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**THE CHEMISTRY OF ZIRCONIUM
SULPHATES AND POLYPHOSPHATES**

PhD

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The chemistry of zirconium sulphates and polyphosphates

by

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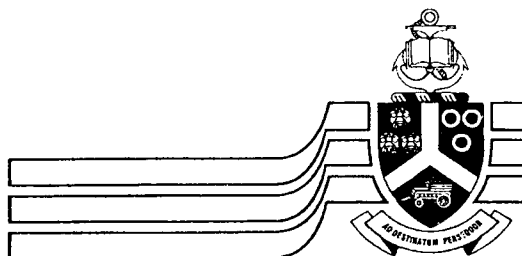


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Henk-Jan de Jager, January 1999

The chemistry of zirconium sulphates and polyphosphates

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Degree: Philosophy Doctor in Chemistry

ABSTRACT

This thesis comprises a combination of fundamental and applied research on aspects of zirconium and phosphate chemistry of importance to the industry, covering the structure and chemistry of zirconium sulphates, the dehydration of phosphates and the hydrolysis of polyphosphates.

The initial purpose was the development of zirconium phosphate-based flame-retardants and catalysts. However, during the course of the investigation it was discovered that important aspects of zirconium and phosphate chemistry that were required for the investigation were not available in the literature. These gaps in the basic understanding and use of this chemistry had to be filled in order to fully exploit the potential of zirconium phosphate compounds as flame-retardants and catalysts, especially on an industrial scale. Of particular importance is the dissolution of zirconium raw materials for purification, which is essential to obtain a zirconium product suitable for catalytic purposes. It is, of course, well known that these materials are highly insoluble in water, and methods were investigated whereby they could be treated. The use of sulphates was one such method, which, in the author's opinion, is potentially one of the most successful ones for this purpose. The chemistry and structures of zirconium sulphates are therefore an important part of the investigation.

$\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ and $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$, are synthesised and their crystal structures resolved by single crystal X-ray diffraction (XRD).

$\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ is solved by the heavy atom method, using the Patterson synthesis. The XRD pattern of a powdered single crystal is in line with the calculated XRD pattern and the spectroscopic features of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ correlate with its structure.

The unit cell of the $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ compound is remarkably large and contains three substructures. Substructure 1 is build of $\text{Zr}_{18}\text{O}_{10}(\text{OH})_{26}(\text{H}_2\text{O})_{22}(\text{SO}_4)_{13}$ clusters. Substructure 2 is an ammonium (bi) sulphate string $(\text{NH}_4)_4\text{H}_2(\text{SO}_4)_3$ and substructure 3 represents parallel channels in the unit cell.

Ammonium zirconium sulphate is an intermediate key component in the upgrading of baddeleyite from the mines, reflecting its potential for an industrial application. Its chemistry is similar to acidic zirconium sulphate and many similar zirconium-based chemicals could be produced in the same way.

Dehydration of phosphates and hydrolysis of polyphosphates are important subjects in the development of zirconium phosphate based flame-retardants and catalysts. Heat treatment of different types of phosphates led to various products and the chemistry of these phosphates had to be re-investigated. The dehydration of phosphates is studied with Raman (in-situ) and infrared spectroscopy. The results of this study are in agreement with thermogravimetric analyses.

Hydrolysis can also be monitored by Raman spectroscopy and is used for quantitative analysis. Rates of acid-catalysed hydrolysis are measured and a mathematical model is developed to explain the behaviour of the reaction. The stability of polyphosphates is explained in terms of the determined activation energy of the hydrolysis.

Since the investigations turned out to be very comprehensive, the development of flame-retardants and catalysts are not reported here, and the topics covered in this thesis are widely divergent. However, the results of this research can be combined and applied in the quest for a good zirconium phosphate flame-retardant and catalyst.

The chemistry of zirconium sulphates and polyphosphates

deur Henk-Jan de Jager

Promotor: Prof. A.M. Heyns

Departement Chemie

Doktorsgraad in Chemie

UITTREKSEL

Hierdie tesis is 'n kombinasie van fundamentele en toegepaste navorsing op sirkonium- en fosfaatchemie, wat vir die industrie belangrik is. Dit handel oor die struktuur en chemie van sirkoniumsulfate, die dehidrasie van fosfate en die hidrolise van polifosfate.

Die oorspronklike doel van hierdie studie was die ontwikkeling van vlamvertragers en katalisatore gebaseer op sirkoniumfosfaat. Dit het gedurende die studie geblyk dat belangrike aspekte van sirkonium- en fosfaatchemie, wat nodig was vir hierdie navorsing, nie in die literatuur beskikbaar was nie. Hierdie leemtes in die onderliggende begrip en gebruik van hierdie chemie is aangespreek, om die volle potensiaal van sirkoniumfosfate as vlamvertragers en katalisatore te benut, veral op industriële vlak. Die oplos van onverwerkte sirkoniummateriale vir suiwering is van groot belang om 'n sirkoniumproduk vir katalitiese toepassings te berei. Dit is bekend dat die materiale hoogs onoplosbaar in water is en verskeie behandelingsmetodes is ondersoek. Die gebruik van sulfate is een daarvan wat, volgens die outeur, die beste potensiaal vir hierdie doel het. Die chemie en strukture van sirkoniumsulfate is daarom 'n belangrike gedeelte in die ondersoek.

$\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ en $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$, is berei en die kristalstrukture opgelos met behulp van enkelkristal X-straaldiffraksie. $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ is met die swaaratoom-metode volgens die Pattersonsintese opgelos. Die X-straaldiffraksiepatroon van 'n kristal wat verpoeier is, kom ooreen met die berekende X-straaldiffraksiepatroon en die spektroskopiese eienskappe van $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ korreleer met sy struktuur.

Die eenheidsel van die $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ verbinding is buitengewoon groot en bevat drie substrukture. Substruktuur 1 bestaan uit $\text{Zr}_{18}\text{O}_{10}(\text{OH})_{26}(\text{H}_2\text{O})_{22}(\text{SO}_4)_{13}$ trosse. Substruktuur 2 is 'n ammonium-(bi)-sulfaat ketting $((\text{NH}_4)_4\text{H}_2(\text{SO}_4)_3)$ en substruktuur 3 verteenwoordig die parallelle kanale in die eenheidsel.

Ammoniumsirkoniumsulfaat is 'n tussenproduk in die verwerking van baddeleyiet in die mynindustrie en het dus potensiaal vir industriële toepassings. Die chemie van ammoniumsirkoniumsulfaat kom ooreen met die van suur sirkoniumsulfaat en verskeie soortgelyke sirkonium-gebaseerde chemikalieë kan op dieselfde wyse geproduseer word.

Dehidrasie van fosfate en hidrolise van polifosfate is belangrike onderwerpe in die ondersoek na sirkoniumfosfaat-gebaseerde vlamvertragers and katalisatore. Verskillende tipes fosfate lei tot verskillende produkte wanneer dit aan hitte blootgestel word en die chemie van hierdie fosfate is her-ondersoek. Die reaksies is met Raman- (in-situ) en infrarooispektroskopie bestudeer en kom met die termogravimetriese analise ooreen.

Hidrolise kan ook met Ramanspektroskopie gevolg word en gebruik word vir kwantitatiewe analises. Die tempo van hidrolise is gemeet en 'n wiskundige model ontwikkel om die reaksiegedrag te verklaar. Die stabiliteit van polifosfate is verduidelik in terme van die aktiveringsenergie wat bepaal is.

Die navorsingsprojek het baie omvangryk geword en die ontwikkeling van vlamvertragers en katalisatore is nie hier gerapporteer nie. Daardeur is die onderwerpe in hierdie tesis baie uiteenlopend, maar die resultate van hierdie navorsing kan gekombineer en toegepas word om 'n goeie sirkoniumfosfaat vlamvertrager en katalisator te ontwikkel.

Preface

The INSTITUTE OF APPLIED MATERIALS at the University of Pretoria forms an interface between the materials industry and the university. Its vision is to initiate and stimulate more research and development on materials to close the gap between raw and processed materials. The dual mission of the institute is to train scientists and engineers and to provide the materials industry with innovative research and development programs.

The institute was founded at the end of November 1996 by its director; Prof. A.M. Heyns. It offers postgraduate students an opportunity to study material sciences from a more practical point of view. I was fortunate to be one of the students and started my studies at the beginning of 1996 before the institute was formally founded. The nature of my education was not to be trained to operate an analytical apparatus or mastering a single technique, but to integrate available techniques in solving a chemical problem. However, single crystal XRD and Raman spectroscopy are heavily represented in this work, because of their practical value in my research. Other techniques like infrared spectroscopy, thermogravimetric analysis, X-ray powder diffraction and to a lesser extent BET surface determination and scanning electron microscopy were also used.

Henk-Jan de Jager

***You may make your plans,
but God directs your actions.***

Proverbs 16:9

To my wife and parents

In remembrance of my best friend Eddy (1967-1998)

Introduction

1.1 Occurrence of Zirconia

Man knew zirconia long before he was able to recognise the compound as a distinctive substance. One of the twelve stones in the breastplate of ancient high priests in Israel was probably a variety of zircon. Much later, in the eighteenth century, colourless zircon compounds were regarded as imperfect diamonds known as Matara diamonds. The name zircon is probably derived from an Arabic precious stone named Zerk or a Persian stone called Zargun.

N. Hassak found Baddeleyite, ZrO_2 , in Brazil in 1892. Soon after that, L. Fletcher found baddeleyite in Ceylon. He gave it the name Baddeleyite that is nowadays commonly used.

In 1923 Von Hevesy discovered the presence of hafnium in zircon by XRD studies. It is difficult to separate them because of the chemical similarity. Both substances have similar atomic radii (Zr $1.452\text{\AA}$ and Hf $1.442\text{\AA}$) and a similar electron distribution in the valence atomic orbitals. This is not sufficient to explain the chemical and physical similarities. Silver and gold for instance also have similar electronic configurations and even have closer atomic radii values. It is suggested that a similarity in the effective nuclear charge on the valence electrons also play a role. [1,2]

Zirconium mainly occurs in zircon minerals, ZrSiO_4 , baddeleyite, ZrO_2 , and other varieties of more complex minerals like silicates. Zircon occurs in all kind of rocks but mainly in granite and syenite rocks. It tends to separate during the cooling process of rock in an acidic

environment. More complex silicates were formed in alkaline environments. Water erosion crumbled and dissolved rock, which finally became clay and soil. Zircon was preserved during the process due to its extreme stability. Rivers dropped disintegrated rocks into the sea, resulting in the formation of shoals along the seacoast. Many beaches contain a considerable amount of zircon and zirconia and therefore, these compounds are widely distributed over the world, ranking twentieth in order of abundance in the crust of the earth [3]. Concentrations of zirconium and hafnium in different rocks are shown in Table I.

*Table I Zirconium and hafnium concentrations
in the earth crust and terrestrial rocks (ppm)*

Rock type	Zr	Hf
Average abundance	165	3
Syenite	500	10
Basalt	100-250	1-4
Sandstone	220	5
Granite	180	4
Shale	160	3
Limestone	20	0.5

Many soils and clays contain zirconium as a minor constituent and are not used as sources of zirconium due to the high costs. Zirconium occurs in more than 20 oxide or silicate minerals and some of them are shown in Table II. Zircon is most commonly used as a source for zirconium, even though separation of silica from zirconia is still a problem. Eudialyte may also become an interesting source of zirconium and hafnium in the future [4].

South Africa is not only accountable for producing 58% of the zirconia from zircon, but is also the major supplier of zirconia from baddeleyite. Baddeleyite is found in Palaborwa (South Africa) and Sao Paulo and Minas Geraes (Brazil). The ore in Brazil delivers poor quality baddeleyite called zirkite due to a high silica contamination. The Palaborwa Mining Company Ltd. (PMC) mines Baddeleyite from South Africa. It is obtained as a by-product

from copper and phosphate extractions and is practically silica free, although it contains some uranium. The Phosphate Development Corporations (Foskor) also mines Baddeleyite. Although Foskor has a capacity of 6,500 TPA, it only utilises ~3,500 TPA. It has invested in an electrofused zirconia facility using zircon sand as its feed stock. The plant produces unstabilised, partially stabilised and fully stabilised zirconia. Baddeleyite from Palaborwa is very unreactive compared to zirconia from other mines. Its inertness can be used to improve its purity by removing impurities with acids [2,5].

Table II Zirconium and Hafnium content in various types of zirconium based minerals.

Mineral	Composition	weight % ZrO ₂	weight % HfO ₂
Baddeleyite ^a	ZrO ₂	59-98.9	0.5-2.1
Catapleite	(Na ₃ Ca)ZrSi ₃ O ₉ ·2H ₂ O	30.5-31.53	0.1-0.6
Elpidite	Na ₂ (Zr,Ti)Si ₆ O ₁₅ ·3H ₂ O	19.8-20.28	0.2-0.4
Eudialyte-eucolite ^b	(Ca,Na) ₅ Zr ₅ Si ₆ (O,OH,Cl) ₂₀	2.0-3.0	0.06-0.7
Polymignite	(Ca,Fe,Y,Zr)(Nb,Ta,Ti)O ₄	28.71-29.11	0.9
Rosenbuschite	(Ca,Na) ₃ (Zr,Ti) ₂ Si ₂ O ₈ F	19.8	0.3
Wohlerite	NaCa ₂ (Zr,Nb)Si ₂ O ₈ (O,OH,F)	15.61-17.55	0.05-0.7
Zircon ^c	ZrSiO ₄	34-67	0.4-17
Zirkelite	(Ca,Fe)Zr ₂ Ti ₂ O ₅	51.7-59.89	1-1.2

a) Caldasite is categorised as baddeleyite

b) Eudialyte from some localities contains 12-20% ZrO₂ and 0.1-0.7% HfO₂.

c) Alvite, cyrtolite, hagatalite, malacon, naegite, oyamalite and yamagutilite are varieties of zircon

1.2 Zirconium Sulphate Structures

Zirconium sulphates appear in a large number of hydrated and anhydrous forms. Crystal structures of many forms are published and will be briefly discussed in this section. Preparation of the various phases starts with a dehydration of the zirconium sulphate tetrahydrate followed by subjecting it to controlled atmospheres. A more detailed discussion can be found in the literature [6]. Zirconium sulphate tetrahydrate can be prepared by dissolving baddeleyite (ZrO_2) in sulphuric acid. It can be used as a starting material to prepare $\alpha\text{-Zr}(\text{SO}_4)_2$ by controlling the H_2SO_4 atmosphere. $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ can be prepared by vapour hydration of zirconium anhydrous sulphate, but the β - and $\gamma\text{-Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ are also isolated. $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 2\text{H}_2\text{O}$ and $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$ are prepared by changing the atmospheric conditions to a high partial pressure of water vapour.

Zirconium phases are directly or indirectly interconvertible as shown in figure 1.1, but $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is the stable phase at all water vapour pressures within a temperature range of -4°C to $+40^\circ\text{C}$. Since energies of direct bonding configurations are very close, the type of structure strongly depends on the experimental conditions, in particular on the sulphuric or water atmosphere [7].

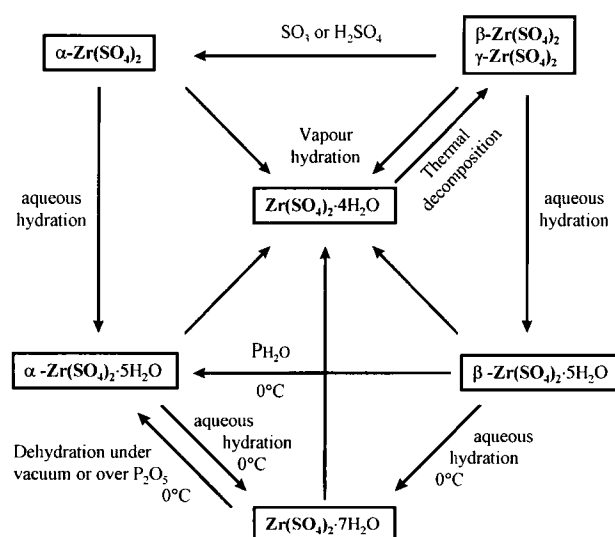


Figure 1.1 Inter relationship between zirconium sulphate compounds.

Zirconium sulphate tetrahydrate is the most well known compound among the zirconium sulphates since it is produced on an industrial scale. Efforts to elucidate the crystallographic structure were performed in 1957 to determine the lattice constants, but it was Singer and Cromer [8] who determined the structure (Table III). Zirconium sulphate tetrahydrate crystallises in an orthorhombic lattice, space group $Fddd$, and is built of $Zr(SO_4)_2 \cdot 4H_2O$ layers normal to the a axis (figure 1.2). Within the layers, each zirconium atom is in contact with four sulphate groups and four water molecules giving it a co-ordination of eight in an antiprism arrangement. Each sulphate group is in contact with two zirconium atoms and the sulphate oxygens that are not in contact with zirconium are linked to water molecules via hydrogen bonding. The antiprism surrounding each zirconium atom is slightly distorted and consists of half of the sulphate oxygen and the hydrate oxygen having an average Zr-O distance of $2.180\text{\AA}$.

Table III Cell parameters of $Zr(SO_4)_2 \cdot 4H_2O$.

Cell parameters	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	No. of reflections
$Z=8$	25.92 ± 0.02	11.62 ± 0.02	5.532 ± 0.005	376

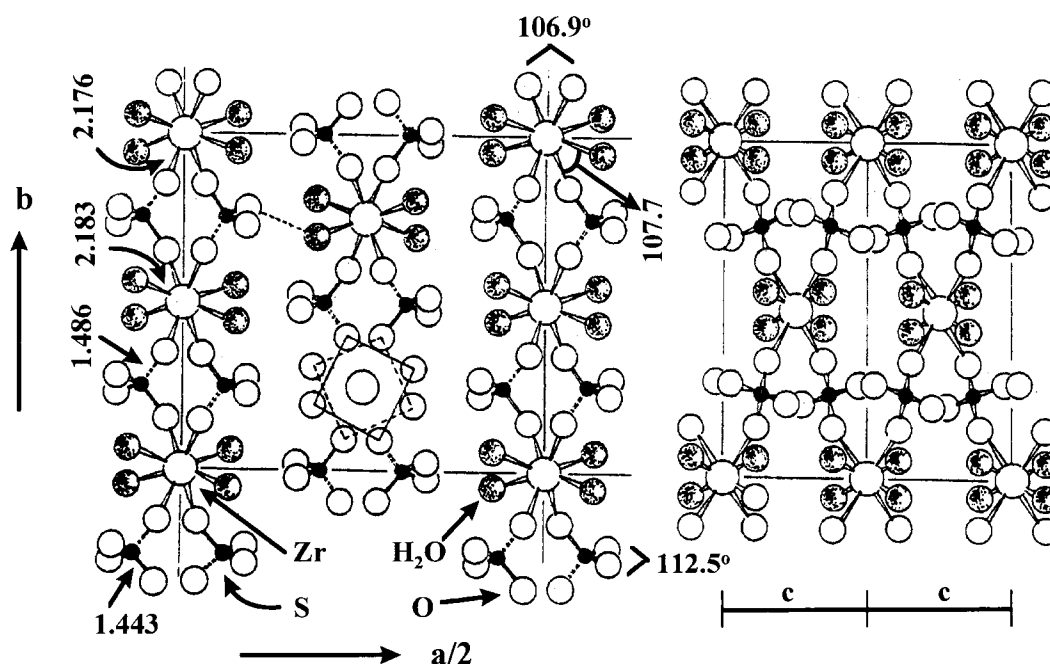


Figure 1.2 Structure of zirconium sulphate tetrahydrate (bond distances in $\text{\AA}$).

Anhydrous $\alpha\text{-Zr}(\text{SO}_4)_2$ crystallises in an orthorhombic structure with space group P_{nma} . Dehydration of the tetrahydrate at a temperature of 250-500°C results in a mixture of the metastable β and γ phases and the stable α phase. The β - and γ -phases convert to the α form upon heating at 650°C or under high partial pressures of sulphuric acid at lower temperatures. Although single crystals of the metastable phases could not be prepared, α single crystals can be grown and the crystallographic data are given in Table IV. Each zirconium is sevenfold co-ordinated with bonds to one oxygen atom of each of the seven sulphate tetrahedra. Two types of sulphate groups can be distinguished, one bonded to four zirconium atoms while the other is bonded to three zirconium atoms, having one terminal oxygen atom. The structure can be visualised as sheets of dimeric rings with zirconium fivefold co-ordinated to the oxygen in the sheet. The sheets are cross-linked by two sulphate bridges per zirconium atom, which are normal to the $[010]$ plane, completing the sevenfold oxygen configuration (figure 1.3).

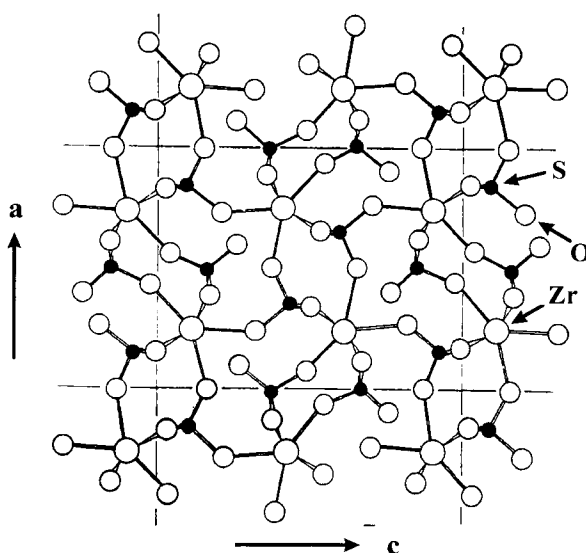


Figure 1.3 Structure of $\alpha\text{-Zr}(\text{SO}_4)_2$ in a (010) projection.

α - $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ [9] is the stable phase of the three possible monohydrates (α , β , γ), formed by equilibration of the γ phase over 75% H_2SO_4 at 120-150°C. The structure is composed of $[\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}]_n$ layers in the (100) plane. Figure 1.4 shows these layers in the (010) projection and the planes are held together by hydrogen bonds. Each zirconium is seven-fold co-ordinated by oxygen atoms of the sulphate and one oxygen of the water molecule. All sulphate groups have three oxygen atoms bridging the zirconium atoms while the remaining oxygen is directed out of the (100) plane. Two types of sulphates are present in the structure; one connects three zirconium atoms by single oxygen bridges, and one sulphate acts as a bidentate ligand. The unit cell parameters are presented in Table IV.

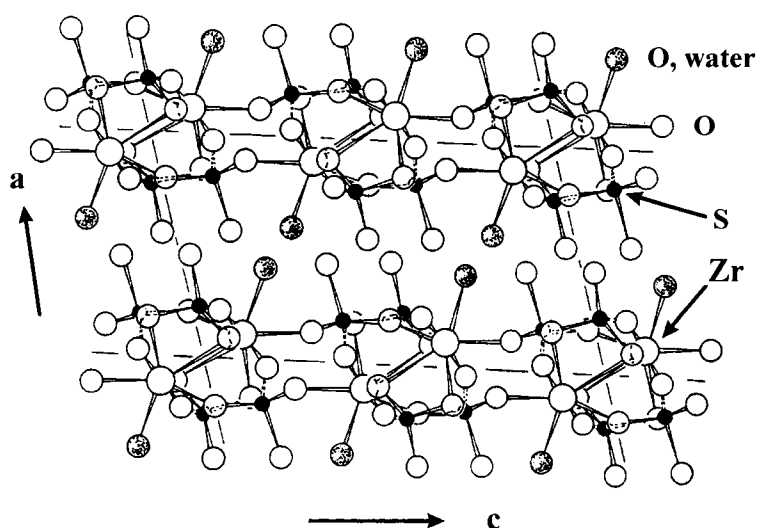


Figure 1.4 Structure of α - $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ in a (010) projection.

β - $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ can be prepared by ageing γ - $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ at room temperature but suitable single crystals could not be obtained.

γ -Zr(SO₄)₂·H₂O [10] is prepared by thermal decomposition of Zr(SO₄)₂·4H₂O at 200°C for 1 hour. It has a triclinic unit cell and space group $P\bar{1}$ and consists of layers of [Zr(SO₄)₂·H₂O]_n along [001]. Zirconium is seven fold co-ordinated having six oxygen ligands originating from sulphate and one oxygen from the hydrate. Sulphates are bridging zirconium polyhedra and each sulphate group is in contact with three zirconium atoms providing double bridging and a build up of zirconium layers. The layers are held together by hydrogen bonding as can be seen in figure 1.5. The γ phase is closely related to the α phase and the cell parameters of all three phases of the monohydrate and the anhydrous structure are given in Table IV.

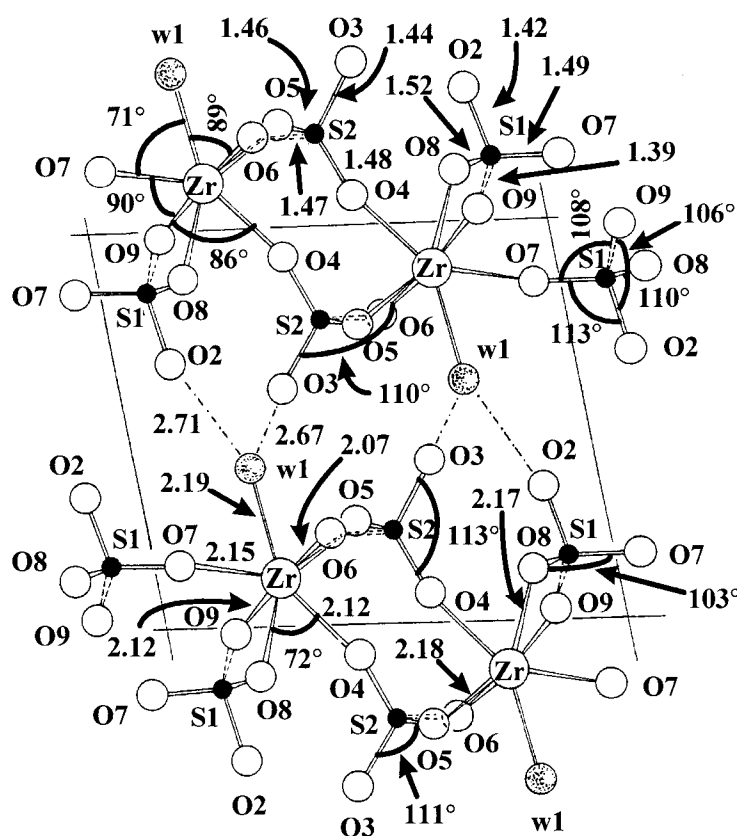


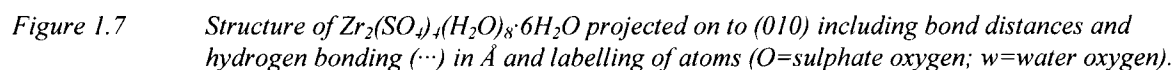
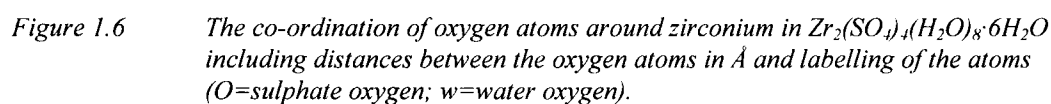
Figure 1.5 Structure of γ -Zr(SO₄)₂·H₂O in a (010) projection) including bond distances and hydrogen bonding (···) in Å and labelling of atoms (O=sulphate oxygen; w=water oxygen)..

Table IV Crystallographic data of anhydrous and monohydrate $Zr(SO_4)_2$.

Cell parameters space group	α - $Zr(SO_4)_2$ Pnma	α - $Zr(SO_4)_2 \cdot H_2O$ P2 ₁ /c	β - $Zr(SO_4)_2 \cdot H_2O$ -	γ - $Zr(SO_4)_2 \cdot H_2O$ P $\bar{1}$
crystal system	orthorhombic	monoclinic	triclinic	triclinic
a / Å	8.61±0.01	7.32±0.01	7.86±0.01	7.89±0.01
b / Å	5.445±0.01	8.54±0.01	5.34±0.01	5.21±0.01
c / Å	10.89±0.01	11.82±0.01	8.97±0.01	8.96±0.01
α / °			91.0±0.1	95.2±0.1
β / °		106.0±0.1	100.7±0.1	99.8±0.1
γ / °			109.4±0.1	109.2±0.1
V / Å ³		710	348	339
Z	4	4	(2) ^a	2
No. of reflections	285	807	-	708
R	0.118	0.131	-	0.126

^a Based on the volume of the cell

Single crystals of $Zr(SO_4)_4(H_2O)_8 \cdot 6H_2O$ [11] were difficult to grow because of decomposition upon drying. The stability depends on the hydrogen bridging between non-bonded water molecules and adjacent $[Zr(SO_4)_2(H_2O)_4]$ layers. The crystal has space group P $\bar{1}$ and the structural unit is composed of $Zr_2(SO_4)_4(H_2O)_8$ dimers with zirconium being eight fold co-ordinated by four water molecules, two bridging sulphate groups and one bidentate sulphate ligand per zirconium atom (figure 1.6). Apart from the bonded water, three non-bonded water molecules are present in the structure lying in sheets parallel to (001). The dimer in the structure has a centre of symmetry, which can be seen in figure 1.7. Oxygen atoms on the bidentate sulphate ligand, which are not bonded to zirconium, are hydrogen bonded to water molecules in the adjacent dimer.



α -Zirconium sulphate pentahydrate (or α -Zr₂(SO₄)₄(H₂O)₈·2H₂O) [12] crystallises from a solution in a triclinic cell with space group $P\bar{1}$. Zirconium is co-ordinated by eight oxygen atoms and the main structural unit is close to the heptahydrate previously discussed (figure 1.8). Sheets of dimeric units (figure 1.9) are held together by hydrogen bridges through both the co-ordinated and the non-bonded water molecules. In this structure however, there are only two non-bonded water molecules in the unit cell lying in sheets parallel to the (101) direction.

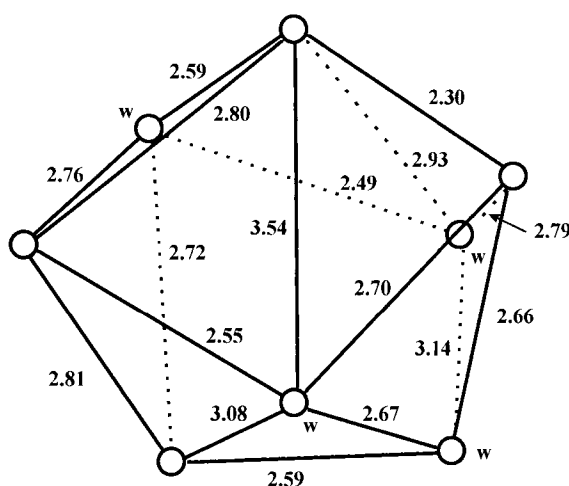


Figure 1.8 The co-ordination of oxygen atoms around zirconium in α -Zr₂(SO₄)₄(H₂O)₈·2H₂O including distances between the oxygen atoms in Å (w=water oxygen).

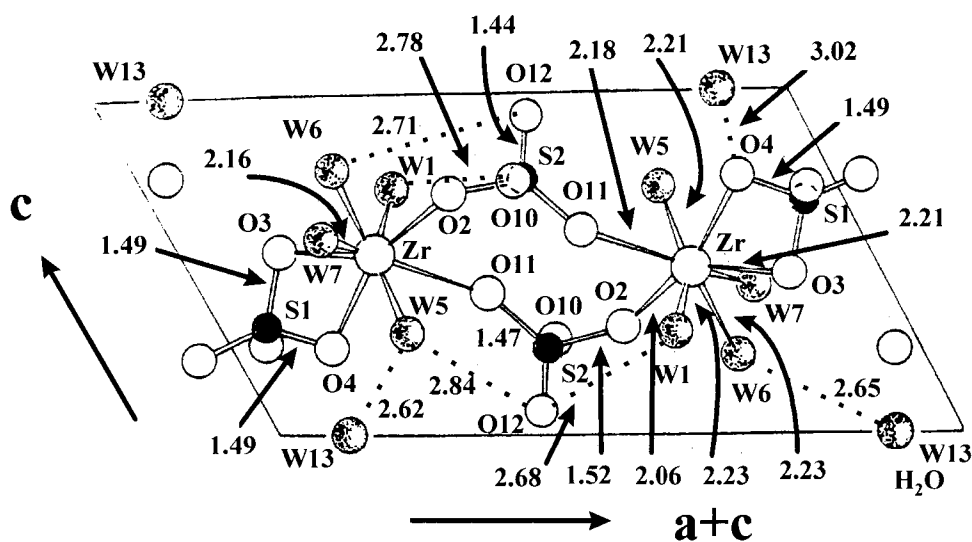


Figure 1.9 Structure of α -Zr₂(SO₄)₄(H₂O)₈·2H₂O projected on to (010) including bond distances and hydrogen bonding (···) in Å and labelling of atoms (O=sulphate oxygen; w=water oxygen).

In the β phase [13] the dimeric units have undergone some distortion and the free water molecules are dispositioned, but the structure is very similar to the α phase. The cell parameters of these hydrates can be found in the table below.

Table V Crystallographic data for the hepta and pentahydrate of zirconium sulphate.

Cell parameters	$\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$	$\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$	$\beta\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
crystal system	triclinic	triclinic	triclinic
$a / \text{\AA}$	12.04 ± 0.01	11.90 ± 0.01	8.55 ± 0.01
$b / \text{\AA}$	6.36 ± 0.01	6.17 ± 0.01	7.60 ± 0.01
$c / \text{\AA}$	8.28 ± 0.01	7.57 ± 0.01	7.71 ± 0.01
$\alpha / ^\circ$	93.0 ± 0.1	106.5 ± 0.1	101.4 ± 0.1
$\beta / ^\circ$	92.4 ± 0.1	95.7 ± 0.1	98.6 ± 0.1
$\gamma / ^\circ$	95.9 ± 0.1	104.6 ± 0.1	89.9 ± 0.1
$V / \text{\AA}^3$			348
Z	2	2	2
No. of reflections	1219	867	754
R	0.159	0.134	0.122

Zirconium dihydroxide sulphate monohydrate ($\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$) [14] has a monoclinic cell and a space group $C_{2/c}$. An oxygen atom from the hydrate completes the pentagonal bipyramidal configuration around zirconium and such a structure is typical for basic sulphates. Figure 1.10 shows the co-ordination of zirconium including some bond distances and bond angles.

Zirconium atoms are connected by hydroxy-bridges (O_1) constituting almost planar zigzag chains and making the Zr-Zr distance $3.568 \text{\AA}$. Chains of $[\text{Zr}(\text{OH})_2]_n^{2n+}$ are interconnected by sulphate groups (O_3), which are almost perpendicular to the zigzag planes. The cell parameters of this structure are shown below.

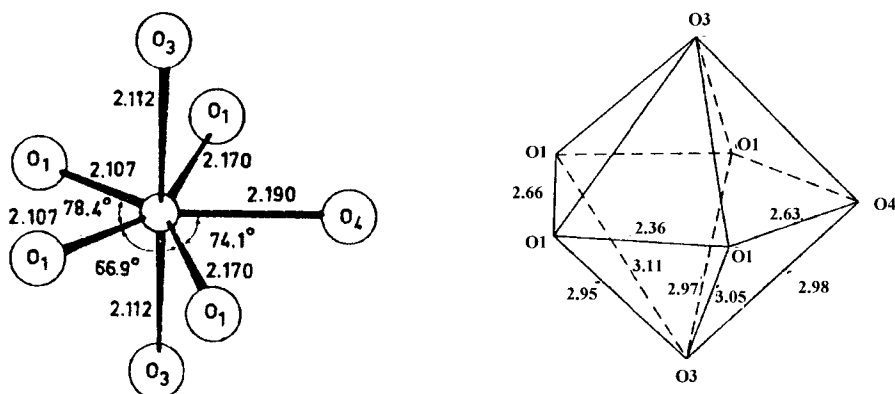


Figure 1.10 The co-ordination of oxygen atoms around zirconium in $\text{Zr}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$ including Zr-O distances (Å). O_1 :OH; O_2 : SO_4 (not bonded to Zr); O_3 : SO_4 ; O_4 : H_2O .

Table VI Cell parameters of $\text{Zr}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$.

a / Å	b / Å	c / Å
6.4969±0.0004	12.4598±0.0010	6.8262±0.0004
No. of reflections	β / °	V=549.2 Å ³
986	96.311±0.004	Z=4

1.3 Research on Zirconium and Phosphates

Zirconium sulphate is industrially prepared by digesting baddeleyite in sulphuric acid at 210°C in an autoclave. Crystalline zirconium sulphate tetrahydrate (AZST) is obtained by crystallising the product from a 45 wt% sulphuric acid solution. The process requires a lot of acid; 600 tonnes of 45 wt% sulphuric acid is needed to process 50 tonnes of ZrO_2 . The sulphuric acid imposes severe environmental problems on the production of zirconium sulphate tetrahydrate due to the corrosive nature of these relatively dilute (less value) and large volumes of acid. Acid zirconium sulphate tetrahydrate can only be prepared from sulphuric acid with almost no cost-effective alternative [15].

Baddeleyite from Palaborwa and zircon deposits are slightly radioactive, since it is contaminated with thorium oxide (ThO_2) and uranium oxide (U_3O_8). Removal of these radioactive elements, beside the other impurities, is therefore essential [16].

Many gaps in the purification of zirconia and the product development of zirconium-based chemicals are still a subject of interest for industries in South Africa [15]. Product development of zirconium chemicals has been a key issue in the INSTITUTE OF APPLIED MATERIALS at the University of Pretoria as well. One of the objects is to produce zirconium-based flame-retardants and catalysts from mined baddeleyite or fused zircon.

Three phases of zirconium phosphate ($\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ $n=0-2$) has been reported [17,18,19], which could be potential candidates for a formulation of flame-retardants. Phosphates and polyphosphates are important ingredients in flame-retardants as well and their use is discussed in the literature [20,21].

Zirconium phosphate dehydrates to zirconium pyrophosphate (ZrP_2O_7) releasing constitutional water when subjected to heat and this pyrophosphate is extremely stable, even at high temperatures (1500°C). These properties are important for effective flame-retardants. Zirconium phosphate exhibits acidic properties as well, which is important for catalytic purposes [22,23]. The purity of the catalyst is extremely important since minor impurities could poison the catalyst and reduce its catalytic activity. Yamanaka reported a α -zirconium phosphate compound having a laminated structure, which was separated by an organic

derivative [24]. More recent papers on the intercalation of zirconium phosphate compounds were published. Yamanaka self (et. al.) reported several n-alkyl derivatives of $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ introducing ester links into the layer structure of γ -zirconium phosphate giving $\text{Zr}(\text{HPO}_4)_{2-x}(\text{ROPO}_3)_x$ compounds [25]. Later a zirconium phosphate catalyst functionalised with sulphonic groups was patented having the formula $(\text{ZrP}_2\text{O}_7)_{1-x}\{\text{Zr}(\text{HPO}_4)_{2-y}[\text{O}_3\text{P-R}(\text{SO}_3\text{H})_n]_y\}_x$ [26]. Pillared zirconium phosphate compounds were reported by Torres et. al. who synthesised a chromia-pillared α -zirconium phosphate compound [27]. Alberti et. al. reported a zirconium phosphite compound also having a pillared structure with a surface area of $375\text{m}^2\cdot\text{g}^{-1}$, which was de-laminated by diphosphonates $(\text{Zr}(\text{HPO}_3)_{1.33}(\text{O}_3\text{P-R-PO}_3)_{0.33})$ [28] and Snover et. al. reported similar zirconium alkyl bisphosphonate multi-layer films [29]. A structure of zirconium phosphate with intercalated organic derivatives is shown in figure 1.11.

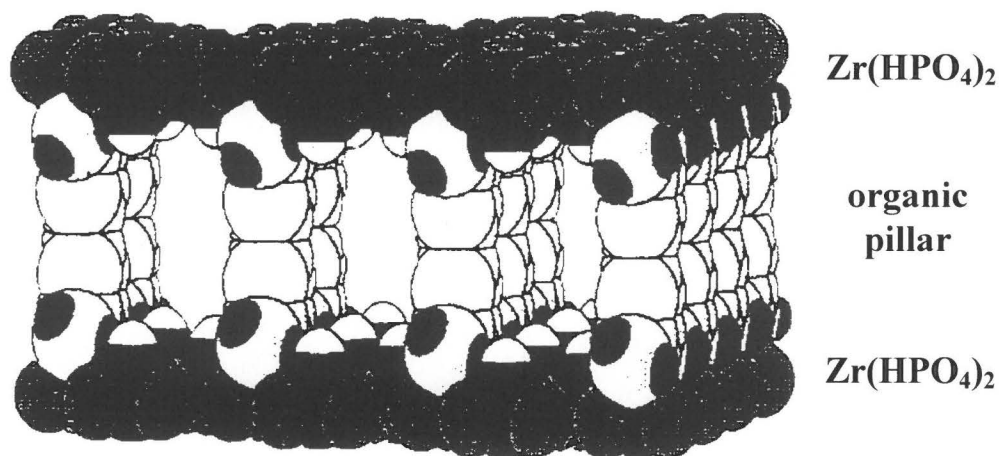


Figure 1.11 Computer generated model of zirconium phosphate layers separated by organic pillars.

The objective was to produce similar zirconium phosphate compounds with the general formula $\text{Zr}(\text{HPO}_4)_{2-x}(\text{O}_3\text{P-R-PO}_3)_x$. R would not represent an organic group, but a condensed phosphate. Polyphosphates or other types of condensed phosphates would separate the zirconium phosphate layers resulting in a structure analogous to figure 1.11. It is believed that these compounds could be effective flame-retardants, especially if they are loaded with

extra phosphates. It is also believed that they could be important catalysts, because the delamination is accompanied by an enormous increase in the surface area (B.E.T.).

Although condensed phosphates could be prepared by dehydration, the stability of the phosphate in acidic aqueous media is a matter of concern and has to be studied in more detail.

The interest in zirconium phosphate for flame-retardants and catalysts originates from the availability of zirconium and phosphate in South Africa [30]. This study is conducted in the context of the development of zirconium phosphate flame-retardants and catalysts from baddeleyite, mined at Palaborwa. It therefore involves a process to upgrade baddeleyite, the dehydration of phosphate and the hydrolysis of polyphosphates.

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2

Experimental

The equipment and techniques employed to tackle the chemical problems discussed in this thesis are described in this chapter. They include,

- Single Crystal X-ray Diffraction (Single Crystal XRD)
- Powder Diffraction (XRD)
- Infrared Spectroscopy (IR)
- Raman Spectroscopy
- Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC)
- Nitrogen Adsorption (BET)
- Scanning Electron Microscopy (SEM)
- pH Meter

2.1 Experimental Set-up and Procedure for X-ray Data Acquisition

2.1.1 Single Crystal XRD

The structure of a single crystal was determined by X-ray diffraction. Primary X-rays were generated in a hot cathode tube under a high vacuum. A tungsten glowing spiral cathode and a molybdenum anode pasted on a copper block are placed in a high vacuum X-ray tube. The spiral cathode was heated by an electrical current (1.5-5A, 4-12V, 1800-2600K) to emit

electrons. Due to an applied potential of 30 kV between the anode and cathode, electrons were accelerated and collided on to the molybdenum anode releasing their kinetic energy. Only a fraction of the energy turned into X-rays (0.2%), the major part was released as heat and water-cooling was therefore essential.

The spectrum of the generated X-rays consists of white radiation and a line spectrum characteristic for the material of the anode. A spectrum of molybdenum and copper radiation is shown in figure 2.1 where K_{α} and K_{β} lines are superpositioned on white radiation [1]. K_{α} of molybdenum is used as an X-ray source in this study. It is actually an unresolved doublet of $K_{\alpha 1}$ and $K_{\alpha 2}$ where the intensity of $K_{\alpha 1}$ is twice the intensity of $K_{\alpha 2}$ and therefore, a weighed average wavelength of $0.7107\text{\AA}$ was used in the determination of the structure.

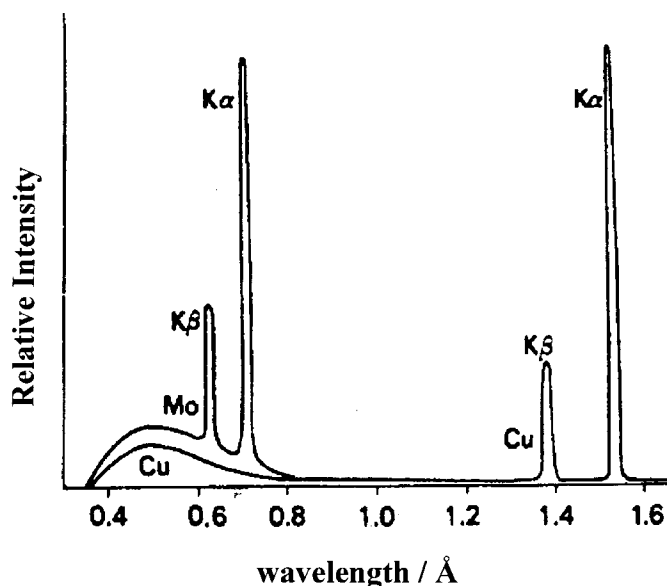


Figure 2.1 *Spectra of molybdenum and copper radiation.*
 Source: *Kristal- en Structuurchemie, Syllabus Structure and Bonding III, Laboratory for Crystal and Structure Chemistry, Faculty of Chemistry, University of Utrecht, Utrecht 1991, 23.*

A crystal was mounted on a gonio-head consisting of movable sledges to keep the crystal centred in the X-ray beam at different settings of the gonio meter. The four-circle diffractometer used in chapter 3, was an ENRAF NONIUS CAD 4 operated by a computer. It is schematically shown in figure 2.2. Incident X-rays passed a collimator in order to filter the divergent parts of the beam, before they were diffracted by the crystal. This process was fully automated and the operation program started with a triclinic primitive cell. The crystal was rotated until 25 strong reflections were found and an orientation matrix was constructed on the basis of these reflections, transforming the triclinic primitive cell to a real crystal cell. When the latter has satisfied the conditions for a crystal system, a unit cell could be established. This process involves complex matrix calculations and since it is fully automated, it is out of the scope of this paper. Once the orientation matrix and the crystal system were known, it was possible to measure structure factors for the h,k,l reflections.

The crystal was oriented in all kinds of directions without displacing its centre of gravity by varying the angles φ , χ and ω around their corresponding axes. The primary X-ray beam, the centre of gravity of the crystal and the detector, defines the measuring plane. The detector could rotate around an axis perpendicular to the measuring plane (angle 2θ) which coincides with the ω axis. A reciprocal lattice vector $\mathbf{H}(h_1, h_2, h_3)$ could be turned into the measuring plane by rotating around axes φ and χ followed by a rotation around the ω axis to intersect this vector with the Ewald sphere. The detector was rotated 2θ around the θ axis to measure the intensity [2].

The structure factor must be corrected for a number of factors:

- 1) Absorption coefficient A . This factor is applied to a strongly absorbing crystal. Absorption is generally high when $\text{Cu } K_\alpha$ radiation is used, but it can sometimes be neglected in the case of $\text{Mo } K_\alpha$ radiation.
- 2) Lorentz factor L . A bandwidth in the radiation, $\Delta\lambda/\lambda$, results in an Ewald shell with a certain thickness instead of a sphere, giving rise to a correction factor $(\cos(\theta) \cdot \sin(\theta))^{-1}$.

- 3) Polarisation factor p . A non-polarised X-ray can excite an electron which in its place emits radiation in the diffraction direction. The primary beam can be decomposed into two orthogonal components perpendicular in the direction of propagation. Likewise, a diffracted beam can be decomposed. One direction is perpendicular to the plane, constituted by the primary and diffracted beam and the other direction is in the plane. The latter has a perpendicular and a parallel component to the direction of propagation. The parallel component does not contribute to the intensity. A factor proportional to $\sqrt{1 + \cos^2(2\theta)}$ corrects this phenomena [3].

Applying the Lorentz and polarisation factor is called data reduction.

In the last phase of the refinement, a scale factor is introduced and the processing of the data could begin.

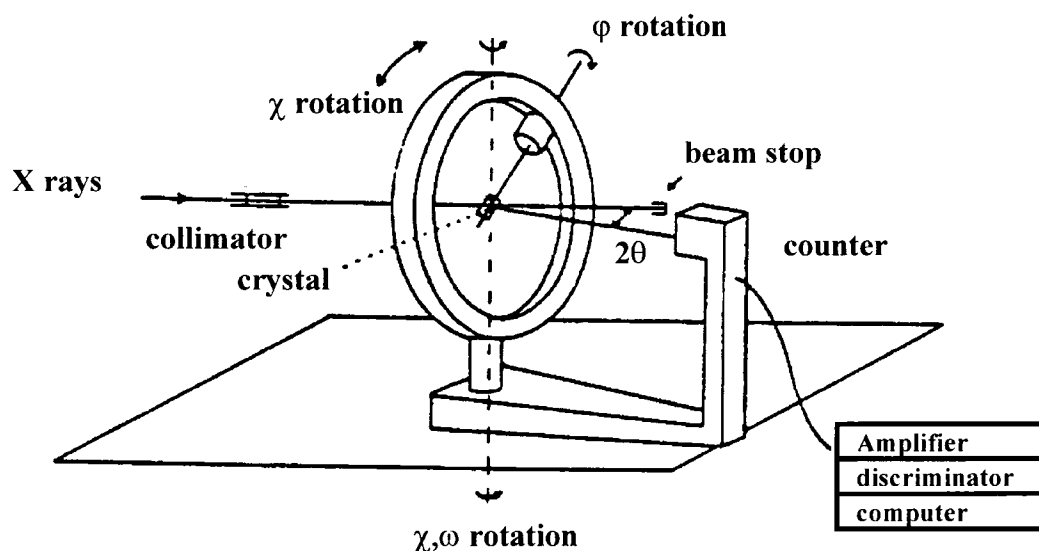


Figure 2.2

A four-circle diffractometer.

Source: *Kristal- en Structuurchemie, Syllabus Structure and Bonding III*, Laboratory for Crystal and Structure Chemistry, Faculty of Chemistry, University of Utrecht, Utrecht 1991, 41.

2.1.2 Powder Diffraction

XRD data were recorded on a Siemens D501 automated diffractometer equipped with a secondary graphite monochromator. The applied potential was 40 kV and the corresponding current 40 mA. The primary X-ray beam was copper K_{α} radiation. A pattern was recorded from 3° to 70° (2θ) in steps of 0.05° . The measure time per step was 1s and the scan speed 3° (2θ) per minute.

2.2 Infrared Spectroscopy

A Bruker IFS 113v FT-IR spectrometer was used for standard analysis. The spectrometer is schematically shown in figure 2.3, which is a simplification of the real set up. It is divided into chambers to reduce interference from stray light. Near infrared (NIR), mid infrared (MIR) or far infrared (FIR) radiation is generated at one of the three sources. The radiation source for the MIR region is a glow bar of tungsten carbide crystal. It is a conductor at room temperature and heated by a current. A mercury lamp is the radiation source for the FIR region, but in this work the glow bar was used as the source for FIR recordings since the irradiance is higher in the $200\text{-}400\text{ cm}^{-1}$ range.

A beam generated by the source is reflected at the movable mirror into the next chamber, filtered and then split by a beam splitter. Part of the light is transmitted and reflected at a movable mirror on one side, while the other part is reflected at the mirror on the opposite side. This whole set up is a Michelson interferometer which records an interferogram based on a difference in path length between two different beams.

Both beams pass the beam splitter again and a joined beam enters the sample chamber. The sample chamber can be opened to insert and remove samples. After interaction with the sample, the beam passes a collimator to filter stray light before reaching the detector. The detector used is a pyro-electric crystal of deuterated triglycidyl sulphate.

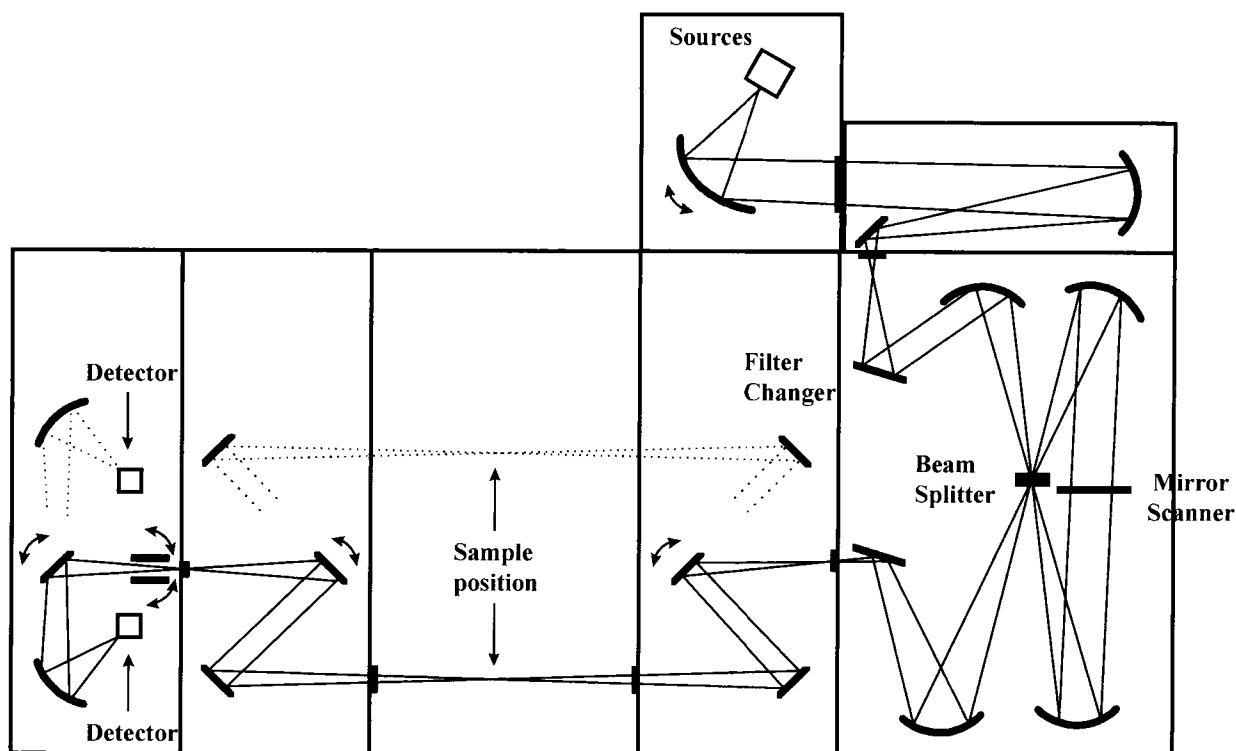


Figure 2.3 Diagram of a Bruker IFS 113v FT-IR spectrometer.

Samples were prepared by mixing 3-5 mg of the compound with 100 mg anhydrous potassium bromide. The powder was transferred into a cylinder and pressed into a pellet using a pressure of $5 \cdot 10^5$ kPa. The cylinder was evacuated during pressing to facilitate pellet formation. After applying a pressure for 1-5 minutes, the sample was taken out of the cylinder and placed into the infrared spectrometer. The sample chamber had been evacuated down to 200 mbar to remove water and CO_2 in the atmosphere. For an analysis in the MIR region, 32 scans were recorded. This is a standard technique for infrared analysis.

Analysis of a sample in the FIR region required 128 scans and the sample was pressed in a poly-ethane pellet at $5 \cdot 10^5$ kPa. 5-7 mg of the compound was mixed with 20 mg poly-ethane since potassium bromide absorbs too much in this spectral region.

2.3 Raman Spectroscopy

The system was a light reflecting confocal DILOR x-y Raman spectrometer with a microscope and a macro-scale chamber, coupled with an intermediate optical arrangement to a x-y spectrograph CCD (multichannel) detector. The advantages of a confocal set up are an enhanced contrast by a spatial filter, an improved depth of field or axial resolution and an improved lateral resolution. A laser beam was generated by an Innova Argon laser, producing a 514 nm excitation line. The beam passed a beam splitter before reaching the objective. This splitter is absent in a transmitted light confocal set up. After the laser beam was reflected at the sample, it propagated in the opposite direction of the incident beam, passing the beam splitter for the second time. The beam splitter diffracted the beam into the direction of the detector consisting of several gratings, amplifiers and a multichannel photo-detector to measure the intensity of the laser beam at different frequencies. A set up of the Raman spectrometer is shown schematically in figure 2.4.

The function of the objective is to illuminate a small zone of the sample, which produces a very high local irradiance (J) at the sample. Thermal relaxation is important because inefficient relaxation of the energy through the sample might induce spectroscopic changes by local heating (chapter 5 and 6).

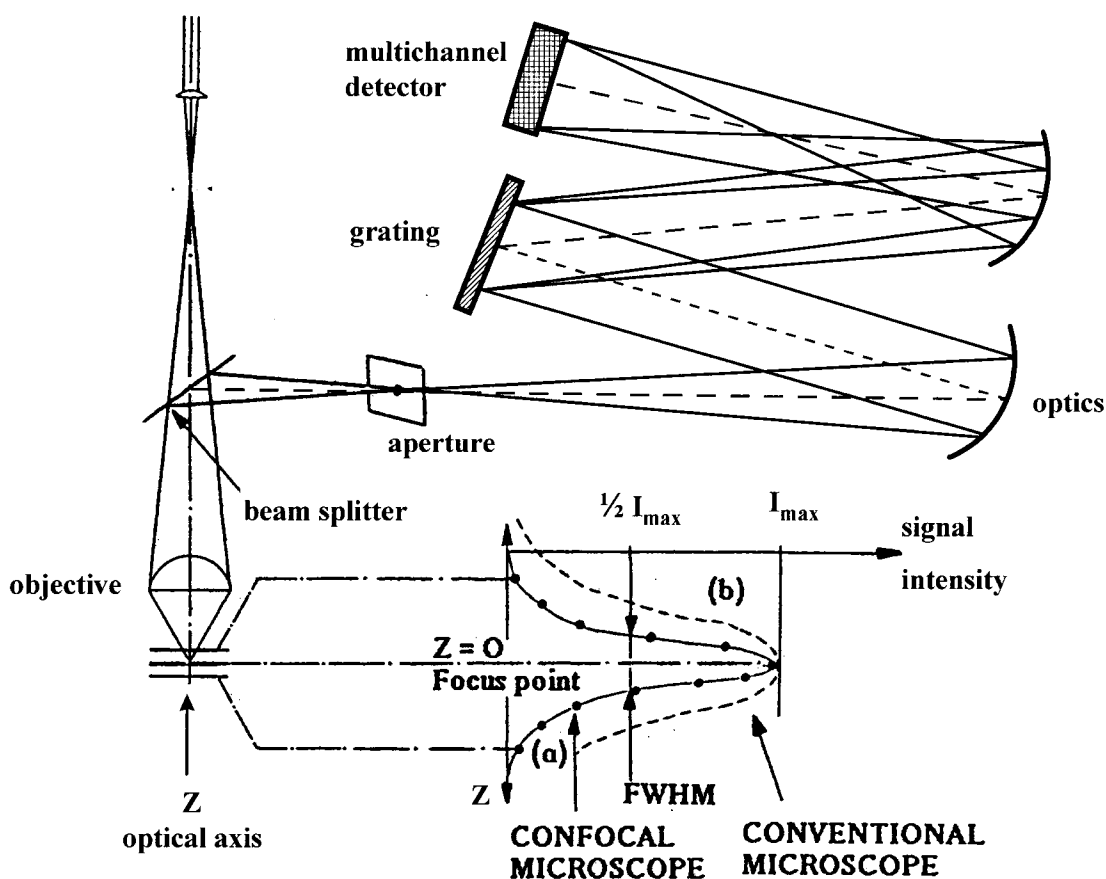


Figure 2.4 Reflected light confocal system and detector including a graph plotting the Raman intensity I versus the axial distance from the focus of the laser beam Z . FWHM is Full Width at Half Maximum.

2.4 Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC)

Thermogravimetric data were collected by a Stanton-Redcroft STA 780 Simultaneous Thermal Analyser. An air-flow was used to remove gaseous decomposition products with a flow rate of $20 \text{ cm}^3 \cdot \text{min}^{-1}$. $\pm 100 \text{ mg}$ of sample was put in a platinum crucible and heated at a scan rate of $5^\circ \text{C} \cdot \text{min}^{-1}$.

Differential Scanning Calorimetry was performed on a Du Pont 910 Calorimeter, controlled by a 1090 Thermal Analyser System.

2.5 Nitrogen Adsorption (BET)

Surfaces of particles were measured by nitrogen physisorption at 77K, a technique developed by Brunauer, Emmett and Teller. Samples were measured using a Micromeritics Flowsorb II 2300. The gas flow was a nitrogen stream (99.7% pure) and the system was calibrated by one single point calibration with 1 μ l of nitrogen gas at room temperature. The offset was tuned to zero and the calibration multiplier was set to the calculated calibration multiplier. 20-60 mg was introduced into the gas stream and cooled to 77K with liquid nitrogen. Desorption was stimulated by a water bath at room temperature. Both the adsorption and desorption values were measured.

2.6 Scanning Electron Microscopy (SEM)

Sample preparation prior to a SEM analysis was essential to avoid a built up of charge on the sample during a scan. Therefore, the powder was spread on an aluminium plate and a 100-120 Å thick layer of gold was sputtered onto the sample using a Polaron Equipment LTD SEM Autocoating Unit E5200. Before sputtering, the chamber was evacuated and flushed with argon three times. The sputtering took place under a reduced pressure of 0.1 mbar. SEM photos were taken by a JEOL JSM840 scanning electron microscope with an electron acceleration potential of 5 kV. The electron source was a heated tungsten filament and the distance between the source and the sample was 5-6 mm.

2.7 pH meter

The pH meter used was a Mettler Delta 340 with a glass electrode. The instrument had an accuracy of ± 0.03 at room temperature. It was calibrated by a two point calibration method using buffers of pH=4 and pH=7.

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tetra-(Dimethyl Sulfoxide) Zirconium Sulphate

3.1 Introduction

Organometallic zirconium compounds have important applications in the paint industry. Zirconium octovates, for instance, are used as paint dryers. They catalyse the oxidation of unsaturated fatty acids in paints, making the paint stiff and hard. The solubility of the zirconium compound in organic solvents is a serious problem. Furthermore, the paint dryer must have appropriate catalytic properties in terms of drying time and it must be resistant to wear and tear. Therefore, the development of new zirconium compounds containing organic ligands is important to improve the quality of the paint dryer. Organometallic zirconium compounds can also be used to catalyse other organic reactions, but this is out of the scope of this study. The development of a suitable paint dryer was the main reason for the synthesis of an organometallic zirconium compound.

A new organometallic zirconium sulphate crystal is reported, containing four dimethyl sulfoxide (DMSO) ligands. The synthesis, determination of the crystallographic structure and some spectroscopic features of this compound are discussed.

The literature reports the existence of zirconium-DMSO compounds. Alcock et al [1] published an article of di- μ -fluoro-bis[bis(dimethyl sulfoxide)-trifluoro zirconium(IV)]. It is a centrosymmetric fluorine bridged dimer which crystallises in a monoclinic space group

$P2_1/n$. The crystal is built of isolated $Zr_2F_8(DMSO)_4$ units (figure 3.1) with two formula units in a unit cell.

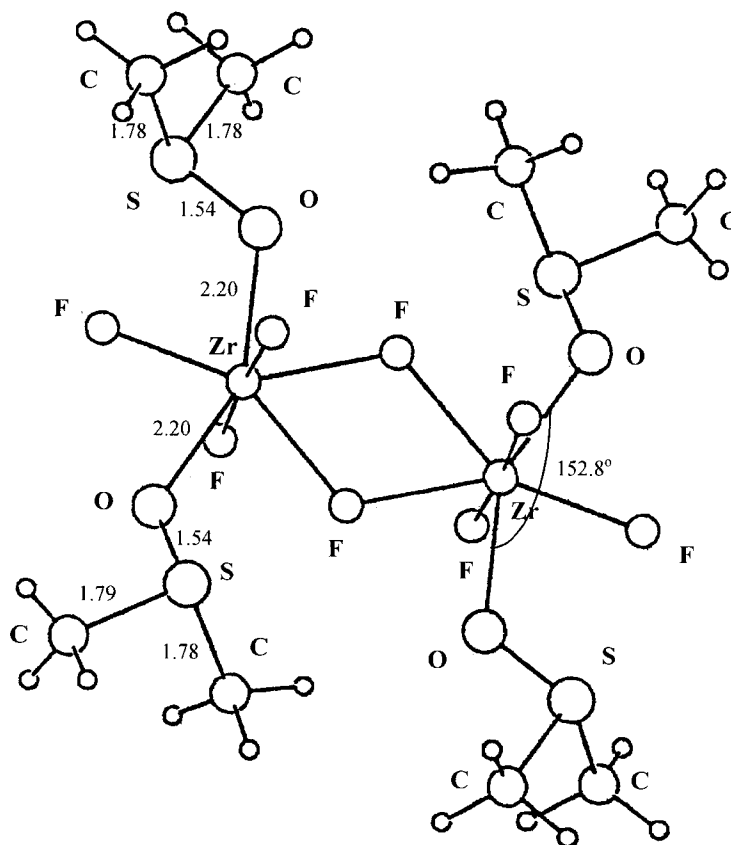


Figure 3.1 View of di- μ -fluoro-bis[bis(dimethyl sulfoxide)-trifluoro zirconium(IV)], including bond length (Å) and angle ($^\circ$).

A di aqua (dimethyl sulfoxide) tetra-fluoro zirconium dihydrate crystal ($ZrF_4(DMSO)(H_2O)_2 \cdot 2H_2O$), shown in figure 3.2, is reported by Gao et. al. [2]. It crystallises in a triclinic structure (space group $P\bar{1}$) of isolated $ZrF_4(DMSO)(H_2O)_2$ pentagonal bipyramids with two non coordinated water molecules. Both types of crystal water participate in the structure by hydrogen bond formation.

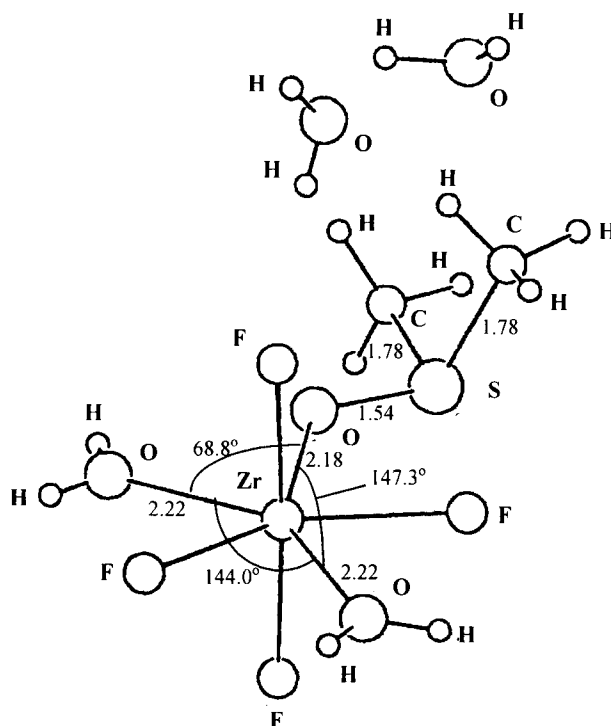


Figure 3.2 View of di aqua (dimethyl sulfoxide) tetra-fluoro zirconium dihydrate including bond length (Å) and angles (°).

Both zirconium compounds are composed of zirconium fluorides with co-ordinating DMSO ligands. A structure of $\text{Zr}(\text{PO}_4)\text{F}(\text{DMSO})$ was also found in the literature [3] but no structures having both sulphate and DMSO ligands were found.

3.2 Preparation of the Single Crystal

Single crystals were grown from a dissolved zirconium sulphate solution for a structure determination by X-ray diffraction. Zirconium sulphate was dissolved in water and ammonia was added until the Zr:NH_3 mole ratio was 1:1. DMSO was added to the solution. It remained in solution in almost all cases, but did not dissolve in a 95% DMSO solution (5% water) even after two days stirring. However, after adding water to the suspension, the zirconium complex dissolved completely and the solution became totally clear. It means that the presence of water is essential in dissolving the zirconium complex. In addition, DMSO seems to stabilise the complex in solution because the solution remained clear during the growth of single crystals. Solutions of zirconium sulphate in water began to precipitate within 24 hours. Once the complex is completely dissolved in a water/DMSO mixture, the liquid starts to evaporate. A 95% solution of DMSO has a boiling range of 188-193°C. The most volatile component in a binary liquid system should evaporate easier, but the rate of evaporation of water in a mixture is also reduced compared to pure water.

An increase in the amount of water of $\text{Zr/H}_2\text{O/DMSO}$ samples dilutes the zirconium complex in the mixture with respect to the water content. Dilution reduces the crystallisation rate but it also takes longer to reach a stage of nucleation. Table I gives several zirconium sulphate/water/DMSO ratios.

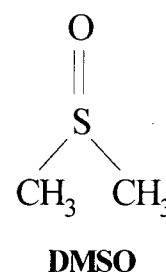
If concentrations of the zirconium solutions are too high with respect to water, a zirconium complex starts to precipitate. A $\text{H}_2\text{O:Zr}$ ratio lower than 2 causes precipitation upon cooling. All samples were set aside for 8- 10 days at room temperature or at 70-75°C (sample E) and all showed crystal formation. Sample A formed large crystals, while crystal formation was slower in samples containing more water. A large amount of DMSO was used in sample E. Evaporation of water in this sample had to be slowed down due to the elevated temperature.

Figure 3.3 shows photos of single crystals prepared by mixture A in Table I.

TABLE I Composition of several zirconium sulphate solutions in water/DMSO mixtures. Zr is the weight of $(\text{Zr}(\text{SO}_4)_2 \cdot \text{NH}_4\text{OH})$ in grams. H_2O and DMSO are expressed in volumes (ml) of water and dimethyl sulfoxide.

Sample	Zr	H_2O	DMSO	solution
A	1	2.5	6	clear
B	1	2.7	5	clear
C	1	3	7	clear
D	1	3	6	clear
E	1	3	55	clear
F	1	<2.5	6	precipitate

All single crystals and even the precipitates are soluble in water. Diluting the samples increases the pH resulting in a precipitation of zirconium hydroxide. Water is a protic solvent containing hydrogen atoms capable of forming hydrogen bonding to solvate anions. Cations are solvated through unshared electron pairs on the oxygen of water. DMSO is a dipolar aprotic solvent which does not contain acidic hydrogen making it unable to form hydrogen bonds. It has a sulfonyl group with two methyl groups attached to it. The sulfonyl group gives the compound a polar character making it miscible with pure water. DMSO can stabilise ions through dipole and induced dipole interactions by its large dipole moment (3.9D) and polarisability ($n_d^{20} = 1.478$). Pure DMSO has a cluster like structure due to this strong dipole interaction, which will break up after adding water. In the presence of weak organic acids some protonation occurs. DMSO can also dissolve ionic compounds through solvating cations by its high electron density on the oxygen of the sulfonyl group. The literature reported that the sulfonyl group mainly determines the chemical properties and that the oxygen atom is the basic centre of this group [4].



A crystal grown in a water/DMSO mixture was selected and completely sealed with glue to avoid the cracking of the crystal caused by evaporation of the liquid. A data set of the single crystal was recorded according to the procedure described in chapter 2 (section 2.1.1).

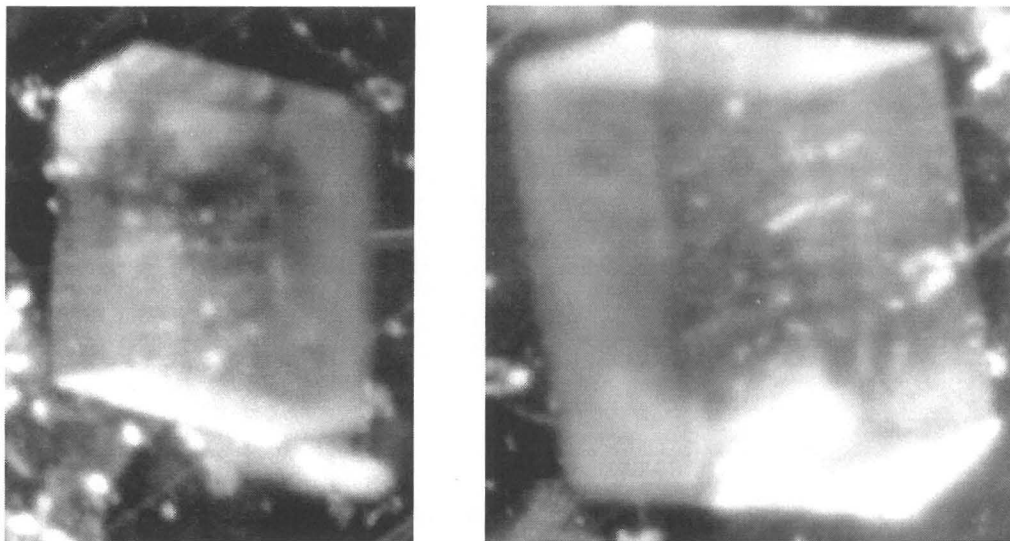


Figure 3.3 Photographs of the zirconium sulphate DMSO single crystal. Size 0.2 mm x 0.2 mm x 0.1 mm.

3.3 Structure Determination

3.3.1 Space-Group and Patterson Synthesis

The unit cell is determined by the systematical absence of certain reflections and the lowest figure of merit corresponds to a C centred monoclinic cell [5]. Table II shows the reflection conditions.

TABLE II *Reflection conditions for a monoclinic C centred unit cell containing a c glide plane.*

h,k,l	$h,0,l$	$0,k,l$	$h,k,0$	$h,0,0$	$0,k,0$	$0,0,l$
$h+k=2n$	$h,l=2n$	$k=2n$	$h+k=2n$	$h=2n$	$k=2n$	$l=2n$

The cell parameters are given in the Table III and figure 3.4 shows the C centred monoclinic cell with the relevant cell parameters.

TABLE III *Cell parameters of the crystal.*

$a = 16.1956 \text{ \AA} (18)$	$\alpha = 90^\circ$
$b = 9.7844 \text{ \AA} (14)$	$\beta = 104.243^\circ (9)$
$c = 14.6308 \text{ \AA} (18)$	$\gamma = 90^\circ$

The following reflections in a monoclinic cell with its unique axis along the b-axis are systematically absent: hkl , $h+k=2n+1$; $h0l$, $l=2n+1$. These extinctions are characteristic for space-groups $C_{2/c}$ (index No.15) and Cc (index No.9) according to the International Tables. From an asymmetric formula unit in the unit cell, it is possible to generate all the other formula units by applying the symmetry operators.

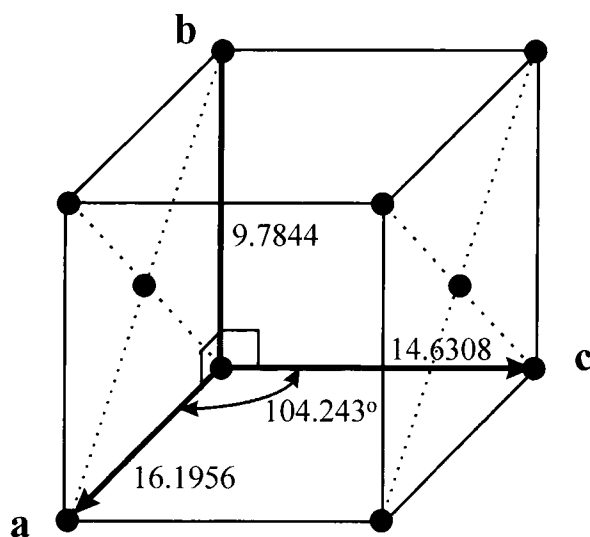


Figure 3.4 Monoclinic C centred cell of the zirconium crystal.

Once the cell parameters are known it is possible to calculate the cell volume; $V=2247\text{\AA}^3$. For a certain composition of a compound, the number of formula units per unit cell can be estimated. As a rule of thumb for organometallic compounds, the volume of each non-hydrogen atom can be taken to be between $18\text{\AA}^3$ and $20\text{\AA}^3$. $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ has 27 non-hydrogen atoms giving an occupation of $Z=2247/(27\cdot 20)\approx 4$ units per unit cell if the volume of a non-hydrogen atom is taken as $20\text{\AA}^3$. Starting with $C_{2/c}$ space-group, 8 general positions are present in the unit cell, meaning that the unit cell contains a half-asymmetric formula unit. Therefore internal symmetry like a two-fold rotation axis or a centre of symmetry is required to generate the other half and consequently, the zirconium atom must be placed on a symmetry position. In that case, the zirconium atom is located at one of the five special positions (Wyckoff symbol a-e).

Table IV shows the possible interatomic vectors (u, v, w) in the Patterson space. Real space co-ordinates in the first row are subtracted from the real space co-ordinates in the first column to obtain the Patterson co-ordinates.

TABLE IV Possible interatomic vectors (u,v,w) in a C_{2c} space-group.

Real space	x, y, z	$\bar{x}, y, \frac{1}{2}-z$	$\bar{x}, \bar{y}, \bar{z}$	$x, \bar{y}, \frac{1}{2}+z$
x, y, z	0, 0, 0	$2x, 0, \frac{1}{2}+2z$	$2x, 2y, 2z$	$0, 2y, \frac{1}{2}$
$\bar{x}, y, \frac{1}{2}-z$	$-2x, 0, \frac{1}{2}-2z$	0, 0, 0	$0, 2y, \frac{1}{2}$	$-2x, 2y, -2z$
$\bar{x}, \bar{y}, \bar{z}$	$-2x, -2y, -2z$	$0, -2y, \frac{1}{2}$	0, 0, 0	$-2x, 0, \frac{1}{2}-2z$
$x, \bar{y}, \frac{1}{2}+z$	$0, -2y, \frac{1}{2}$	$2x, -2y, 2z$	$2x, 0, \frac{1}{2}+2z$	0, 0, 0

$C_{2/m}$ is the symmetry of the Patterson function for a monoclinic cell according to the International Tables for crystallography and this symmetry can be traced from the Table. In this symmetry the following relations exist: $I(u, v, w) = I(u, \bar{v}, w) = I(\bar{u}, v, \bar{w}) = I(\bar{u}, \bar{v}, \bar{w})$; I being the intensity of the peaks in the Patterson space. A Patterson function is calculated with space-group symmetry $C_{2/m}$ and the reduced intensities, i.e. $F^2(hkl)$. The 20 strongest peaks in the Patterson space are listed in Table V.

Table V Interatomic vectors in Patterson space for a C_{2c} space-group in a descending order of peak intensity.

	X	Y	Z	Intensity
1	0	0	0	999
2	0	0.6348	0.5	295
3	0.9405	0	0.2046	289
4	0.1723	0.1946	0.0266	157
5	0.0563	0.3697	0.2947	152
6	0.3267	0.0582	0.4739	146
7	0.8646	0.8264	0.4204	131
8	0.1363	0.1912	0.0797	129
9	0.4091	0	0.4397	83
10	0	0	0.5	67
11	0.0362	0.3691	0.4531	61
12	0.8019	0.8924	0.1001	60
13	0.771	0.8107	0.1785	58
14	0.1131	0.1876	0.2312	53

15	0.9672	0	0.0532	53
16	0.8859	0	0.4169	52
17	0	0.2496	0.5	52
18	0.8067	0.7967	0.1323	52
19	0.0773	0.1984	0.2842	49
20	0.2301	0.4377	0.3215	49

The heavy atom method is used to locate the zirconium atom by identifying interatomic vectors for the zirconium atoms (with a high intensity) in the Patterson space. It is verified whether the peaks observed in the Patterson peak summation (Table V) can be fitted to the possible vectors in Table IV. The peak with the second highest intensity in the Patterson summation is most likely to originate from Zr-Zr interatomic vectors. If the zirconium atom is located at the 4a or 4b position (Wyckoff symbol) then the Patterson peak at co-ordinate $(0, 0, \frac{1}{2})$ should be intense. In fact there is no peak with this co-ordinate and therefore the position of the zirconium atom is not in a 4a or a 4b site. The interatomic vectors for a 4c and a 4d site are $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$ respectively, which are both absent in the first twenty peaks. The latter is present as number 37 in the list (not shown) having an intensity of only 34 with respect to an intensity of 1000 at the origin. Based on the low intensity, it is not likely that the zirconium atom is located in a 4d site. It can now be concluded that the site of the zirconium atom does not have a centre of inversion. The remaining position is a 4e site with an interatomic vector of $(0, v, \frac{1}{2})$ which is in accordance with $(0, 0.6348, \frac{1}{2})$; peak number 2 in Table V. Since $v=2y=0.6348$; $y=0.3174$ or $v=1.6348$ and $y=0.8174$. Another possible interatomic vector is $(u, 0, w)$ corresponding to peak number 3 in Table V with co-ordinate $(0.9405, 0, 0.2046)$. From these co-ordinates, x and z can be calculated i.e. $u=2x=0.9405$; $x=0.4703$ and $w=0.2046$ or $1.2046=\frac{1}{2}+2z$; $z=0.3523$. Now that the zirconium co-ordinate is known, it is possible to determine a co-ordinate in the Patterson space to test the validity of the procedure. Real space co-ordinate $(0.4703, 0.3174, 0.3523)$ can be transformed to a co-ordinate $(2x, 2y, 2z)$ in Patterson space and the new Patterson co-ordinate is $(0.9405, 0.6348, 0.7046)$. Applying a similarity transformation to this co-ordinate results in an indistinguishable co-ordinate $(0.0595, 0.3652, 0.2954)$, which is in agreement with peak number 5 in Table V.

Accepting $C_{2/c}$ as the correct space-group, it is possible to calculate a Fourier summation and a difference Fourier summation to find the atom positions of the lighter atoms and to assign the types of elements. Positions were refined by the non-linear least-squares refinement lowering the disagreement factor of residual to 0.18.

A subsequent addition of more atoms to electron density peaks is followed by isotropic refinement. In the final step atoms were anisotropically refined and hydrogen atoms were added to the structure. By inspecting the structure, it became clear that certain carbon atoms bonded to sulphur must be replaced by oxygen. If the types of atoms were wrong, it would be visible in the atomic displacement factor. For instance, if a sulphur atom, with 16 electrons, is swapped by oxygen, with 8 electrons, the atomic displacement factor will decrease due to a shortage of electrons. In order to match the 16-electron system, the 8-electron model will sharpen its position by decreasing its atomic displacement factor. A condition for peak sharpening is that $\int_{\text{cell}} \rho_i(\mathbf{r}) d\mathbf{r}$ (ρ is electron density) for atom i remains the same.

The replacement was supported by the geometry of the relevant ligand and on the infrared spectrum showing the presence of S-O bonding originating from sulphate groups. The remaining peaks after a calculation of the Fourier difference were small. Atomic displacement factors were again isotropically refined and the disagreement factor of residual converged to a value of 0.0581.

All carbon atoms in DMSO have large atomic displacement ellipsoids. Atomic displacement factors for carbon are generally large and SHELXL-97 even warned that the position could be split. The ellipsoids increase with an increasing distance from the zirconium atom. For molecules this is not uncommon, but compact structures like this should not have such large atomic displacements and some scepticism about the assignment or space-group is in place. Disorder could cause large atomic displacement ellipsoids but the symmetry could also be too high. The latter forces a two folded rotation axis determining the remaining atom positions in the asymmetric unit. Atoms generated by this symmetry element are superpositioned on the electron density map and if this symmetry element is absent, large atomic displacement factors are necessary to match the measured electron density with atomic positions in the structure. For these reasons the space-group is changed to Cc and the

structure is further refined. Space-group Cc differs from $C_{2/c}$ as the latter contains a two-fold rotation axis on basis vector **b**. After the final refinement, the disagreement factor of residual was 0.0474.

The question is whether the change in space-group from $C_{2/c}$ to Cc was actually warranted, and a statistical procedure to determine the significance of the change was required [6]. Weighted residual factors (R_w) were used to evaluate the space-groups on their statistical significance.

$$R_w = \left[\frac{\sum_{i=1}^n \sigma_i^{-2} (F_i^{\text{obs}} - F_i^{\text{calc}})^2}{\sum_{i=1}^n \sigma_i^{-2} (F_i^{\text{obs}})^2} \right]^{1/2} \quad [3.1]$$

σ_i is the experimental standard deviation of observation F_i and the square inverse the weighed factor. F_i does not necessarily have to be structure factors, but can be any experimental parameter. For the optimum value of R_w the following conditions must be valid:

$$\frac{\delta R_w}{\delta p_j} = 0 \text{ for } j=1 \text{ to all parameters and}$$

$$\frac{\delta^2 R_w}{\delta p_j^2} > 0 \text{ to ensure } R_w \text{ has a minimum value.}$$

R_w is usually calculated using the non-linear least-squares method. SHELXL-97 calculates R_w and also gives the corresponding numbers of the parameters and the reflections. To determine whether R_w of space-group $C_{2/c}$ is significantly larger compared to R_w of Cc , a ratio **R** is defined.

$$R = \frac{R_w(C_{2/c})}{R_w(Cc)} \quad [3.2]$$

Ratio R is compared with a tabulated value R_α at a given level of significance α . If R is larger than R_α then the probability is less than α (or $\alpha \cdot 100\%$) that the $C_{2/c}$ space-group is rejected while it is actually $C_{2/c}$.

R is calculated based on the information of SHELXL-97 for the space-groups $C_{2/c}$ and Cc after anisotropical refinement including hydrogen atoms (Table VI). It has a value of 1.164.

Table VI Data produced by SHELXL-97 for the statistical significance test.
 R_w is the weighed residual, n is the number of parameters,
 $n(F_i)$ the number reflections used.

	$C_{2/c}$	Cc
R_w	0.1320	0.1134
n	128	250
$n(F_i)$	3272	3390

The dimension of the test is 122 and the degree of freedom is 3140. The difference in the number of reflections between space-groups $C_{2/c}$ and Cc is very small and has no impact on the test. In fact, for $C_{2/c}$, $m-n_1$ equals 3144 and for Cc , $m-n_2$ is 3140. In the Table for the test of significance with $\alpha=0.005$, the dimension lies very close to the tabulated value of 120. As far as the reflections are concerned, $m-n_2$ is close to 3000 observations. Interpolation formulas to calculate R_α for the dimension and observations are available, but in this case not necessary. R_α for 3000 observations and 120 degrees of freedom is 1.0271, which is smaller than R . Increasing the number of observations only reduces R_α . The tabulated value for 200 degrees of freedom is 1.0394 which is still smaller than R . This test proves that $Zr(SO_4)_2(DMSO)_4$ crystallises in a Cc space-group instead of a $C_{2/c}$ space-group with a certainty of more than 99.5%.

3.3.2 Discussion of the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ Structure

The structure of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ is shown in figure 3.5. Two sulphate groups (S1 and S2) are bonded as bidentate ligands co-ordinated to zirconium through oxygen as was anticipated. Both sulphate ligands in the figure direct backwards while two DMSO ligands (S3 and S4) point forward. The remaining two DMSO ligands are located at the left (S5) and the right (S6) of the zirconium. The pseudo C_2 axis can also be located perpendicular to the figure, slightly bent to the right. If this symmetry element were present, it would rotate $\text{S1} \rightarrow \text{S2}$, $\text{S3} \rightarrow \text{S4}$ and $\text{S5} \rightarrow \text{S6}$.

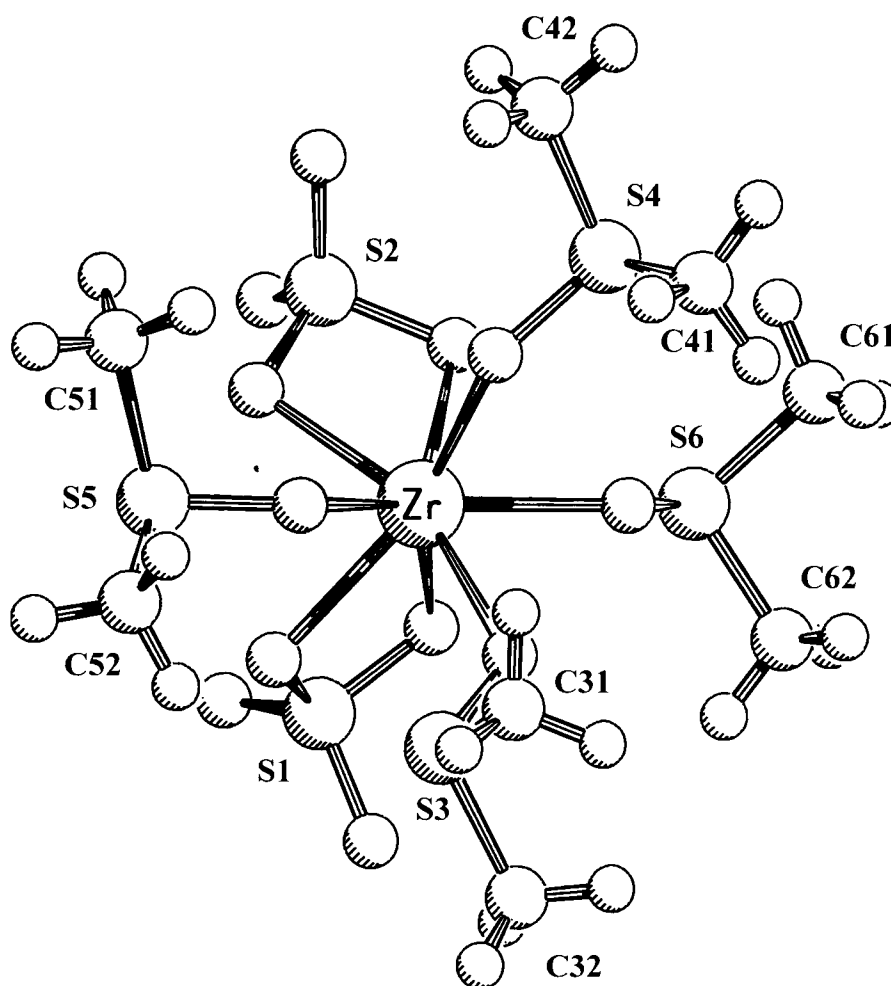


Figure 3.5 View of the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ molecule showing the labelling of Zr, O and C atoms.

In figure 3.5, atoms are represented by spheres and placed on the electron density map. A better representation of atomic positions would be obtained when atomic displacement factors are put into the structure. Atoms are now illustrated in figure 3.6 by ellipsoids, their sizes and shapes depending on the atomic displacement factors.

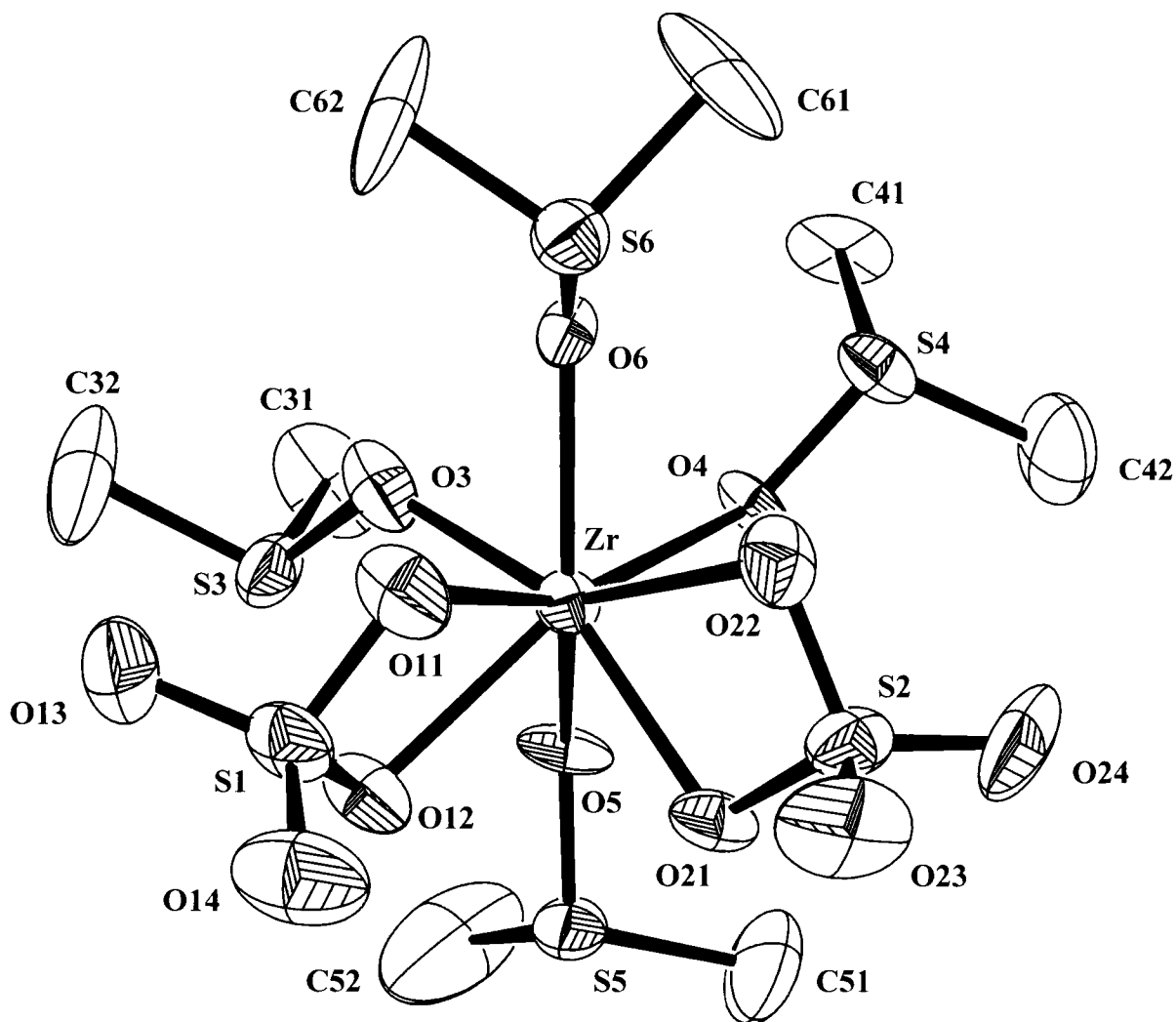


Figure 3.6 View of the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ molecule including atomic displacement factors showing non-H atoms and their labelling.

Although the space-group has been changed from $C_{2/c}$ to Cc , carbon atoms C32, C61 and C62 still display large atomic displacement ellipsoids, but the disagreement factor of residual is low enough to accept the proposed structure ($<5\%$).

At this stage, matrix calculations are introduced to obtain more insight in the orientation of the oxygen ligands with respect to the zirconium atom. Fractional co-ordinates of the first oxygen co-ordination shell around zirconium in a monoclinic lattice (x',y',z') are transformed to real space co-ordinates (x,y,z) in Å in a fixed orthogonal co-ordinate system:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & \cos(\beta) \\ 0 & 1 & 0 \\ 0 & 0 & \sin(\beta) \end{pmatrix} \cdot \begin{pmatrix} x' \cdot a \\ y' \cdot b \\ z' \cdot c \end{pmatrix} \quad [3.3]$$

β is the angle between vector **a** and **c** in the monoclinic cell and a, b, c are the cell lengths of the unit cell. Table VII shows the results of this co-ordinate transformation where the presence of the pseudo C_2 axis can easily be seen. Upon such a two-fold rotation; x changed to -x and z to -z leaving y unchanged and consequently O11→O21, O12→O22, O3→O4 and O5→O6.

TABLE VII Co-ordinates of the oxygen ligands in Å around zirconium in a fixed orthogonal co-ordination system.

Atom	x	y	z
Zr	0.00	0.00	0.00
O11	-0.55	1.41	-1.58
O21	0.47	1.43	1.53
O12	-1.95	1.04	0.18
O22	1.98	1.06	-0.16
O3	-1.30	-1.53	-0.86
O4	1.28	-1.51	0.85
O5	-1.03	-0.83	1.78
O6	1.00	-0.87	-1.74

Taking a closer look at the immediate surroundings of the zirconium atom, it can be seen that zirconium is co-ordinated by eight oxygen atoms in rather an unusual way (figure 3.7). The structure can be described by two distorted pyramids, sharing a base edge under an angle of $30.15^\circ (\pm 4)$. The odd co-ordination is probably due to steric hindrance of the large DMSO ligands. An advantage of co-ordinate transformation is the possibility for easy vector

calculation to describe the oxygen configuration. Figure 3.7 suggests a flat base of each pyramid, which is actually not the case. The angle between the normals of the planes constituted by O12-O21-O4 and O12-O3-O4 is $8.61^\circ (\pm 4)$ and not 0° in the case of a plane. Likewise, the angle between the normals of the planes O11-O22-O4 and O11-O3-O4 is $9.15^\circ (\pm 4)$ showing the distortion of the structure.

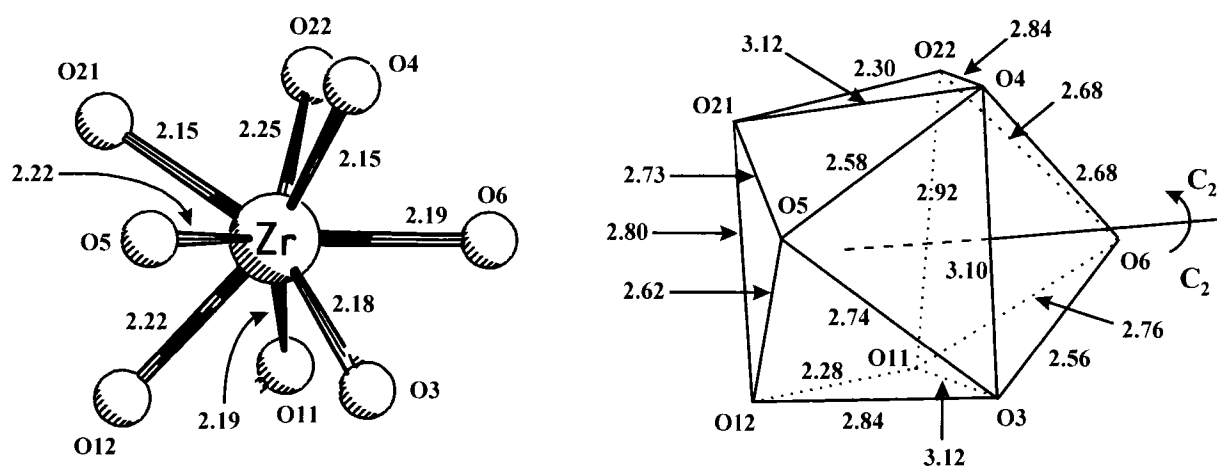


Figure 3.7 Co-ordination of zirconium by oxygen, showing its corresponding oxygen configuration including distances in Å and the pseudo C_2 axis.

By comparing Zr-O distances and co-ordination configurations of the first oxygen shell with the literature values of zirconium sulphates, it can be concluded that no extreme deviations are present. Distances and co-ordination compare quite well confirming the existence and stability of the structure. Zr-O distances vary from 2.15Å to 2.25Å which is in the range of the zirconium sulphates reported earlier. Although the distances between oxygen in the co-ordination configuration compare to other zirconium sulphate polyhedra, the shape of the polyhedra is unique. Bipyramidal structures are common, also in zirconium sulphates. $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ has a pentagonal bipyramidal structure sharing a common base while the oxygen co-ordination of zirconium in $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ has a bipyramidal structure with a split base.

Figure 3.8 shows the structure in an orthogonal co-ordination system projected along the y-axis. Transformation of the y-co-ordinates is only a multiplication of the y-co-ordinate by

cell length b of the unit cell (eq.3.3) and therefore the y -axis is parallel to basis vector b . The figure is a map with the height of each atom printed next to its location. In this view, both sulphate groups lie above the x,z plane at $y=0$ while the DMSO ligands point downwards.

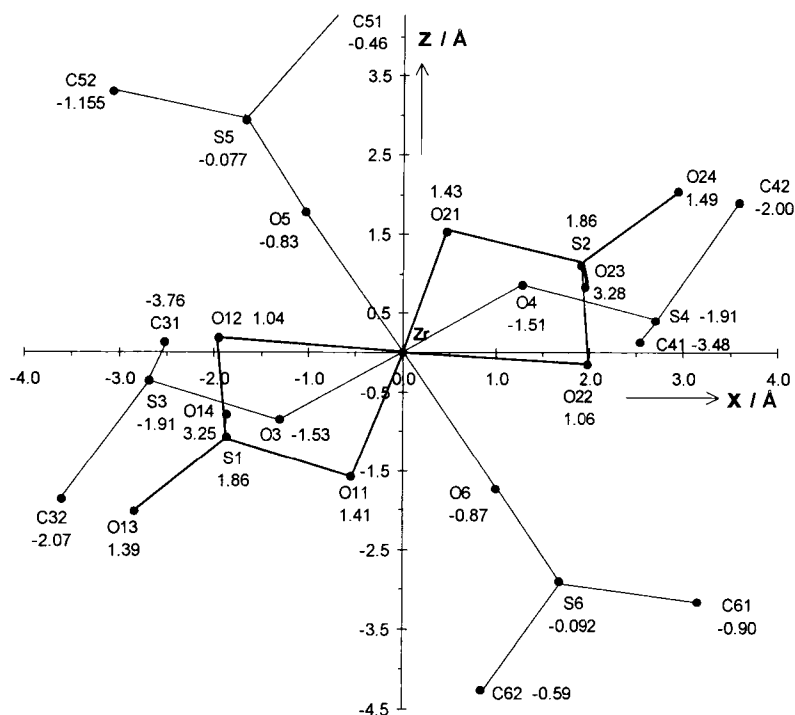


Figure 3.8 Co-ordinates of $Zr(SO_4)_2(DMSO)_4$ in an orthogonal co-ordinate system in a projection along the y -axis. y -co-ordinates are printed next to the atom positions in the (x,z) plane.

Bonding distances are shown in figure 3.9 and the exact (x,y,z) co-ordinates of the atoms can be found in Appendix A (Table A1). Distances within the sulphate groups are in agreement with those found in zirconium sulphates. Terminal oxygens have S-O distances ranging from $1.42\text{\AA}$ to $1.45\text{\AA}$ which is in accordance with distances in other zirconium sulphate structures. S-O distances of bridging oxygen in the sulphate groups are somewhat larger than in terminal oxygen, also showing a larger deviation due to the interaction with zirconium and steric hindrance with DMSO ligands. Once again, these distances are in line with those found in the literature. The S=O distances are $1.51\text{\AA}$ for S3-O3 and S5-O5 while they are $1.55\text{\AA}$ for S4-O4 and S6-O6, the latter comparing well with the S=O distance of $1.56\text{\AA}$ in $Zr_2F_8(DMSO)_4$.

The variation in C-S distances ranging from 1.67Å to 1.83Å is remarkable. In other zirconium-DMSO structures the distance is 1.71Å to 1.79Å [3]. This large variation was anticipated by the inspection of the large atomic displacement factors of the methyl groups (figure 3.6).

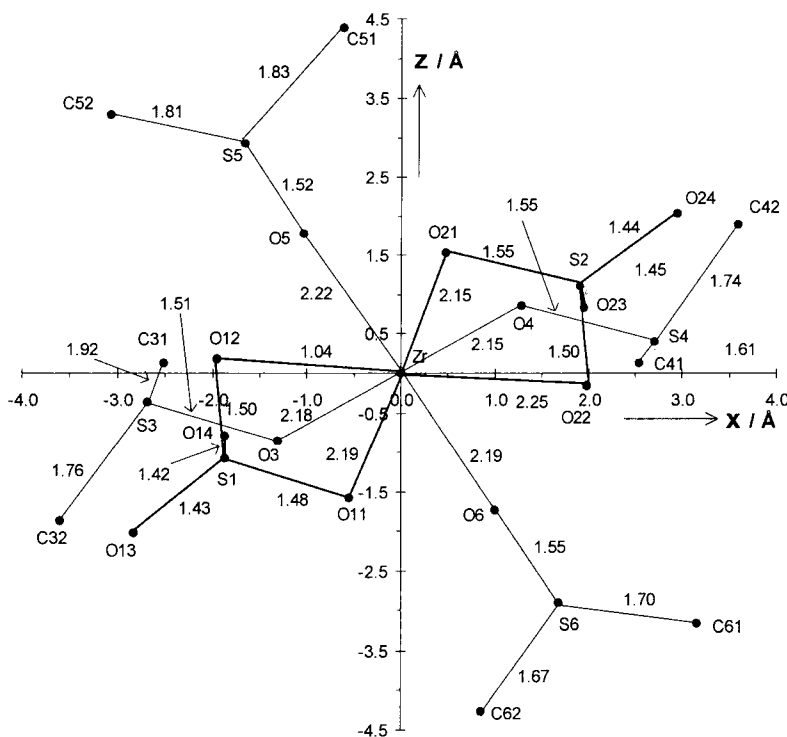


Figure 3.9 Bond distances of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ in an orthogonal co-ordinate system in a projection along the y-axis.

Interatomic angles are shown in figure 3.10. Bond angles in the sulphate group deviate from the ideal tetrahedron. Angles of O11-S1-O12 and O21-S2-O22 are 99.82° and 97.62° respectively, which are lower than the angle of 109.5° in a perfect tetrahedron. An eight-fold co-ordination of zirconium, accommodated by two sulphate ions and four DMSO ligands, puts a restriction on the oxygen configuration. Sulphate must act as a bidentate ligand decreasing the bidentate angle in order to match the zirconium co-ordination. Such a distortion is often accompanied by a change of S-O bond distances and angles to minimise the configurational energy caused by strain and steric hindrance, which is also the case. The

bidentate angles are lower than those found in α - $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (107°), γ - $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (106°), $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$ (103°) and the α - and β -forms of $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$ (101° and 100° respectively). All these structures and also α - $\text{Zr}(\text{SO}_4)_2$ have further bridging sulphate groups connecting different zirconium atoms. In this way zirconium dimers are formed with O-S-O angles closer to 109.5° releasing strain on the sulphate groups. $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ does not form dimers and maintains this extra strain on the sulphate ligands.

DMSO ligands are almost maximally separated from each other with interatomic angles ranging from 71.5° to 77.1° . Zr-O-S (126.5° - 128.0°), O-S-C (102.0° - 104.6°) and C-S-C (98.3° - 100.2°) angles are very well in line with Zr-O-S (126.1° - 129.0°), O-S-C (103.0° - 105.5°) and C-S-C (97.3° - 99.9°) angles found in $\text{Zr}_2\text{F}_8(\text{DMSO})_4$.

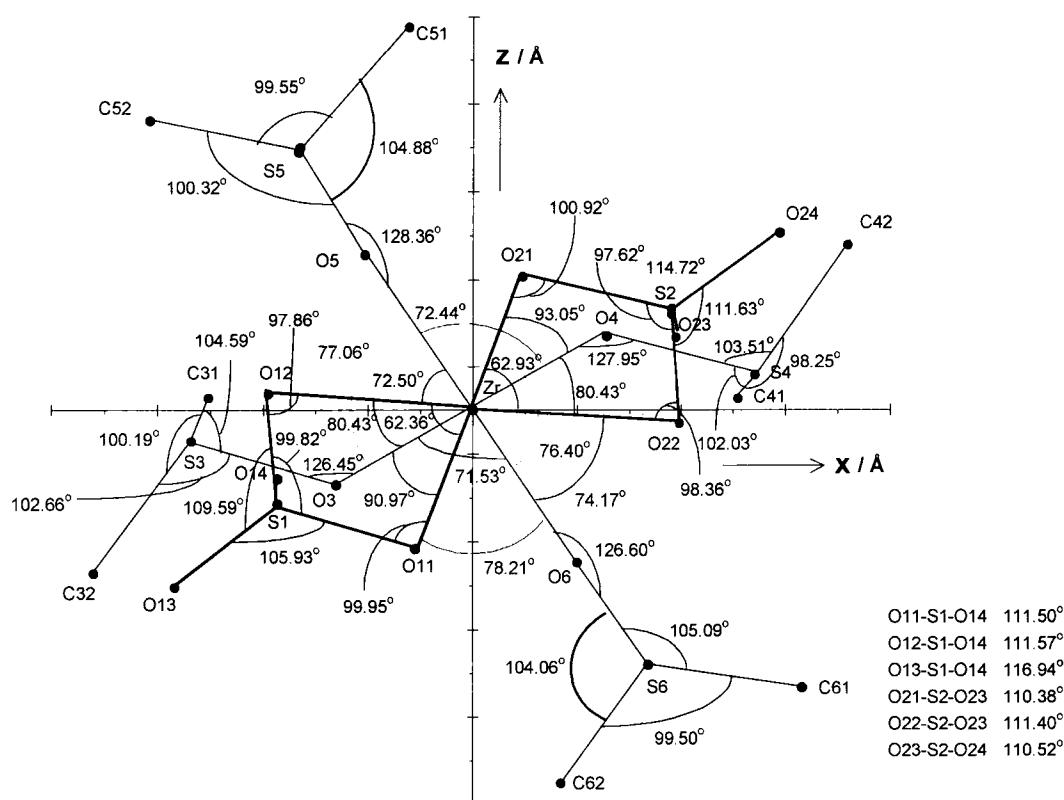


Figure 3.10 Bond angles of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ in an orthogonal co-ordinate system in a projection along the y-axis.

Figures 3.9 and 3.10 confirm the actual absence of the C_2 axis by the large differences in bond lengths and angles between pairs of bonds and angles, which transform into each other by a twofold rotation. Although the pseudo symmetry is clear from these figures, discrepancies in co-ordinates between pairs of symmetry related atoms are too large to accept a $C_{2/c}$ space-group.

The packing of formula units in the cell differs considerably with those in the literature. Hydrated zirconium sulphates forms layers connected by hydrogen bonding, but $Zr(SO_4)_2(DMSO)_4$ in a crystal could be considered as a packing of individual formula units without any direct bonding between them (figure 3.11). A $Zr_2F_8(DMSO)_4$ crystal is also built from isolated formula units, but a $ZrF_4(DMSO)(H_2O)_2 \cdot 2H_2O$ crystal shows hydrogen bonding.

Two $Zr(SO_4)_2(DMSO)_4$ structures could clearly be seen in the middle of the unit cell in figure 3.11 with the two sulphate groups sideways. The c glide plane is also visible by taking the mirror image of the upper structure in the middle of the unit cell, followed by a translation over half a translation unit in the c direction. In this way the lower structure in the middle of the unit cell is obtained.

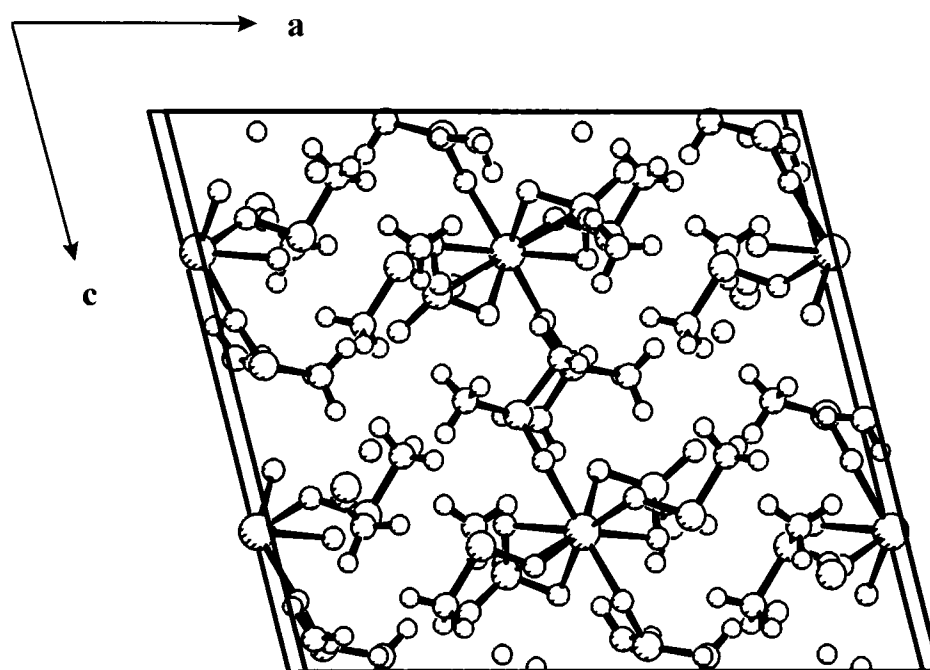


Figure 3.11 The monoclinic unit cell of $Zr(SO_4)_2(DMSO)_4$ in a projection along the b vector.

Crystal data of $\text{Zr}_2\text{F}_8(\text{DMSO})_4$, $\text{ZrF}_4(\text{DMSO})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ are given in Table VIII to compare the unit cell parameters of these structures.

TABLE VIII Crystal data for various zirconium-DMSO compounds.

$\text{Zr}_2\text{F}_8(\text{DMSO})_4$ Monoclinic $Z=2$ $V=1087 \text{ \AA}^3$	$\text{ZrF}_4(\text{DMSO})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ Triclinic $Z=2$ $V=536 \text{ \AA}^3$	$\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ Monoclinic $Z=4$ $V=2247 \text{ \AA}^3$
$a = 8.831 \text{ \AA}$ $\alpha = 90$	$a = 7.357 \text{ \AA}$ $\alpha = 99.95$	$a = 16.1956 \text{ \AA}$ $\alpha = 90$
$b = 11.955 \text{ \AA}$ $\beta = 108.12$	$b = 8.318 \text{ \AA}$ $\beta = 98.76$	$b = 9.7844 \text{ \AA}$ $\beta = 104.24$
$c = 10.834 \text{ \AA}$ $\gamma = 90$	$c = 9.627 \text{ \AA}$ $\gamma = 9108.61$	$c = 14.6308 \text{ \AA}$ $\gamma = 90$

Although it is difficult to compare zirconium fluoride with sulphate structures, it can be concluded that cell parameters differ considerably. Counting the number of non-hydrogen atoms, estimated cell volumes of $1040 \text{ \AA}^3$ and $2160 \text{ \AA}^3$ for $\text{Zr}_2\text{F}_8(\text{DMSO})_4$ and $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ respectively are calculated, which correspond to the cell volumes in Table VIII. Cell expansion is due to the larger number of non-hydrogen atoms in the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ unit cell with respect to $\text{Zr}_2\text{F}_8(\text{DMSO})_4$.

Zirconia-DMSO compounds are limited in number but these show crystal structures in which DMSO is co-ordinating zirconium in a variety of ways.

An XRD powder pattern can be calculated from the single crystal data. In practice, calculating an XRD powder pattern is complicated because additional parameters like peak-width at half maximum, must be taken into account. The mathematical procedure is based on a Rietveld refinement, which is out of the scope of this book due to its complexity. However, computer programs are available on the market and a program called DBWS 9411 is used to generate the XRD data. It basically calculates the pattern from the atom positions in the unit cell. Hydrogen is excluded for simplicity and therefore the structure contains 27 atoms with $Z=4$. Besides the co-ordinates, a background count of 200 is used and the scale factor is set to 0.02. The wavelengths of the radiation are $\text{Cu K}\alpha_1=1.54051 \text{ \AA}$ and $\text{Cu K}\alpha_2=1.54433 \text{ \AA}$.

1200 reflections are calculated to generate the pattern with 2θ ranging from 3° to 65° in steps of 0.05° . Figure 3.12 shows the calculated pattern and the experimental pattern of powdered single crystals (see also figure A1 and Table A2 in Appendix A). Although the intensities differ, calculated peak positions occur on the measured pattern. Powdered single crystals might still have some preferred orientations in contrast with its precipitated analogue, leading to different intensities. A close inspection reveals some additional peaks in the measured spectrum at $2\theta = 14.1^\circ$, 27.1° , 55.3° and a shoulder at 9.9° indicating the presence of another phase. Fortunately they have a minimal intensity and it can be concluded that the structure of the measured single crystal represents the general structure of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$.

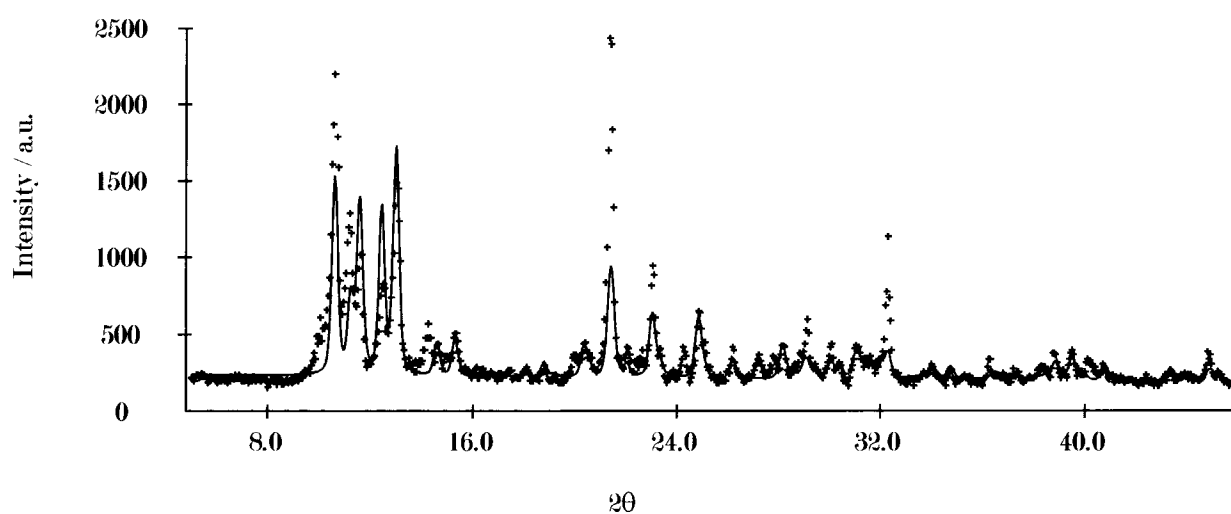


Figure 3.12 An XRD pattern of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$, a) powdered single crystal measured (+)
 b) calculated from the single crystal structure (solid line).

3.4 Thermal Analysis and Spectroscopy

Figure 3.13 shows a TGA/DSC curve of the zirconium compound revealing a decomposition of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ in roughly four steps. The TGA curve shows a small mass loss below 100°C , indicating the release of crystal water. No further mass loss is observed up to 170°C shown by the plateau in the figure. At 200°C , two DMSO ligands are released, followed by the release of the remaining DMSO ligands at 370°C . Liberation of the first type of DMSO ligands is just above the boiling temperature of a 95% DMSO solution. Since the mass loss corresponds to two ligands per zirconium atom, it is believed that the DMSO ligands dissociate from the zirconium atom as a whole, without leaving any remains. The temperature range of the decomposition of the second type of DMSO is wider compared to the range of the first DMSO type indicating rearrangement of the structure during decomposition. The decomposition of the second type of DMSO ligands overlaps with the decomposition of zirconium sulphate to zirconia which is completed at 800°C . The TGA curve shows some interesting features related to the symmetry of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$. As stated before, the oxygen in DMSO is the basic centre of the ligand while zirconium is a Lewis acid. A bonding between the two species could be interpreted as an acid-base reaction with a certain bonding strength. The structure has a pseudo internal C_2 axis, giving rise to two types of DMSO ligands making the two ligands in each type almost identical. Therefore, the two ligands in a pair are expected to decompose at the same temperature, but decomposition temperatures of both types differ, reflecting the different bond strengths between the zirconium atom and the oxygen of the DMSO pairs. Bond strengths could not explain the differences in the bond lengths observed. Zr-O3 and Zr-O4 bond lengths are $2.18\text{\AA}$ and $2.15\text{\AA}$ respectively while the Zr-O5 and Zr-O6 distances are $2.22\text{\AA}$ and $2.19\text{\AA}$. In general the former type is shorter than the latter, but the difference between Zr-O4 and Zr-O6 is very small compared to the variation in distances in each type. Release of the DMSO ligands can not entirely be explained in terms of Zr-O bond lengths. Stability of the ligand in the crystal must also play a role.

The BET surface of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ was too small to be measured, but after calcination to zirconia, the surface was $60\text{ m}^2\cdot\text{g}^{-1}$. Organic ligands and sulphate were burnt off, increasing

the surface of the powder considerably. The surface of a zirconia particle prepared by calcining $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ is shown in figure 3.14. The particle shows many, brain like, grooves, which could have potential for catalytic applications.

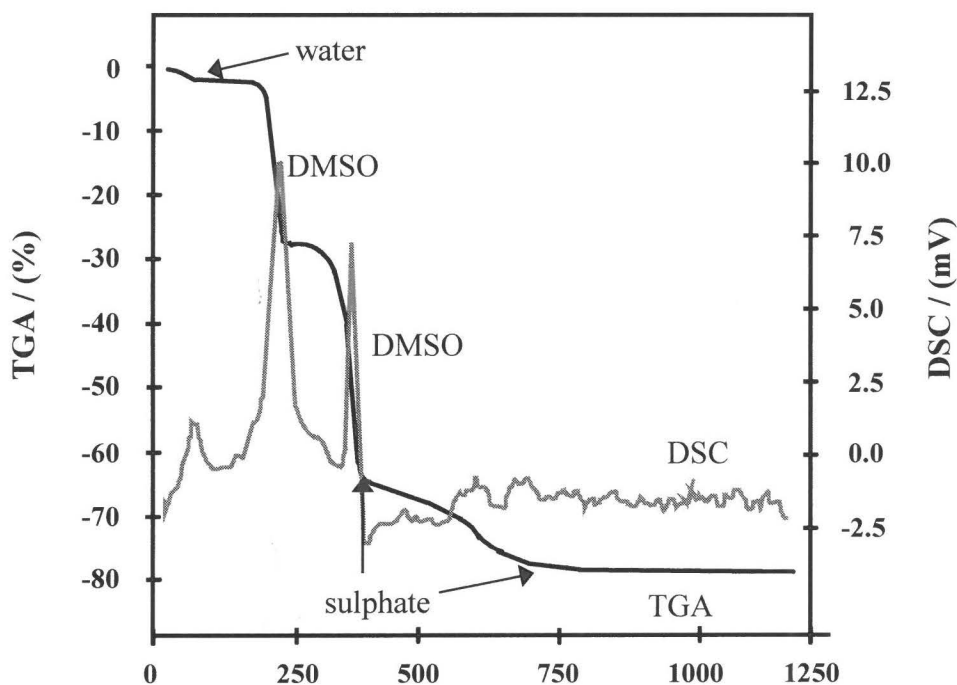


Figure 3.13 TGA (black) and DSC (grey) curves of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$. Scan rate $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

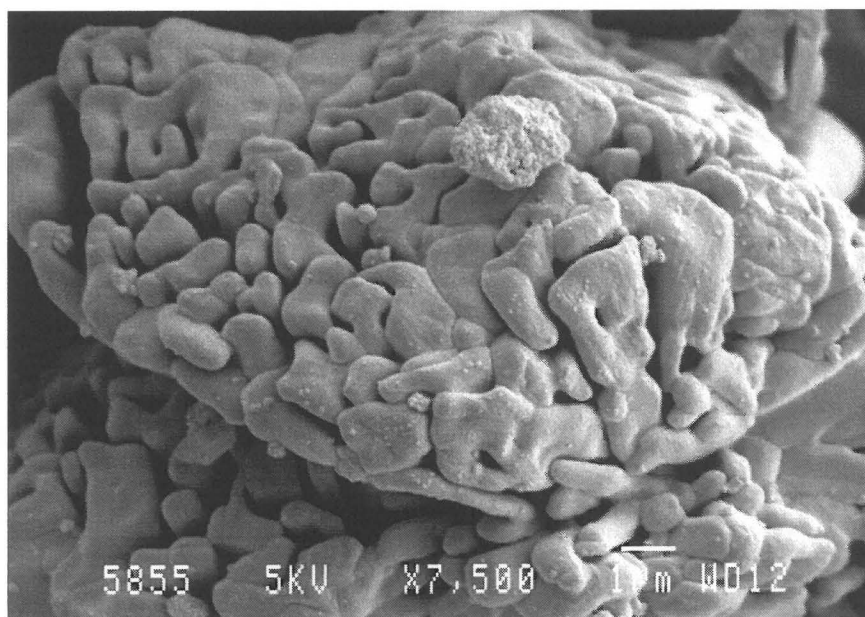


Figure 3.14 SEM photo of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ after calcining at $800\text{ }^\circ\text{C}$ for 2.5 hours. Magnification 7,500x.

Infrared and Raman spectra were recorded prior to the structure determination to verify the presence of certain groups in the structure. An infrared spectrum of different $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ powders are shown in figure 3.15. Spectrum A is the spectrum of a single crystal, grown in a water/DMSO medium and ground until a powder was obtained. In spectrum B the powder was obtained by recrystallization of the product in water (3 times). Spectrum C is a spectrum of the zirconium compound precipitated in a water/DMSO mixture by evaporating water from the mixture followed by heating at 80°C for three hours. All the spectra are similar except that water bands at 1635 cm^{-1} , 3480 cm^{-1} and 3564 cm^{-1} are absent in the precipitated powder due to the evaporation of water. This water is not crystalline because it is not visible in the XRD pattern and it is weakly bonded to the zirconium crystal. The release of water does not change the crystal structure and is in accordance with the TGA curve. The sulphate bands sharpen upon dehydration because water, which is apparently hydrogen bonded to sulphate, tends to broaden the sulphate bands.

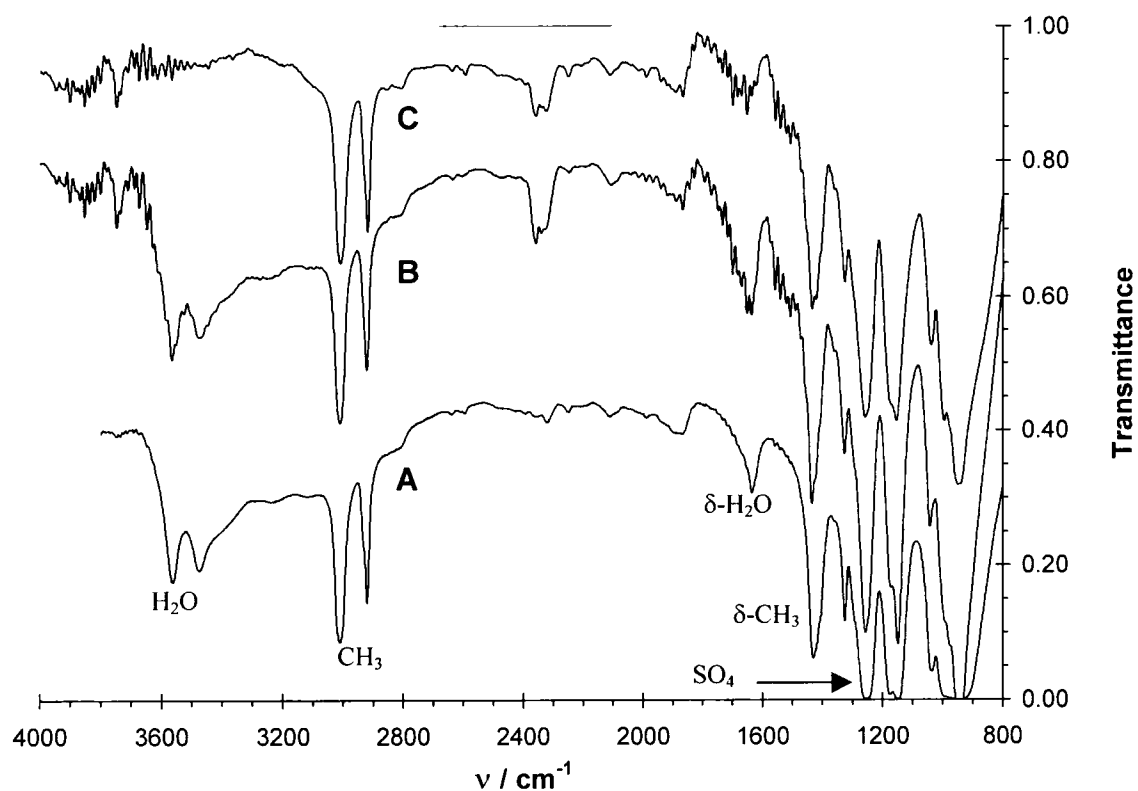


Figure 3.15 Infrared spectrum of a powdered $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ single crystal in (A) a water/DMSO mixture, (B) a powder precipitated from water and (B) a powder precipitated from a water/DMSO mixture and heated at 80°C for three hours. See appendix A (Table A3) for exact band positions.

$\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ is soluble in water and could be hydrolysed. Therefore, the compound had been recrystallised from water three times before an infrared spectrum was recorded. It is clear that the methyl bands in DMSO at 2920 cm^{-1} and 3009 cm^{-1} remain, indicating that no hydrolysis occurs on dissolution. The sulphate bands are also identical to those in $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$. Figure 3.16 displays the infrared spectrum of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ at lower wavenumbers showing well resolved bands.

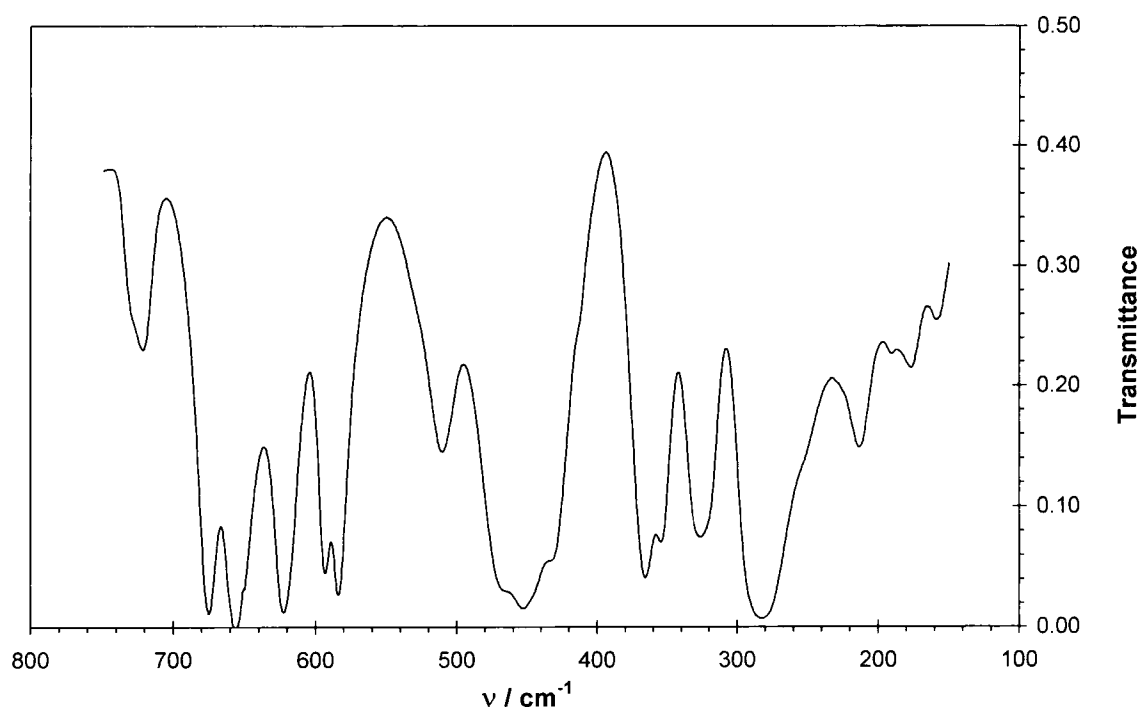


Figure 3.16 Infrared spectrum of a powdered single $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ crystal pressed in a polyethene pellet ($50\text{-}400\text{ cm}^{-1}$) and in a KBr pellet ($400\text{-}800\text{ cm}^{-1}$). See appendix A (Table A3) for exact band positions.

The Raman spectra of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ and DMSO are shown in figure 3.17. The Raman spectra of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ shows multiple bands in the fingerprint area which were difficult to assign, but they involve Zr-O stretch and bending vibrations [7]. It has been mentioned that $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ has a pseudo C_2 axis with two pairs of DMSO ligands and therefore zirconium is considered to be located in a C_2 site, surrounded by eight oxygen atoms (figure 3.7). Based on this, the number of modes of the Zr-O stretch vibrations is

eight and $\Gamma=4A+4B$ with all modes being infrared and Raman active. If zirconium is placed in a C_1 site, all eight bands would have A symmetry. Most of the Raman bands between 250 cm^{-1} and 650 cm^{-1} could be traced in the infrared spectrum, although some bands shifted slightly. Some discrepancies exist, such as the Raman band at 409 cm^{-1} which is completely absent in the infrared spectrum. The Raman bands at 188 cm^{-1} and 529 cm^{-1} can be found in the infrared spectrum at 213 cm^{-1} and 511 cm^{-1} respectively, which is a remarkable shift. The reason for this is not clear but might involve the presence of some variable amounts of water. Note that the remaining Raman bands at 278 cm^{-1} , 314 cm^{-1} , 358 cm^{-1} , 364 cm^{-1} , 443 cm^{-1} , 454 cm^{-1} , 587 cm^{-1} and 618 cm^{-1} are in line with the infrared spectrum. The Raman bands at 670 cm^{-1} and 694 cm^{-1} are also present in the infrared spectrum at 658 cm^{-1} and 680 cm^{-1} respectively, which is somewhat lower. Raman bands at 726 cm^{-1} and 732 cm^{-1} can also be found as one band at 721 cm^{-1} in the infrared spectrum.

Above 800 cm^{-1} the two spectra compare very well. The sulphate bands between 900 and 1000 cm^{-1} are present in both spectra. The two Raman bands at 1174 cm^{-1} and 1250 cm^{-1} are also visible as strong absorption bands in the infrared spectrum. Furthermore, a weak Raman band at 1323 cm^{-1} can also be found in the infrared spectrum at the same position. At first it was thought that this Raman band corresponded to the remains of some free DMSO molecules in the sample, but this option was cancelled out by the presence of a distinctive absorption band in the infrared spectrum of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$. The broad band at 1425 cm^{-1} is clearly present in both the Raman and infrared spectra.

A DMSO solution has Raman bands between 625 cm^{-1} and 750 cm^{-1} corresponding to S-CH_3 vibrations according to the IRSCOT correlation tables [8]. The symmetric stretch vibration has a band at 669 cm^{-1} while the antisymmetric stretch vibration can be found at 698 cm^{-1} . In $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$, these vibrations have shifted towards higher wavenumbers and are split due to the different crystallographic sites of the DMSO ligands. The overtone of the symmetric stretch vibration in DMSO is at 1308 cm^{-1} and also higher at 1323 cm^{-1} in $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$.

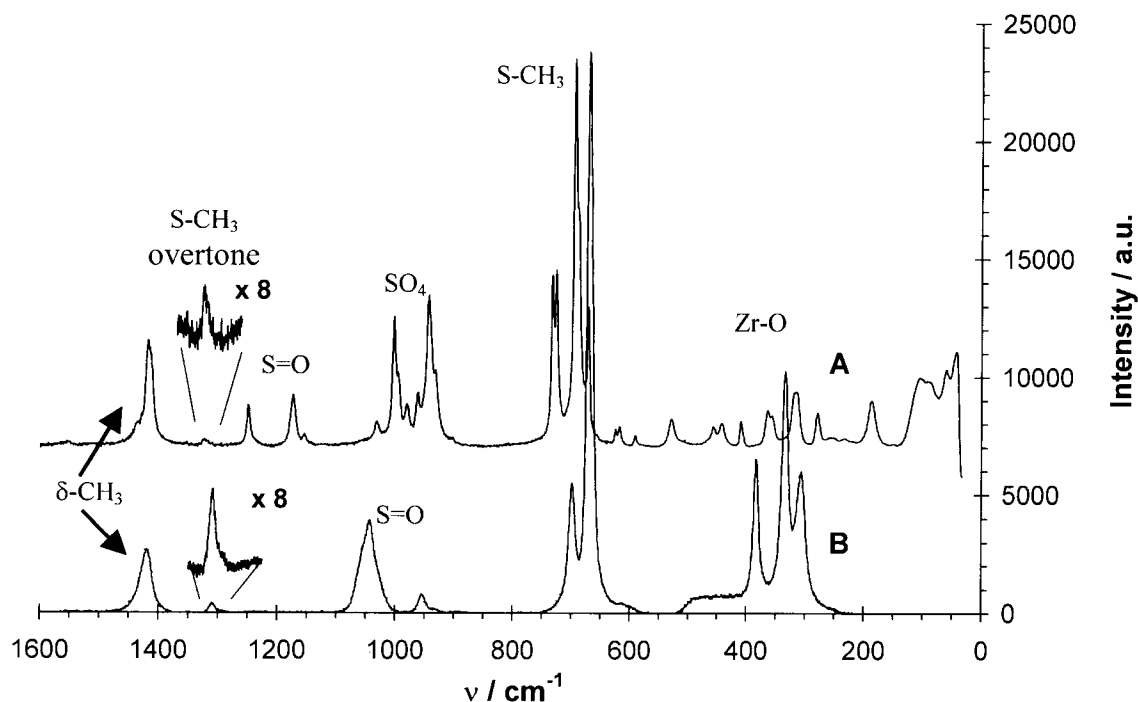


Figure 3.17 Raman spectrum of (A) a $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ powder and (B) a 95% DMSO solution. Both spectra are recorded in the macrophase. Integration time 150s; laser power 75 mW. See appendix A (Table A4) for exact band positions.

The sulfuryl band in the Raman spectrum of a 95% DMSO solution is located at 1042 cm^{-1} and has actually shifted towards lower wavenumbers due to $>\text{S}=\text{O}\cdots>\text{S}=\text{O}$ intermolecular bonding. It rises $10\text{--}20\text{ cm}^{-1}$ in non-polar solvents [9] and it is also expected to be higher in crystals if there is no direct intermolecular interaction. In the Raman spectrum of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$, the two bands at 1174 cm^{-1} and 1250 cm^{-1} are believed to be S=O modes in the DMSO ligands. They also appear in the infrared spectrum. O3-S3 and O5-S5 distances are $1.51\text{ \AA}$ while O4-S4 and O6-S6 distances are $1.55\text{ \AA}$. If a direct relation between S-O bond distance and bond strength exists, it means that the S-O bonds are not symmetry related, but the explanation of two sulfuryl bands representing two types of S-O bonds still holds.

The band at 1425 cm^{-1} can be ascribed to methyl deformation modes, but the methyl stretch vibrations of the DMSO ligands also deserve some attention (figure 3.18). Pure DMSO has two identical methyl groups in C_{2v} symmetry with two intense bands; one band at 2911 cm^{-1}

representing the total symmetric C-H stretch vibration (A_1) and another band at 2998 cm^{-1} corresponding to the degenerate stretch mode (E). In $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$, the methyl bands have been split because they are located at different sites, just as the S-CH₃ vibrations. It is not possible to assign the vibrations to the specific methyl groups in the structure, only the splitting of the Raman bands due to the different crystallographic locations is visible. Please note that this splitting is not visible in the infrared spectrum.

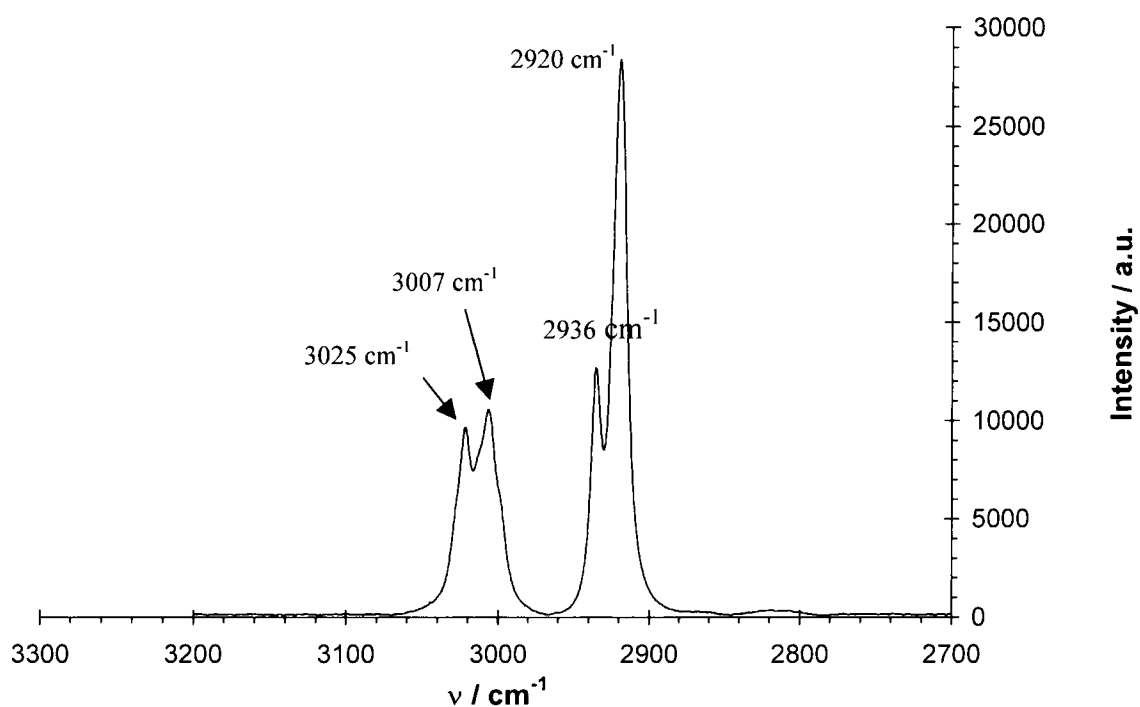


Figure 3.18 Raman spectrum of the CH₃ group in $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ powder recorded in the macrophase. Integration time 150s; laser power 75 mW. See appendix A (Table A4) for exact band positions.

3.5 Conclusion

$\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ crystallises in a monoclinic C centred cell. The structure was determined by the heavy atom procedure since zirconium is the heavy atom in the compound. From the systematic absence of reflections it was concluded that the possible space groups were $C_{2/c}$ and Cc. The structure was resolved for both space groups and the statistical procedure of Hamilton revealed that Cc is the proper space group. $C_{2/c}$ and Cc only differ in a two-fold rotation axis, which is absent in the Cc space group. However, it is helpful to consider this rotation axis to understand the spatial arrangement of the ligands around zirconium.

The unit cell contains four formula units, which could be regarded as isolated monomers with zirconium as the central atom. Each zirconium atom has eight-fold co-ordination in the form of two pyramids sharing a base edge. Both pyramids would transform into each other when applying the two-fold rotation symmetry if the space group were $C_{2/c}$. Zr-O bond distances do not reveal extreme deviations.

The methyl groups of the DMSO ligands show quite large atomic displacement ellipsoids, due to some imperfect crystallisation. Variations in bond distances between the C and S atoms in the DMSO ligands are large, but the average distance corresponds to the average C-S distance in other DMSO compounds. All the DMSO ligands are almost maximally removed from each other to reduce steric hindrance. Bond angles in the sulphate groups deviate from the perfect tetrahedron, which is due to strain and steric hindrance. Only the S-O groups carrying a negative charge are connected to zirconium. The S=O groups in the sulphate ligands are not bonded to the central atom and this is reflected in the S=O and S-O bond distances.

The XRD powder pattern calculated from the single crystal data is in line with the pattern of a ground single crystal, although the intensities differ somewhat due to a orientation preference of the small crystallites.

The Raman spectra and the IR spectra of the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ powder are in agreement with each other. They are also in accordance with the single crystal structure of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$. The sulphate groups and DMSO ligands are clearly present. IR spectra

also showed that the compound does not hydrolyse in water, which means that it is stable towards hydrolysis.

Dissolution in organic solvents (ethanol, acetone and 95% DMSO) is poor, reducing the application possibilities in paints. It might be possible to replace the sulphate ligands by more appropriate ligands to produce better zirconium-based paint dryers. Although a new and stable organometallic zirconium compound is prepared, this particular compound is not suitable for the use of paint dryers. However, this chapter discussed the structure of a zirconium sulphate compound interacting with DMSO molecules. It is expected that similar interactions exist between DMSO and other (water-soluble) zirconium salts. This compound might be a first step in the production of an improved paint dryer, but more research is required.

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Ammonium Zirconium Sulphate

4.1 Introduction

Zirconia from the mines is very impure and it is important to devise a cost-efficient process to purify the mineral. In addition, it is also important to convert zirconia into a water-soluble compound for the synthesis of many other zirconium-based chemicals. A new compound in the class of ammonium zirconium sulphates is developed and its chemistry and structure are discussed.

Zirconia can be digested by sulphuric acid as outlined in chapter 1.



Also interesting is the formation of zirconium basic sulphate (ZrOSO_4), because it is an important starting material for the preparation of many other zirconium chemicals as well. Zirconium basic sulphate can be precipitated from acid solutions. Addition of sulphate (H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$) to zirconium oxychloride replaces two chloride ions by a sulphate ligand. Metal oxides except titania remain in solution as ions and are removed. Titania precipitates because it is also a d^0 ion. It is in the same group of the periodic system, making its chemistry similar to zirconium.

Figure 4.1 shows several zirconium-based compounds prepared from basic zirconium sulphates.

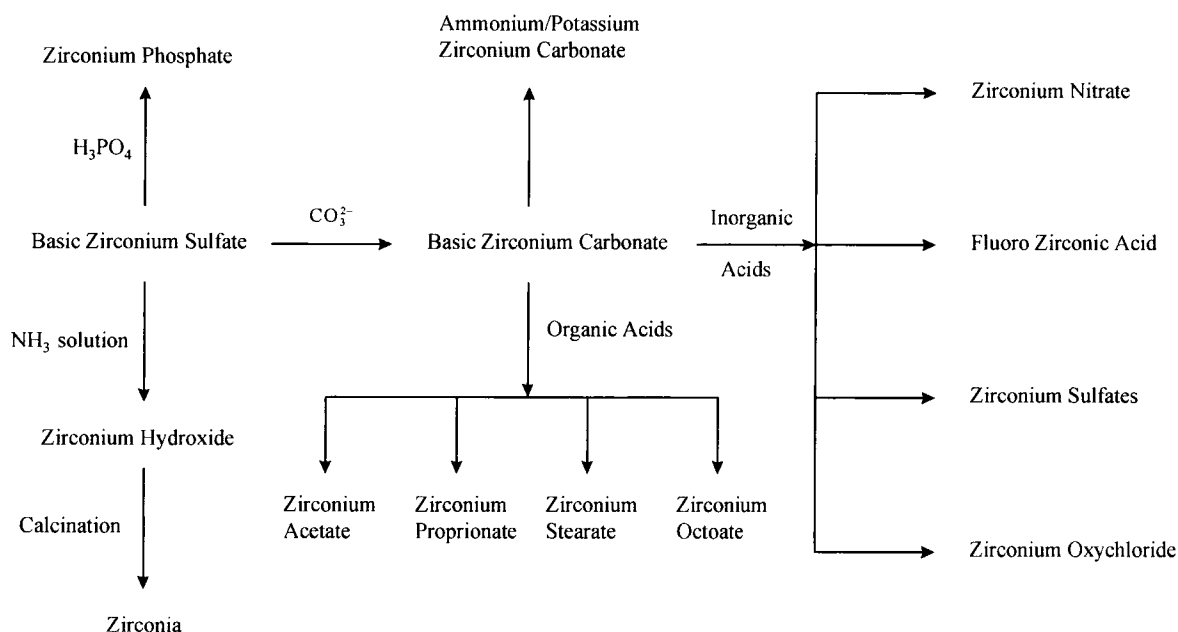
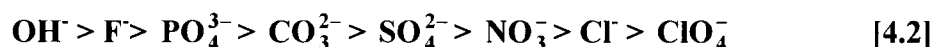


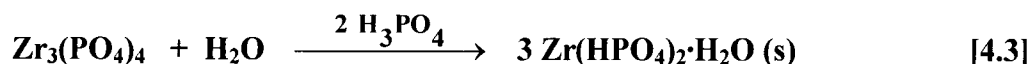
Figure 4.1 Zirconium chemicals derived from basic zirconium sulphate.

The tendency for inorganic ligands to form zirconium complexes can be expressed in a series in a descending order of ligand affinity for zirconium [1].



Complexing zirconium by hydroxyl groups strongly depends on the pH. Adding a mineral acid to a freshly prepared zirconium hydroxide precipitate ($\text{ZrO}_x(\text{OH})_{4-2x}$; $0 < x < 2$) redissolves the precipitate forming the mineral salt. In this way the hydroxyl ligands are displaced by an acid-base reaction, although they are the strongest ligands in the series.

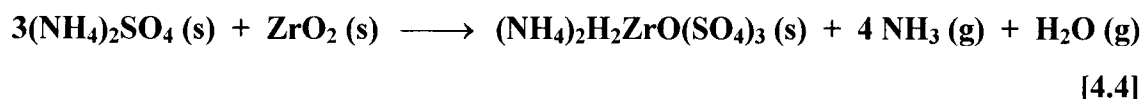
The affinity of ligands is applicable to zirconium in an aqueous medium. In this work it is found that refluxing zirconium phosphate in orthophosphoric acid at $\sim 110^\circ\text{C}$ forms $\text{Zr}_3(\text{PO}_4)_4$ according to XRD. This compound is soluble in orthophosphoric acid and cannot be precipitated with an almost saturated solution of sodium hydroxide up to a pH of 12. If water is added to the solution, $\text{Zr}_3(\text{PO}_4)_4$ reacts with water forming $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, which precipitates:



$\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is very stable. Hydroxyl groups could not replace phosphate ligands even if zirconium phosphate is suspended in water with a pH of 13. It is also impossible to remove the ligands by heating (1200°C). All the other ligands will come off, but zirconium phosphate reacts to ZrP_2O_7 , which is extremely stable.

From the examples above it is clear that the ligand series is a general series, which can only be used as an indication for the ligand strength in the synthesis of zirconium salts in aqueous medium.

Blumenthal claimed in 1950 a patent for a process to produce a soluble zirconium salt [2]. He ground ammonium sulphate and baddeleyite in a ratio of 3:1, spread the mixture in thin layers and heated it between 400°C and 600°C for from 5 minutes up to 2 hours. He postulated the following reaction based on his analysis of the components in the products:



Cations can not be bonded to zirconium directly, but they act as counter cations of the sulphate and oxo ligands. In case of bidentate sulphate ligands, the number of cations is too large. Monodentate ligands can carry all the cations, but the oxygen, which is not bonded to a sulphate, must then originate from a hydroxyl group. Another way of writing the formula is $\text{Zr}(\text{OH})_2(\text{HSO}_4)(\text{NH}_4\text{SO}_4)_2$. This is also impossible with zirconium in the fourth oxidation state and each ligand carrying a formal charge of -1.

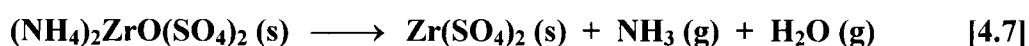
Shumenko et. al. also claimed to have found an ammonium sulphate zirconate salt by reacting baddeleyite with ammonium sulphate [3]. They even used a $(\text{NH}_4)_2\text{SO}_4 : \text{ZrO}_2$ molar ratio of 1:10, which was heated at 500°C for two hours. The first step according to Shumenko involved the release of ammonia:



followed by the attack of NH_4HSO_4 on zirconia:



They stated that an ammonium sulphate zirconate is formed between 240°C and 500°C and increasing the temperature to 580°C decomposes the zirconate to zirconium sulphate:



High amounts of ammonium sulphate were used to increase “zirconate” formation.

Motov and Ritter studied the solubility of a $\text{ZrO}_2\text{-H}_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ ternary system [4]. They claimed to have found many soluble ammonium zirconium sulphate compounds; e.g. $(\text{NH}_4)_4\text{Zr}(\text{SO}_4)_4\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Zr}(\text{SO}_4)_3\cdot 1.5\text{H}_2\text{O}$, and $(\text{NH}_4)_4\text{Zr}_4\text{O}_5(\text{SO}_4)_5$, based on molar ratios of initial mixtures. Their ternary system has never been studied before and they submitted some d/n values of XRD patterns. Neither a chemical analysis nor single crystal work was performed to prove the actual existence of these compounds.

Kuznetsov et. al. reported several sodium or ammonium zirconium sulphate salts [5]. The ammonium sulphate salt was $(\text{NH}_4)_2\text{Zr}(\text{SO}_4)_3\cdot 2\text{H}_2\text{O}$, while the sodium salts were $\text{Na}_2\text{Zr}(\text{SO}_4)_3\cdot 3\text{H}_2\text{O}$, $\text{Na}_4\text{Zr}(\text{SO}_4)_4\cdot 3\text{H}_2\text{O}$ and $\text{Na}_6\text{Zr}(\text{SO}_4)_5$. They described the structures as double salts of sodium/ammonium sulphates and zirconium sulphates.

Rogachev et. al. also studied ammonium zirconium sulphate compounds [6]. Their crystal structures are described of $(\text{NH}_4)\text{Zr}(\text{OH})(\text{SO}_4)_2\cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Zr}(\text{OH})_2(\text{SO}_4)_2\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_5\text{Zr}_6\text{O}_4(\text{OH})(\text{SO}_4)_{10}(\text{H}_2\text{O})_7$. All these structures were determined by X-ray powder diffraction only, making a comprehensive crystal structure determination impossible. Single crystals of ammonium zirconium fluoride sulphate hydrate; $(\text{NH}_4)_3\text{Zr}_2\text{F}_9(\text{SO}_4)\cdot 2\text{H}_2\text{O}$, and its potassium analogous were solved by Kuznetsov et. al. [7].

Many hafnium analogues were also reported because of the chemical similarity between hafnium and zirconium. Rogachev et. al. published a single crystal structure of an ammonium hafnium sulphate compound, $(\text{NH}_4)_4\text{Hf}(\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$ [8] and studied many similar structures by X-ray powder diffraction [9]. The powders were $(\text{NH}_4)_2\text{Hf}_2\text{O}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Hf}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$. $(\text{NH}_4)_4\text{Hf}(\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Hf}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ were previously reported by Chalyi et. al. [10].

4.2 Preparation of the Powder

The products formed by fusing ammonium sulphate and zirconia have not been studied in great detail except by Blumenthal's patent in 1950 and Shumenko in 1973.

In this study, the salt was prepared in different ways. The first method was fusing zirconia from Phalaborwa Mining Company Ltd. (PMC) with ammonium sulphate (mole ratio 1:3) at 500°C overnight (12 hours). The product obtained was dissolved in hot water (90°C) and filtered to remove the non-reacted part. After filtration, the product was recrystallised from the solution. The crystals were washed with concentrated hydrochloric acid to remove impurities (e.g. iron). Impurities dissolve readily in concentrated HCl, but the product dissolves poorly when a mother liquid of the dissolved product is used.

A major disadvantage is the use of concentrated hydrochloric acid, limiting the practical application of the synthesis. Nitric acid can be substituted for hydrochloric acid, reducing acidic fumes considerably. The ligand strength of nitrate is still lower than sulphate, leaving nitrate ions in solution (eq. 4.2).

The product can be recrystallised in an acidic medium eliminating the washing procedure in acid afterwards. In the first method, impurities could be included in the crystal during crystallisation, causing isolation from the solvent medium, which hampers their removal. In the alternative route, the fused product was dissolved in hot water and heated at 80°C. After the product had been dissolved, it was filtered to remove unreacted baddeleyite and non soluble impurities (silica particles from crucibles).

Ammonia was added to the solution to enhance crystallisation at a later stage. A shortage of ammonia results in a paste, which is difficult to filter. The addition of ammonia is accompanied by a rise of the pH, which is compensated for by the addition of nitric acid, therefore keeping the impurities in solution and preventing zirconia from hydrolysis. The product was recrystallised from the solution, which became more acidic with the evaporation of water ($\text{pH} < 0$), and was dried at 150°C overnight. This alternative process is used as the standard method to prepare the product.

4.3 Composition and Structure

Results of the chemical analysis of the product are shown in Table I. The content of zirconium and sulphate are determined by ICP analysis. Ammonium is determined by UV/VIS spectroscopy. Details of the analysis could be found in Appendix B.

Table I Chemical analysis of zirconia fused with ammonium sulphate.

	NH ₄	Zr	SO ₄
mass %	5.48	27.81	50.31
mole	0.9987	1	1.72

The ratio of NH₄:Zr is 1:1 and SO₄:Zr almost 2:1. A composition as stated above has a net positive charge. Taking the charge balance and the results of the loss on ignition into account, the fusion product could be (NH₄)HZrO(SO₄)₂.

The composition of the reaction product can also be written as a combination of zirconium sulphate and ammonium hydroxide (Zr(SO₄)₂+NH₄OH). To verify whether fusion of ammonium sulphate with zirconia forms such a combination, several analyses were conducted.

(NH₄)HZrO(SO₄)₂ was dissolved in water, recrystallised and used as a reference. A combination composition was prepared by adding dropwise a 28% ammonia solution to an acid zirconium sulphate tetrahydrate (Zr(SO₄)₂·4H₂O) solution until the intended NH₄:Zr ratio of 1:1 (mole/mole) was obtained. The mixture was stirred until a clear solution was obtained while the temperature was kept below 60°C. Zirconium sulphate did not precipitate to zirconium hydroxide and the product was obtained by evaporating water to crystallise the salt from the solution.

The first experiment was a simple pH measurement of Zr(SO₄)₂+NH₄OH and NH₄HZrO(SO₄)₂ in water. The pH of the former compound varied between 1.8-1.9 in a

concentration range from $0.26 \text{ mole}\cdot\text{l}^{-1}$ to $0.31 \text{ mole}\cdot\text{l}^{-1}$. $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ had a pH of 2.02 at a concentration of $0.28 \text{ mole}\cdot\text{l}^{-1}$, indicating a similar acidity of both zirconium compounds in water.

Infrared spectra of $\text{Zr}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ (A), $\text{Zr}(\text{SO}_4)_2+\text{NH}_4\text{OH}$ (B) and $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ (C) were also recorded and are shown in figure 4.2. The samples were pressed in a potassium bromide pellet according to the standard technique. Spectra were recorded between 4000 cm^{-1} and 400 cm^{-1} . Above 3000 cm^{-1} ammonium and water bands were present in $\text{Zr}(\text{SO}_4)_2+\text{NH}_4\text{OH}$ and $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ which were confirmed by a band at 1652 cm^{-1} ($\delta_s \text{ H}_2\text{O}$) and 1399 cm^{-1} ($\delta_s \text{ NH}_4$). More interesting were the bands between 1000 cm^{-1} and 1250 cm^{-1} representing SO_4^{2-} vibrations. Using IR spectra as a fingerprint analysis, bands originating from $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ and $\text{Zr}(\text{SO}_4)_2+\text{NH}_4\text{OH}$ coincided, suggesting a close similarity in the structural composition.

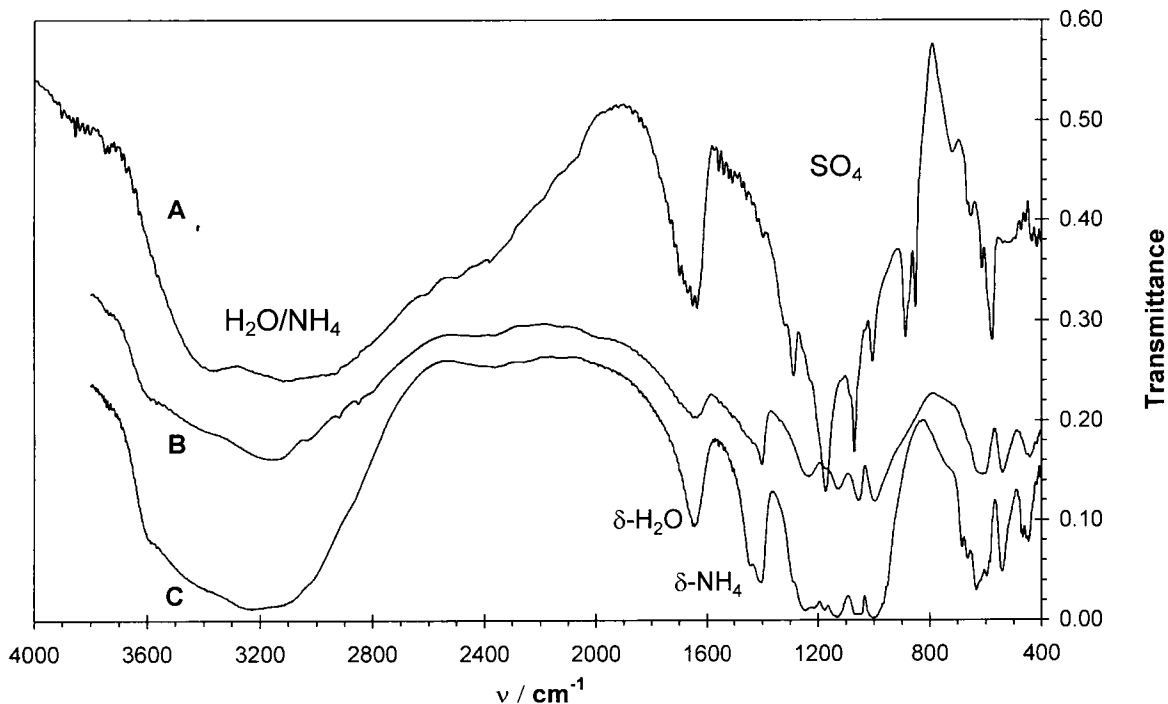


Figure 4.2 Infrared spectra of A) $\text{Zr}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$, B) $\text{Zr}(\text{SO}_4)_2+\text{NH}_4\text{OH}$ and C) $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$. See appendix B (Table B1) for exact band positions of spectrum C.

The spectral range in figure 4.2 mainly represents stretch vibrations. Similar groups bonded to a central Zr atom may show bands at similar positions if the vibrations of those groups are group characteristic. Bending vibrations, visible in the far infrared region, are more affected by the surrounding of the vibrating species, resulting in larger band shifts (figure 4.3). Samples of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (A), $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$ (B) and $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ (C) were pressed in a polyethylene pellet to measure spectra in the far infrared region. According to the spectra in figure 4.3 there is a very close resemblance between the spectra of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ and $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$. Although assignment is very difficult in this region, it can be concluded that bands are similar and the structures of both samples seem to be identical.

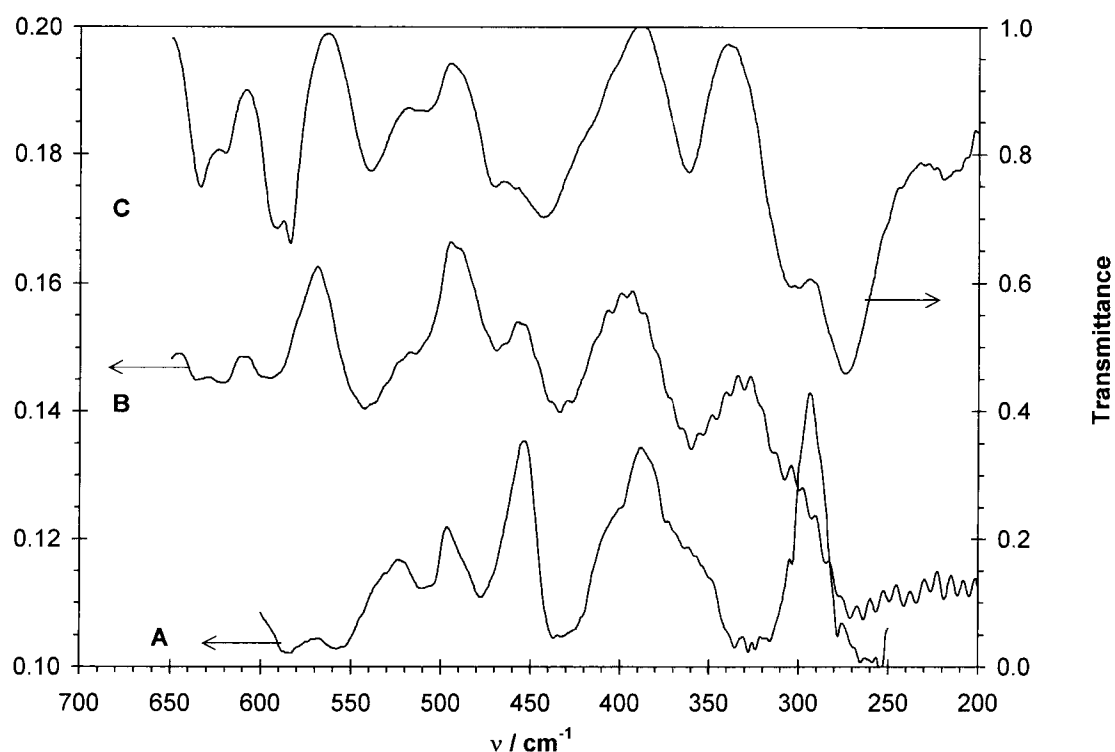


Figure 4.3 Infrared spectra of A) $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, B) $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$ and C) $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$. See appendix B (Table B1) for exact band positions of spectrum C.

Finally, XRD patterns of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ and $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$ (mole ratios $\text{Zr}:\text{NH}_4 = 1:1$ and $1:2$) were recorded and are shown in figure 4.4. Pattern A is zirconium sulphate tetrahydrate. Pattern B is a combination of zirconium sulphate and ammonium hydroxide with a ratio of $1:1$ and the sample of pattern C is the same as B, except that the $\text{Zr}:\text{NH}_4$ ratio is $1:2$. The last spectrum (D) is the spectrum of $(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ recrystallised from water. The pattern of $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$ does not correspond to the pattern of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, indicating that the former compound recrystallises in a different structure. The patterns of $(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ and $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$ are similar, but in the latter some remains of zirconium sulphate tetrahydrate are still visible at $2\theta = 13.7^\circ$ and 20.5° . It is quite clear that pattern A does not correspond to the other spectra, proving a different crystal structure. Patterns B and C are similar although some peaks from spectrum A are still present suggesting that some $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is left. These peaks vanish when using an excess of ammonium hydroxide. A Zr to NH_4 ratio of $1:2$ may suggest a different composition, but during crystallisation some ammonia has evaporated and a quantitative analysis is not reliable. Comparing spectra A, B and D, it can be concluded that $(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ and $\text{Zr}(\text{SO}_4)_2 + \text{NH}_4\text{OH}$ are isostructural.

The XRD pattern of $(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ recrystallised from water is of a poor quality and only used for comparison. It is enhanced when it is recrystallised from a more acidic solution ($\text{pH} = 0-1$), in this case a nitric acid solution, according to the process outlined in the experimental section. The XRD pattern of this compound has peaks at the same diffraction angles, but they are better resolved and their signal to noise ratio is much higher (figure 4.5).

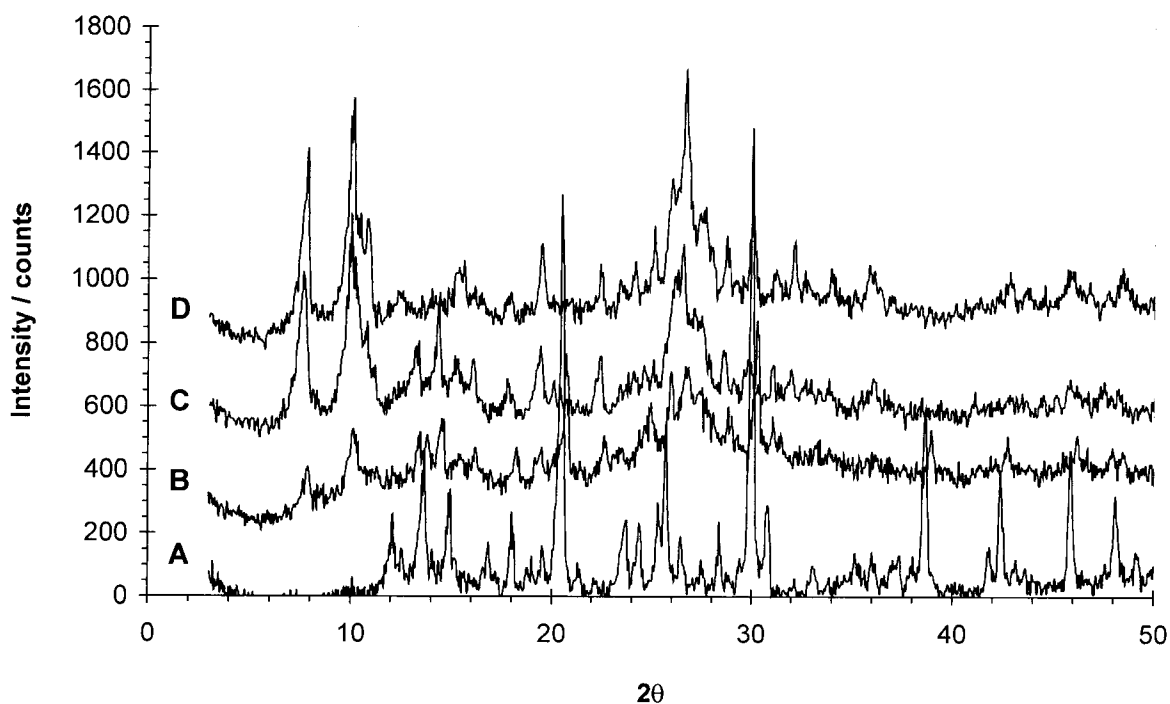


Figure 4.4 XRD patterns of A) $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, B) $\text{Zr}(\text{SO}_4)_2 + 1 \text{NH}_4\text{OH}$, C) $\text{Zr}(\text{SO}_4)_2 + 2 \text{NH}_4\text{OH}$ and (D) $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$.

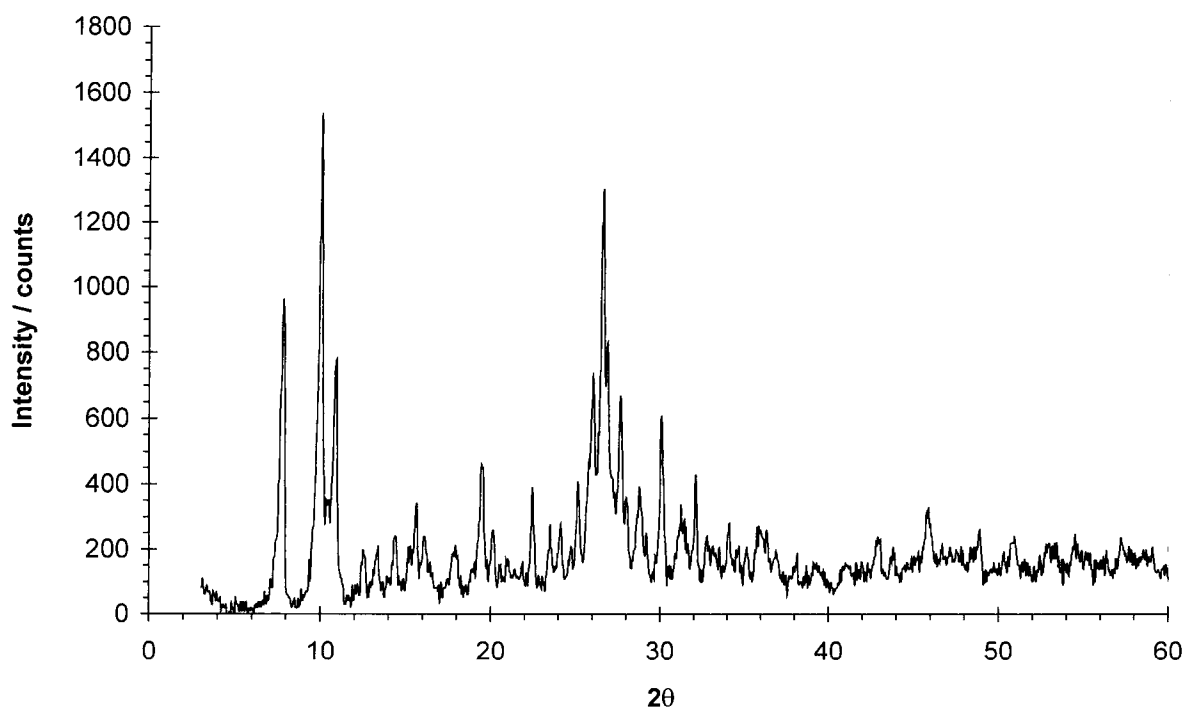


Figure 4.5 XRD pattern of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ recrystallised from an acidic solution ($\text{pH}=0$). See Appendix B (Table B3) for the exact peak positions.

4.4 Preparation of the Single Crystal

Many attempts were made to grow a single crystal and it proved to be extremely difficult. Growing a single crystal over sulphuric acid in a desiccator resulted in a glassy substance (figure 4.6). Evaporating water at a slower pace at 5°C and 22°C also didn't have the intended result. Neither did the use of thread and scratches in the glass of the sample beaker to facilitate nucleation work. Decreasing the concentration of the mother liquid could also not produce single crystals.

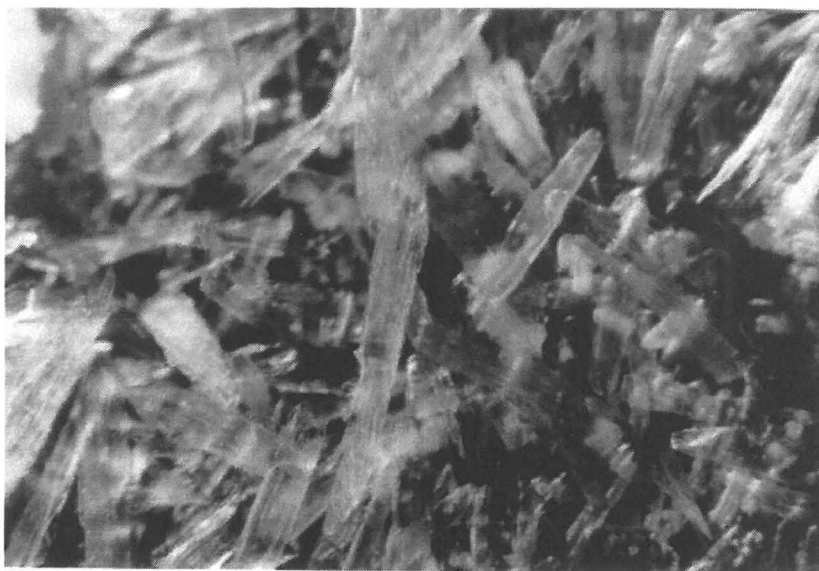


Figure 4.6 Glass formation of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$. Magnification 10x.

La Mer proposed a diagram (figure 4.7) explaining nucleation and crystal growth. Nucleation depends on the concentration because nuclei are formed and grow above the nucleation concentration. Between the nucleation and saturation concentration, existing crystals will grow but no new crystal will be formed. The concentration of the species falls during crystal growth and this continues until the saturation concentration is reached. The diagram of La Mer is also applicable to crystal formation and growth here. The concentration of dissolved zirconium is kept high due to evaporation of the solvent. The actual concentration depends

on the rate of evaporation and the crystal growth rate. Decreasing the rate of solvent evaporation reduces fluctuations above the nucleation concentration, producing larger single crystals. It is expected that the saturation and nucleation concentrations are very close, reducing the concentration range of the growth stage.

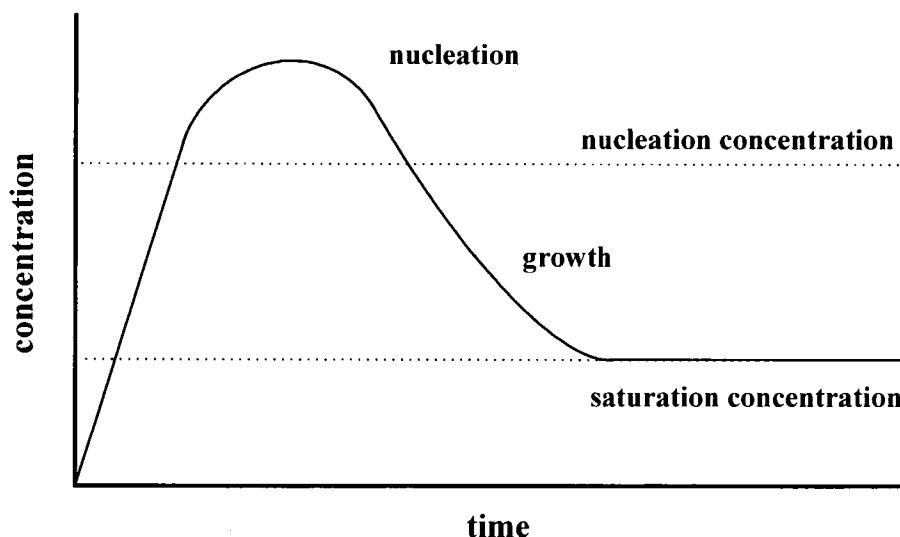


Figure 4.7 Diagram according to La Mer explaining the process of crystal nucleation and growth in terms of concentration.

Crystals formed in each sample are polydisperse because nucleation and growth does not take place consecutively. Both processes overlap causing a distribution in crystal size.

Nucleation is hampered by a large surface energy and nuclei with a radius below the critical radius are unstable and redissolve. The addition of condensation nuclei lowers the surface energy since initial radii of the crystals are larger than the critical radius if crystallisation takes place on these condensation nuclei.

After nucleation, a dissolved particle collides with the crystal by diffusion making crystal growth dependent on the collision frequency. Flux J of the particles at a radius r from the origin of the crystal is according to Fick's first law:

$$J = 4\pi r^2 \cdot D \cdot \frac{dc}{dr} \quad [4.8]$$

D is the diffusion constant and c is the concentration of the particles in solution. It is obvious that r must be larger than radius R of the crystal and that $C(r=R)=0$. Another formulation of flux J can be written down by integrating eq.4.8 and assuming a stationary diffusion with the condition that $C(r \rightarrow \infty)=C_{\infty}$ (C_{∞} =bulk concentration):

$$J = 8\pi \cdot D \cdot C_{\infty} \cdot R \quad [4.9]$$

J is proportional to the crystal growth and it is clear that the rate depends on the concentration. Note that the rate is not necessarily of a first order in concentration. Crystallisation is faster at high concentrations, but if it is too fast, a polycrystalline or glassy material will form because particles do not have time to align to the crystal structure. Duration of alignment is very important especially for zirconium in aqueous media at a relative high pH ($\text{pH} \approx 2$). It is known that zirconium forms clusters, even in acidic solutions [11,12,13]. When the pH is increased these clusters also tend to aggregate making the duration of alignment even more important.

If an aqueous zirconium sulphate system follows La Mer's model, it is important to control the flux J and the concentration in order to grow single crystals. Therefore a glass cylinder was filled with mother liquid, closed with a stopper and sealed with parafilm to minimise evaporation. Variations in the temperature causes variations in the solubility of the crystal in its mother liquid which in its turn cause a change in the saturation and nucleation concentration, inducing precipitation instead of crystal growth.

Fluctuations in temperature also cause variations in the flux. For a single crystal to grow slowly, the flux must be as small as possible, but large enough to obtain a crystal within a certain time. During the crystallisation, the temperature of the mother liquid was kept at 22°C and not exposed to sunlight. After 4-5 months the zirconium crystals were large enough for a single crystal determination. Figure 4.8 shows single crystals grown over a period of 6 months. They are heavily aggregated and randomly oriented in the solid. By comparing figure 4.8 and the glassy rods in figure 4.6, it is clear that close control of the experimental conditions is of major importance.

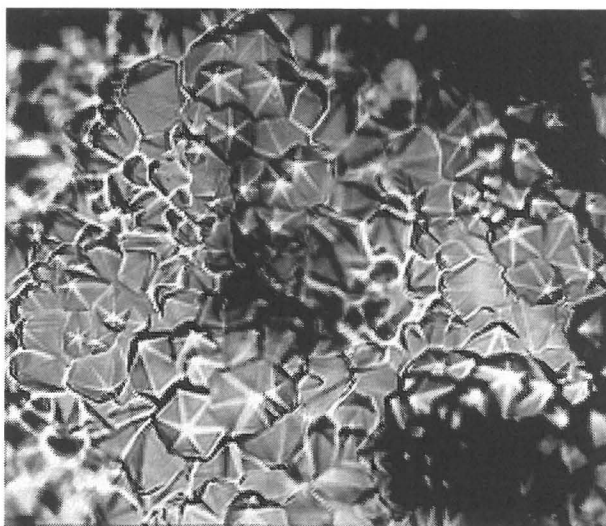


Figure 4.8 Aggregated single crystals of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$
Magnification 20x.

Isolating a single crystal was very difficult due to the immediate cracking of the crystals, making them unsuitable for crystal structure analysis. To overcome this problem, a drop of mother liquid containing an isolated crystal was put on a glass plate in the vicinity of a drop of glue. The crystal was slowly and extremely carefully transferred into the glue and when the glue was partially dry, it was put onto a needle and left to dry for at least 24 hours. The needle was put into the sample holder of the four-circle diffractometer and firmly kept in its place by bee wax. The chance of preparing a suitable sample in this way was less than 10% because most of the crystals cracked during the transfer to the glue or upon drying. A high surface tension of the glue causes cracking upon drying. The 10% chance of preparing a suitable sample originated from a mere count of the number of single crystals successfully transferred on to the needle.

4.5 Resolving the Structure

After a suitable crystal was mounted on the goniometer of the diffractometer, the standard procedure for single crystal determination was executed with an acceleration potential of 30kV and a current of 1.5 mA. After 25 strong reflections were measured, a hexagonal unit cell was established. The macroscopic shape of the single crystal (figure 4.8) confirmed the type of unit cell. The six-fold rotation symmetry was clearly visible by inspection of one single crystal.

The intensities of the h,k,l reflections were only 10% of the intensity required to solve the structure. Low intensities for a zirconium sulphate compound is not expected since zirconium is normally a good scatterer. It is possible that the compound can disintegrate during preparation and therefore the same crystal was subjected to another analysis three days later. Special attention was paid to the intensity of h,k,l reflection (6,-6,6). The intensity of this relative strong reflection, measured during the first analysis (1511 counts), was similar to the intensity of the second measurement (1585 counts) proving that the crystal remained stable with time.

Another crystal was sucked from the mother liquid into a capillary and sealed at both ends with glue. The critical step was to anchor the crystal to the glue without encapsulating the crystal. The capillary was also fixed with bee wax into the sample holder and once again 25 strong reflections were collected to establish the unit cell. The reflections confirmed the existence of the hexagonal cell, but did not gain in intensity.

Merely boosting the acceleration of the electrons to generate X-rays in order to increase the intensity is impossible, even if the anode is water-cooled. Higher X-ray intensities can be achieved by using a rotating anode to avoid burning of the anode, but the construction is more complicated and the output more susceptible to noise compared to the hot cathode X-ray tube discussed in chapter 2 (section 2.1.1).

Another possibility is cooling the sample to increase the signal to noise ratio. The sample was therefore cooled down to 150K. The structure was resolved by a combination of direct method and heavy atom method. Although the structure contains a heavy element (zirconium), it could not be resolved by the heavy atom method only. As the unit cell is

large, it contains many zirconium atoms giving rise to many inter-atomic vectors. A structure containing N atoms has $N(N-1)$ peaks (+ N peaks on the origin) in Patterson space. If those peaks are broad, it is difficult to distinguish between separate peaks. The direct method is a mathematical technique using normalised structure factors to identify positions of atoms, e.g. the atoms are considered as point atoms. This method is not within the scope of this study and computer programs like SHELX-97 are available in order to solve the structure.

New data were recorded using a NONIUS KAPPCD area detector system having a rotating water-cooled anode as a source and a CCD detector. The set-up is similar to the four-circle diffractometer described in chapter 2, except that a CCD detector collects multiple reflections simultaneously. 240 scans with an acquisition time of 100 s per scan were recorded (100s per degree around Ω). Each reflection was measured twice to filter out noise. 84855 reflections were measured, but 12380 reflections were unique. The total measure time was 13.2 hours. Data were recorded at a power of 60kV, 50mA and nitrogen was blown over the sample to cool the sample to 150K.

Reflections with identical h,k,l parameters were measured more than once. h,k,l and $\bar{h},\bar{k},\bar{l}$ reflections are identical, since the reciprocal lattice is centro-symmetric according to the law of Friedel, reducing the number of unique reflections even more. It does not mean that only 12380 measured reflections were used while the remaining ones were discarded. All identical reflections were averaged to produce a unique reflection. The reflections are expressed in their structure factors and SHELX-97 calculates two types of average indices; e.g. $R(\text{int})$ and $R(\sigma)$.

$$R(\text{int}) = \sum |F^2 - F^2(\text{mean})| / \sum |F^2| \quad [4.10]$$

$$R(\sigma) = \sum \sigma(F^2) / \sum F^2 \quad [4.11]$$

These indices give information about the distribution of identical reflections around the average.

The cell dimensions measured at 150K and at room temperature are shown in Table II. According to the table, no phase change occurred on cooling down to 150K. The space group

of the crystal is $P6_3$ or $P6_3/m$, based on the systematic absence of reflections. During the determination of the structure having space group $P6_3$, it became clear that the structure contained a mirror symmetry element at $c=1/4$ and that a zirconium cluster was located on that symmetry element. Therefore a unit cell must contain six clusters, since it has 12 symmetry-related positions. The space group $P6_3/m$ (no. 176) is accepted to describe the structure of the zirconium complex. All the symmetry operations can be found in the International Tables for Crystallography [14]. Zirconium is the heaviest atom in the compound and was placed first on the electron density map.

Table II Cell parameters of a zirconium sulphate compound at a temperature of 150K and 298K.

Cell	Temperature	
parameters	150K	298K
a	34.9167	34.891(3)
b	34.9439	34.891(3)
c	18.8260	18.8022(16)
α	90.0345	90
β	89.9915	90
γ	119.9721	120

Figure 4.9 shows a zirconium cluster projected along the c-axis of the unit cell and figure 4.10 is the same cluster along the mirror plane. The unique zirconium atoms in a cluster are labelled, while the remaining zirconium atoms are generated by symmetry operations. Zirconium atoms 1 to 3 and 8 are located on the mirror plane and will therefore be transformed into their own upon reflection. Zirconium atoms 4 to 7 and 9 to 11 produce a mirror image, giving rise to a total of 18 zirconium atoms per cluster. The zirconium atoms form the skeleton of a cluster and it is clear that the structure consists of a bending plane of zirconium with zirconium atoms sticking out above and below that plane (figure 4.9). Once the zirconium atoms were positioned, the structure was refined and a new electron density map calculated.

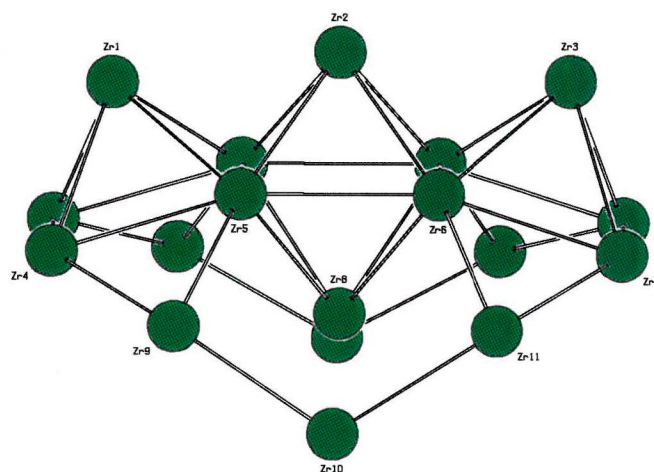


Figure 4.9 *Skeleton of a zirconium cluster in a projection along the c-axis of the unit cell. Bonds between zirconium atoms do not exist, but are drawn to visualise the skeleton.*

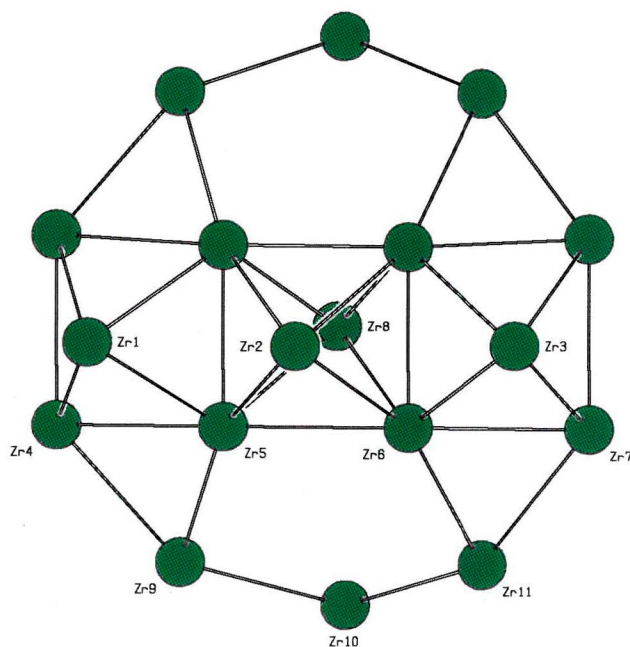


Figure 4.10 *Skeleton of a zirconium cluster along the mirror symmetry element of the unit cell. Bonds between zirconium atoms do not exist, but are drawn to visualise the cluster skeleton.*

The next step was the determination of the positions of oxygen and sulphate ions (figure 4.11). The latter could be discerned by their tetrahedral arrangement with oxygen atoms. From other structures as described in section 1.2, it is known that sulphate groups can act as bidentate ligands or as bridges connecting zirconium atoms by forming dimers (figure 1.9+1.11+1.13+1.15). However, not all the sulphate ions act as ligands, but this will be discussed later.

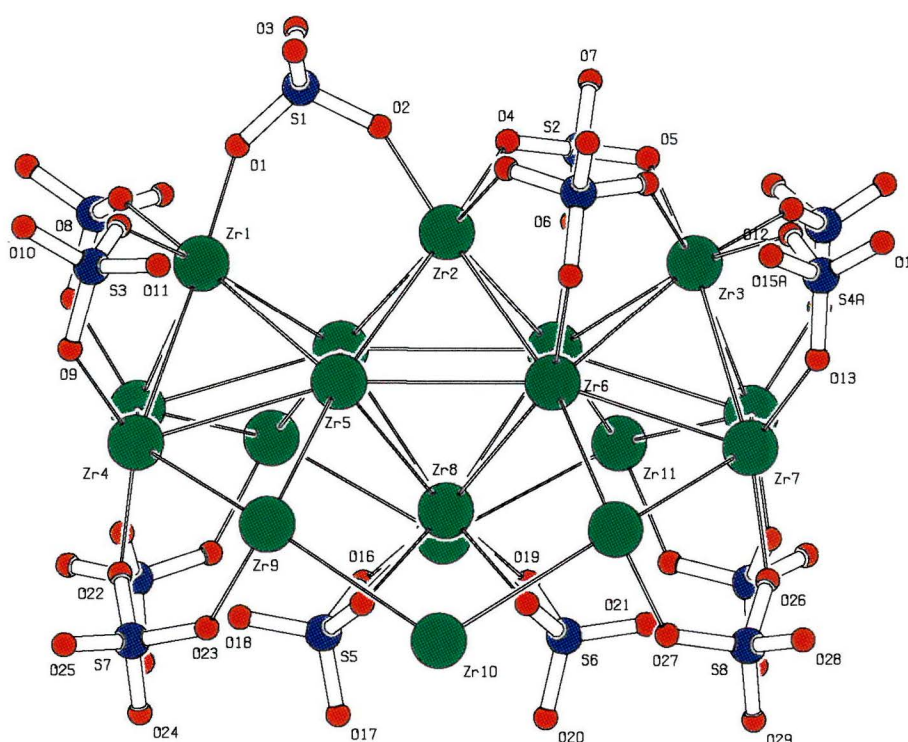


Figure 4.11 Zirconium cluster including the bridging cluster sulphates. Bonds between zirconium atoms do not exist, but are drawn to visualise the cluster skeleton.

After placing the sulphate ions and refining the structure, the remaining oxygen had to be placed. This was quite difficult because of the different types of oxygen. Some oxygen atoms could originate from water, while others could be O^{2-} or OH^- . In addition, oxygen could be mono-fold, two-fold, three-fold or four-fold co-ordinated by zirconium. Before tackling this

problem, all oxygen atoms were initially placed as O^{2-} and the structure was anisotropically refined. The factor of residual dropped to 8.1%.

Water as a ligand is quite common and is bonded to zirconium through the lone pair of oxygen (figure 1.10-1.16). Based on the structures in section 1.2, it is expected that water is a monodentate ligand, capable of forming multiple hydrogen bonds. Water can therefore only be assigned to terminal oxygen peaks in the electron density map. However, these terminal peaks do not necessarily originate from water. It can also originate from terminal oxygen atoms ($Zr=O$) or terminal hydroxy groups ($Zr-OH$). The former has bond lengths of $1.8\text{\AA}$ [15,16], while the latter has bond lengths smaller than $2.05\text{\AA}$ [17-20]. In this zirconium structure, the distances between zirconium and oxygen are $2.2\text{\AA}$ meaning that the oxygen atoms must originate from water molecules. The water ligands were placed and the zirconium skeleton including these ligands can be found in figure 4.12.

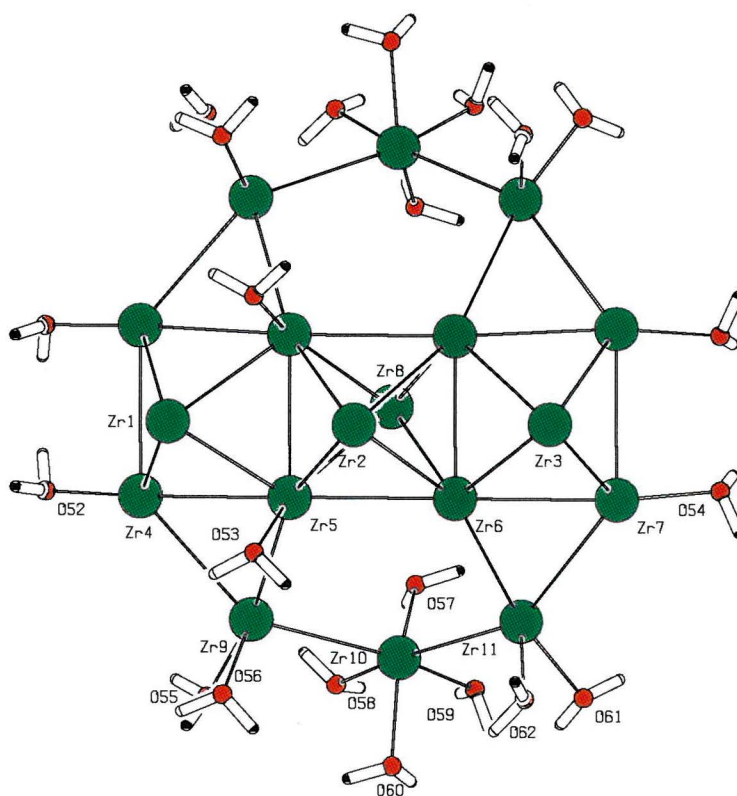


Figure 4.12 Zirconium cluster including co-ordinating water ligands. Bonds between zirconium atoms do not exist, but are drawn to visualise the cluster skeleton.

Oxygen co-ordinated by four zirconium atoms must participate in an oxo bond. Each zirconium atom has a formal charge of +4, which is a very high positive environment for an oxygen atom and therefore these oxygen atoms are expected to be present as O^{2-} . Two-fold co-ordinated oxygen is expected to be a hydroxy group (section 1.2). It is more difficult to assign the type of oxygen when it is co-ordinated by three zirconium atoms. A number of published zirconium compounds contain oxygen atoms, which are co-ordinated by three zirconium atoms [21-32].

An important criterion to determine the type of oxygen is the bond length between zirconium and oxygen. According to the literature, average Zr-O bond lengths of Zr_3O species are larger than 2.27Å for hydroxy groups, while they are smaller than 2.14Å in oxo bonds.

Another criterion is the sum of the three angles between the zirconium atoms co-ordinating the same oxygen atom. In case of hydroxy groups, this sum is smaller than 275° , while it is larger than 295° for oxygen in oxo bonds. The three zirconium atoms around an oxygen repel each other and the most favourable geometry, based solely on electrostatic repulsion, is a flat structure with a Zr-O-Zr angle of 120° . The sum of the angle of this geometry is 360° . Introducing an extra ligand changes the geometry towards a tetrahedral arrangement, decreasing this sum of angles.

All the oxygen atoms co-ordinated by 3 zirconium atoms were evaluated using the two criteria specified above. Each criterion resulted in the same assignment of hydroxy groups or oxo bonds to the peaks in the electron density map (Table III), increasing the reliability of the proposed structure in figure 4.13.

Table III *Assignment of the type of oxygen ligand in three-fold co-ordinated oxygen by zirconium.*

OH	O31	O36	O38	O41	O44
O	O32	O34	O35	O40	O43

Please note that some oxygen atoms are located on the mirror symmetry element, while the others have mirror images.

The positions of hydrogen atoms in Zr_2OH and Zr_3OH species were added to the structure by considering each $\text{Zr} \rightarrow \text{O}$ direction as a vector. The resultant vector of the vectors around an oxygen atom is the direction of the O-H bond and its length is taken as $0.85 \text{ \AA}$. After anisotropic refinement of the structure, the factor of residual dropped just below 8%. Although this seems to be very small, this drop must be seen in the context of the whole structure containing many electrons.

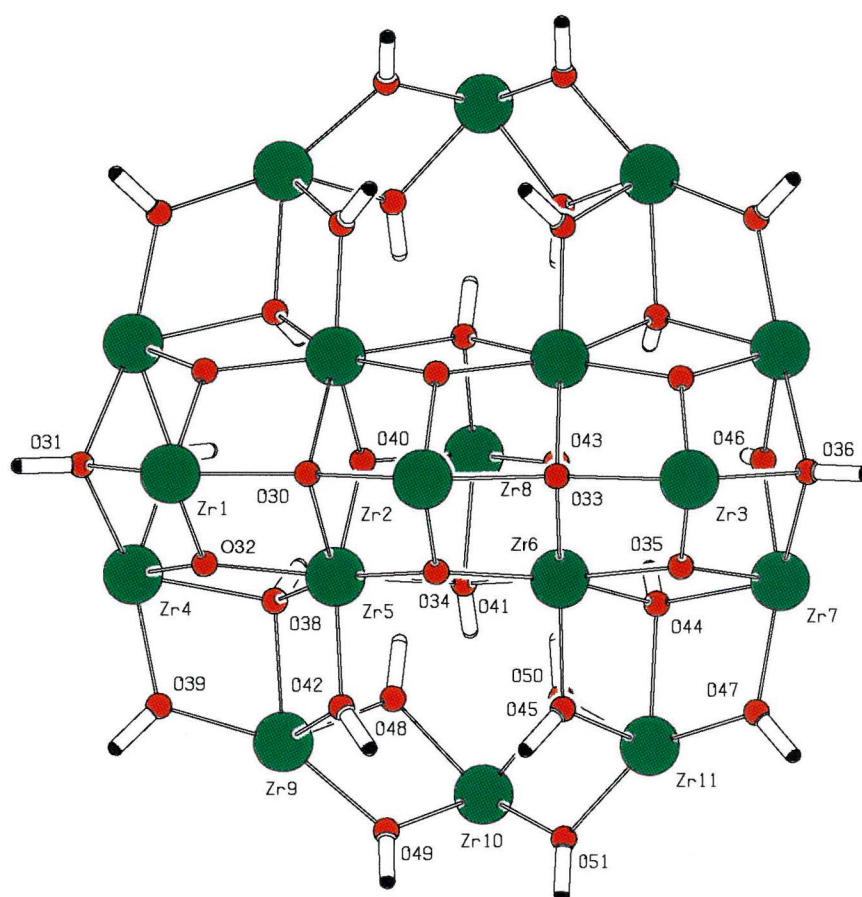


Figure 4.13 Zirconium cluster including the hydroxy groups and oxo bonds.

Figure 4.14 shows the unit cell of the crystal along the c-axis, which clearly contains a solvent part. The volume fraction of the solvent part in the unit cell is 0.25 (V/V) and the packing of the cell is not very economical. The location and size of the solvent part is determined as follows. A three dimensional grid is put over the entire unit cell and each point of the grid is evaluated for the presence of an atomic neighbour. If no atom of the structure is present within the Van der Waals radii of neighbouring atoms, the point is considered to be located in the solvent part of the cell. Each point is associated with a certain volume making it possible to determine the volume of this solvent part.

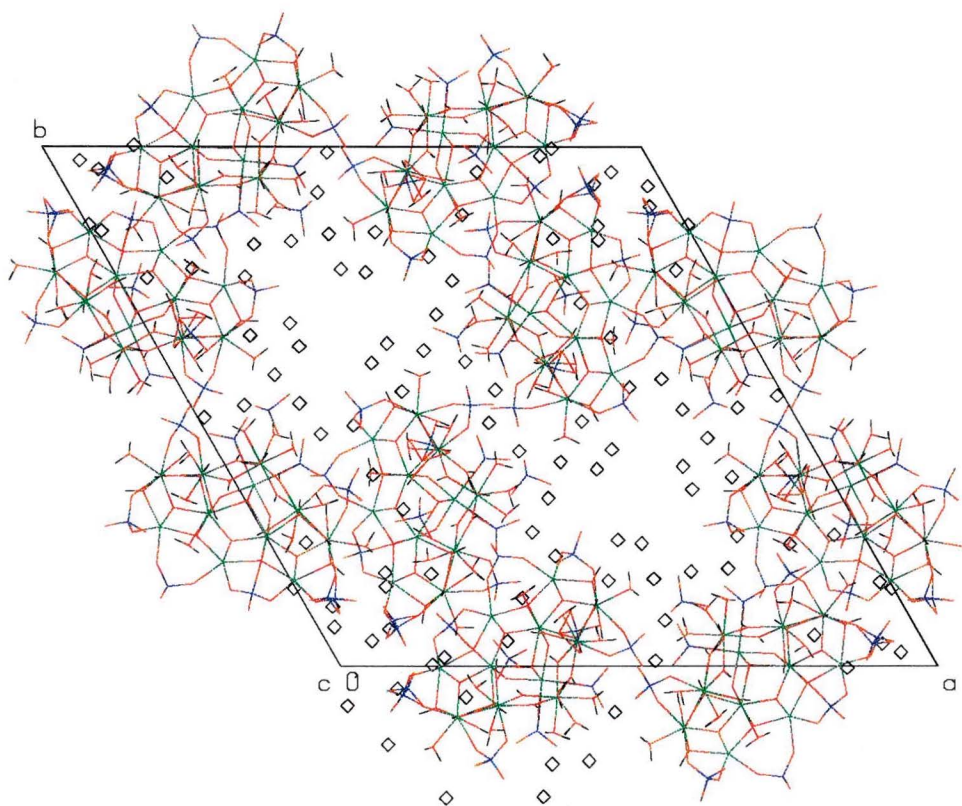


Figure 4.14 The unit cell of the zirconium compound in the (001) projection ($\diamond$ = unassigned electron density).

The solvent part consists of three types of channels running parallel to the c-axis. These channels contain electron density, which is more diffuse in nature, and interferes with the electron density from the zirconium compound. The density from the solvent part contributes to the structure factors of the zirconium compound, particularly for lower order reflections, thus slightly blurring the electron density map. The total structure factor of a unit cell reflection can be considered as a combination of two separable structure factors. They are the structure factor of the compound (F^0) and the structure factor of the solvent (F^{solv}). The sum of both structure factors gives the total structure factor:

$$\mathbf{F} = \mathbf{F}^0 + \mathbf{F}^{\text{solv}} \quad [4.12]$$

Subtracting the structure factor from the total structure factor removes electron density in the channels enhancing the electron density map of the zirconium structure. In other words, the solvent is squeezed from the structure making it easier to find the hydrogen atoms and to identify the remaining atoms. The removal of the solvent contribution is called the “squeeze technique” which was developed by the University of Utrecht in the Netherlands.

This technique lowers $R(\text{int})$ and $R(\sigma)$, but the factor of residual increases to 8.8%. Hydrogen atoms in many water ligands remained to be invisible after squeezing out the solvent, probably due to the many rotational conformations. Therefore, water is inserted as a rigid species before the next refinement.

The non-co-ordinated sulphate S300 was split into two sulphate ions due to disorder. O303 had to be split as well, due to high atomic displacement factors (Appendix B, Single Crystal XRD Data). In the Fourier difference map, some remaining density popped up, which was only $1/2\text{\AA}$ separated from a neighbouring oxygen atom. The actual occurrence of two atoms being that close is impossible and this extra density is a split of the oxygen atom due to disorder. In the unit cell, it is manifested as two incorporated sulphate tetrahedra meaning that this sulphate could adopt different orientations.

A new Fourier differential map that included the solvent in the channels showed electron densities smaller than 4 electrons per $\text{\AA}^3$ (figure 4.14). These densities could not represent other sulphur atoms, because sulphate ions are relatively heavy and they have a strong charge, which should be visible in the structure. Based on the chemical analysis, electron densities larger than 3 electrons per $\text{\AA}^3$ were initially interpreted as nitrogen. These assignments were an issue of debate because it could not only be NH_4^+ or NH_3 , but H_3O^+ , H_2O or OH^- as well. Nevertheless, assignment of nitrogen to these peaks dropped the factor of residual to 6.33%. After all the refinements, only one peak with a density of 3.5 electrons per $\text{\AA}^3$ remained unassigned. It is located on the mirror plane at a distance of 2.1 $\text{\AA}$ from O36 and O54. Although there is a cavity in the structure, these distances are very short for hydrogen bonds. It is believed that this peak shows some remaining density, which belongs to the solvent part, and that it can be considered as an artefact.

The structure is refined until the factor of residual for F^2 (wR_2) is minimised. This factor is more stable than the factor of residual for F (wR_1), but a disadvantage is its dependency on the weighting scheme. The choice of weighting scheme is purely arbitrary and does not alter the structure¹.

¹ The weighting scheme is: $[\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P]^{-1}$, with $P = (\max F_o^2 + 2 \cdot F_c^2)/3$ and the Goodness of Fit (GooF) equals $\sum \frac{(F_o^2 - F_c^2)}{n - p}$. n is number of reflections (12380) and p is the number of parameters (855).

SHELX-97 automatically chooses A and B to reduce the Goodness of Fit (GooF) to 1. SHELX-97: $wR_1=6.33\%$ and $wR_2=18.47\%$ with $\text{GooF}=1.073$. As a rule of thumb: $wR_2 \approx 2 \cdot wR_1$. Choice: $A=0.01300$, $B=300$ results in $wR_2=14.77\%$ at the expense of $\text{GooF} = 1.350$.

4.6 Substructures in the Unit Cell

4.6.1 Overview

Resolving the structure is an iterative process and a part of the structure has already been discussed in the previous section. The structure is composed of aggregates of zirconium clusters. Each cluster has 18 zirconium atoms, while an aggregate contains 6 clusters, which are symmetry-related by the 6_3 screw axis on the origin of the unit cell. The dimensions of the unit cell (Table II) are quite extraordinary compared to the cell parameters of other zirconium sulphate compounds (Table III to VI in section 1.2). This is probably due to a growth in cluster size upon neutralisation. Addition of a base introduces OH groups, which can act as bridging groups between zirconium atoms.

The whole structure can be divided into three substructures. The first substructure is the polymeric zirconium cluster, the second the three non-co-ordinating or “free” sulphates and the third the solvent part. The location of the centre of each cluster in fractional co-ordinates (x_c, y_c, z_c) and the chemical composition of the compound of the first two substructures can be found in Table IV.

Substructure 1 is located on the mirror plane and electrically neutral. It has the molecular formula $Zr_{18}O_{10}(OH)_{26}(H_2O)_{22}(SO_4)_{13}$. Substructure 2 contains three free sulphates per zirconium cluster, located on the mirror plane with a total charge of 6-. The third substructure includes all the so-called nitrogen in the solvent part. Five of these N atoms are positioned on the mirror plane, while the remaining atoms have a site symmetry of 1. Six ammonium ions or protons must be present in order to maintain the charge balance.

Table IV Location in fractional co-ordinates and composition of substructure 1 and 2 per zirconium cluster.

Substructure	X_c	Y_c	Z_c	Zr	SO_4	O	OH	H_2O
1	0.307	0.010	$\frac{1}{4}$	18	13	10	26	22
2	0.359	0.428	$\frac{1}{4}$		1			
	0.276	0.288	$\frac{1}{4}$		1			
	0.493	0.368	$\frac{1}{4}$		1			

4.6.2 Substructure 1

The zirconium cluster has been well resolved and is illustrated in figure 4.9 to 4.13. The zirconium skeleton is held together by bridging sulphates, hydroxy groups and oxygen. The sulphate and hydroxy ligands from substructure 1 are also involved in hydrogen bonds with the other substructures. Water ligands in the zirconium cluster stick out of the cluster and participate in hydrogen bonds with substructures 1, 2 and 3 forming a well defined water interface between the zirconium cluster and the solvent part (figure 4.12).

The zirconium atoms are co-ordinated by oxygen atoms from the various ligands in the cluster. Zr1 and Zr2 are co-ordinated by 7 oxygen atoms while Zr3 to Zr11 have a co-ordination number of 8. Zr1 has only one bridging sulphate, while Zr3 has two bridging sulphates to Zr2. This leaves an open gap for Zr5 (and Zr5a) to attract an extra water molecule. The structure has a mirror plane through Zr1, Zr2, Zr3 and Zr8. A mirror plane can also be forced through Zr1, Zr2 and Zr3, if the two water ligands (O53 and O53a) were replaced by a bridging sulphate, which must be the mirror image of sulphate S1 through the plane Zr1, Zr2 and Zr3.

Zr1 is connected to oxygen from three different sulphates, one hydroxy bridge and two oxygen atoms, which are co-ordinated by three zirconium atoms (figure 4.15). A co-ordination number of seven is not uncommon and also occurs in monoclinic zirconia [33,34]. The position of the zirconium atom on the mirror plane is interesting. Zr1, O1, O30 and O31, generating the mirror images of O8 and O32, compose this plane. This is an extra symmetry element in a ZrO_7 species, which is not uncommon. $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ in figure 1.16 also has a mirror plane, bisecting oxygen around a zirconium atom. Bond lengths are in line with section 1.2.

Zr2 is also positioned on the mirror symmetry element and atoms Zr2, O2, O30 and O33 constitute the mirror plane. O4 and O34 are reflected to complete the seven-fold co-ordination (figure 4.16). The zirconium polyhedral of Zr1 is similar to the polyhedral of Zr2, which is a capped trigonal bipyramid with the mirror plane as base. Since this is difficult to visualise, it is easier to show the co-ordination shell by connecting some O-O distances (figure 4.17).

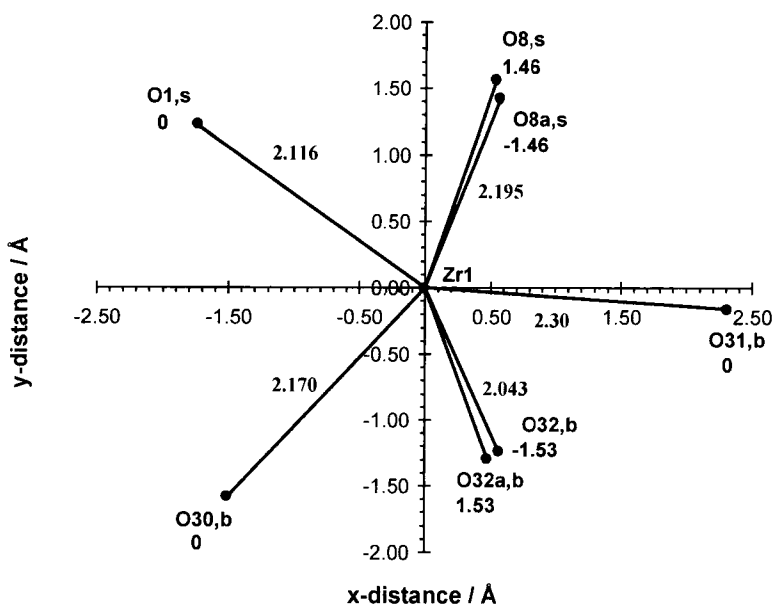


Figure 4.15 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr1 (a=mirror image, b=bridging oxygen, s=sulphate). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

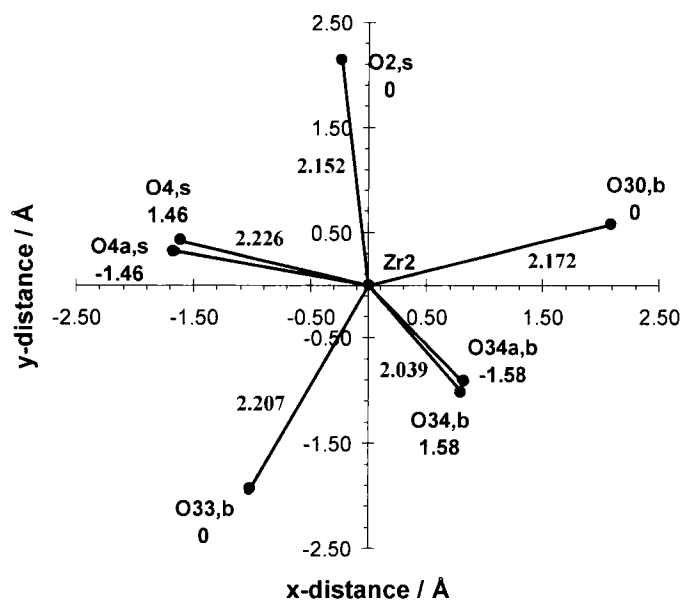


Figure 4.16 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr2 (a=mirror image, b=bridging oxygen, s=sulphate). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

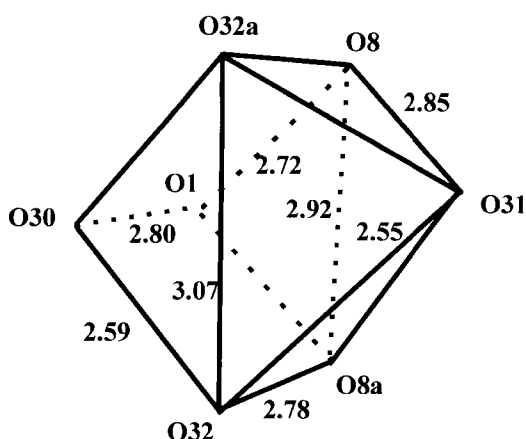


Figure 4.17 Oxygen configuration around Zr1. O1, O30 and O31 constitute the mirror plane. Distance between atoms in Å.

The next zirconium atom, Zr3, has also mirror symmetry, but in this case there are three oxygen atoms generated by reflection. Atoms Zr3, O33 and O36 constitute the mirror plane, producing the mirror images of O5, O12 and O35 to give a total co-ordination of eight (figure 4.18). O5, O12 and their mirror images form a rectangular, since their heights are the same (two decimals in Å) while O33, O35, O35a and O36 can be interpreted as a plane puckering into the structure. It is easier to understand the oxygen configuration if only a part of the polyhedral is drawn (figure 4.19). The mirror plane can be found easily by comparing the atoms with their mirror images.

Co-ordinates of the first oxygen shell around zirconium Zr4 to Zr11 are shown in figures 4.20 to 4.27. Their polyhedra are omitted since they do not contain any symmetry, except for Zr8, which is similar to Zr3 (figure 4.19). Almost all the other polyhedra differ in geometry, just as those reported in section 1.2. It is therefore not relevant to discuss all kinds of angles within these polyhedra but it can be confirmed that zirconium can be co-ordinated in various ways.

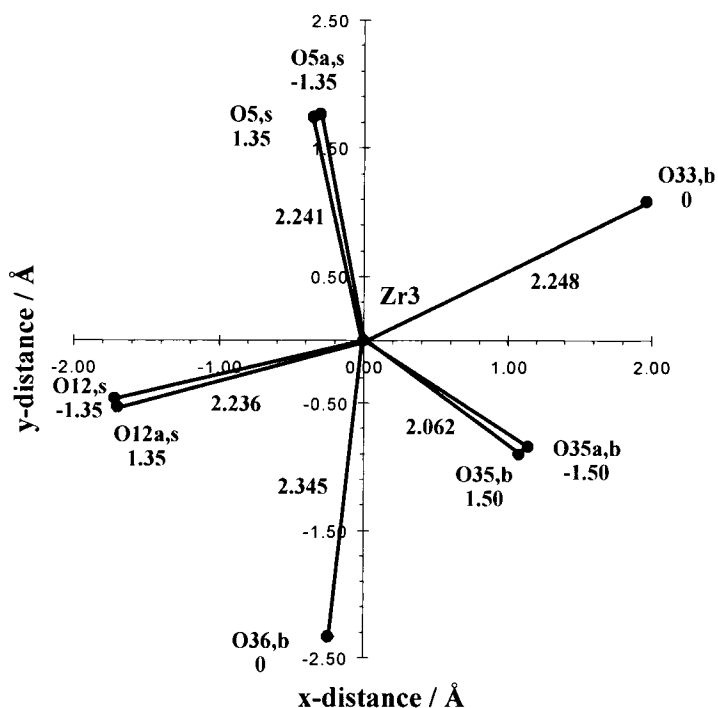


Figure 4.18 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr3 (*a*=mirror image *b*=bridging oxygen, *s*=sulphate). Z-axis is parallel to the *c*-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

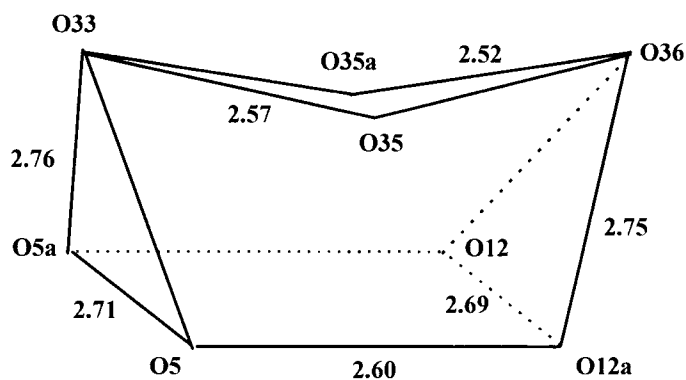


Figure 4.19 Oxygen configuration of Zr3. Distance between atoms in Å.

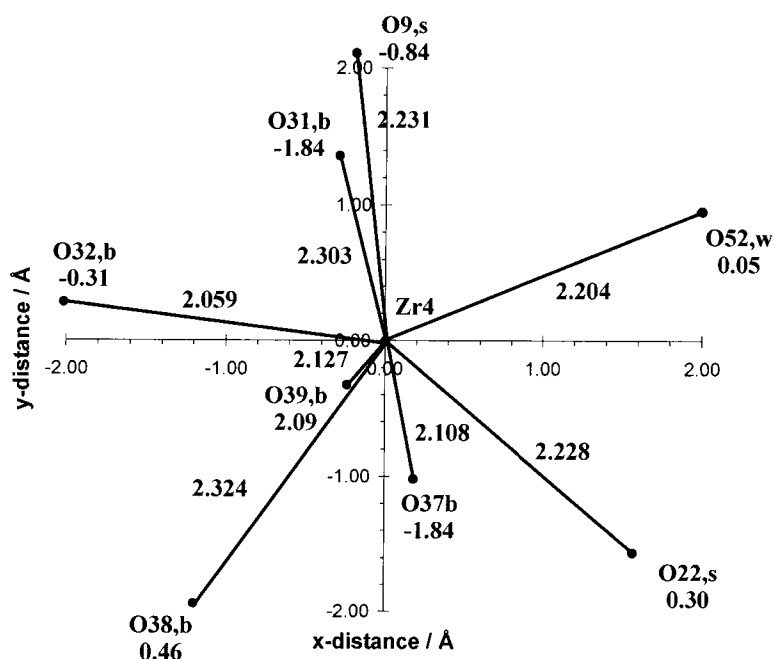


Figure 4.20 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr4 (b=bridging oxygen, s=sulphate, w=water). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

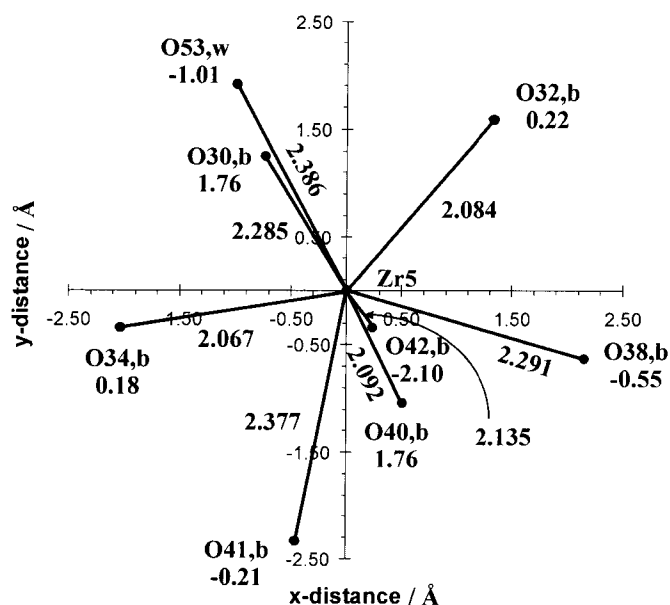


Figure 4.21 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr5 (b=bridging oxygen, s=sulphate, w=water). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

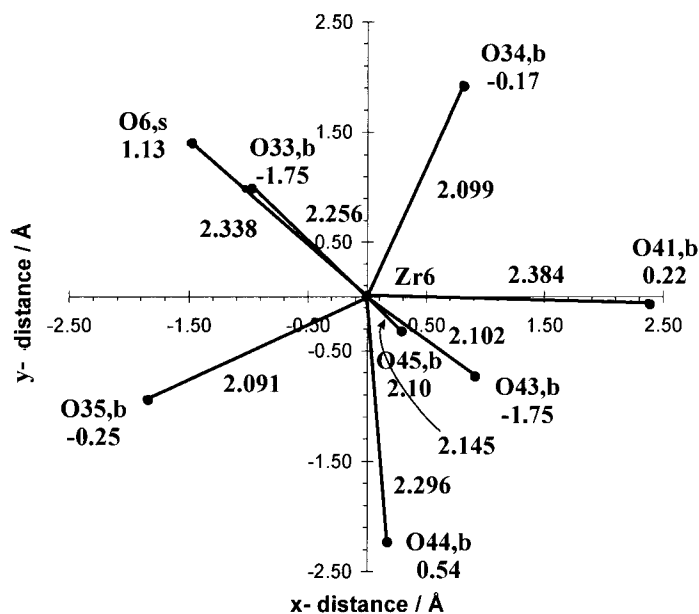


Figure 4.22 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr6 (b=bridging oxygen, s=sulphate). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

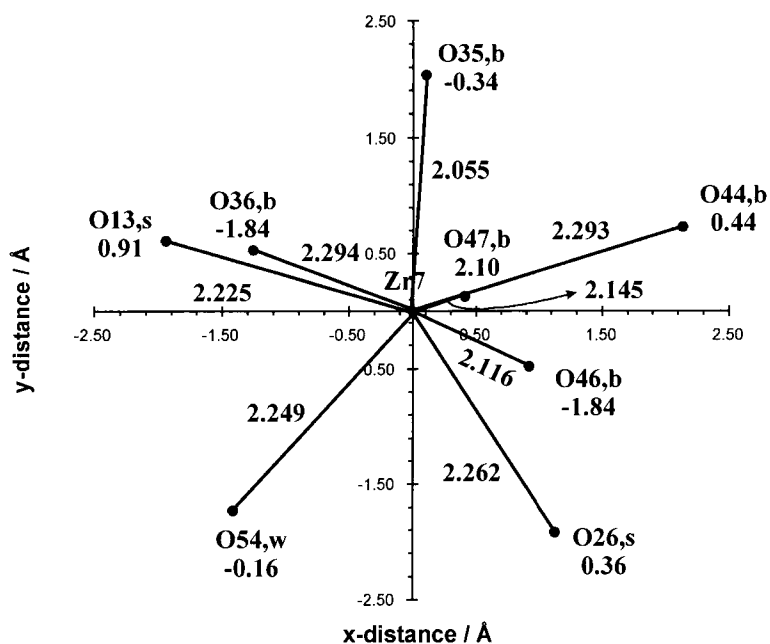


Figure 4.23 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr7 (b=bridging oxygen, s=sulphate, w=water). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

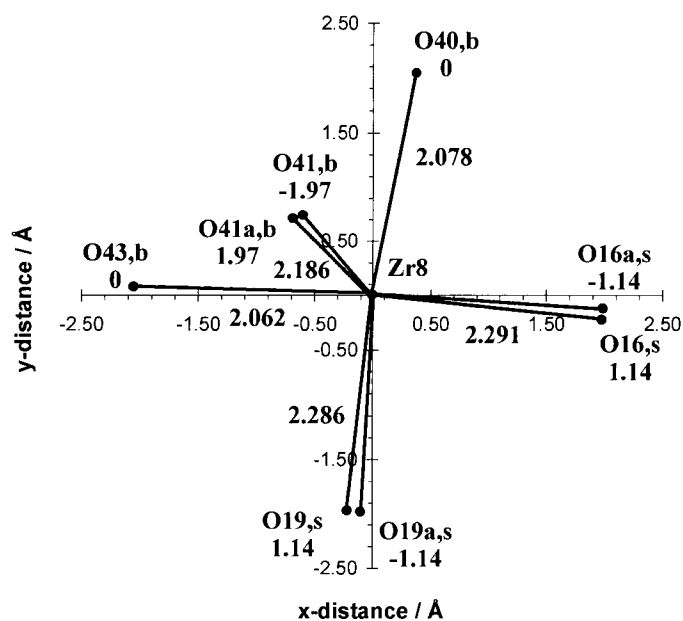


Figure 4.24 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr8 (b=bridging oxygen, s=sulphate). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

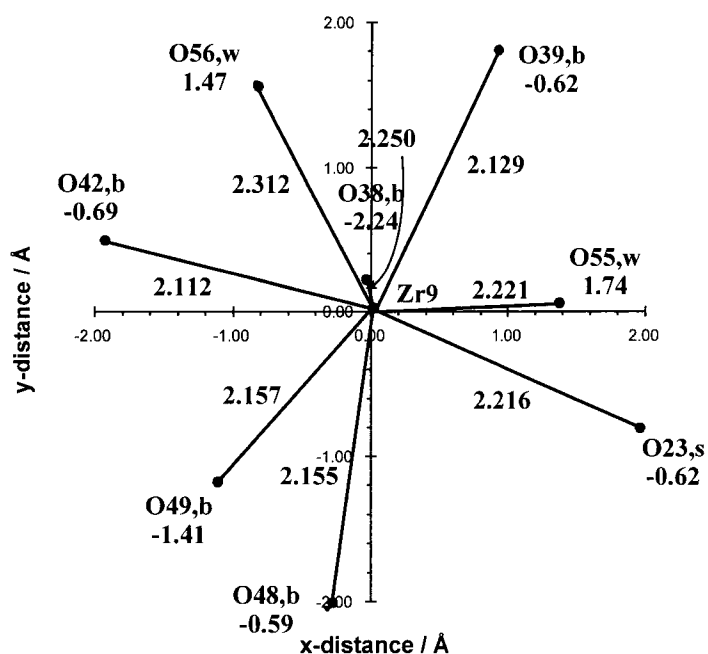


Figure 4.25 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr9 (b=bridging oxygen, s=sulphate, w=water). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

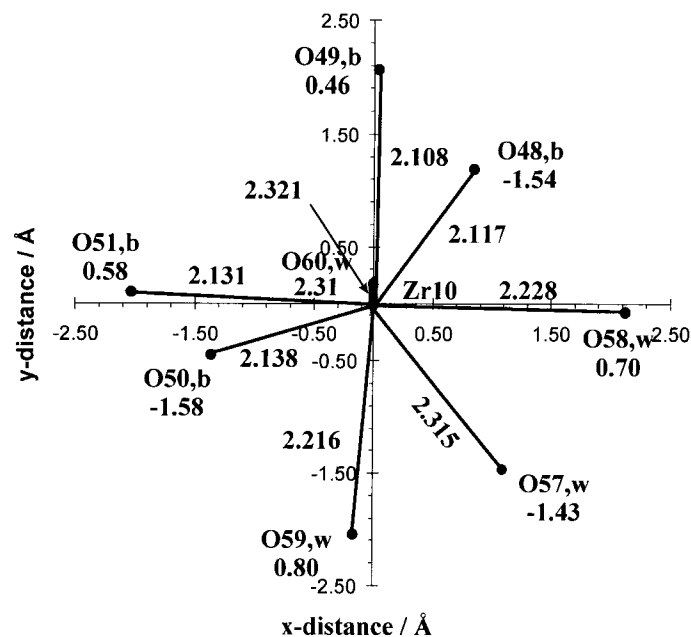


Figure 4.26 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr10 (b=bridging oxygen, s=sulphate, w=water). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

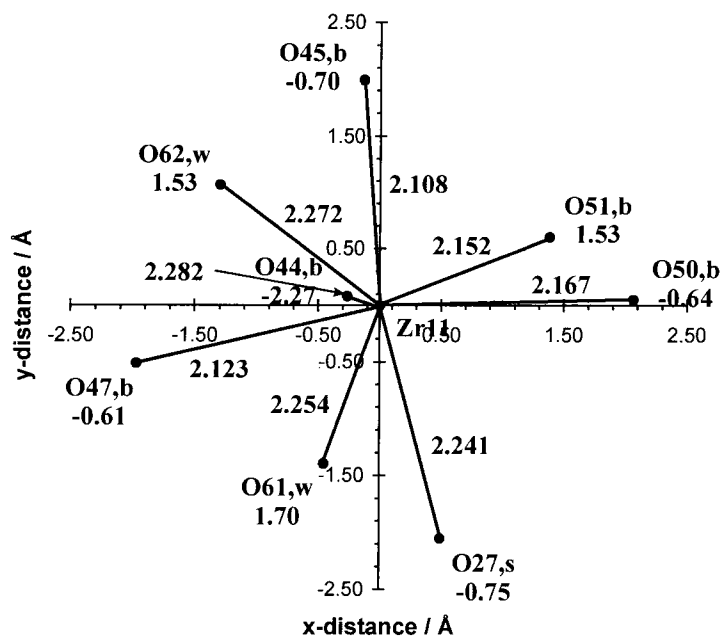


Figure 4.27 Co-ordinates of atoms in an orthogonal co-ordination system with respect to Zr11 (b=bridging oxygen, s=sulphate, w=water). Z-axis is parallel to the c-axis of the unit cell and z-co-ordinates are printed down the atomic label. Bond lengths are printed along the bonds.

Oxygen atoms co-ordinated by three zirconium atoms have Zr-O bond lengths between 2.04Å and 2.10Å ($\bar{x}$ =2.067, σ =0.021, n =16)². Zr-O bond lengths of oxygen which are connected to four zirconium atoms vary between 2.17Å and 2.29Å ($\bar{x}$ =2.223, σ =0.043, n =6). The average bond length is higher than in the previous type of oxygen, because oxygen must provide space for four zirconium atoms in its co-ordination shell. It can accommodate the extra zirconium atom by expanding its Zr-O bonds.

The next kind of oxygen is a hydroxy group in Zr₃OH species. The Zr-O bond lengths range from 2.18Å to 2.38Å ($\bar{x}$ =2.302, σ =0.049, n =13). Despite the difference of 0.20Å between the minimum and maximum distance, the standard deviation is still of the same order. Zr-OH bonds co-ordinated by three zirconium atoms are larger than oxo bonds having the same co-ordination number. This is due to a decrease in the partial charge of oxygen, according to the principle of electronegativity equalisation [35]. A reduced electronegativity of the oxygen by a hydrogen atom leads to longer Zr-O bonds.

The next type of oxygen is the hydroxy bridge with bond lengths between 2.11Å and 2.17Å ($\bar{x}$ =2.132, σ =0.018, n =18), which are in line with the Zr-OH distance in figure 1.16. The bonds are smaller than in the Zr₃OH species due to a reduction in the number of co-ordinating zirconium atoms.

All the hydroxy groups point out of the cluster to enable the formation of hydrogen bonding. Water ligands, co-ordinating zirconium directly, have Zr-O distances between 2.20Å and 2.39Å ($\bar{x}$ =2.271, σ =0.054, n =11). Zr1 to Zr3, Zr6 and Zr8 have no water ligands. O52, O54, O57, O59, O62 and O54 are directed to the channels, while O52, O54, O55, O56, O58, O60 and O62 interact with sulphates from substructure 2. Not all the water ligands function as an interface to the solvent part. O53, O55, O58, O59 and O61 form connections to other clusters through hydrogen bonds with cluster sulphates.

The last type of oxygen originates from cluster sulphates with Zr-OS distances ranging from 2.12Å to 2.34Å ($\bar{x}$ =2.23, σ =0.049, n =19). The average distance is slightly higher, but still in agreement with the reported values in section 1.2. The sulphates normally connect two different zirconium atoms. Sulphate S2 and its mirror image is an exception. It co-ordinates

² $\bar{x}$ =average, σ =standard deviation, n =number of bonds.

three different zirconium atoms (figure 4.28), which is rather unusual, but the bond lengths are in agreement with those in section 1.2.

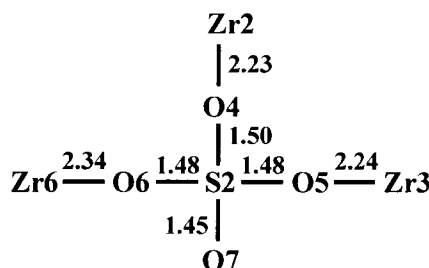


Figure 4.28 Co-ordination of S2 sulphate ion.
Bond lengths (in Å) are printed near the bonds.

The other S-O distances in the cluster are also in the range from 1.42Å to 1.51Å, except for S4-O14. Therefore, sulphate S4 needs some special attention. S4 must be split into S4a and S4b, each having a site symmetry number of one and an site occupancy of ½. It means that S4 in 50% of the unit cells crystallises in position S4a, while the other 50% in S4b. Both positions are symmetry related by a mirror plane through O12, O13 and O14 of the same sulphate. O15 has consequently a mirror image with a site occupancy of 50% and this type of disorder is accompanied by a large atomic displacement factor (figure 4.29).

The S4a-O14 and S4b-O14 are 1.29Å and 1.30Å and not in line with section 1.2 because the position of O14 is not well defined. The large atomic displacement factor of O14 is probably due to the position of O14 just off the mirror plane. This spreads the electron density and SHELLX-97 compensate for this effect by increasing the atomic displacement factor.

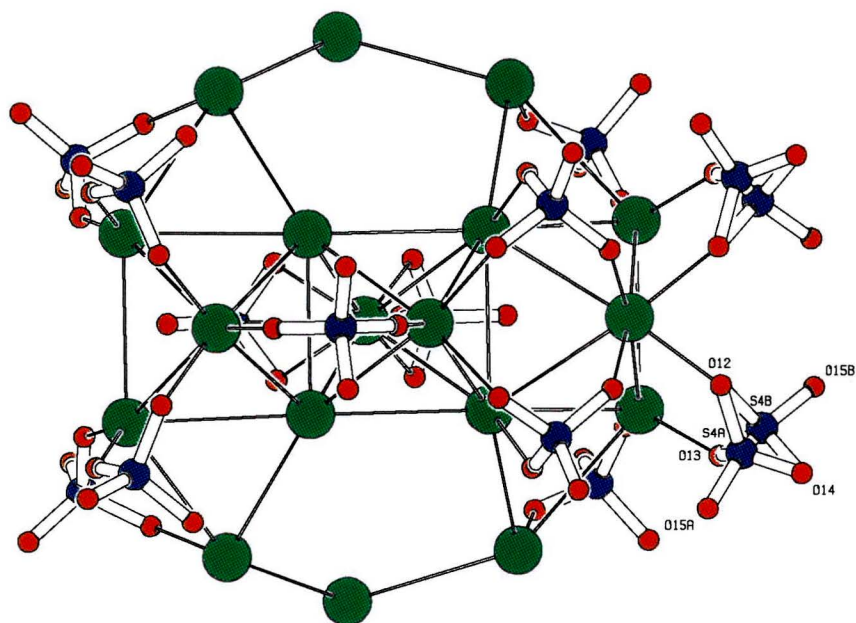


Figure 4.29 Splitting positions of S4 and O15 through the mirror plane O12, O13 and O14. O14 is just off the plane.

4.6.3 Substructures 2 and 3

Many electron densities are found around the zirconium cluster (designated N), forming a sort of interface between the zirconium cluster and the solvent part. The extent of disorder of atom N increases with increasing distances from the zirconium cluster.

N(401) forms hydrogen bonds with donors O42 and O45 and acceptor O28 of the zirconium cluster. O28 originates from a bridging sulphate in the zirconium cluster and can only accept hydrogen. N(401) is also hydrogen bonded to a free sulphate through O(302). Since it is connected to four hydrogen, it is not expected that an extra hydrogen atom is involved. It is therefore concluded that N(401) is actually a water molecule, which occurs twice per cluster. N402 can be found near O21 and O29 of the zirconium cluster sulphates S6 and S8 respectively. It is also connected to the oxygen O104 and O301 of the two free sulphates. All the oxygen atoms can participate in hydrogen bonds as acceptors and it is believed that N402 is an ammonium ion. Also note that the Pk_a of ammonium is 9.24, which means that all the real nitrogen species are ammonium ions and not NH_3 ligands in a solution with $pH=2$. The N402-O bond lengths vary between 2.99Å and 3.04Å.

The free sulphate S300 is kept in position and is attached to the zirconium cluster by hydrogen bonds. The sulphate configuration deviates slightly from a tetrahedron, due to the hydrogen bonding. O49, O51, O54 and O60 connect the free sulphate directly, while they are indirectly linked to (O21, O29) and (O28, O42, O45) through ammonium and water respectively. The hydrogen bond structure is shown in figure 4.30.

The positions of O60 and O101 need some special attention. Atom O101 originates from another sulphate and will be discussed later. O60 is linked to O304 by some sort of hydrogen bonding. The hydrogen involved is not visible in the electron density map, but might be hidden in the background noise. SHELX-97 listed the O304-O60 distance, but not the O304-H60 distance (H60A or H60B). Since the positions of H60A and H60B are known, it means that the latter distance is too far from O304 and the concealed hydrogen must be associated with O304. If this is the case, the whole structure in figure 4.30 will be $(NH_4)HSO_4 \cdot H_2O$.

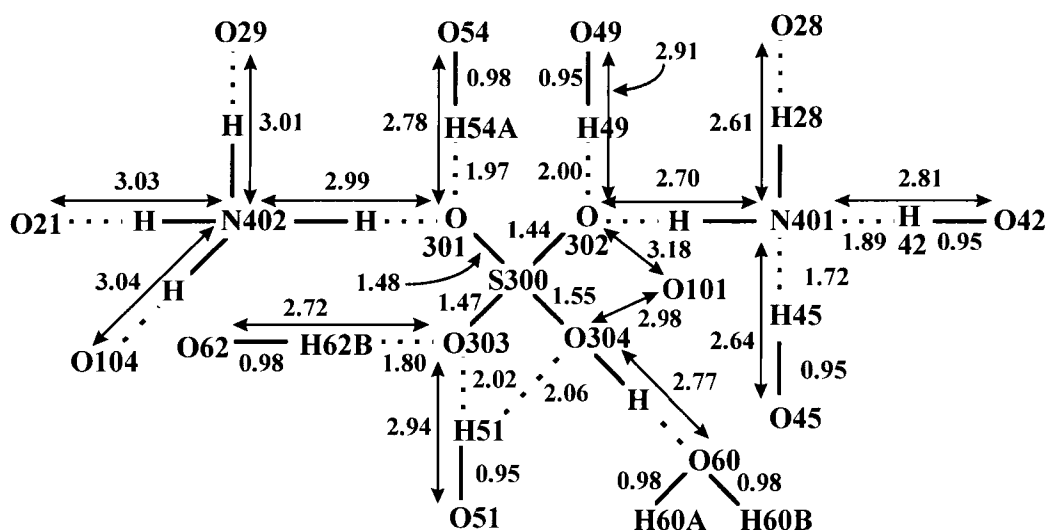


Figure 4.30 Proposed hydrogen network of the N401-S300-N402 structure in the solvent part (—covalent bond; ...hydrogen bonding; bond lengths in Å). All hydrogen in covalent N-H bonds are part of the N atom.

The free sulphate S100 is bonded to N402 through O104 and to S300 through O101 (see also figure 4.31). If O304 carries a hydrogen atom, which is hydrogen bonded to O60, O101 must also possess a hydrogen for a hydrogen bond with O304. O103 is hydrogen bonded to O55 and O102 connects S100 to N406. N406 donates hydrogen to the cluster sulphates S5 and S7 through O18 and O24 respectively. Ammonium is associated with the sulphate ion to maintain charge neutrality and is expected to be located near the sulphate. It is suggested that N406 is an ammonium ion, analogous to figure 4.30 and if this is correct, the S100-N406 combination represents $(\text{NH}_4)\text{HSO}_4$.

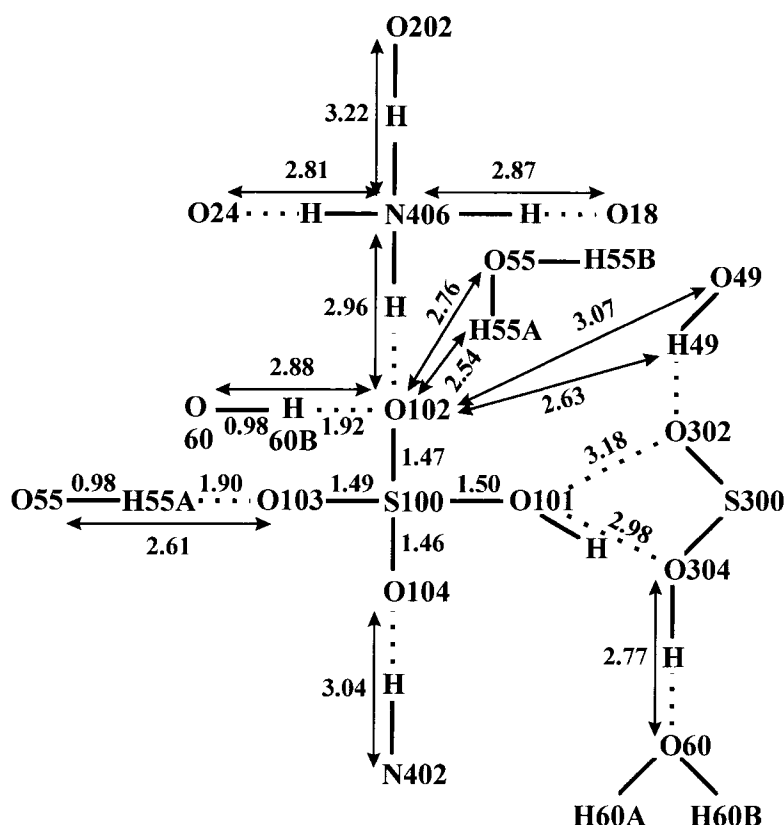


Figure 4.31 Proposed hydrogen network of the N406-S100 structure in the solvent part (—covalent bond; ...hydrogen bonding; bond lengths in Å). All hydrogen in covalent N-H bonds are part of the N atom.

The distance between N406 and the oxygen of the next sulphate (O202) is 3.22Å, which is too long for a normal hydrogen bond. O202 is connected to cluster water through O52 and O58. O201 is hydrogen bonded to a water ligand of the zirconium cluster (O60) at conventional distances, while O203 is connected to N404 at 3.23Å (figure 4.32). In other words, the S200 sulphate is more isolated compared to the other free sulphates.

N404 is not only bonded to the S200 sulphate, but also to N417 and O59 from a water ligand in the zirconium cluster. The former is in its turn linked to N403 and N414 at specific hydrogen bond distances. N403 must donate hydrogen atoms to O17, O25 and O57. Although O57 is a water ligand, it can not use its hydrogen atoms for a hydrogen bond with N403 since the N403-H57A (or B) distances are too long. N403 must be an NH₃ or a NH₄⁺ species. N403 is the nearest “nitrogen like” density peak in the electron density map to

balance the charge of the structure. Also note that the mother solution is acidic (pH=2) and it is therefore believed that N403 represents an ammonium ion. In such a case, N404 and N417 could be bridging water molecules, connecting N403 and sulphate S200. However, the reader must bear in mind that this is only a hypothesis to complete the free sulphate structure. N403, N404 and N417 are not located on a mirror plane and occur twice per zirconium cluster.

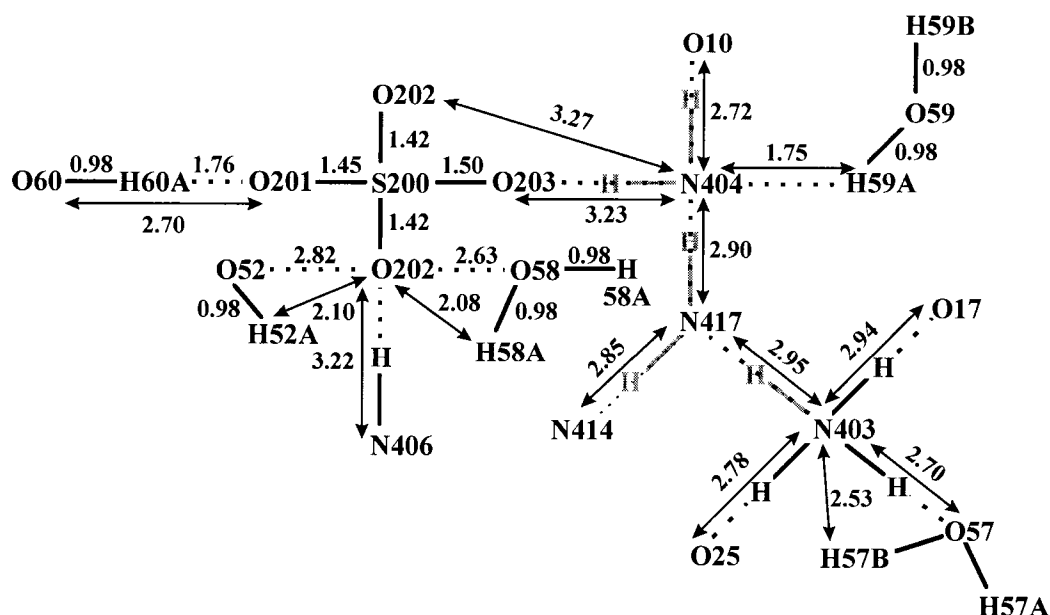


Figure 4.32 Proposed hydrogen network of the N4061-S100 structure in the solvent part (—covalent bond; hydrogen bonding; ---suggested covalent bond; bond lengths in Å). All hydrogen in covalent N-H bonds are part of the N atom.

It seems that the free sulphates and ammonium ions form a string along the edge of the zirconium cluster. The string is attached to substructure 1 through many hydrogen bonds in order to support the structure of the cluster as shown in figure 4.33. The figure also reflects the observed disorder of the oxygen atoms in the free sulphates.

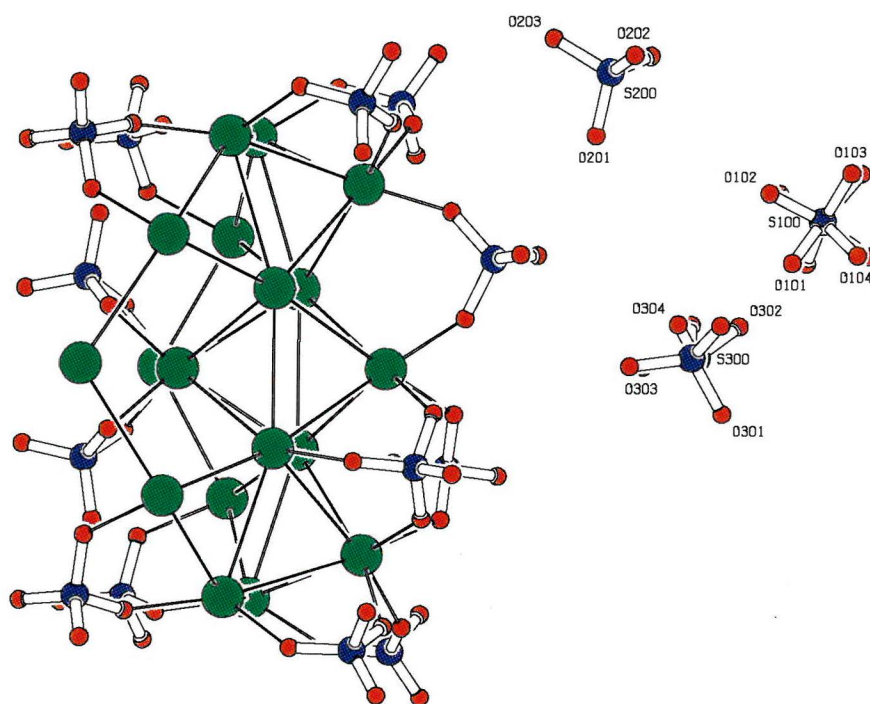


Figure 4.33 Positions of the free sulphates with respect to substructure 1.

N405 is linked to O6 and O15A from two sulphates S2 and S4A in the zirconium cluster. The sulphates can only accept hydrogen in hydrogen bonds and should accept hydrogen from N405. O54 and O62 are donating water ligands and N405 must be a water molecule. This water is connected to the zirconium cluster in four directions (figure 4.34).

N413 is bonded to O54 at a distance of $2.75\text{\AA}$ and H54B at $2.82\text{\AA}$. This atom can only donate hydrogen to O54, since H54A and H54B are too far to form a hydrogen bond. O15B is also bonded to N413 at $2.04\text{\AA}$ and can only accept hydrogen since it is a cluster sulphate. The next atom in the vicinity is H36, originating from a hydroxy bridge in the zirconium cluster at a large distance of $2.63\text{\AA}$. Since there are no other atoms present, it is concluded that N413 corresponds to a water molecule.

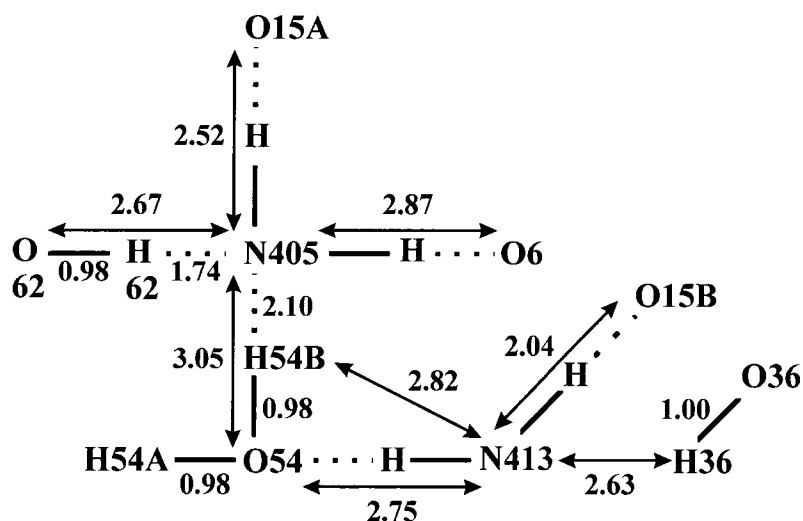


Figure 4.34 Hydrogen bonds in the N405-N413 structure (— covalent bond; ... hydrogen bond). All hydrogen in covalent N-H bonds are part of the N atom.

The N peaks in the electron density map were isotropically refined and Table V shows their isotropic atomic displacement parameters.

Table V Isotropic atomic displacement factors for peaks in the solvent part (*u*=unknown).

Atom label	Species	U_{iso}	Atom label	Species	U_{iso}
N401	H ₂ O	0.035	N408	u	0.091
N402	NH ₄ ⁺	0.041	N410	u	0.029
N403	NH ₄ ⁺	0.042	N411	u	0.130
N404	H ₂ O	0.047	N412	u	0.148
N405	H ₂ O	0.048	N414	u	0.165
N406	NH ₄ ⁺	0.050	N415	u	0.197
N413	H ₂ O	0.066	N416	u	0.300
N407	u	0.083	N417	H ₂ O	0.240

From the table it is clear that the assigned peaks N401 to N406 and N413 (except N417) have lower atomic displacement factors compared to the unknown species in the solvent part. The factors of the known species are somewhat higher than the (anisotropic) values for the atoms in substructure 1, but they are still acceptable. The atomic displacement factors reflect the extent of disorder for the unassigned peaks in the solvent part and the higher order of the assigned peaks in the sulphate string. The unassigned atoms are present, but they can not be identified with certainty. They are probably water molecules, hydrogen bonded to the zirconium cluster and not NH_3 ligands. If they were ammonium ions, they would have to be accompanied by an anion (SO_4^{2-} , OH^-) to preserve the charge balance.

The unit cell contains three channels, two of them being identical in size and shape (figure 4.35). Type O runs through the origin of the cell and has the smallest cross section of the channel. Assuming a cylindrical channel, its diameter is $6.5\text{\AA}$. Type A and B are identical having a diameter of $12\text{\AA}$. Their positions in the unit cell are related by swapping the (x,y) fractional co-ordinates (Table VI).

The density of the cell can be calculated by adding the mass of all the atoms in the unit cell and dividing this sum by the unit cell volume. The atoms, designated as N, are not taken as nitrogen, but as water or ammonium, both having the same mass. The corresponding density is $2.326\text{ g}\cdot\text{cm}^{-3}$.

It is now possible to calculate the inner surface of channels O, A and B, based on their volumes. Channel O is a cylinder, but channels A and B are in between a cylinder and a triangular pipe. The corresponding surfaces are calculated for both types of A and B (Table VII.).

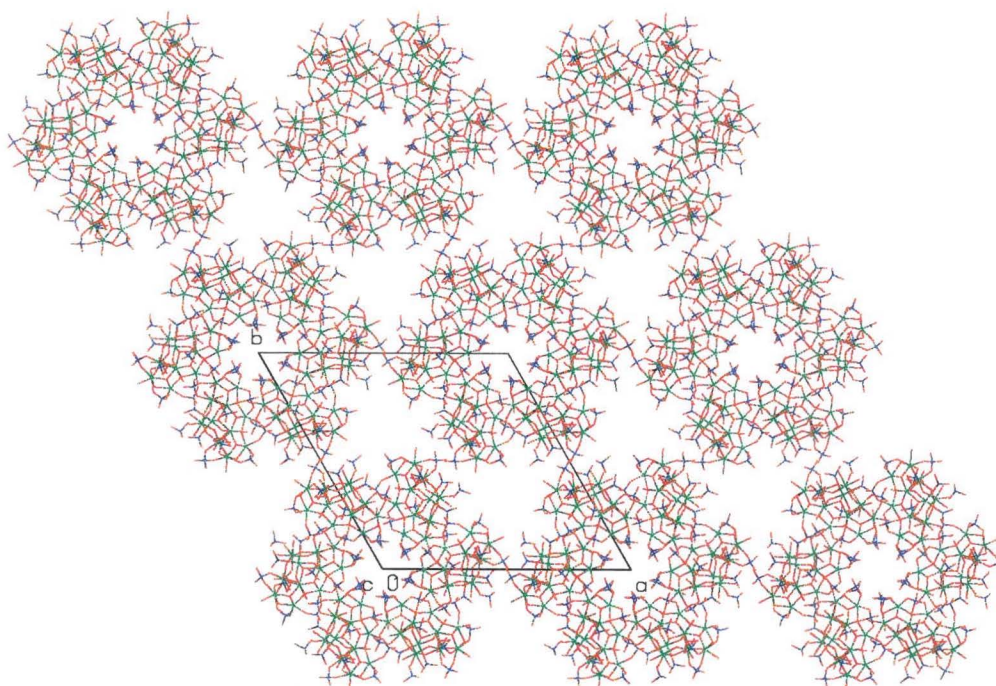


Figure 4.35 Four adjacent unit cells showing the channels in the single crystal structure.

Table VI Position, diameter and volume of the channels in the ammonium zirconium sulphate unit cell.

Type	Position (x,y) fractional co-ordinates	Diameter Å	Volume Å ³
O	(0,0)	6.5	625
A	($\frac{1}{3}, \frac{2}{3}$)	12	2100-2300
B	($\frac{2}{3}, \frac{1}{3}$)	12	2100-2300

Table VII *Inner surfaces of the channels in a unit cell for circular and triangular pipes, including the total surface area, expressed in $\text{m}^2 \cdot \text{g}^{-1}$. Channel O is a cylinder.*

Channel type	Surface / ($\text{m}^2 \cdot \text{g}^{-1}$)	
	Circular	Triangular
O	83	-
A/B	153-160	196-205
Total	389-403	475-493

The surfaces in Table VII are quite high when compared to zirconia (see Table VIII), but the question is whether the surfaces are accessible. The compound is soluble in water and cracks upon drying. BET values were measured, but no surface area could be determined. Drying the compound has severe consequences for the structure. The channels are very narrow and filled with water, introducing enormous surface tensions upon drying (surface tension water; $\gamma = 73 \text{ mN} \cdot \text{m}^{-1}$). The structure collapses and in addition, the water ligands and hydroxy bridges form oxo bonds with neighbouring clusters, destroying the channels and the surfaces. Consequently, the structure shrinks as was indeed observed.

4.6.4 Modelling the Structure

It is possible to model the structure similar to the modelling of zirconia stabilised by yttrium oxide. Introducing Y^{3+} into the zirconia lattice stabilises cubic zirconia in the fluorite structure. Depero and Zocchi modelled the phase of yttria-stabilised zirconia by defining building blocks of zirconia clusters to gain insight in the stabilisation of the structure without including lattice energies [36].

The structure described in this chapter can be treated similar. The zirconium clusters are already defined (figure 4.9). They are located around the origin of the unit cell in figure 4.18 and are symmetry related by a 6_3 -screw axis. Figure 4.36 shows the spatial arrangement of the clusters schematically after applying the 6_3 -screw axis.

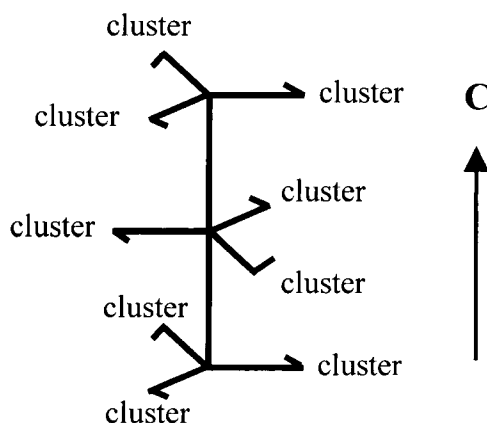


Figure 4.36 Cluster orientation in a 6_3 -screw axis parallel to basis vector c of the unit cell.

Three clusters constitute a layer perpendicular to the c -axis and this layer is called layer A. The remaining clusters in this layer can be constructed by translation over the basis vectors $\mathbf{a}$ and $\mathbf{b}$ of the unit cell. The next layer is 60° rotated around the screw axis and it is therefore not the same as the previous layer. It is called layer B and the stacking sequence of the layers is ABAB.....

Negative charged sulphate groups point out of the cluster, giving the cluster a negative outer layer. It is believed that these electrostatic repulsive forces and steric strain between clusters are responsible for the conformation of alternating layers. Each cluster in a layer is maximal removed from its lateral neighbour clusters (120°) to reduce repulsion and steric strain (figure 4.37). It is separated from its neighbour clusters in the next layer by 60° from a top view to experience minimal repulsion.

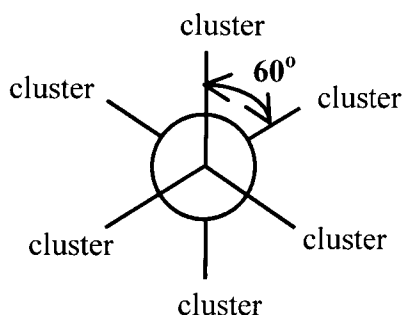


Figure 4.37 *Spatial conformation of two cluster layers in a projection along the c axis of the unit cell*

However, all these clusters must be held together to form the structure of the single crystal. Inter- and intra-hydrogen bonds stabilise the clusters and the structure as a whole. Substructure 2 facilitates this stabilisation through a complex of hydrogen bonds as discussed in the previous section. Note that there are no direct bonds between the clusters, except hydrogen bonds. This makes the structure very unstable and substructure 2 act as a support between clusters. It is the fine balance between electrostatic repulsive forces and the attractive forces from hydrogen bonds, which is responsible for the type and stability of the structure.

All the clusters around the screw axis constitute a pillar of clusters. The single crystal can be constructed by translating a pillar over the basis vectors **a** and **b** of the unit cell. In this way, the structure is considered as a set of parallel pillars (figure 4.35) instead of alternating layers.

4.7 Powder and Single Crystal

The importance of ammonium in crystallisation is also reflected in the synthesis of the ammonium zirconium sulphate powder in section 4.2. Ammonium hydroxide is added during the synthesis of the powder. If the addition of extra ammonium hydroxide is omitted, the substance becomes a paste instead of a filterable powder.

In case of the single crystal, the total number of crystallised ammonium ions amounts to four per zirconium cluster if the assignment in section 4.6.3 is correct. The ratio of ammonium to zirconium is 2:9, which is appreciably lower compared to the chemical analysis of the ammonium zirconium sulphate powder. Some amorphous ammonium hydroxide or sulphate may be randomly present in the channels of the single crystal, but it can not compensate for the shortage of ammonium.

Substructure 1 has the molecular formula $\text{Zr}_{18}\text{O}_{10}(\text{OH})_{26}(\text{H}_2\text{O})_{22}(\text{SO}_4)_{13}$. Neutralising an acidic zirconium sulphate solution increases the pH and replaces sulphate ions with hydroxy groups. The Zr to SO_4 ratio is 1:0.72 in substructure 1 of the single crystal, while it is 1:1.72 in a powder. Both crystals originate from the same zirconium sulphate solution, but have different crystallisation rates. In this solution the Zr to SO_4 ratio ranges from 1:2 to 1:3. Please note that the powder is obtained by heating the solution to boost evaporation of water, while the single crystal is grown at room temperature. During the preparation of the powder, the solution becomes more concentrated due to water evaporation forcing the zirconium compound to crystallise. Beside the zirconium compound, ammonium sulphate could also be salted out³. Assuming the zirconium structure of the powder has the same molecular formula as substructure 1, the Zr: SO_4 ratio of the zirconium structure in the powder is 1:0.72, while the Zr: NH_4 ratio is 1:1 (Table I). If this is correct, then ammonium sulphate must co-precipitate with a NH_4 : SO_4 ratio of 1:1. It means that ammonium sulphate precipitates as NH_4HSO_4 , being a matrix for the crystallisation of the zirconium compound.

³ Solubility $(\text{NH}_4)_2\text{SO}_4$: $5.78 \text{ mol}\cdot\text{l}^{-1}$ at 298K.

This is in line with the pK_a value of HSO_4^- ($pK_a=1.92$) with respect to the pH of the solution ($pH=2$). During the evaporation of water, the solution becomes more acidic.

Figure 4.38 shows the Raman spectra of a $NH_4HZrO(SO_4)_2$ powder and a (cracked) single crystal dried at $130^\circ C$. Zr-O bands are expected in the 560 cm^{-1} to 745 cm^{-1} range and the sulphate bands can be found between 971 cm^{-1} and 1200 cm^{-1} [37]. Both spectra are identical except for an extra band at 1428 cm^{-1} in the powder spectrum. The ammonium band at 1428 cm^{-1} in the spectrum of $NH_4HZrO(SO_4)_2$ is very weak because of the ionic nature of the species [38]. The absence of the 1428 cm^{-1} band in the spectrum of the dried single crystal is due to the different $NH_4:Zr$ ratios of both samples confirming the hypothesis above. OH bands are present in both spectra at 3160 cm^{-1} (not shown) and are very broad due to hydrogen bonding.

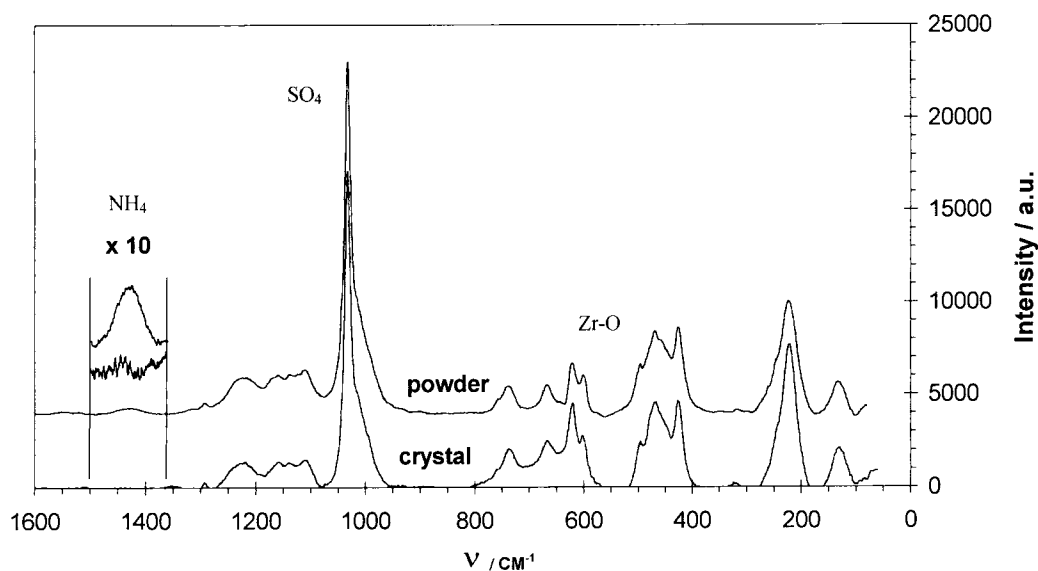


Figure 4.38 Raman spectra of $NH_4HZrO(SO_4)_2$ powder and a single crystal. Laser power 75 mW, integration time 150s, sample: macro phase. See appendix B (Table B2) for exact band positions of the powder.

4.8 Decomposition

A TGA/DSC curve of single crystals and the powder were recorded (figure 4.39). The samples were first heated up to 130°C to remove all loosely bonded water molecules. This temperature was maintained for 30 minutes before the rest of the analysis took place.

A continuous mass loss below 600°C indicates the volatilisation of (constitutional) water. Hydroxy groups will dehydrate forming oxo bonds and ammonium will be released as NH_3 . Heating the sample completely destroys the supporting hydrogen bond network and zirconium clusters will be joined together. The whole crystal structure will be destroyed as well, resulting in an amorphous zirconium oxy sulphate compound (figure 4.41A).

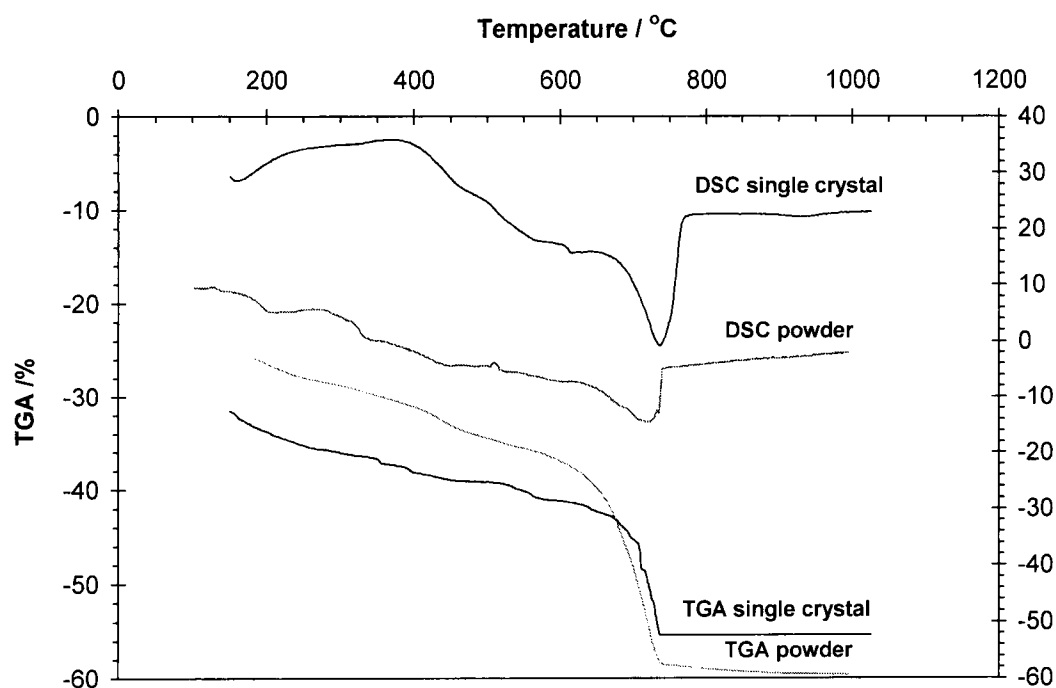
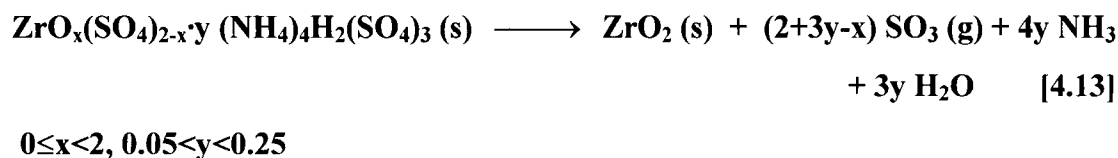


Figure 4.39 TGA/DSC curve of ammonium zirconium sulphate; single crystal (black) and powder (grey). Scan rate 5 °C/min.

During the thermogravimetric analysis, SO_3 (or SO_2 and O_2) was released from 650°C and the sample had been completely decomposed to zirconia at 800°C. A total decomposition reaction can generally be written as follows:



According to the TGA curves, the sulphate content in a powder is much higher compared to the single crystal, due to the co-precipitation of ammonium (bi) sulphate during the preparation of the powder. During heating, the sulphate in the powder started to come off at a slightly lower temperature than in the single crystal, probably due to the extra ammonium (bi) sulphate present in the sample.

The original molecular mass of both samples can be calculated on the basis of the mass fraction of zirconia after calcination. According to the TGA curve, the molecular mass of the single crystal was 276 gram per mole zirconium. The molecular mass, determined by single crystal analysis, is 260 gram per mole zirconium¹. The difference in mass might involve some amorphous water, invisible in the single crystal analysis, but contributing to the initial mass in the TGA curve. This water is just an experimental artefact and not part of the compound. Nevertheless, the error in mass is just 5.8% and it can be concluded that the masses are in line with each other.

The molecular mass of the powder is 304 gram per mole zirconium. The extra mass is due to the co-precipitation of ammonium (bi) sulphate. It is not known whether this is ammonium sulphate, ammonium bisulphate or a combination of both.

The mass losses of sulphate in both samples between 650°C and 800°C are not in agreement with the expected losses. In both cases the mass loss is too low, indicating that the amount of sulphate in the sample is in fact lower than expected or that sulphate is being released at lower temperatures. Therefore, a new experiment was conducted.

¹ The molecular mass is determined by adding the masses of the three substructures and dividing it by the number of zirconium atoms per cluster. Substructure 1: $\text{Zr}_{18}\text{O}_{13}(\text{OH})_{26}(\text{H}_2\text{O})_{22}(\text{SO}_4)_{13}$, substructure 2: $(\text{NH}_4)_4\text{H}_2(\text{SO}_4)_3$ and substructure 3: $21 \text{H}_2\text{O}$.

The powder and the single crystal were dried at 500°C for 3 hours, placed in a furnace tube and heated again to 500°C. Steam was generated and heated in a 6m coiled copper pipe (Ø2mm) over a flame. The gas had a temperature below 500°C, but well above 350°C, and was blown over the sample. The experimental set up is shown in figure 4.40. The evolving decomposition products, condensed at the end of the furnace tube, were highly acidic and consisted of H₂SO₄. Acidic gas also evolved. The reaction was continued until no acidic gas evolved from the sample. According to the XRD spectrum of the powder, obtained during decomposition (figure 4.41B), the samples dissociated to zirconia. The release of the sulphate groups was confirmed by infrared spectra (not shown), recorded before and after the decomposition. The samples decomposed to zirconia within 4 hours in the presence of steam, while it degraded much slower in a dry atmosphere (air) (>4 weeks).

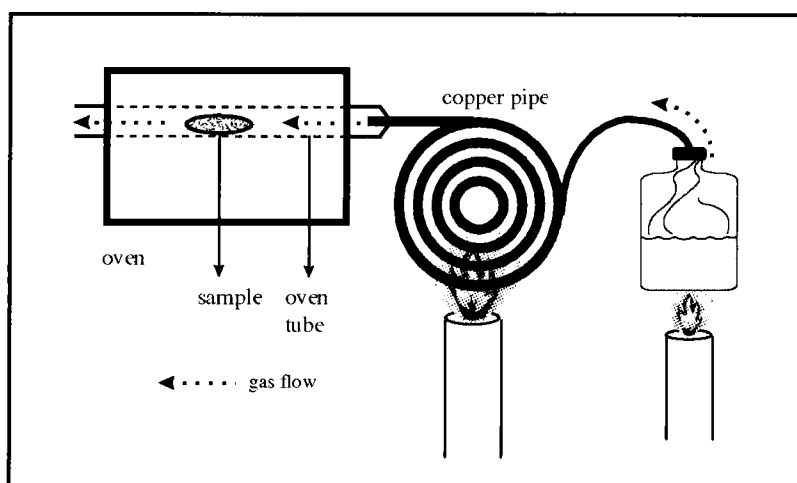


Figure 4.40 Experimental set up for the decomposition of the zirconium sulphate sample.

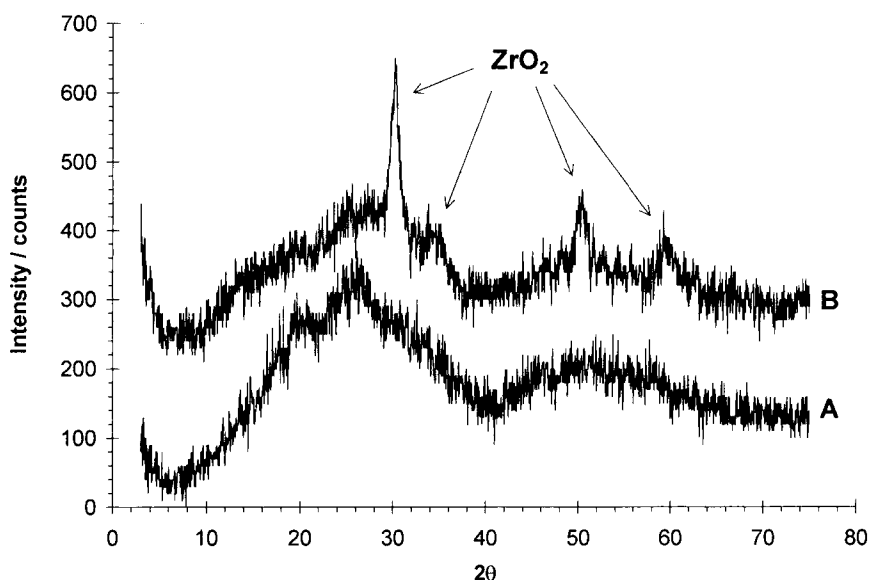
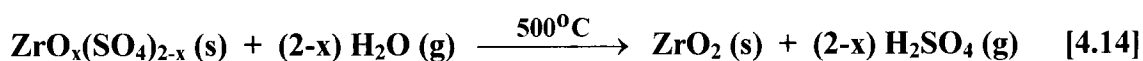


Figure 4.41 XRD pattern of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$; A) heated at 500°C for 1 day and B) during decomposition by water vapour at 500°C .

SEM photos of the powder were taken to study the surface of the samples before decomposition (A), after heating at 500°C for 5 weeks in air (B) and after decomposition by water vapour for 3.5 hours (C). Sample C was thermally treated for 3 hours at 500°C prior to decomposition. The particles looked similar at a magnification of 1,000x, although sample C showed more cracks. An increase in the magnification to 15,000x revealed the unruffled exterior of the powder before decomposition and after decomposition in air at 500°C (figure 4.42). The powder decomposed in water vapour has a roughened surface.

The powder slowly decomposes to zirconia in air, probably reacting with water in the atmosphere. At this decomposition pace, the gaseous products slowly diffuse through the sample without extensively disturbing the morphology. In case of decomposition by blowing water vapour over the sample, decomposition is complete within hours, affecting the particle's morphology. The samples must react with water to produce sulphuric acid.



This reaction is the opposite of dissolving zirconia in sulphuric acid. The Gibbs energy for the reaction under these experimental conditions must be negative.

The decomposition of the single crystals follows a similar path and their SEM photos look identical to those in figure 4.42.

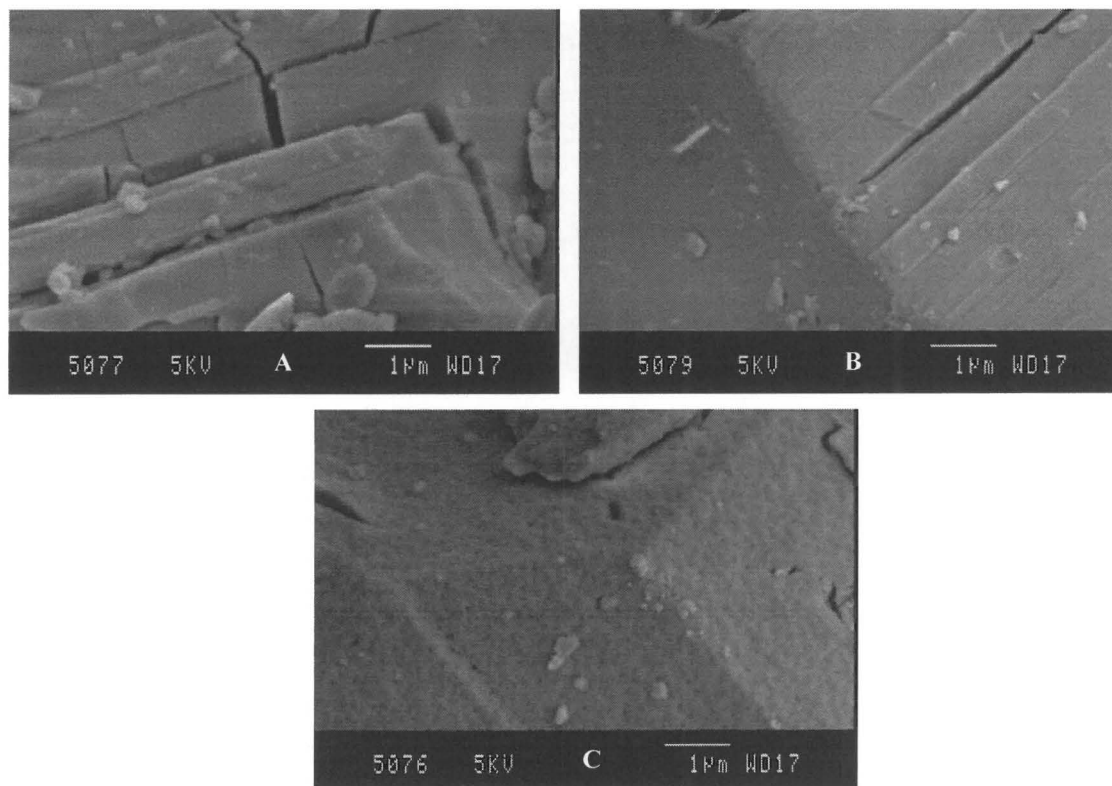


Figure 4.42 SEM photos of zirconium sulphate powders; A) powder before decomposition B) powder annealed at 500 °C for 5 weeks in air and C) powder decomposed by water vapour at 500 °C. Magnification 15,000x

Zirconia, prepared by water vapour decomposition, might find applications in the field of catalysis. For catalytic purposes, the surfaces might contain many stacking faults and dislocations, which are potential reactive sites of a catalyst. The decomposition is accompanied by an increase in the surface area. Powders and single crystals before calcination do not have measurable BET values, but after water vapour decomposition they have a larger surface area ($30 \text{ m}^2 \cdot \text{g}^{-1}$). However, other routes producing zirconia with higher surfaces at similar calcination temperatures are available [39].

Samples annealed at 800°C in air have surface areas between 65 m²·g⁻¹ and 85 m²·g⁻¹. Electron microscopy photos of the particles show a smooth surface, but after calcination the surfaces are cracked and rough (figure 4.43). SO₃ gas is released, building a pressure inside a particle, which causes the cracking of the crystal. This cracking is accompanied by an increase in the surface, explaining the increase in BET surfaces on heating.

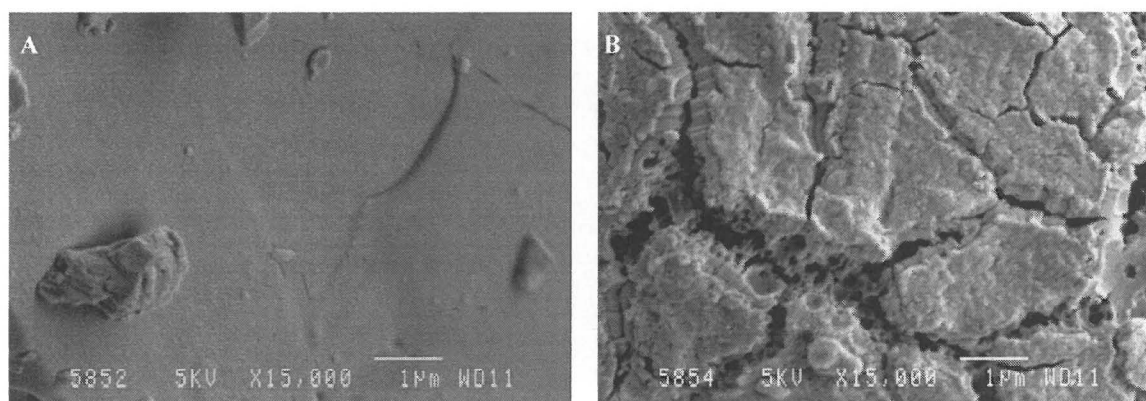


Figure 4.43 SEM photo of a zirconium sulphate powder A) before and B) after calcination at 800°C. Magnification 15,000x

Table VIII shows the surface areas of the powder calcined in air at 800°C and the powder decomposed by water vapour at 500°C. Calcining the powder at 800°C resulted in the largest surface area. Zirconium hydroxide (ZrO_x(OH)_{4-2x}, 1 ≤ x ≤ 2) can be precipitated by addition of ammonia to a zirconium oxychloride solution. According to figure 4.44, there is a negative relationship between the surface area and the calcination temperature. Annealing a zirconium hydroxide precipitate at 800°C results in a much lower surface. The table also includes the surface area of zirconia from Merck for comparison. The surfaces, obtained by decomposition, are higher than commercially available high-grade zirconia.

Decomposition of both the powder and the single crystal can proceed according to two routes. Sulphate can be released by a reaction with water forming sulphuric acid, which is a slow decomposition at temperatures below 600°C, while SO₃ is rapidly driven off at higher temperatures.

Table VIII BET surfaces of zirconia particles.

Initial composition	Calcination temperatures / °C	BET surface / m ² ·g ⁻¹
NH ₄ HZrO(SO ₄) ₂	800	65-85
NH ₄ HZrO(SO ₄) ₂	500 (water vapour)	30
ZrO ₂ (Merck)	-	2

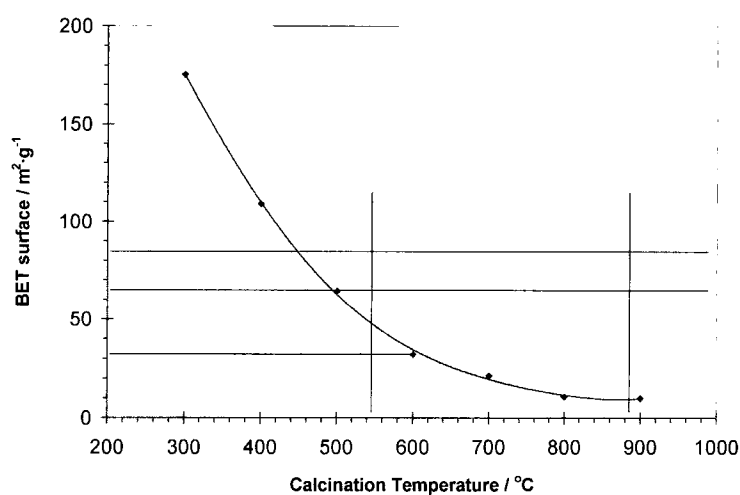
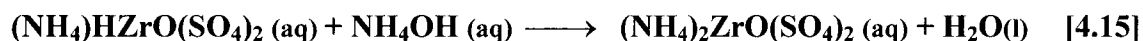


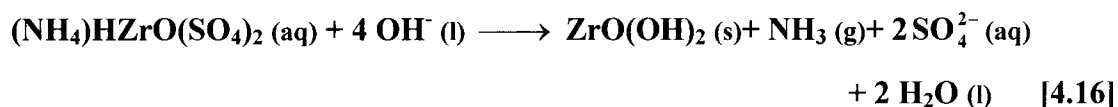
Figure 4.44 Surface area of ZrO₂. ZrOCl₂ is hydrolysed by 28% aqueous ammonia and dried at 100 °C for 24h. followed by calcination. K. Tanabe, *Mat. Chem. Phys.*, 13, (1985), 347

4.9 Zirconium Derivatives

If ammonium hydroxide is added to a $(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ solution, an acidic proton is abstracted by OH^- from the zirconium complex, exchanging the proton by an ammonium ion. Addition is continued until zirconium hydroxide just starts to precipitate. The solvent is evaporated forcing recrystallisation of the product. The hydroxide will redissolve when the precipitate is washed with (hydrochloric) acid, but the complex does not significantly dissolve.



The amount of added ammonia must be carefully controlled because ammonium hydroxide does not only substitute ammonium ions for protons, it can also hydrolyse the zirconium complex due to a raising pH.

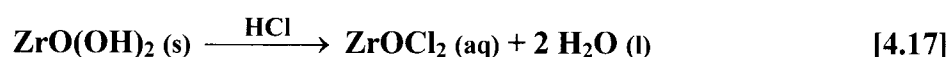


Filtration is slow due to the gelling nature of the filtrate. The precipitate is washed twice with ethanol resulting in a soft and fine powder. Suspending the product in ethanol after washing it in water considerably enhances filtration, making it possible to dry the product at relatively low temperatures (80°C). Unfortunately, ethanol interacts with zirconium hydroxide and can not be completely evaporated upon drying. Upon calcination it is converted into carbaceous deposits, which initially blackens the powder before it eventually completely decomposes to carbon dioxide. Temperatures above 500°C are needed to remove these deposits, causing a degradation of the product. Therefore, ethanol is not a suitable option to dry the product.

Hydroxyl groups on zirconium can form OH bridges polymerising the zirconium compounds. Below a pH of 1.8, a solution of $0.3 \text{ mol}\cdot\text{l}^{-1}$ zirconium sulphate does not

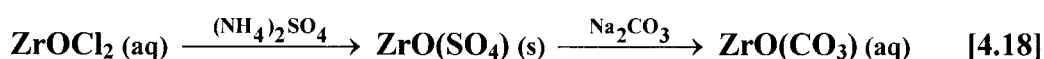
precipitate but zirconium hydroxide eventually precipitates after adding more ammonium hydroxide.

This precipitate can be redissolved in various acids. Nitric acid, sulphuric acid or hydrochloric acid are suitable, forming zirconium oxy nitrate, zirconium oxy sulphate and zirconium oxy chloride respectively. Acids dehydrolyses and prevents (premature) crystallisation. Redissolution by hydrochloric acid results in zirconium oxy chloride, which can be crystallised from solution.



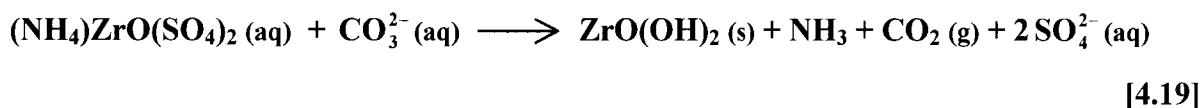
In this way a process to produce zirconium oxy chloride is established which might be interesting for industrial production. Costs of reagents are relatively low if zirconia is readily available. Zirconium oxy chloride can be used as an end product or it could be an intermediate for the production of various zirconium-based chemicals. A problem may arise in washing the zirconium hydroxide because of the difficulty in filtration. The precipitate retains a lot of water and filtration times are quite long, which is an important factor for large-scale production.

The sulphate in the complex can be displaced by carbonate adding a sodium carbonate solution. Displacement reactions progress according to the strength of the ligands. Ligand strengths are given in eq.4.2 and although this is the ligand strength for zirconia, it also seems to be valid for zirconium oxy compounds. Sulphate is a stronger ligand than chloride while a carbonate ligand is the strongest of the three.



Directly adding a carbonate solution to a zirconium oxy chloride solution does not displace chloride with carbonate, although carbonate is the strongest ligand. The carbonate solution only increases the pH, hydrolysing the zirconium oxy chloride to zirconium oxy hydroxide.

Addition of a sodium carbonate solution to ammonium zirconium oxy sulphate in water will not form the carbonate analogue as well. Zirconia hydrolyses to form zirconium oxy hydroxide, similar to the case of adding sodium carbonate to a zirconium oxy chloride solution. The carbonate increases the pH and the complex is hydrolysed by water.



Zeiss and Gieseke studied the formation of basic zirconium carbonate by a simple one step carbonation from zirconium sulphate tetrahydrate [40]. They added a 0.6M solution of ammonium carbonate to a 100 ml 0.1M zirconium sulphate solution under continuous stirring until the pH reached a value of 6.75. According to Zeiss and Gieseke the Zr to CO_3 ratio was 1.08. The product was thoroughly washed by centrifugation to remove the sulphate and ammonium ions. This process was evaluated and the procedure repeated with some minor modifications. After every washing cycle, the product was filtered by vacuum filtration instead of centrifugation and the filtrate was collected to check for the presence of sulphate and carbonate ions. Barium chloride was also added to a part of the filtrate because it precipitates with carbonate and sulphate. Another part of the filtrate was acidified with nitric acid to a $\text{pH} < 0.5$ and heated to 80°C to remove carbonate. It was neutralised by a sodium hydroxide solution until a pH of 6.5-7.5 was reached and tested for sulphate. After no sulphate and carbonate could be detected in the filtrate, the sample was dried by vacuum filtration. Infrared spectroscopy showed in this case no carbonate bands, which are clearly present in zirconium oxy carbonate compounds.

Zeiss and Gieseke reported a molar Zr to CO_3 ratio of 1:0.8 before any washing procedure. The presence of carbonate not bonded to zirconia is very likely if a solution of zirconium sulphate tetrahydrate is neutralised by ammonium carbonate to a pH of 6.75 and vacuum filtered only once after some centrifuging cycles. Centrifugation is useful for separation by sedimentation, but it is not a washing technique. Even after vacuum filtration the precipitated

zirconium product retains a lot of water and might therefore also contain some “free” carbonate.

Furthermore the authors mentioned briefly the analytical methods employed to analyse carbonate. They determined the carbonate content by acid distillation and total carbon analysis. Acid distillation probably involves the release of carbon dioxide. When an acid is added to the precipitated zirconium product and the evolving gas is bubbled through lime water, calcium carbonate will precipitate. If such a technique is used, the results are expected to be very inaccurate.

The author believes that the results reported by Zeiss and Gieseke are disputable and that only a fraction of the precipitated zirconium product contains basic zirconium sulphate. The majority is zirconium hydroxide. Ammonium carbonate only raises the pH and it is the pH, which forces zirconium sulphate tetrahydrate to precipitate as zirconium hydroxide ($\text{ZrO}(\text{OH})_2$) resulting in a wet paste containing carbonate ions.

4.10 Upgrading of Baddeleyite

$(\text{NH}_4)\text{HZrO}(\text{SO}_4)_2$ obtained by the standard method was calcined at 1000°C for 5 hours to decompose the product back into ZrO_2 . Both the calcined product and baddeleyite were analysed for several metal (trace) elements and for sulphate ions. The results are shown in Table IX.

Table IX *Elemental analysis of baddeleyite and calcined $(\text{NH}_4)_2\text{ZrO}(\text{SO}_4)_2$.
Contents of Zr and Hf are measured by X-ray fluorescence.
Sodium and sulphate are determined by ion chromatography.
All remaining components in the samples are determined by ICP.
nd=non detectable by ICP.*

	Baddeleyite	ZrO_2
% Zr	71.6	71.5
% Hf	1.3	1.6
% Si	0.3	0.1
mg U /kg	591	nd
mg Th /kg	72	nd
mg Ti /kg	1142	305
mg Fe /kg	2247	nd
mg Ni /kg	nd	nd
mg Cu /kg	432	nd
mg Na /kg	41	222
mg Ca /kg	107	246
mg P /kg	533	262
mg SO_4^{2-} /kg	1300	1200

The amount of zirconium in both samples was the same. It is therefore possible to compare concentrations of each element in both samples directly.

Since the chemistry of hafnium and zirconium are similar, a change in the hafnium concentration is not expected. The decrease in silica is also negligible.

Most striking is the reduction of uranium and thorium after crystallisation. Uranium drops from 591 mg per kg zirconia to a concentration under the detection limit.

Thorium falls from 72 mg per kg to a non-detectable concentration. Almost all the uranium and thorium remain in solution upon crystallisation. This reduces the radio-activity of zirconia to a minimum, making recrystallisation of $(\text{NH}_4)_2\text{ZrO}(\text{SO}_4)_2$ from an acidic solution a valuable process in this regard.

The transition metals (Ti, Fe, Cu) also show an enormous decrease in concentration while iron and copper are below the detection limit in purified zirconia. Nickel was not present in baddeleyite in the first place. Titanium remains present in purified zirconia, because it is in the same group of the periodic table of the elements as zirconium. Their chemistry is similar (both d^0 electron configuration) obstructing the separation of both elements.

Although the concentration of almost all elements decreases, the concentration of sodium and calcium increases. In the process of recrystallisation, ordinary water from the tap was used, containing high concentrations of these elements. They are included in the crystals during recrystallisation, thus causing the rise in their concentration. This issue is quite important since it is too expensive to use distilled water when producing on a large scale. The impact on the quality in terms of the requirements of the product needs to be assessed.

The content of phosphorous is reduced by a factor of two. In general, phosphates are very strongly bonded to zirconium and zirconium phosphate is easily formed upon heating. Zirconium phosphate does not dissolve in concentrated acid nor will it decompose at 1000°C to zirconia. If phosphate is present as a soluble salt, it will immediately precipitate with dissolved zirconium. This precipitate is removed during filtration in order to remove the unreacted baddeleyite and non-soluble impurities, therefore accounting for the reduction obtained.

4.11 Conclusions

Ammonium zirconium sulphate can be prepared by fusing zirconia with ammonium sulphate. The product can be dissolved in water and recrystallised from solution. A powder is obtained when the solution is heated to evaporate water, while single crystals are produced on prolonged standing. Single crystals can only be produced by carefully controlling reaction conditions. Glass formation can be avoided by stimulating crystal growth and reducing nucleation. This is achieved by reducing the rate of evaporation of the solvent (water). Spectroscopic analysis of the powder and a dried/ground single crystal shows the sulphate groups and the ammonium ion. The ammonium ion is not visible in the Raman spectrum of the single crystal, because of the low $\text{NH}_4\text{:Zr}$ ratio. Ammonium zirconium sulphate powder can also be prepared by mixing acid zirconium sulphate and ammonia in water. According to IR spectra and XRD patterns, the acid-base reaction results in a compound identical to the powder. The IR spectra are almost identical, showing the group characteristic similarities, while the XRD patterns show similar structures and/or phases. $\text{NH}_4\text{HZrO}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ is the empirical formula for the powder, according to a chemical analysis.

The single crystal structure crystallises in a hexagonal structure and can be resolved at 150K. The cell is very large compared to the ammonium zirconium sulphates and their hafnium analogous in section 4.1. The structure of the single crystal consists of three substructures. Substructure 1 is a set of zirconium oxy dihydroxy sulphate clusters having 18 zirconium atoms per cluster. It includes bridging sulphates, oxygen and hydroxy bridges. Sulphate ions could be placed easily because of the tetrahedral structure of the ions, but difficulty was experienced in the assignment of the hydroxy groups. This was tackled by comparing the relevant Zr-O bond lengths and Zr-O-Zr angles with those reported in the literature. In this way the hydroxy bridges and the oxo bridges could be identified. Water ligands are also present in the structure, completing the co-ordination number of zirconium to 7 or 8. Some zirconium atoms are located on a mirror symmetry element introducing symmetry in the first co-ordination shell of zirconium. No extreme deviations in the Zr-O bond lengths are present, although distances might vary somewhat. Zr-O bond lengths with a co-ordination number of four are larger than bond lengths with a co-ordination number of three in order to

accommodate all the oxygen atoms. If the ligand is a hydroxy group, but the co-ordination number is the same as in oxo bonds, the Zr-O distance will be longer due to a decrease in the partial charge of oxygen. The sulphates also form bridges with between two different zirconium atoms. Some structures reported in the literature have sulphate bidentate ligands co-ordinating the same zirconium ion, but all the sulphate ligands in this structure form bridges between zirconium atoms. One sulphate even co-ordinates three different zirconium atoms and the bonds can not be explained by electrostatic interaction only. Substructure 1 has the molecular formula $\text{Zr}_{18}\text{O}_{10}(\text{OH})_{26}(\text{H}_2\text{O})_{22}(\text{SO}_4)_{13}$, which is electrically neutral. It is believed that hydroxy bridges and water ligands form inter- and intra-oxo bonds upon heating resulting in hard and dense agglomerates. Hydroxyl groups replace sulphate ions if the pH is increased, precipitating zirconium oxy hydroxide.

Substructure 2 is an ammonium (bi) sulphate string of $(\text{NH}_4)_4\text{H}_2(\text{SO}_4)_3$ forming a hydrogen bond network with the cluster to support the cluster structure. It is not part of the main structure (substructure 1), but it is an essential ingredient for the crystallisation, because it stabilises the hexagonal structure. Resolving the structure is difficult due to electron density interference from substructure 3. A network is proposed by including the direct environment of the structure in terms of hydrogen donation. The stabilising purpose of substructure 2 becomes apparent if the hydrogen bonds between substructures 1 and 2 are identified.

Substructure 3 consists of the channels, formed by the arrangement of zirconium clusters in the unit cell. The single crystal collapses upon heating due to the release of ammonia and water. Hydroxy ligands form oxo bonds connecting the clusters.

The single crystal and the powder show identical decomposition behaviour. They decompose with water vapour at a moderate temperature (500°C), forming sulphuric acid, or they degrade to zirconia at a higher temperature (600°C), releasing SO_3 .

The layers of zirconium clusters perpendicular to cell basis vector **c** has an ABAB..... stacking sequence. This sequence forms parallel pillars of clusters around the screw-axes.

Although the structure can be prepared by a combination of ammonium hydroxide and acid zirconium sulphate with some variation in the ammonium to zirconium ratio, the compound can not be considered as a solid solution. A solid solution has a crystalline phase that can have variable compositions, but the ammonium part is located at crystallographic sites in the crystal structure. The ammonium to zirconium ratio in the single crystal structure is therefore fixed and the ammonium part (substructure 2) is an integral part of the structure.

The single crystal could function as an inorganic membrane or it might find applications in catalysis and/or molecular sieving due to the presence of large, parallel channels in the structure. No work on the practical application has been done in this study and potential applications could be explored in subsequent research projects.

The formula of the powder can be approximated by $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$, although this is not the real composition. The powder has a zirconium oxy hydroxy sulphate structure, which might be similar to substructure 1 of the single crystal. Ammonium sulphate is co-precipitated, enhancing crystallisation of the product from the mother solution and stabilising the structure. The exact structure of the powder is not known but it involves ammonium sulphate, which act as a matrix for the water-soluble zirconium oxy hydroxy sulphate. It is possible that the powder could be a solid solution, but more work needs to be done to obtain insight in the structure of the powder.

The powder can be used as a starting material for the production of other zirconium based chemicals. Most of the trace elements are removed and a very pure product is obtained. This opens opportunities for large-scale production, although some obstacles have to be tackled first. A major disadvantage is the release of ammonia and some SO_x gasses during fusion of zirconia and ammonium sulphate. Society's awareness of environmental issues like pollution and conservation imposes severe restrictions on emissions and waste. Treatment of emissions and waste is subjected to government regulation and an important factor in large-scale production. A more detailed study is required to assess the viability of the process and more work needs to be done to optimise this process.

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5

Dehydration of Phosphates

5.1 Introduction

5.1.1 Phosphate Mining

Phosphorous was often applied to light bearing materials in the eighteenth century, but modern phosphorescent materials do not even contain the element. The discovery of phosphorous is attributed to Hennig Brand (1669), but it was Boyle who characterised its combustion product in 1694. Six years later the presence of phosphorous in bones and teeth was discovered becoming the main source of phosphate from the end of the eighteenth century. During the first half of the following century the value of phosphorous in fertilisers was realised, making it extremely important in the agriculture. Soon, deposits were discovered in Europe (1850) with phosphorous in the fully oxidised state. It is widely distributed in rocks and soils and over 200 different phosphate minerals are known today. Apatite is the most important group since it occurs in sufficient abundance for commercial mining. These deposits mainly consist of fluorapatite $\text{Ca}(\text{PO}_4)_6\text{F}_2$, chlorapatite $\text{Ca}(\text{PO}_4)_6\text{Cl}_2$ and hydroxyapatite $\text{Ca}(\text{PO}_4)_6(\text{OH})_2$. Sedimentary rock deposits of apatite are called phosphorite and are of marine origin. Large deposits are found in Morocco, USA (Florida, North California), Kazakhstan, China and Tunisia, but commercial interesting deposits are also found in Togo, Senegal, South Africa, Algeria, Jordan, Turkey, Israel and Brazil.

Apatite in igneous rock is less common, but also occurs in Russia, South Africa and Brazil. It is believed that apatite is widely distributed over the world, ending up in rivers and oceans by weathering and leaching, but concentrating phosphorous from sea water is commercially not feasible since the concentration is too low ($\sim 1 \text{ mg}\cdot\text{l}^{-1}$). The phosphate content varies seasonally and geographically and increases with depth up to 1000 m where it reaches a constant level. However, phosphate is concentrated in shell fragments, skeletal remains of marine organisms and terrestrial animals. It is accumulated on the ocean floor becoming sedimentary deposits due to geological uplifting and movement.

Several deposits are found in South Africa. Marine deposits are mainly confined to southern and western coastal regions comprising both onshore and offshore deposits. The overwhelming phosphate production in South Africa (95%) originates from igneous deposits in Phalaborwa. The geology of the Phalaborwa complex has a 2030 million years old pipe-like intrusion embodied in granite gneiss (gneiss = a type of hard rock with light and dark bands formed from earlier rocks which were pressed together under heat). It is made up of three concentrically coalescing lobes designated Northern Pyroxenite, Loolekop and Southern Pyroxenite formed by concentric volcanic intrusions over 1300 million years. This caused an enormous variability in its mineralogy especially in crossing zones between successive volcanic pipes. For further information about the process of phosphate mining, the reader is referred to the literature [1]

5.1.2 Classification of Phosphates

An inorganic polymer is a substance with large molecules composed of atoms other than carbon, linked together mainly by covalent bonds [2]. A polyphosphate is generally classified as an inorganic polymer and also regarded as a condensed phosphate formed by repeated condensation of tetrahedral PO_4 units linked through common oxygen atoms. These tetrahedra retain their structural tetrahedral arrangement and a maximum of three oxygen corners could be shared ($\text{P}=\text{O}$ excluded) resulting in chain, sheet or three dimension structures.

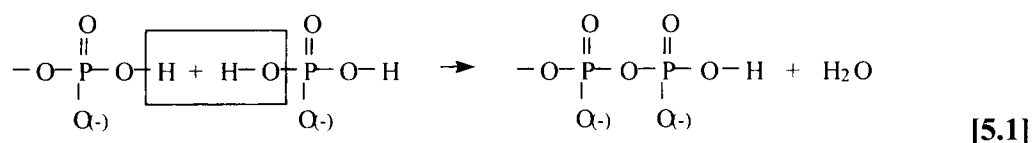
Structural isomerism also occurs because of the different arrangement or packing of the PO_4 tetrahedra but tetrahedra never share edges or faces. Phosphorus atoms have a formal charge of +5 and are located in the centre of the tetrahedra. A maximum P-P distance of 2 P-O distances is obtained if two octahedra are sharing a corner in which the P-O-P bridging angle is 180° . Sharing edges reduces the P-P distance to $1.16 \cdot \text{P-O}$ because the O-P-O angle is theoretically $\sim 70.5^\circ$. Face sharing tetrahedra decreases the distance further to $0.67 \cdot \text{P-O}$. Normally the shortest interatomic distance is a cation to anion distance, meaning that structures with shorter distances of like charged ions are unlikely to exist. These structures are energetically unfavourable due to electrostatic repulsion between phosphorus [3].

Berzelius discovered different types of phosphoric acids in 1816, but it was Thomas Clark who in 1827 prepared tetrasodium pyrophosphate by dehydrating monobasic sodium phosphate [4]. Pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) is the simplest form of a condensed phosphate. It exhibits five crystalline forms, which are soluble in water. The structures are determined by the angle at the shared oxygen atom and the rotation of the two tetrahedra around the same oxygen atom.

Triphosphates and tetraphosphates are not considered as oligophosphates but condensed phosphates with a composition $\text{P}_n\text{O}_{3n+1}^{(n+2)-}$ $4 < n < 50$ are classified as oligophosphates [5]. They are usually obtained as mixtures in amorphous compositions because of their reluctance to crystallise as individual salts.

A long chain polyphosphate is a condensed phosphate with more than 50 monomers ($n > 50$). Thomas Graham discovered, in 1833, different varieties of phosphates including the phosphate melt causing confusion in naming the phosphate species. Everett Partridge presented a paper in 1949 to reform the nomenclature in the designation of different phosphate compounds [4], which is nowadays still used with some minor modifications. Although a polyphosphate salt or solution has a chain length distribution, the chains are long enough to exhibit the same properties and can be regarded as a pure compound.

The reaction to prepare a polyphosphate can be considered as a condensation polymerisation forming P-O-P linkages while constitutional water molecules are released. The condensation polymerisation of phosphate can be visualised as follows:



with cations balancing the negative charged PO_4 units. Condensed phosphates can be roughly divided into three classes:

- Ultra phosphates
- Meta phosphates
- Linear polyphosphates

Condensed phosphates consist of a metal oxide (M_2O) or a H_2O part and a phosphorous pentoxide part (P_2O_5). Together they form the polyphosphate. The positions of the classes are schematically presented in figure 5.1 where the ratio of M_2O to P_2O_5 identifies the type of phosphate [5].

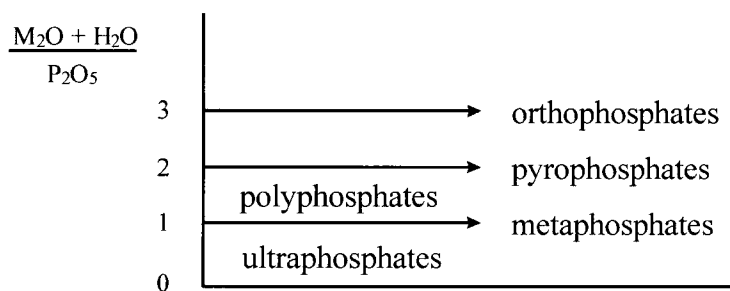


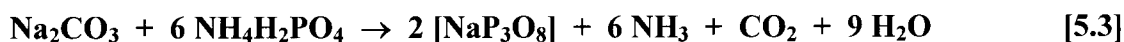
Figure 5.1 Position of the types of phosphates with respect to the $(M_2O+H_2O) : P_2O_5$ ratio.

A ratio of 3 defines orthophosphoric acid or a monophosphate salt ($M_3PO_4 \equiv 1\frac{1}{2} M_2O : \frac{1}{2} P_2O_5$). Pyrophosphates and metaphosphates have a ratio of 2 and 1 respectively and linear polyphosphates are located between these two types. A decreasing $M_2O:P_2O_5$ ratio corresponds to an increasing chain length. A linear polyphosphate tends to an infinite chain length if the ratio approaches 1. A ratio of 1 defines cyclic metaphosphates while ultraphosphates are positioned below a ratio of unity, with its cross-link density increasing with a decreasing ratio.

5.1.3 Ultraphosphates

Ultraphosphate glasses are amorphous polyphosphates with a phosphate to cation ratio below unity and a general molecular formula $P_n O_{3n-m}^{(n-2m)-}$ ($m, n \in \mathbb{N}$; $0 < 2m \leq n$) with protons, ammonium ions or metal cations balancing the negative charged phosphates. Additional oxygen cross-linking substitute pairs of metal ions to form 3 dimensional networks such as cages and sheets. These networks are amorphous because cross-linking is random.

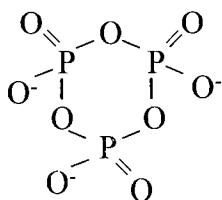
Ultraphosphates are prepared by heating a mixture of ammonium dihydrogen phosphate and sodium dihydrogen phosphate (eq.5.2). Cross-linking can be controlled using different molar ratios of reagents. To obtain the same product it is also possible to heat ammonium dihydrogen phosphate with sodium carbonate (eq.5.3), the ratio of Na:P in the polymer is important.



Dehydration up to about 500°C produces linear polyphosphate chains. The linear polymer contains acidic hydroxyl groups and is soluble in water. Firing the mixture above 600°C causes cross-linking between separate chains. Complete dehydration is not possible, because the corresponding reaction is reversible [6].

5.1.4 Metaphosphates

A metaphosphate has the general anionic formula $P_nO_{3n}^{n-}$ ($n \in \mathbb{N}$; $n > 2$). Although this expression does not look complicated, confusion existed in defining phosphates with this general formula. In 1848 Fleitmann classified metaphosphates using chemical analysis [4]. A sodium polyphosphate glass, also known as a Graham's salt, was erroneously labelled hexa metaphosphate. Metaphosphates are in a true sense ring anions. A meta diphosphate anion ($n=2$) has never been reported because it is highly strained due to edge sharing tetrahedra. Meta triphosphate (cyclic triphosphate) $Na_3P_3O_9$ can be prepared by heating sodium dihydrogen phosphate from 500°C to 620°C followed by slowly cooling to room temperature (See also the phase-relations scheme in figure 5.2). This type of phosphate is also referred to as $NaPO_3$ I.



Meta triphosphate

Higher metaphosphate anions up to $n=8$ have been isolated from mixtures containing even larger rings [7].

5.1.5 Linear Polyphosphates

A linear polyphosphate anion could be represented by the general formula $P_nO_{3n+1}^{(n+2)-}$ ($n \in \mathbb{N}$).

Only alkali metals and ammonium polyphosphates are soluble in water. Linear metals or ammonium polyphosphates of high molecular weight can be prepared by thermal dehydration of the corresponding dihydrogen phosphate. Figure 5.2 shows a scheme, which relates the phases of condensed sodium dihydrogen orthophosphate with temperature.

Thermal condensation of sodium dihydrogen phosphate must be controlled very carefully since the existing phases depend very much on the temperature. Heating sodium dihydrogen phosphate result in the formation of the pyrophosphate ($Na_2H_2P_2O_7$). Increasing the temperature to above 240°C could give rise to a number of compounds; three varieties of triphosphates ($Na_3P_3O_9$) could be obtained designated by $NaPO_3$ I, I', I''. These can be formed by carefully controlling cooling conditions. Each type can be distinguished by XRD, but in solution they show the same behaviour. Other forms of phosphates obtained upon thermal dehydration are linear polyphosphates. Two forms are referred to as $NaPO_3$ II and III or collectively as Maddrell's salts, named after a German chemist R. Madrell. These polyphosphates consist of tetrahedral PO_4 chains, parallel aligned along the cell axis. The arrangement and number of repeating units along the axis determine the sizes of the crystallographic unit cell axis. The structure of the salt is shown in figure 5.3 and it is clear that the repeating distance of PO_4 tetrahedra in the polymer is 3 phosphate units [4,8].

Another variety of a polyphosphate is a Kurrol's salt. Chain lengths of 5,000 to 10,000 PO_4 tetrahedra could be obtained by crystallising the polyphosphate from molten sodium polyphosphate at proper crystallisation rates from 650°C to 550°C using a seed followed by reheating to promote crystallisation. These polymers consist of helical chains aligned along the longest cell axis with a repeating distance of 4 PO_4 units (figure 5.3). Both polymers are insoluble in water because the helical chains spiral into each other in opposite directions of the screw axis. The chains are held together so tight that water cannot easily penetrate the crystal. However introducing a foreign cation such as lithium ions enhances the solubility considerably.

It is found that potassium ions also increase the solubility, but not to the extent as lithium. By

incorporating foreign ions, the packing of the crystal is disturbed [9], which is reflected by the increase in the solubility. The smaller the cation (K^+ , Na^+ , Li^+) the easier it is for the cation to penetrate the crystal.

Quenching a melt of sodium phosphate at 630°C results in a water soluble glass, which is designated a Graham's salt or $NaPO_3$. It is an undercooled liquid and not a substance with a certain composition. The general composition is $Na_{n+2}P_nO_{3n+1}$.

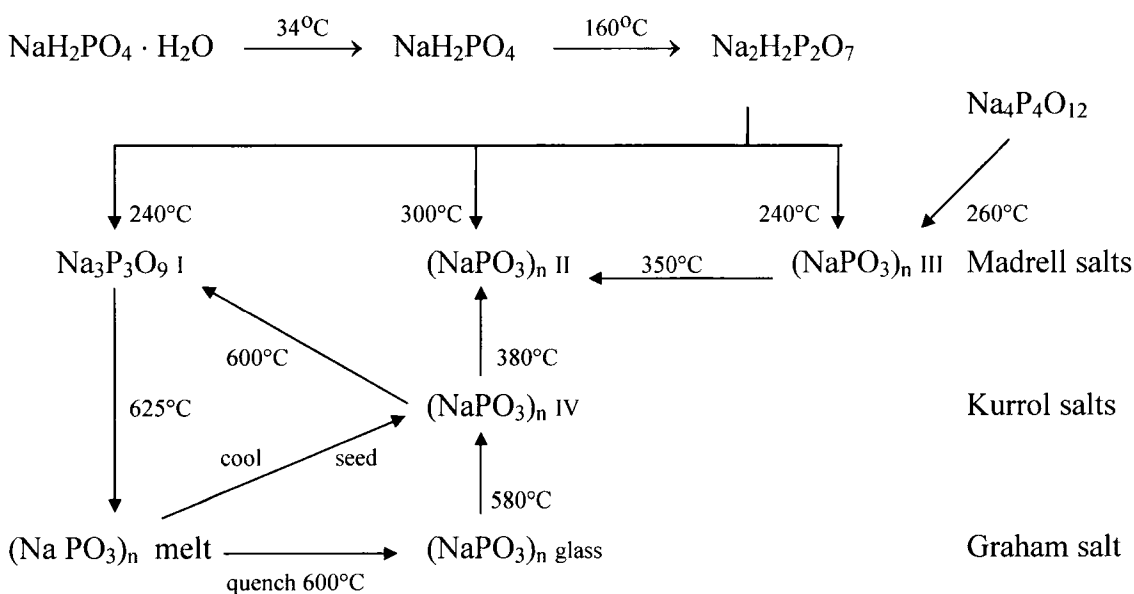


Figure 5.2 Relations between the different phases of condensed sodium phosphates. Corbridge, D.E.C., *Phosphorus An outline of its Chemistry, Biochemistry and Technology*, 2nd ed., Elsevier Scientific Publishing Comp., Amsterdam 1980, 124

Partridge regarded condensed sodium phosphates as metaphosphates because all general formulas reduce to the general formula of cyclic metaphosphates for large values of n .

The formula for ultraphosphate glasses reduces in the same way if $n \gg m$. However, cyclic meta phosphate differs in constitution from other types of condensed phosphates. It is therefore recommended to reserve the name of metaphosphate to cyclic compounds.

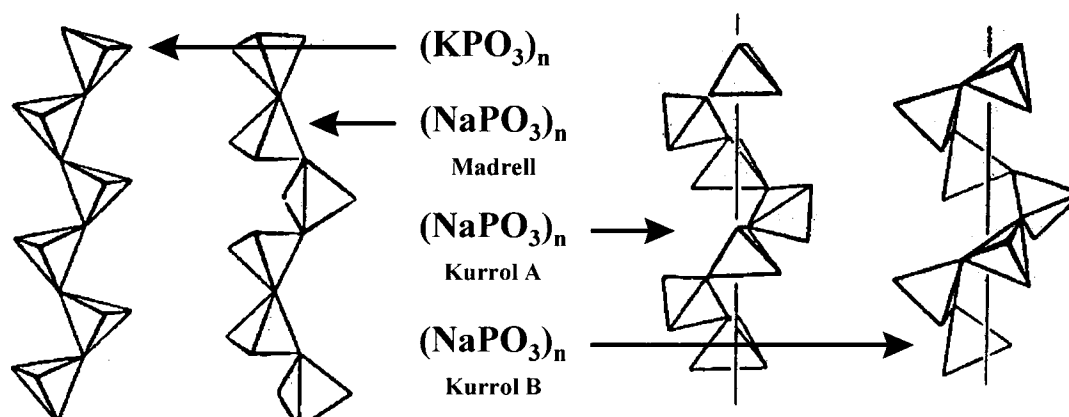


Figure 5.3 Chain configurations of polyphosphates [8].

A dissolved polyphosphate can be precipitated after adding divalent cations. The precipitate is an elastomeric product that retains a lot of water. Divalent or higher valent cations are able to attract multiple polymer chains according to a formal electrostatic count. These ions function like bridges between polymer chains producing a network precipitate [10], which can be re-dissolved by decreasing the pH with acid. Protons can replace divalent cations resulting in a water-soluble polymer and a salt. Polyphosphate glasses consist of discrete linear chains randomly arranged in a solid form with a chain length distribution depending on the cation to phosphorous ratio. The solid contains high molecular weight species plus a small amount of cyclic rings. The main chain length increases with decreasing water vapour pressure in the atmosphere. Heating the sodium polyphosphate above its melting temperature of 627.6°C produces a molten polymer, which forms a glass on quenching (Graham's salt). The glass dissolves easily in water.

Potassium polyphosphate is formed during dehydration above 250°C, but this polymer dissolves very slowly in water. Heating this polymer above its melting point, followed by rapid cooling gives a translucent, partially vitreous solid, but it is difficult to make these glasses. Potassium polyphosphate dissolves in water and has a lower viscosity compared to sodium polyphosphate due to a much higher liquidus temperature.

At such a temperature the distribution of polymer size is shifted to a low molecular species which is frozen after quenching. A high molecular weight equilibrium is reached on cooling down slowly and a corresponding high molecular weight polymer could be crystallised [10]. Potassium glasses can be obtained by lowering the $M_2O:P_2O_5$ ratio below unity. A ratio of 1 corresponds to a P_2O_5 weight mass of 60% in the phase diagram of potassium phosphate in figure 5.4. Changing $NH_4H_2PO_4$ to KH_2PO_4 ratio varies the $K_2O:P_2O_5$ composition. Although sodium Kurrol's salt is metastable with respect to sodium meta triphosphate, potassium Kurrol's salt with a $K_2O:P_2O_5$ ratio near unity is stable in this regard because of the absence of meta triphosphate in such a system [11].

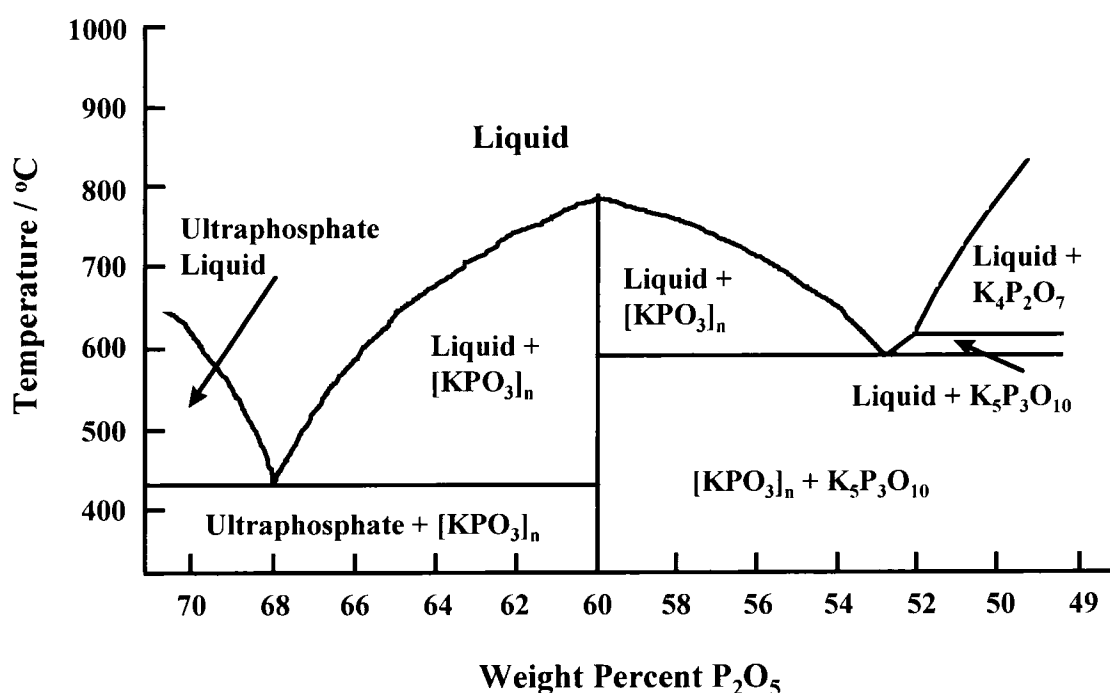
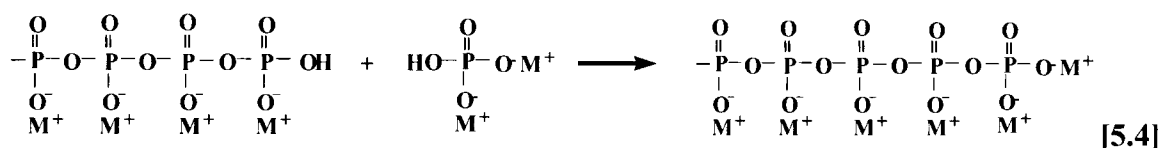


Figure 5.4 Phase diagram of potassium phosphate.

5.1.6 $M_2O:P_2O_5$

A phosphate polymer is formed during the heating process of dihydrogen phosphate and if 100% pure reagent is used, in theory, chains of infinite length could be obtained. However, in practice the reagents always contain some monohydrogen phosphate, which acts as a chain growth terminator:



The $M_2O:P_2O_5$ ratio, where M is the metal cation, plays a dominant role in the chain length of crystalline and amorphous polyphosphates. Increasing the $M_2O:P_2O_5$ ratio results in shorter polymers because M_2O acts as a chain growth terminator. For example, a polymer with an average chain length of 1000 P_2O_5 units differs from a polymer with a length of 500 in just one M_2O group per 1000 P_2O_5 units. A M_2O to P_2O_5 ratio above unity introduces chain growth terminators and a ratio below unity introduces branches. The latter is the basis of ultraphosphate glasses and the polymer could not be regarded as linear anymore. At a $M_2O:P_2O_5$ ratio higher, but near unity, formation of branches is possible. Consequently, chain lengths must be reduced to compensate for the excess M_2O left by the branched points. Polymers with different degrees of cross-linking can be isolated by interrupting the condensation process or by using different condensation temperatures. Ray [6] offered a technique to calculate the cross-link density. Suppose the mole fraction of phosphoric pentoxide is y:

$$y = \frac{P_2O_5}{P_2O_5 + M_2O} \quad [5.5]$$

M_2O is the metal part of the phosphate, but in this case it does not include H_2O . The mole fraction of M_2O is (1-y). Therefore:

$$\frac{1-y}{y} = \frac{M_2O}{P_2O_5} \quad [5.6]$$

The fraction of M_2O equals the fraction of P_2O_5 associated with metal cations. In other words, the fraction of P_2O_5 with hydroxyl groups, capable of cross-linking, is:

$$\frac{P_2O_5 - M_2O}{P_2O_5} = \frac{P_2O_5 - \frac{1-y}{y} \cdot P_2O_5}{P_2O_5} = \frac{2y-1}{y} \quad [5.7]$$

If the cross-link density is x , the fraction of P_2O_5 carrying a residual hydroxyl group is:

$$\frac{2y-1}{y} - x = \frac{\text{mole } H_2O}{\text{mole } P_2O_5} \quad [5.8]$$

The number of moles of water per gram of glass is:

$$\text{mole } H_2O = \frac{\text{gram } H_2O}{\text{gram glass}} \cdot \frac{1}{M(H_2O)} \quad [5.9]$$

in which $M(H_2O)$ is the molar mass of water. The weight of water divided by the sample weight is the weight fraction (W) of bonded water in hydroxyl groups. For the number of moles of glass a similar procedure is followed:

$$\text{mol } P_2O_5 = \frac{\text{gram } P_2O_5}{\text{gram glass}} \cdot \frac{1}{M(P_2O_5)} \quad [5.10]$$

$M(P_2O_5)$ is the molar mass of anhydrous polymer. The weight of P_2O_5 divided by the sample weight is the weight fraction of anhydrous polymer ($1-W$). Combining the last three expressions gives a formula to calculate the cross-link density:

$$x = \frac{2y-1}{y} - \frac{W}{1-W} \cdot \frac{M(P_2O_5)}{M(H_2O)} \quad [5.11]$$

W can be measured by the loss of weight on ignition up to 700°C in the presence of an excess base to avoid any loss of phosphoric oxide. Ray suggested using litharge (PbO). The loss of weight must be in accordance with the water content present in the glass.

After dissolving a polyphosphate all branches disappear and a solution will only contain linear chains. In a condensed sodium phosphate the $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio will not change upon fusing or heating [12]. Chain length is also influenced by rates of crystallisation and thermodynamics. During a slow crystallisation process, impurities and even chain growth terminators are forced out of the crystals. Impurities have time to migrate out of the crystal but will be captured in the crystal upon fast cooling. If the phosphate system is thermodynamically unstable, slow cooling could also lead to a reduction in chain length.

Sodium Kurrol's salt is unstable with respect to sodium cyclic triphosphate and is converted to this metaphosphate at atmospheric pressure. Controlling rates and in this case seeding (figure 5.2) is therefore required.

Phosphate units must be transported from the melt to the crystal interface during crystal growth. Long polymers could move to the crystal surface, not as a whole because of the stress placed on the chain, but segment by segment. Clayton et. al. determined the degree of polymerisation of $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ melts using surface tension techniques and density measurements. They found a polymerisation degree of 8-9 in the melt near the liquidus for a $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio near unity, which is low compared to glasses and crystals [13,14]. Phosphates in melts undergo continuous reorganisation and chains are very short. It is also difficult to fit large polymer chains directly into the crystal lattice and therefore crystals grow by addition of short movable chains. This results in a wide distribution of species (chains) on quenching. A maximum average of 400 phosphate units can be obtained by quenching a sodium polyphosphate melt [11].

Polyphosphates are not very reactive since the phosphorus atoms are in their complete oxidation state (V). However, they are not stable to hydrolytic attack in acidic solutions, but this part will be dealt with in chapter 6.

5.2 Experimental

All polyphosphates were prepared by heating alkalimetal dihydrogen phosphate (KH_2PO_4 Merck), ammonium dihydrogen phosphate (Merck) or combinations of the phosphates. Sodium phosphate glasses were prepared by simply heating monobasic phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ Kanto Chemical Co., Inc.) above the melting temperature. The melt was quenched in air at room temperature and dissolved in water. Raman spectra of dissolved glasses were recorded at various pH. Furthermore, Raman spectra of the crystalline forms were also recorded. All data were obtained at room temperature. The spectra were recorded with the Raman spectrometer described in chapter 2 (section 2.3).

5.3 Results and Discussion

5.3.1 KH_2PO_4

A free KH_2PO_4 unit has C_{2v} symmetry and $\Gamma=2A_1+B_1+B_2$ which are all Raman active. The two total symmetric vibrations correspond to symmetric P(OH)_2 and PO_2 stretch vibrations. B_1 and B_2 correspond to their antisymmetric counterparts.

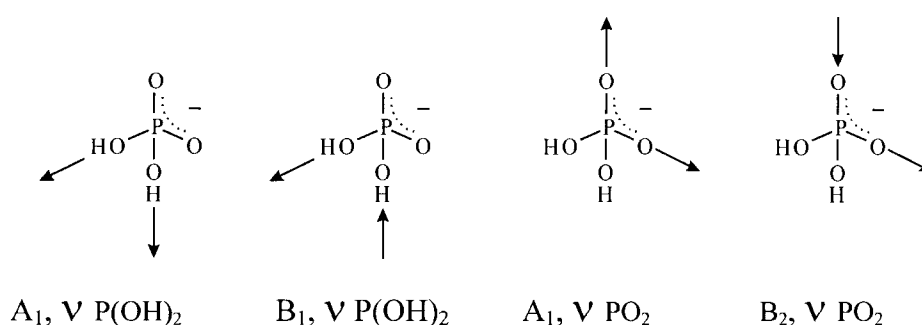


Figure 5.5(a) shows the Raman spectrum of a sodium dihydrogen crystal. The spectrum has only one large band at 914 cm^{-1} and not the expected four bands. At least the two symmetric bands were expected since total symmetric vibrations of species with mainly covalent bonds are generally visible in Raman spectra. A spectrum of the potassium dihydrogen crystals dissolved in water is shown in figure 5.5(b). It shows two strong bands at 879 cm^{-1} and 1074 cm^{-1} plus some weak bands at 939 cm^{-1} and 1151 cm^{-1} .

Potassium dihydrogen phosphate crystals have a tetragonal structure. Figure 5.6 shows the projection along the tetragonal axis. Each tetrahedron is hydrogen bonded to four others. Two hydroxyl groups are donors of protons and the former conjugated oxygen atoms are acceptors. In the structure K^+ lies $\frac{1}{2}c$ above each phosphate tetrahedron [15].

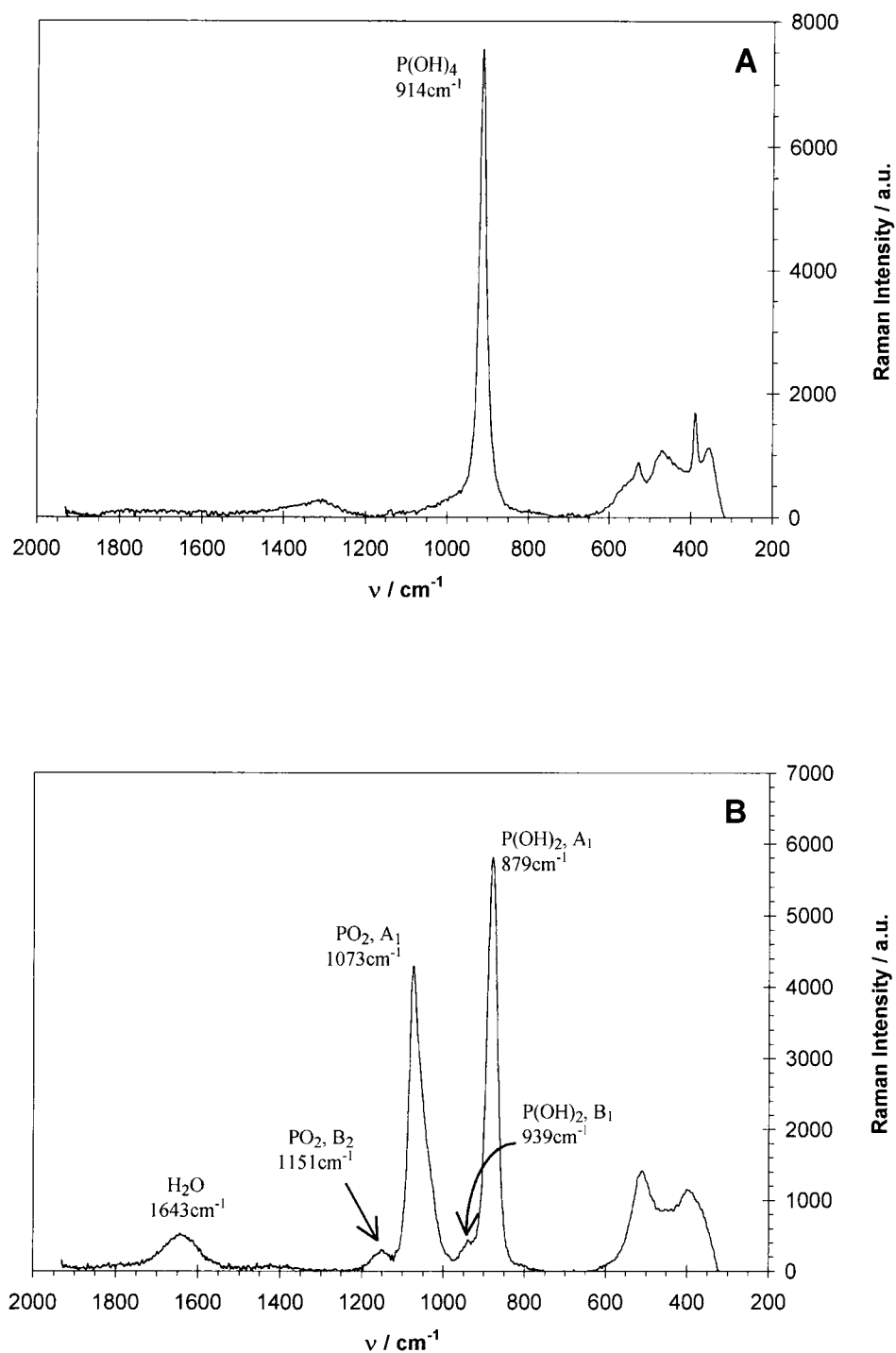


Figure 5.5 Raman spectra of potassium dihydrogen phosphate A) crystal B) saturated solution. Laser power 50 mW. Integration time 60s. Band positions can be found in Appendix C (Table C1).

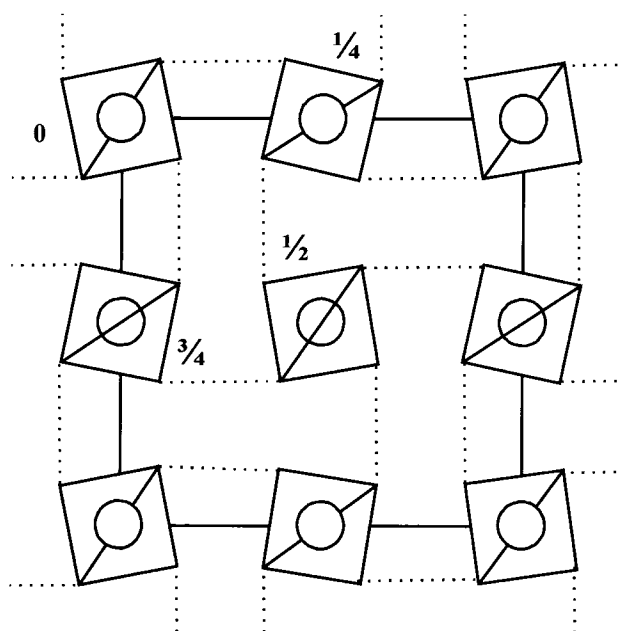
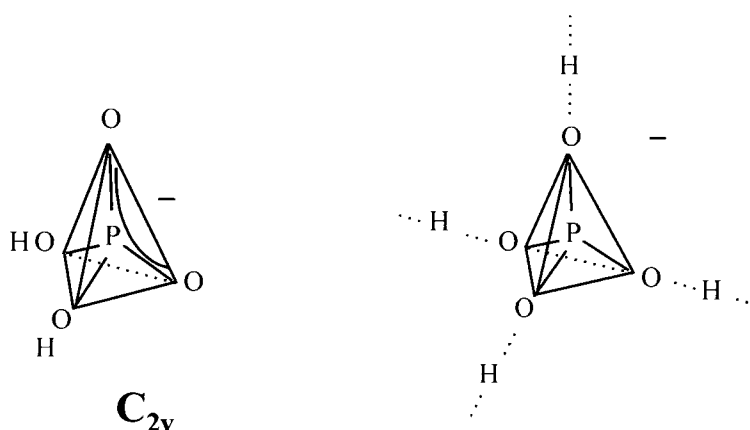


Figure 5.6 Structure of KH_2PO_4 . Broken lines represents H bonding and numerals denote z values

Protons are now equally shared between oxygen atoms of two different phosphate units, making all the oxygen ligands identical and increasing the symmetry of the phosphate species in the crystal. Consequently, the band at 914 cm^{-1} is the total symmetric breathing stretch vibration $\text{P}(\text{OH})_4$. The increase in symmetry by hydrogen bonding can be seen in the structure below.



However, the phosphate species does not have T_d symmetry. According to She et. al., [16] the monobasic phosphate species occupies a S_4 site in the crystal. They also showed that the tetrahedral phosphate ion could be treated as an “individual” molecule in the crystal, according to the analysis of the spectral structures above 300 cm^{-1} . The local crystalline field of S_4 symmetry splits the vibrational modes. She et al concentrated on the Raman spectrum of the crystal below 700 cm^{-1} . S_4 symmetry is lower than T_d symmetry, but a split of the band at 914 cm^{-1} is not observed. The difference between S_4 and T_d symmetry is only due to a slight difference in spatial orientation and since the vibrational modes behave essentially as individual molecular vibrations, it is concluded that the splitting effect on the phosphate band is negligible small.

It must be noted that Ratajczak and Baran [17] published an article on Infrared and Raman polarised spectra of KD_2PO_4 . The Raman spectra they recorded had multiple phosphate bands between 800 cm^{-1} and 1200 cm^{-1} due to the lower symmetry of the structure. The crystal was monoclinic and contained four chemically different phosphate groups on positions of C_1 symmetry.

Dissolving the crystal in water breaks the high symmetry, lowering it to C_{2v} , or even lower due to hydrogen bonding with water. Hydrogen bonding with water does not have such an impact on the symmetry and the $P(OH)_4$ band splits into two new bands, which are both totally symmetric in C_{2v} .

The structure of potassium dihydrogen phosphate also explains the differences in the positions of the bands. In the crystals, the bond order is slightly higher than a single P-O bond due to conjugation of the negative charge of a phosphate unit. The charge is distributed over the four P-O bonds resulting in a bond order of $1\frac{1}{4}$, which could be somewhat lower due to hydrogen bonding. On dissolution, the $P(OH)_2$, A_1 vibration has a bond order of one, shifting the band to lower wavenumbers (879 cm^{-1}). The PO_2 , A_1 vibration has a bond order of $1\frac{1}{2}$, resulting in a band shift towards higher wavenumbers (1073 cm^{-1}).

Figure 5.5(b) also shows the $P(OH)_2$, B_1 band at 939 cm^{-1} and the PO_2 , B_2 band at 1151 cm^{-1} . The broad band at 1640 cm^{-1} is the bending vibration of water.

Heating KH_2PO_4 crystals up to 180°C has no effect on the Raman spectra, but increasing the temperature from 230°C to just 260°C has an enormous effect on the spectrum (figure 5.7(a)). A tail to higher wavenumbers at the A_1 band is observed accompanied by a growing broad band at 705 cm^{-1} . The A_1 band of the monophosphate has almost disappeared at 320°C and a band at 678 cm^{-1} and 1149 cm^{-1} is clearly visible. Increasing the temperature from 320°C up to 360°C does not influence the Raman spectra, except that the A_1 band of the monophosphate has disappeared completely. The A_1 stretch vibration of the $\text{P}(\text{OH})_4$ species of KH_2PO_4 at 914 cm^{-1} is replaced by the A_1 stretch vibration of the PO_2 species in the polyphosphate at 1149 cm^{-1} . It is a shift to higher wavenumbers showing the increase in the bond strength. A P-O-P band also arises, starting at 705 cm^{-1} at 230°C and shifting to 670 cm^{-1} at 360°C , indicating the polymerisation reaction forming linkages between monophosphates through oxygen. At 360°C no significant changes in the spectrum could be observed, except the minor shift of the P-O-P band. Polymerisation is complete and only condensation between polymers could occur at higher temperatures.

TGA/DTA curves were also recorded to study the influence of temperature on the Raman spectra. A potassium polyphosphate could be prepared directly by thermal dehydration of potassium dihydrogen phosphate. Figure 5.8 shows a TGA/DSC curve of the process. At these experimental conditions, water evolves from 200°C . The total mass loss between 200°C and 350°C corresponds to one water molecule for every KPO_3 unit. The peak at 810°C without any loss of mass indicates the transition to the melt.

According to the Raman spectra, condensation takes place without the formation of stable and detectable intermediates. Knowing metaphosphate will not form upon heating [11], polymerisation of potassium dihydrogen phosphate could be monitored using Raman spectroscopy. The Raman spectra are consistent with the TGA/DSC curve. Irregularities in the DSC curve are probably due to the condensation between polymer strings with different lengths and configurations.

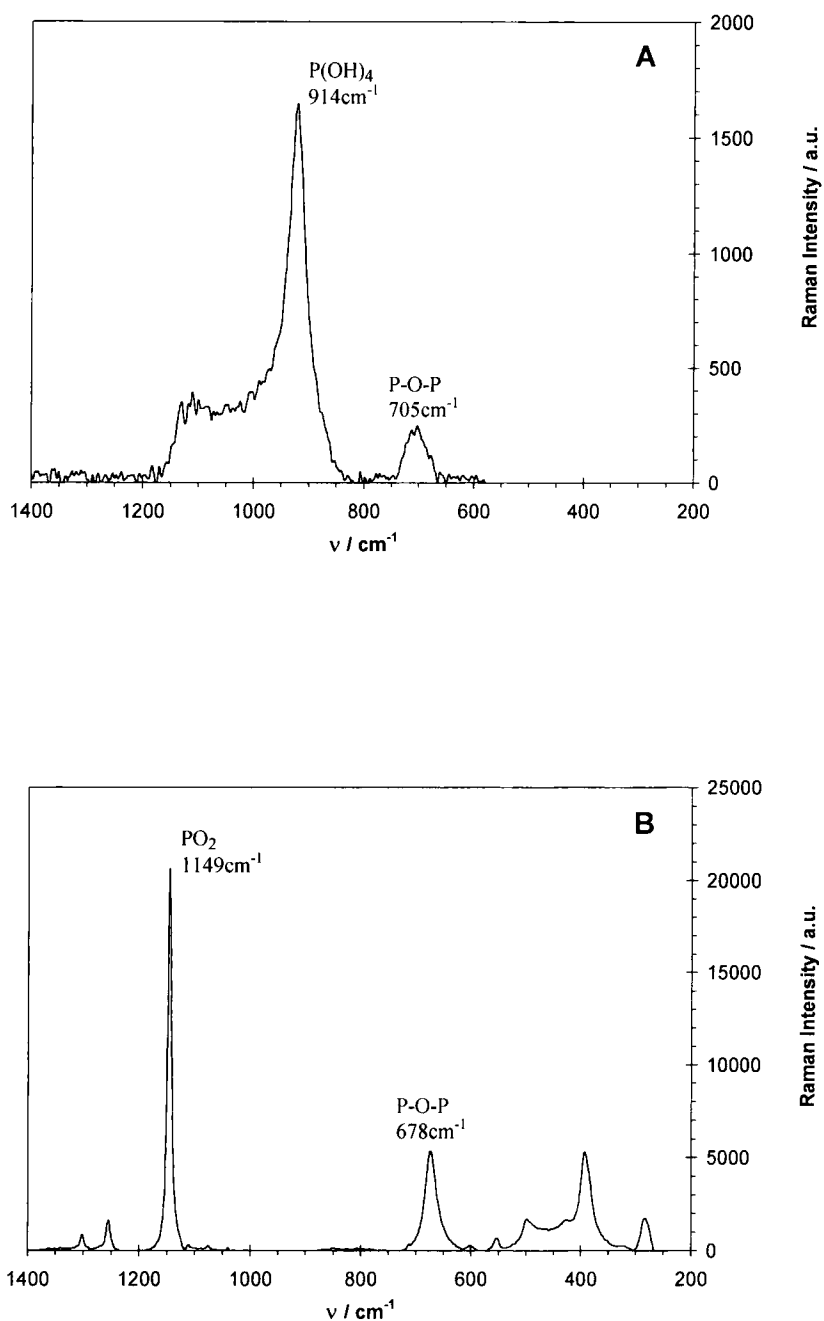


Figure 5.7 A+B Macro phase Raman spectra of KH_2PO_4 at A) 230°C and B) 360°C. Laser power 75mW, integration time 50s. Band positions can be found in Appendix C (Table C2).

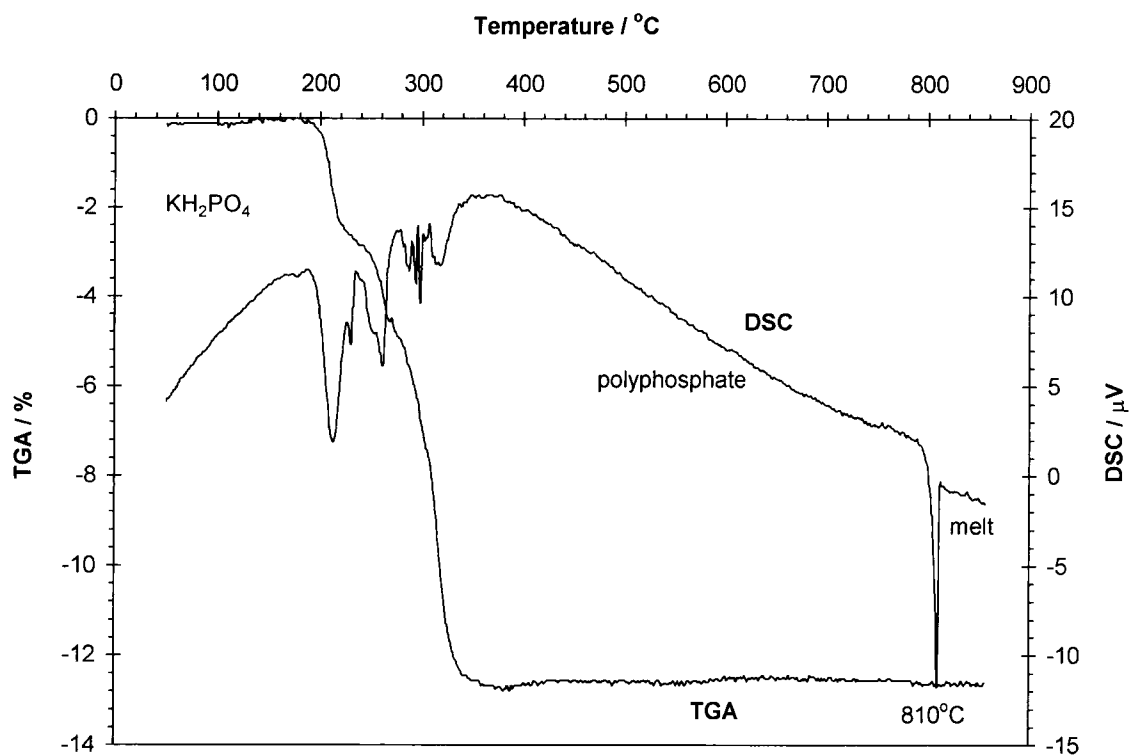


Figure 5.8 TGA/DSC curve of potassium dihydrogen phosphate
Scan Rate $5^{\circ}\text{C}\cdot\text{min}^{-1}$.

5.3.2 NaH_2PO_4

Figure 5.9 shows TGA/DSC curves of the dehydration of NaH_2PO_4 . The TGA curve could roughly be divided into three sections. The first section corresponds to the loss of two crystal water molecules below a temperature of 150°C .

The next section represents the loss of one constitutional water molecule per two phosphate units at a temperature between 150°C and 250°C .

Finally, one constitutional water molecule per two phosphate units is released in a temperature range from 280°C to 350°C .

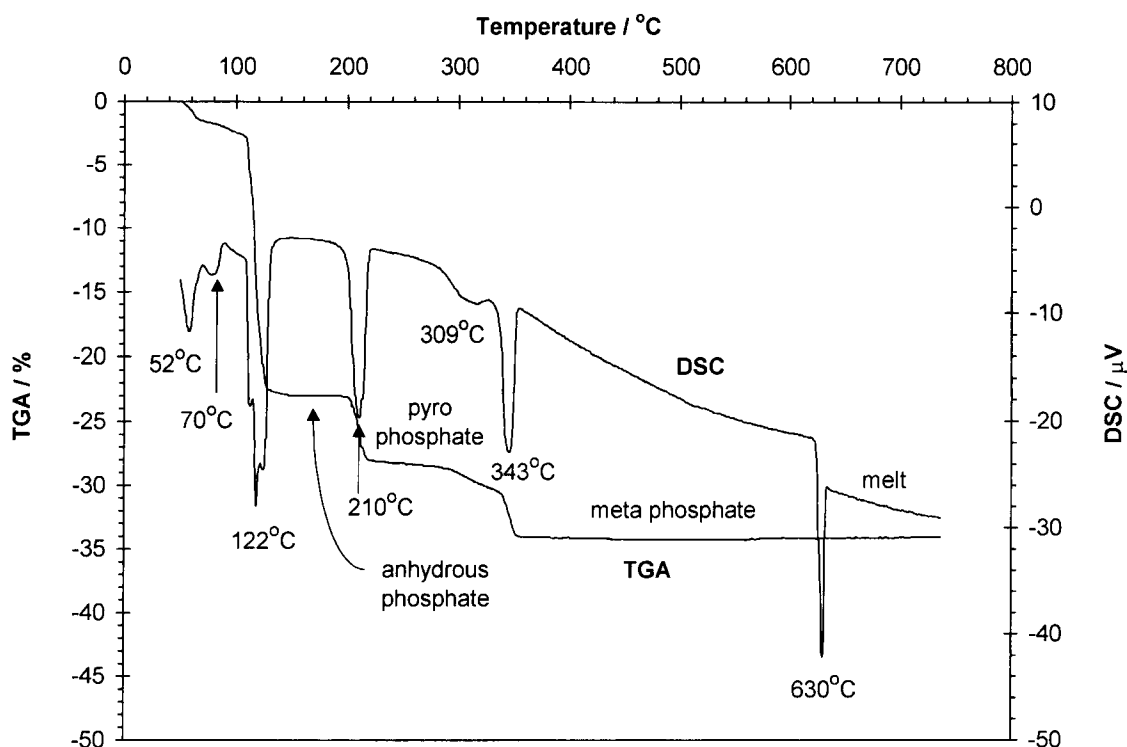


Figure 5.9 TGA/DSC curve of sodium dihydrogen phosphate
Scan rate $5^\circ\text{C}\cdot\text{min}^{-1}$

Taking a closer look at the process of loosing crystal water, the loss seems to proceed in at least two steps indicating the presence of at least two different sites for water molecules.

The IR spectra also show the loss of crystal water. They were recorded after the system was pumped down to 170 mbar at room temperature. Since crystal water is very loosely bonded, evaporation due to reduced pressure occurs. Water might even be evaporated during sample preparation. Therefore, two KBr pellets were pressed and the sample was inserted between the two pellets. Both pellets were pressed onto each other with a pressure of $5 \cdot 10^5$ kPa before recording the IR spectra. The results are shown in figure 5.10.

At 3450 cm^{-1} the OH stretch of the phosphate and/or crystal water can be seen. A band at 1650 cm^{-1} with a tail to higher wavenumbers represents the bending vibration of crystal water. An interesting peak occurs at 3570 cm^{-1} corresponding to loosely bonded crystal water. The peak is very sharp also reflecting the very weak interaction with phosphate. After removing this water, the sharp peak has disappeared but the large OH band at 3450 cm^{-1} is still present. The 1650 cm^{-1} band becomes more symmetric in appearance when the weakly bonded crystal water is removed.

After removing all the crystal water, no water band could be observed anymore. In fact, even the hydroxy groups originating from the phosphates cannot be seen in the spectrum, although they are still present. It is therefore suggested that the large hydroxy band at 3450 cm^{-1} in figure 5.11(b) represents the strongly bonded crystal water only.

The phosphate bands are located around 1000 cm^{-1} . Their exact positions after heating at various temperatures can be found in Table I and will be discussed in the next section.

Chapter 5 Dehydration of Phosphates

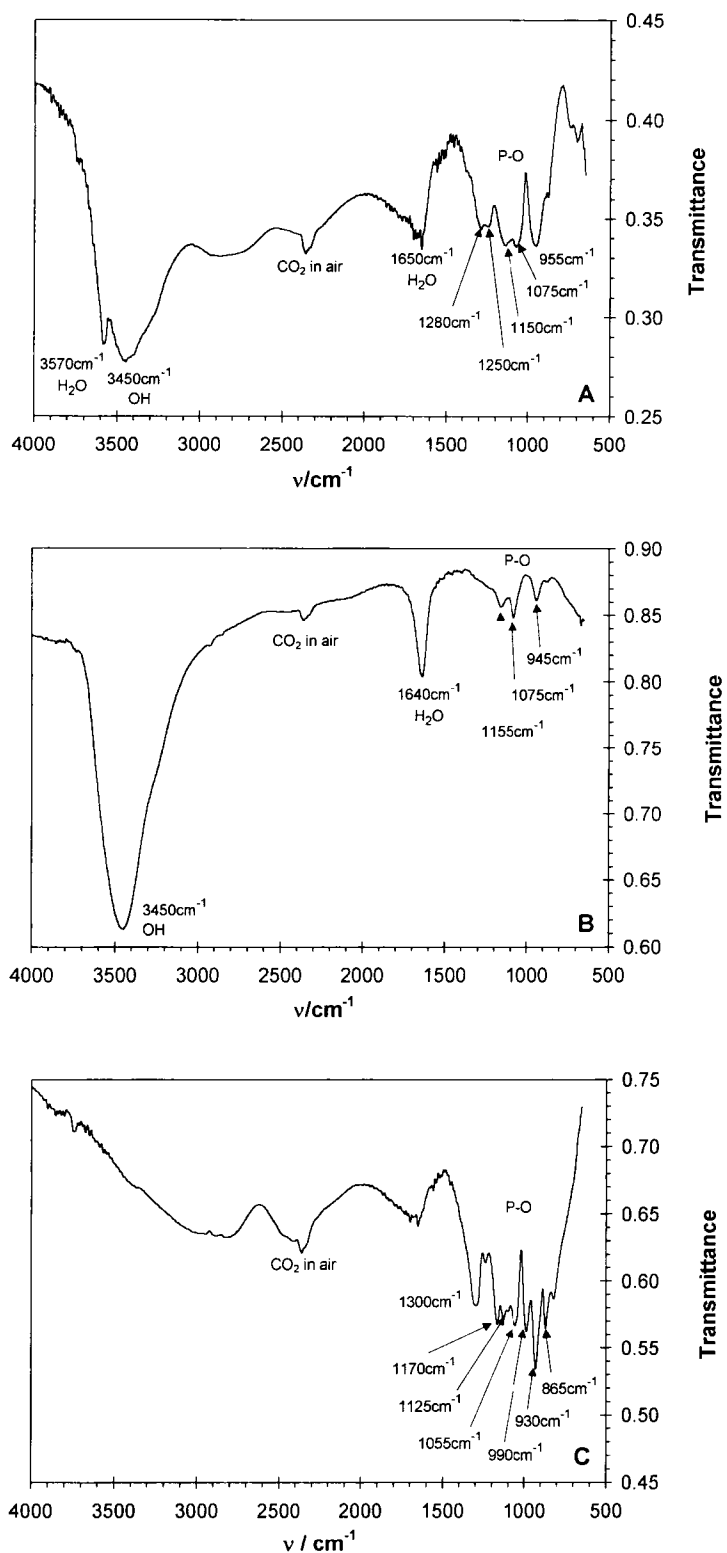


Figure 5.10 IR spectra of sodium dihydrogen phosphate after heating at A) 22 °C B) 65 °C C) 170 °C for 2 hours. Band positions can be found in Appendix C (Table C10).

Table I Positions of phosphate bands (cm^{-1}) in infrared spectra of phosphates dehydrated at several temperatures [18-20].

22°C	65°C	170°C	Vibration
		865	$\nu_s \text{P(OH)}_2$
		930	$\nu_{as} \text{P(OH)}_2$
955	945		$\nu_s \text{PO}_2$
		990	$\nu_s \text{PO}_2$
1075	1075	1055	$\nu_{as} \text{PO}_2$
		1125	$\nu_{as} \text{PO}_2$
1150	1155	1170	$\nu_{as} \text{PO}_2$
1250			$\delta \text{P-O-H}$
1280		1300	$\delta \text{P-O-H}$

5.3.3 Raman Spectra of Phosphates Releasing Crystal Water

The figures in this section show the Raman spectra of the loss of crystal water recorded in-situ at various temperatures. Some spectra were recorded after dehydrating the sample in an oven.

A full interpretation of the Raman spectra involves factor group analysis, which is out of the scope of this work. Raman and crystallographic studies on sodium dihydrogen phosphate crystals have already been published [21-24]. The main focus is to monitor the process of dehydration of sodium phosphate.

The Raman spectra of sodium phosphate can be subdivided into three frequency regions:

- 1) A bending region of the phosphate species between 300 cm^{-1} and 600 cm^{-1} . These bands originate from O-P-O bending vibrations but are blurred at higher temperatures due to structural disorder and evaporation of water. At 150°C all water is driven off making the bands visible.
- 2) A skeletal P-O stretch region of the phosphate species between 600 cm^{-1} and 1400 cm^{-1} . Bands of actual interest originate from water and P-O vibrations. Release of crystal water is also visible in the Raman spectra. From 20°C to 200°C , the phosphate is still present as sodium dihydrogen phosphate, but evaporation of crystal water induces changes in the crystal structures according to the XRD analysis (appendix C). This also influences the phosphate band positions and will be discussed in more detail later. Phosphate starts to condense above 200°C , which can be clearly seen in the spectra.
- 3) A stretch region of water between 3000 cm^{-1} and 4000 cm^{-1} . Water molecules are hydrogen bonded to the phosphate groups. The loss of water, visible in the Raman spectra, is in agreement with the DSC curve.

H_2PO_4^- with C_{2v} symmetry has 4 bands which should all be active in Raman and IR spectroscopy. This symmetry could be obtained best by dissolving the species in water (figure 5.11). Its deuterated analogue is also shown and prepared by dissolving anhydrous NaH_2PO_4 in D_2O .

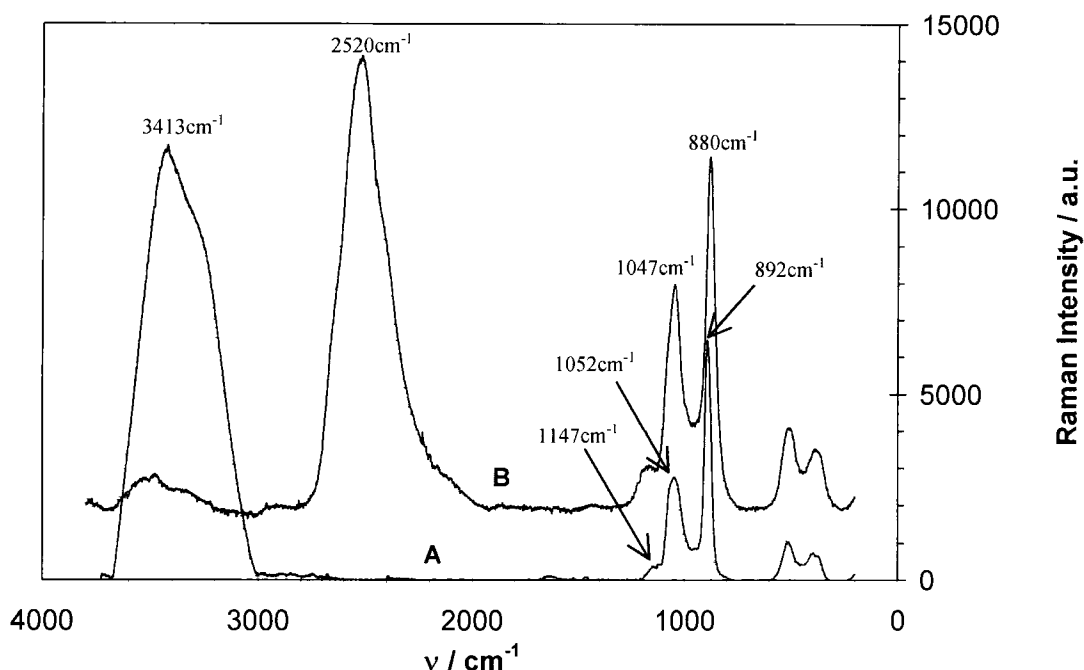


Figure 5.11 Raman spectra of (A) NaH_2PO_4 dissolved in water and (B) NaD_2PO_4 in D_2O . Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C3).

Only three P-O vibrations of sodium phosphate in water are visible at 892 cm^{-1} , 1052 cm^{-1} and a shoulder at 1147 cm^{-1} . Since the phosphate is in solution, it is believed that the two large bands are total symmetric group characteristic vibrations of $\text{P}(\text{OH})_2$ at 892 cm^{-1} and PO_2 at 1052 cm^{-1} when compared to KH_2PO_4 . The shoulder at 1147 cm^{-1} must be the PO_2 , B_2 vibration. The $\text{P}(\text{OH})_2$, B_1 band is probably hidden under the tails of the 892 cm^{-1} and the 1052 cm^{-1} bands. The deuterated analogue shows the large shift of the medium band, but only a 12 cm^{-1} shift of the $\text{P}(\text{OH})_2$ band to lower wavenumbers is observed. No significant shift in the PO_2 vibration is present.

Figure 5.12 shows the spectra of sodium dihydrogen phosphate dihydrate at room temperature. Three large bands at 910 cm^{-1} , 945 cm^{-1} and 992 cm^{-1} are present. The deuterated species shows a 39 cm^{-1} shift of the 910 cm^{-1} bands to lower wavenumbers, indicating that a $\text{P}(\text{OH})_2$ vibration is involved. The shoulder of the 871 cm^{-1} band is due to an exchange of H^+ for D^+ . A P-O band at 949 cm^{-1} has shifted slightly while the 992 cm^{-1} band shows a larger shift to higher wavenumbers and both bands must be involved in PO_2 vibrations. Bartl et al [21] reported a large distortion of the phosphate tetrahedron in $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. Three phosphate oxygen atoms (O1, O2, O3) co-ordinate Na^+ , while the remaining oxygen atom (O2) does not. This oxygen is an acceptor of three hydrogen bonds, originating from an acidic hydrogen and two water molecules. O1 and O3 are donors and acceptors of acidic framework bridges only. The phosphate tetrahedron is far from ideal and the symmetry of the phosphate should therefore be low, although this is not explicitly reported.

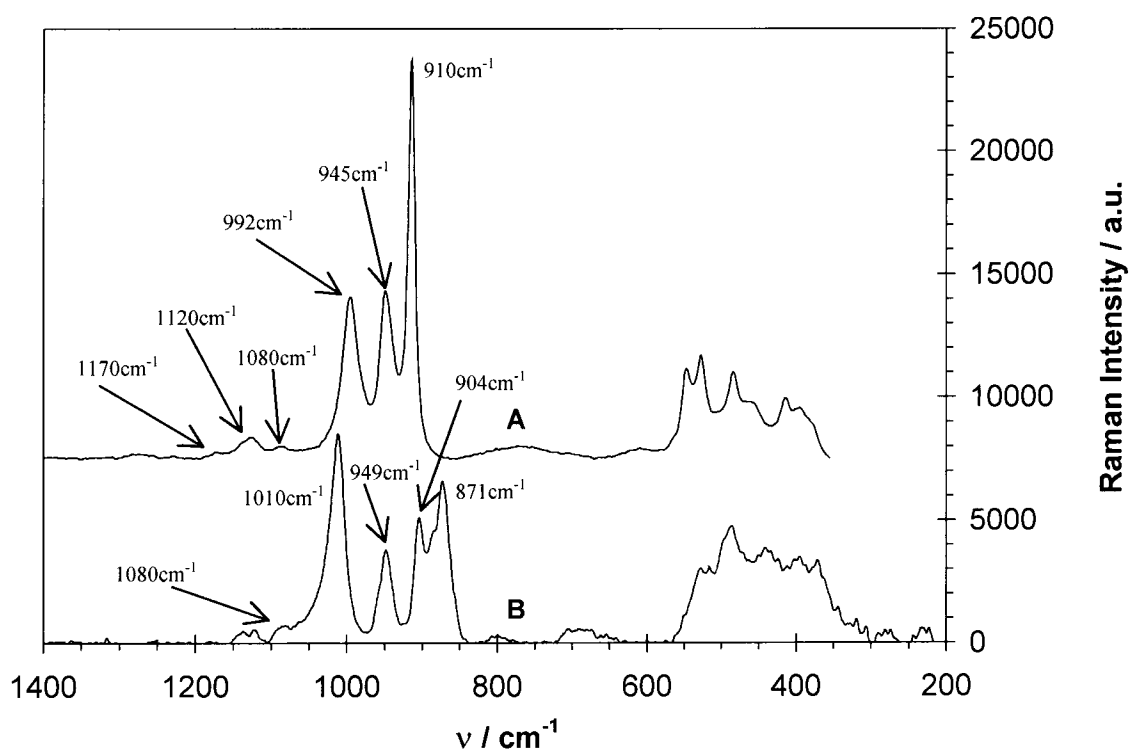


Figure 5.12 Raman spectra of (A) $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and (B) $\text{NaD}_2\text{PO}_4 \cdot 2\text{D}_2\text{O}$. Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C4).

The Raman spectra of the deuterated and non-deuterated phosphate dihydrate crystals in the water region are shown in figure 5.13. They contain three broad bands plus a sharp band, indicating the presence of two water molecules. It must be noted that the XRD analysis (appendix C, not in-situ) revealed traces of $\text{NaH}_2\text{PO}_4 \cdot 1\text{H}_2\text{O}$.

The sharp peak at 3577 cm^{-1} represents the water molecule loosely bonded to the phosphate species. This peak can also be found in the IR spectrum recorded at 22°C . It disappears in the Raman and IR spectra (figures 5.10, 5.13 and 5.15) if the temperature is increased up to 60°C , which is perfectly in accordance with the TGA curve in figure 5.9. A small difference in hydrogen bonding probably splits the DSC curve into two peaks. The strength of the hydrogen bonding, however, is so weak that the difference in this bonding is not substantial.

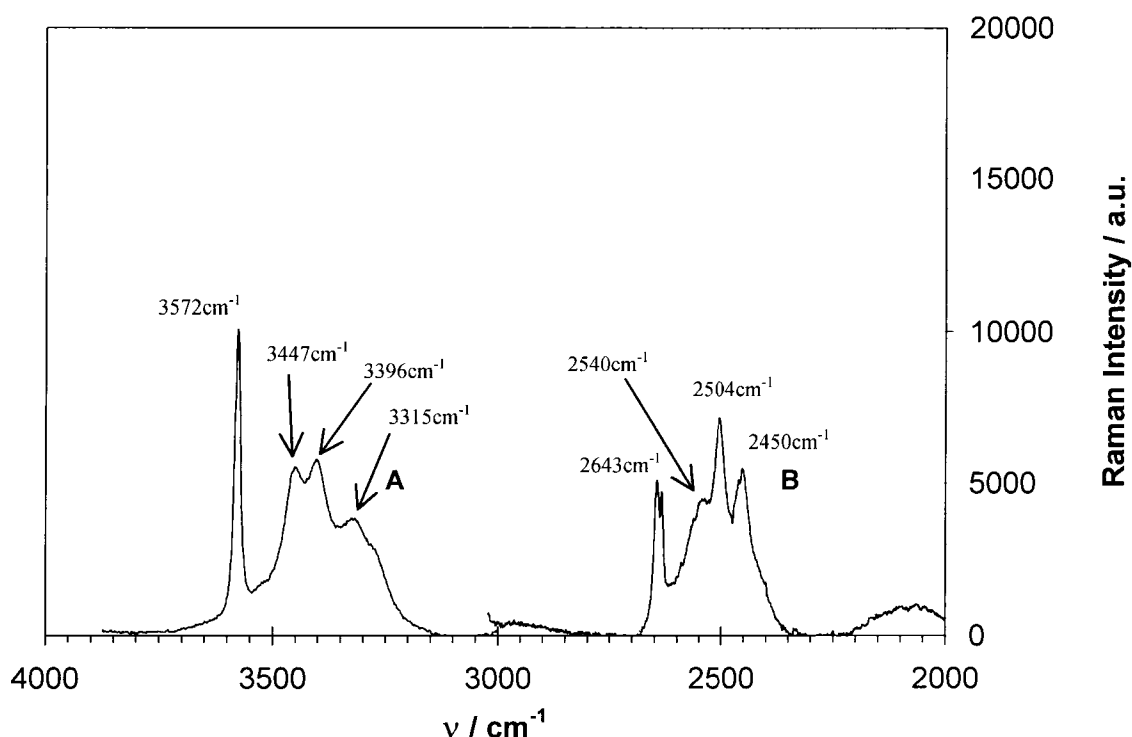


Figure 5.13 Raman spectra of (A) $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and (B) $\text{NaD}_2\text{PO}_4 \cdot 2\text{D}_2\text{O}$. Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C4).

Bartl et al [21] reported a water molecule (W1) having a very long and bent contact with phosphate oxygen atoms and they suggested that this water lies at the boundaries of very weak hydrogen bonds. This must be the loosely bonded water molecule and its Raman band is sharp because of the weak interaction with the phosphate. The other water bands are broader and disappear at 150°C, reflecting a much stronger interaction with the phosphate species in the crystal.

Heating the sample to 60°C removes the loosely bonded crystal water and the resulting spectrum is shown in figure 5.14, with only two large P-O bands present. The presence of the remaining crystal water is quite obvious, but the sharp band of the loosely bonded water molecule has disappeared (Figure 5.15).

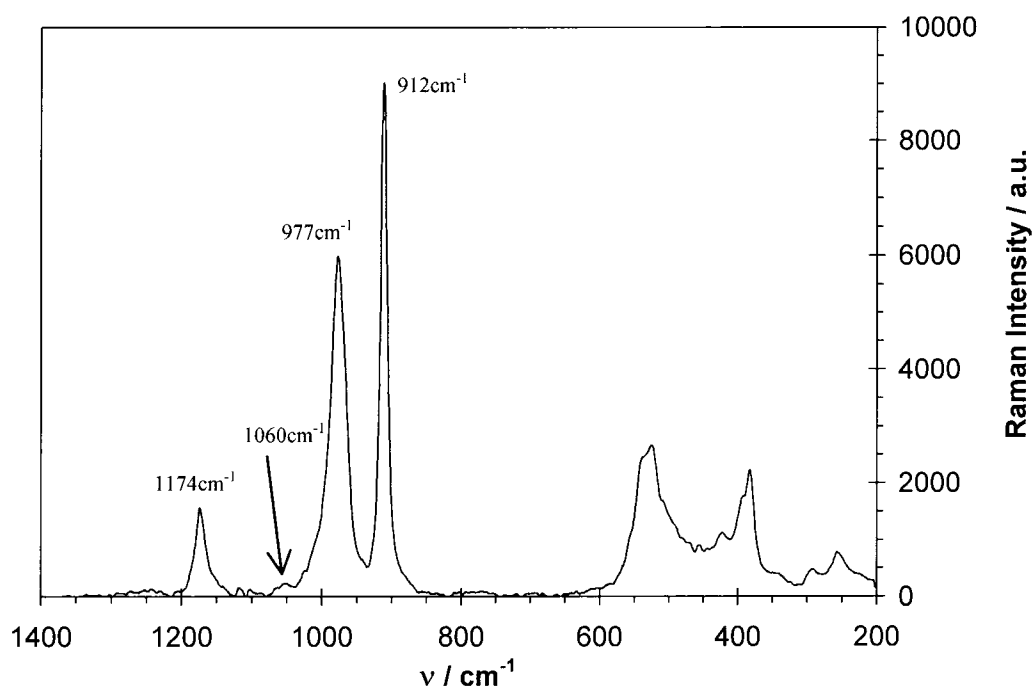


Figure 5.14 Raman spectra of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ recorded in-situ at 60°C. Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C5).

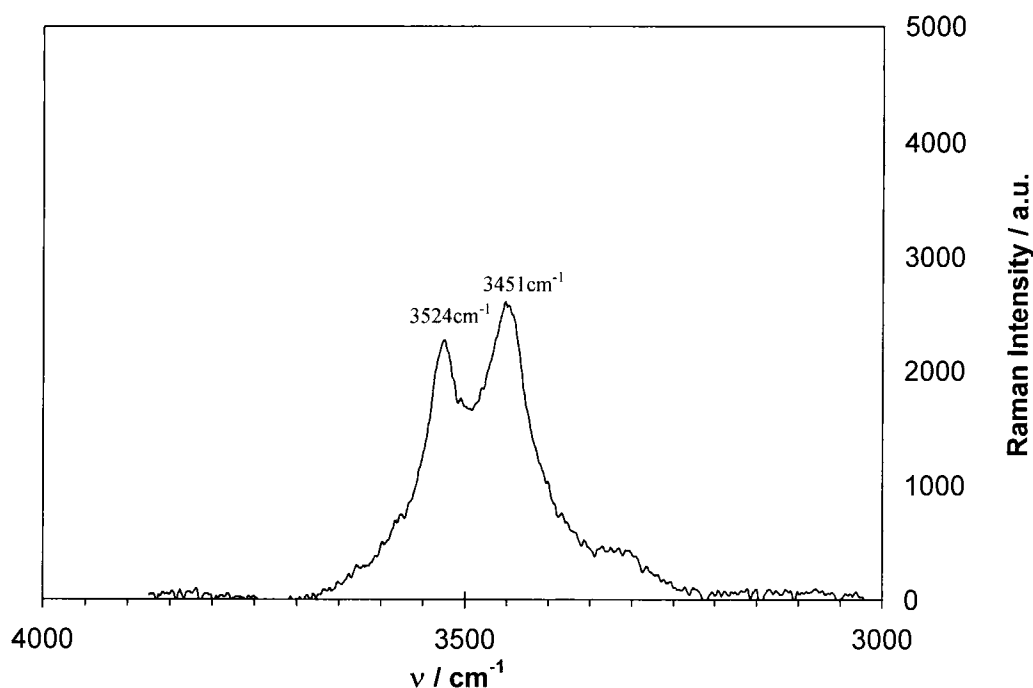


Figure 5.15 Raman spectra of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ recorded in-situ at 60 °C. Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C5).

Catti and Ferraris [22] suggested a mechanism for the transition from the phosphate dihydrate to the monohydrate and pointed out the structural similarity between them.

Although it was difficult to obtain the monohydrate by heating the samples in a drying oven, this phase could be obtained when the dehydration process is monitored by recording Raman spectra of the heated sample. Samples that dehydrated overnight at only 68 °C consisted of anhydrous phosphate with some minor remains of the monohydrate. This caused problems in the interpretation of the spectra. A combination of bands from the monohydrate and the anhydrous phosphate determined the appearance of the spectrum in the area of the P-O vibrations, but crystal water from the remaining monohydrate was still present. The Raman spectrum in figure 5.16(A) is a superposition of the monohydrate and anhydrous phosphate spectra obtained after dehydration in a drying oven. A reference of the anhydrous phosphate is shown in figure 5.16(B).

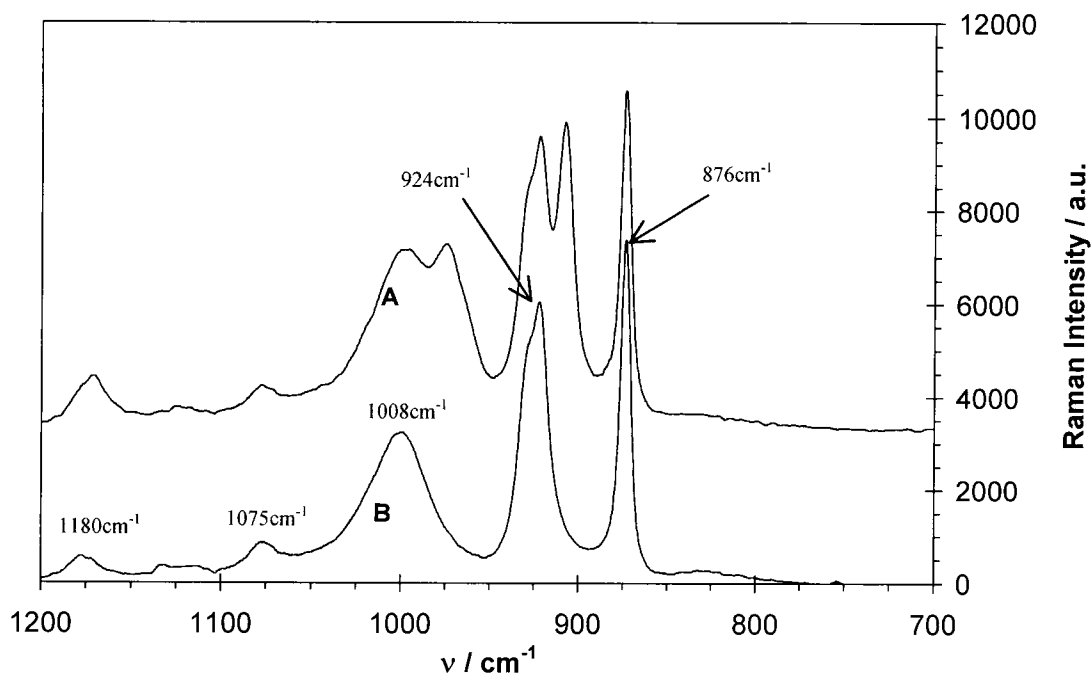


Figure 5.16 Raman spectra of NaH_2PO_4 : (A) monohydrate and anhydrous phosphate dehydrated at 68°C overnight and (B) anhydrous phosphate recorded in-situ. Temperature 150°C . Laser power 75 mW . Integration time 100 s .

The spectrum of the anhydrous phosphate shows a new band at 876 cm^{-1} , while the former P(OH)_2 and PO_2 bands of the monohydrate phosphate are displaced towards higher wavenumbers.

To determine whether the band of the anhydrous species at 924 cm^{-1} is truly a P(OH)_2 vibration, it is compared with the spectrum of a deuterated phosphate (figure 5.17).

The P(OH)_2 vibrations shift to lower wavenumbers while the PO_2 vibration moves towards higher wavenumbers on deuteration.

The unit cell of the anhydrous phosphate contains two different types of phosphates (designated P1 and P2). According to Catti and Ferraris [23], the P1 tetrahedron has three oxygen atoms forming hydrogen bonds with P2 tetrahedra. Two oxygen atoms act as donors and one as acceptor. The P2 tetrahedron has two oxygen atoms involved in two hydrogen bonds with its centro-symmetric equivalent. One oxygen atom is a donor, while the other is an acceptor.

The two other oxygen atoms are involved in hydrogen bonds with three P1 tetrahedra. The bands at 874 cm^{-1} and 924 cm^{-1} could reflect the two types of phosphates, but the assignments of bands might not be so straightforward. Choi et al [24] studied the Raman spectrum of the anhydrous phosphate in detail using factor group analysis and reported 96 Raman active normal modes.

The sharp bands in the bending region of the spectra in figure 5.17 deserve some attention. Six modes between 300 cm^{-1} and 600 cm^{-1} can be clearly discerned and will also move to lower wavenumbers on deuteration, indicating that these modes are involved in P-O-H bending vibrations.

P-O bands in the IR spectra overlap heavily. However, in Raman spectroscopy, the bands and the shifts of the bands are clearly visible and the transitions between the crystallographic phases can easily be monitored. The P-O positions are summarised in table II.

Changes in the Raman and IR spectra correspond to the peak positions in the DSC curve and the mass loss in the TGA curve, implying that thermogravimetric analysis and spectroscopy are consistent with each other.

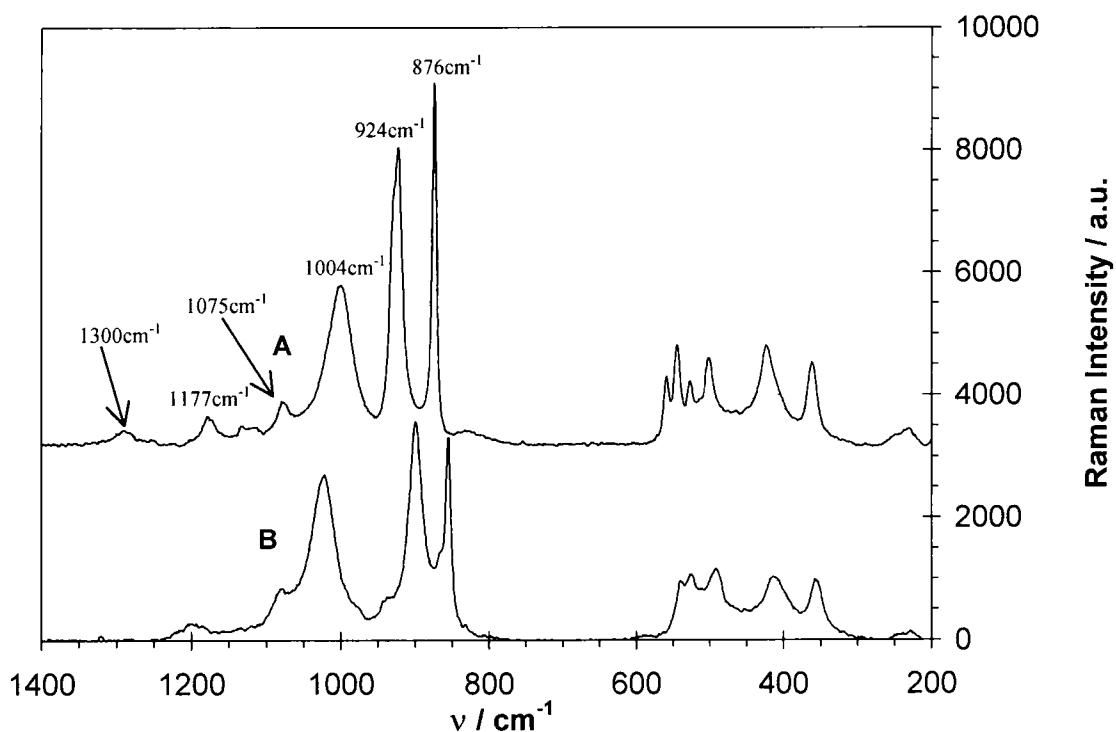


Figure 5.17 In-situ Raman spectra of (A) anhydrous NaH_2PO_4 and anhydrous NaD_2PO_4 . Both spectra are recorded in-situ at 150°C . Laser power 75 mW . Integration time 100 s . Band positions can be found in Appendix C (Table C6).

TABLE II Assigning stretch vibrations of NaH_2PO_4 to bands [18-20].
s=strong, m=medium, w=weak, sh=shoulder.

25°C	60°C	68°C 1 night	150°C - 180°C	Vibration
		873	874 s	$\nu_s \text{P(OH)}_2$
910 s	912 s	907		$\nu \text{P(OH)}_2 A_1$
		924	922 s	$\nu_s \text{P(OH)}_2$
945 s	977 s	973		$\nu \text{PO}_2 A_1$
992 s		998	1004 s	$\nu_s \text{PO}_2$
1080 w	1060 w	1075 w	1075 w	
1120 w			1124 w	$\nu_{as} \text{PO}_2$
1170 w	1174 m		1177 w	$\nu_{as} \text{PO}_2$
			1300 w	
3315 s				water
3396 s	3451 s	3451 s		“
3447 s	3524 s	3524 s		“
3572 s				“

5.3.4 Condensation of Monobasic Phosphate

Above 200°C NaH_2PO_4 starts to condense forming disodium pyrophosphate (figure 5.9). This temperature is higher than expected. Although a scan rate of 5°C per minute was used in thermogravimetric analysis, these differences in temperatures are quite large. Corbridge (figure 5.2) did not explain his experimental procedure, nor did he mention the source. Measurements were probably not conducted in-situ and phases were determined afterwards.

Raman spectroscopy also shows the transition from anhydrous phosphate to pyrophosphate. The band at 737 cm^{-1} represents the linkage between the two phosphate units (P-O-P) while the band at 1023 cm^{-1} corresponds to the PO_2 vibration. The Raman spectrum of $\text{Na}_2\text{D}_2\text{P}_2\text{O}_7$ shows a definite shift of the 737 cm^{-1} band towards lower wavenumbers when compared to $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, proving a coupling between hydrogen and the P-O vibrations. At first, the 737 cm^{-1} band was assigned to a P-OH vibration, but Raman spectra of $\text{Na}_4\text{P}_2\text{O}_7$ and cyclic metaphosphates showed a similar band (not shown) and ruled out this option. The literature assigned this band to a P-O-P vibration [25,26]. The author believes that the P-O-P and P-OH vibrations cannot be regarded separately and both vibrations must be combined to one symmetric vibration in the Raman spectrum. Therefore, the 737 cm^{-1} band is a symmetric H-O-P-O-P-O-H vibration, which is confirmed by the absence of a separate P-OH band between 800 and 950 cm^{-1} . The vibration of such a species would also shift towards lower wavenumbers upon deuteration.

The PO_2 bands shift towards higher wavenumbers as expected.

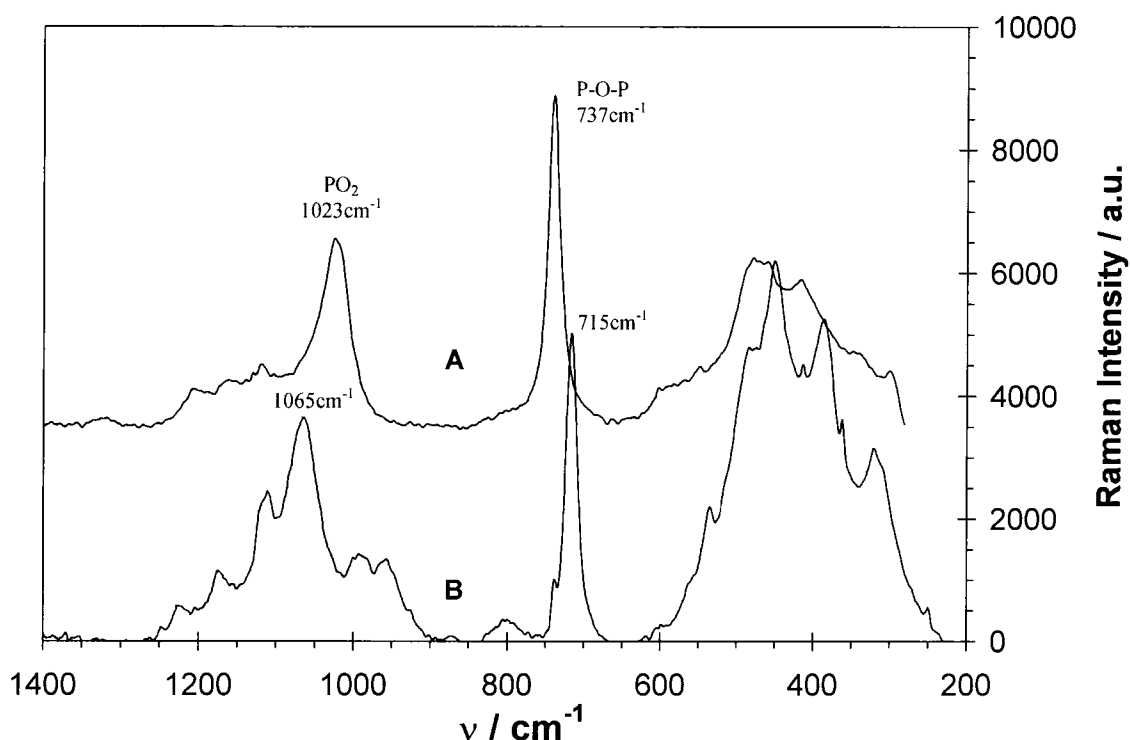
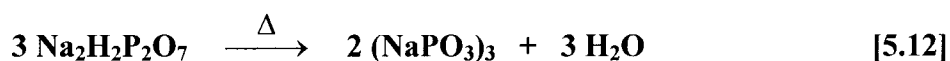


Figure 5.18 In-situ Raman spectra of (A) $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and (B) $\text{Na}_2\text{D}_2\text{P}_2\text{O}_7$. Both spectra are recorded in-situ at 250 °C. Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C7).

Sodium polyphosphate cannot simply be prepared by thermal dehydration of monosodium dihydrogen phosphate. Metaphosphate formation starts above 300°C. It appears that this process takes place in two steps, one at 310°C and the other at 345°C. According to mass loss calculations, a combination of the two steps accounts for the loss of water in the formation of the meta triphosphate. In this temperature range, the Raman spectra also changes. The bands of the pyrophosphate are replaced by bands at 1151 cm^{-1} and 694 cm^{-1} , which correspond to the symmetric stretch of the PO_2 and the $-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}-$ backbone species of cyclic meta triphosphate respectively (figures 5.19 + 5.20).

Meta triphosphate can only be formed from pyrophosphate; bonds need to be broken and new bonds must be formed. The simplest reaction is:



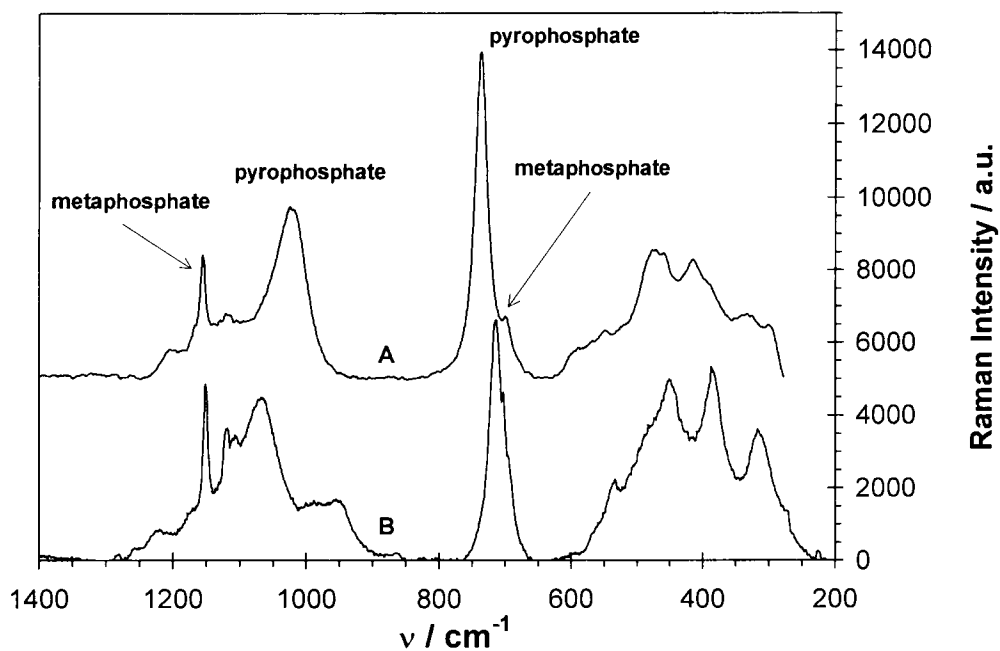


Figure 5.19 Raman spectra of (A) $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + \text{Na}_3\text{PO}_3$ and (B) $\text{Na}_2\text{D}_2\text{P}_2\text{O}_7 + \text{Na}_3\text{PO}_3$ recorded in-situ at 320 °C. Laser power 75 mW. Integration time 100s.

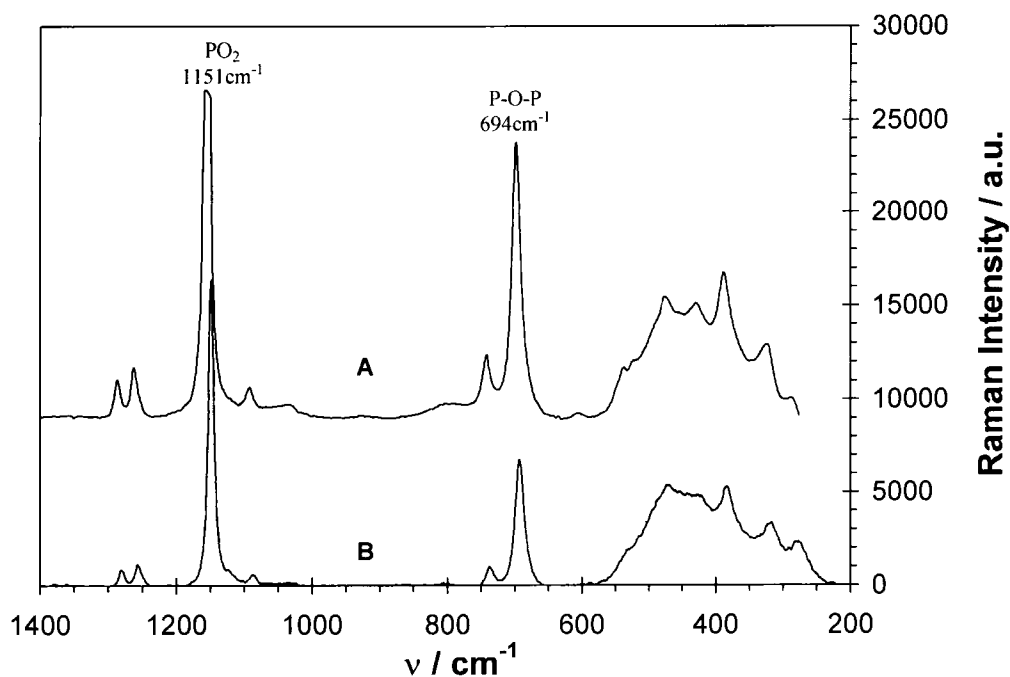
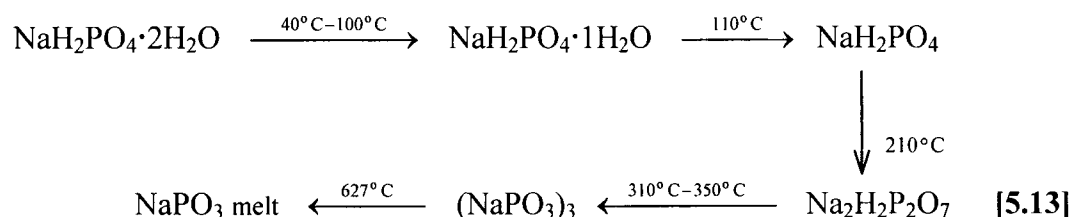


Figure 5.20 Raman spectra of Na_3PO_3 from (A) NaH_2PO_4 and (B) NaD_2PO_4 recorded in-situ at 400 °C. Laser power 75 mW. Integration time 100s. Band positions can be found in Appendix C (Table C8).

No sodium polyphosphate is formed upon heating NaH_2PO_4 below the melting point and under these experimental conditions a mixture of two sodium meta triphosphate phases is obtained (XRD, appendix C). Since metaphosphates do not contain hydrogen atoms, the spectra of metaphosphate prepared from NaH_2PO_4 and NaD_2PO_4 must be identical, which is indeed the case. From 360°C the TGA shows no further mass loss and the DSC peak at 630°C indicates the transition to the melt.

Below is a summary of the total thermogravimetric analysis of the condensation of sodium dihydrogen phosphate.



The melt can be quenched in air at room temperature to form a glass essentially containing linear polyphosphates. The degree of branching depends on the $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio. Even at $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ below unity, branching could still occur according to Strauss and Treitler [12]. They showed that hydrolysis of branches in a polyphosphate solution accounts for the decrease in the viscosity of the solution. All branches should have disappeared after 24 hours. A titration curve of a known aliquot of polyphosphate in water with a sodium hydroxide solution is shown in figure 5.21. An inflection point near $\text{pH}=9$ represents a state in which all hydrogens at both ends of all the chains are replaced by sodium ions. From the amount of sodium hydroxide used, the average length of a polymer can now be calculated. For the present study, a typical degree of polymerisation for a sodium polyphosphate polymer prepared by quenching a melt in air is 85, which is low compared to the values in the literature (400 [11]). An important factor is the purity of the reagents as well as residual moisture. Dibasic orthophosphates terminates chain growth and polyphosphate formation is very sensitive for the amount of this phosphate species present in the sample.

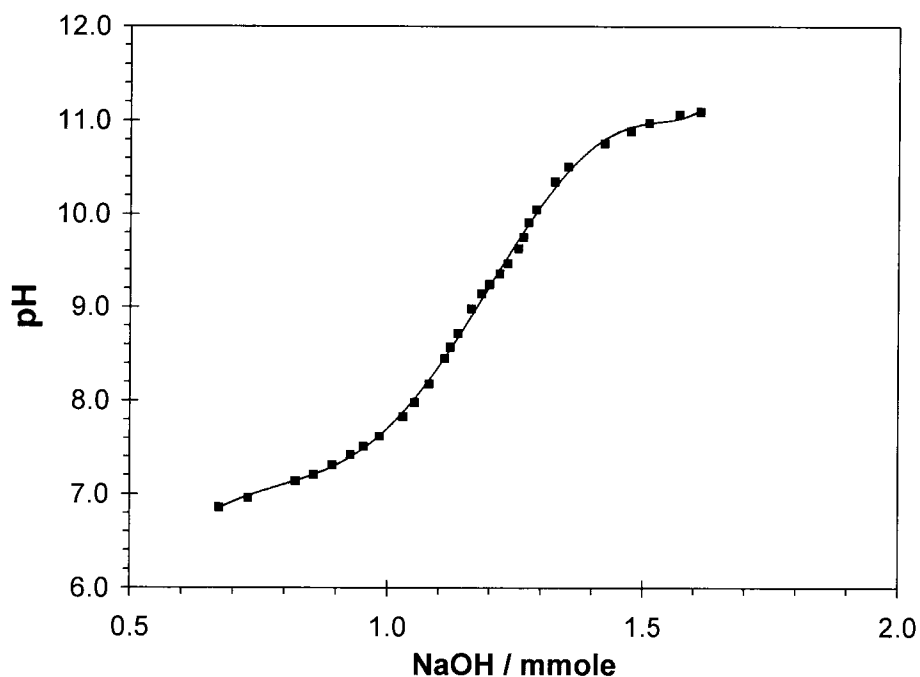


Figure 5.21 Titration curve of $2.58 \cdot 10^{-3}$ mole NaH_2PO_4 in water.
 NaH_2PO_4 is quenched from the melt in air and dissolved in water

A major difference between the condensation of sodium dihydrogen phosphate and potassium dihydrogen phosphate is the absence of potassium pyrophosphate during the dehydration of the latter. Potassium polyphosphate is thermodynamically stable towards potassium pyrophosphate, while sodium polyphosphate is not stable with respect to sodium meta triphosphate. The literature also reported the ease at which a sodium polyphosphate is converted to a meta triphosphate [11].

5.3.5 Phosphate Mixtures

Dehydrating a mixture of potassium dihydrogen phosphate and sodium dihydrogen phosphate does not give a water-soluble salt. A combination of ammonium dihydrogen phosphate and sodium dihydrogen phosphate, however, produces a glass after dehydration between 400°C and 600°C ($K_2O:P_2O_5 < 1$). A TGA/DSC curve of this dehydration process is shown in figure 5.22. During the first step, up to a temperature of 100°C, crystal water of NaH_2PO_4 is released. Between 150°C and 600°C, water and ammonia evolve. Up to 350°C, mainly water is released and above this temperature the ammonium counter cation decomposes to ammonia leaving a proton behind, as suggested by the DSC curve.

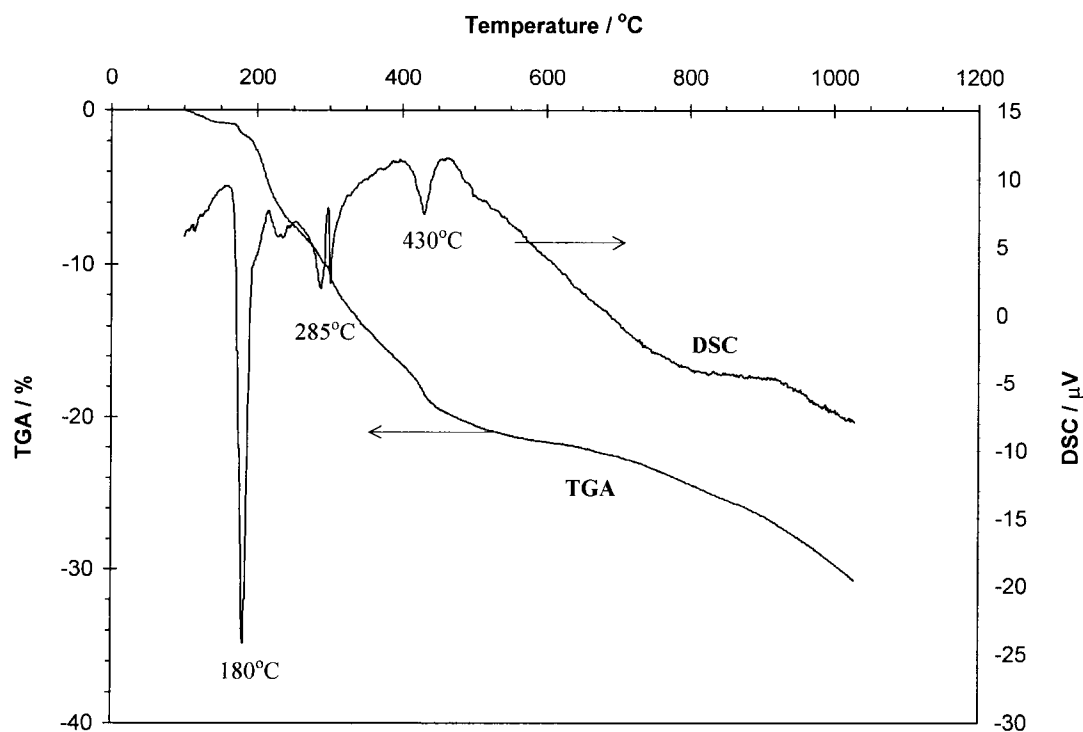


Figure 5.22 TGA/DSC curve of a 1:1 (mole/mole) mixture of $(NH_4)H_2PO_4$ and NaH_2PO_4 . Scan rate $5^\circ C \cdot min^{-1}$.

At 500°C the phosphate sample has turned from a liquid state to a glass, which no longer dissolves in water. An analysis of the shape of the DSC curve reveals that branching begins at 500°C. The DSC curve shows a small plateau from 810°C and continues to decrease above 920°C, which is accompanied by a high mass loss. Up to 800°C mainly branching is involved, but above 920°C the sample sublimates/evaporates.

A mixture of ammonium dihydrogen phosphate and potassium dihydrogen phosphate also produces a glass above 200°C (figure 5.20). Comparing the TGA and DSC curve, the phosphate units condense from 200°C. Between 350°C and 400°C ammonia evolves and branching occurs from ~450°C (figure 5.23).

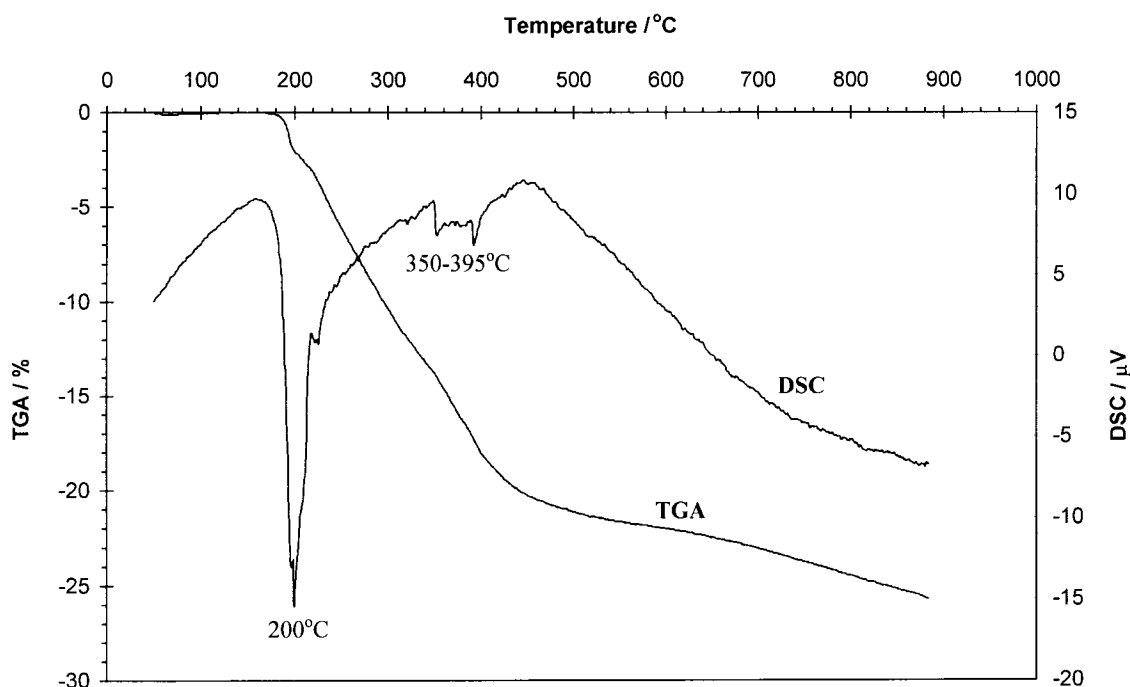


Figure 5.23 TGA/DSC curve of a 1:1 (mole/mole) mixture of $(\text{NH}_4)\text{H}_2\text{PO}_4$ and KH_2PO_4 . Scan rate $5^\circ\text{C}\cdot\text{min}^{-1}$.

Raman spectra of the condensation process are shown in figure 5.24. At room temperature only one band is visible, because the structure of $\text{NH}_4\text{H}_2\text{PO}_4$ is similar to the structure of KH_2PO_4 [15]. Therefore $\text{NH}_4\text{H}_2\text{PO}_4$ also has one total symmetric $\text{P}(\text{OH})_4$ stretch vibration located at the same position as the analogue KH_2PO_4 vibration. The band at 1660 cm^{-1} is the total symmetric stretch of the ammonium ion. It disappears upon heating at 350°C . After condensation, the $-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}$ vibration at 700 cm^{-1} and the PO_2 vibration at 1155 cm^{-1} replace the band at 920 cm^{-1} .

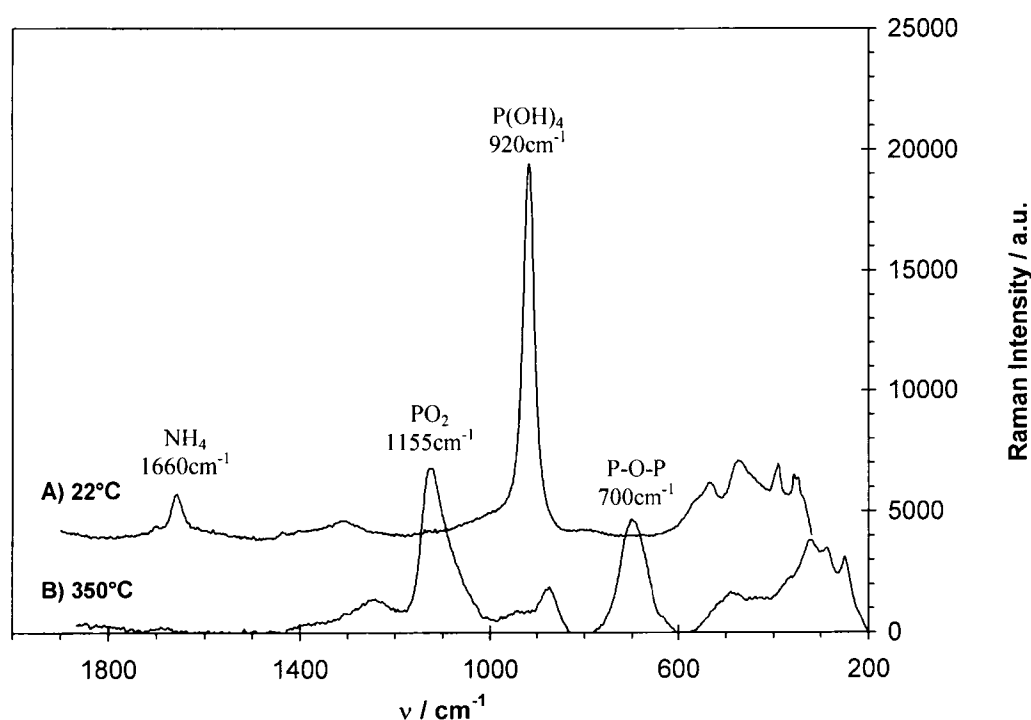
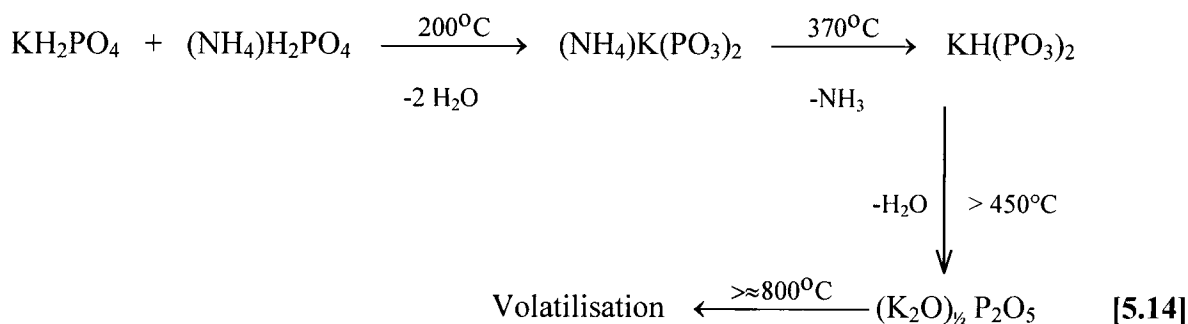


Figure 5.24 Raman spectra of a 1:1 (mole/mole) mixture of $(\text{NH}_4)\text{H}_2\text{PO}_4$ and KH_2PO_4 . A) spectrum at 22°C B) spectrum at 350°C recorded in-situ. Band positions can be found in Appendix C (Table C9).

Raman spectra and TGA/DSC curves are in agreement with each other and all the reactions are summarised in the reaction sequence.



The ammonium ions on the phosphate units are decomposed upon heating the polymers to 400°C. Ammonia gas is released and protons are left behind forming hydroxy groups. Since the temperature for this process is higher than the temperature for condensation, branching is expected to happen immediately after the release of ammonia. However, this is not the case. Branching occurs over a temperature range starting at a higher temperature than for a normal condensation. Hydroxyl groups must be in each other's vicinity in order to condense. In a crystal packing, a fraction of the hydroxyl groups will be close enough and the polymers must rearrange their orientations to make condensation possible. Rearrangement depends on the mobility of the polymers, which is higher at elevated temperatures. Therefore these temperatures, which are the driving force for branching, are higher compared to the condensation temperatures for linear polymers. The presence of different types of metal counter cations disturbs the packing of polymers inducing glass formation. Extensive branching stabilises polyphosphate glasses towards dissolution in water and only a certain temperature range is appropriate to produce linear soluble glasses.

Determination of cross-link density is not as simple as outlined in section 5.1.6. During dehydration, ammonia evolves, which must be accounted for. If the mass loss of ammonia and the process of branching overlap, subtraction of the appropriate mass of the ammonia part from the total mass loss is not possible. Fortunately, ammonia is released in the last stage of the formation of linear phosphates below 450°C. Cross-linking becomes statistically apparent from 500°C onwards. Please note that some branching might occur during the formation of linear phosphates at the expense of the linear chain length.

Cross-link density x is calculated from the mass loss curve in figure 5.23 by using the formula in eq.5.15. In this figure, the mass loss curve is given in a mass loss percentage versus the temperature, which could easily be transformed in a mass loss fraction m versus the temperature. $(1-m)$ is the fraction of the remaining polyphosphate and has to be multiplied by the molecular mass of the phosphate (M_p) to obtain the mass of the sample at each temperature. M_p is the sum of the molecular masses of KH_2PO_4 and $(\text{NH}_4)\text{H}_2\text{PO}_4$. Furthermore, $(1-m) \cdot M_p$ must be subtracted from the molecular mass of linear polyphosphates (M_L) to get the mass loss due to cross-linking. This corrected mass loss must be divided by the difference between the molecular mass of the linear phosphate and the completely dehydrated condensed phosphate, which includes the loss of all constitutional water ($M_{\max} = \text{mass of } (\text{M}_2\text{O})_{1/2}\text{P}_2\text{O}_5$), to obtain the cross-link density.

$$x = \frac{M_L - (1-m) \cdot M_p}{M_L - M_{\max}} \quad [5.15]$$

Unfortunately, M_L and $M_{\max}$ are not exactly known, introducing an error in the calculation. An alternative calculation is the subtraction of the molecular masses of ammonia (MNH_3) and two water molecules ($\text{M}_{\text{H}_2\text{O}}$) from the total mass loss ($m \cdot M_p$). The two water molecules account for the formation of linear polyphosphates while the ammonia is released upon heating before cross-linking takes place. The corrected mass loss must be divided by the molecular mass of water to obtain the fraction of water released upon cross-linking. An extra factor of a $\frac{1}{2}$ is introduced to account for the initial K to NH_4 ratio of 1:1.

$$x = \frac{m \cdot M_p - 2 \text{ M}_{\text{H}_2\text{O}} - \text{M}(\text{NH}_3)}{\frac{1}{2} \text{ M}_{\text{H}_2\text{O}}} \quad [5.16]$$

Specifying the cross-link density is very important since it can be defined in various ways. Beside the definition above, cross-link densities could also be expressed in the fraction of cross-links per phosphate atom or the fraction of phosphate atoms being cross-linked. In the former definition, the ceiling of the cross-link density is 0.25 while the latter has a maximum of 0.5 due to the K to NH_4 ratio.

The cross-link density curve is plotted versus the temperature in figure 5.25 and in this case the ceiling value is 1. At temperatures lower than 500°C the polymer is statistically not cross-linked, but at higher temperatures branching occurs. The curve in figure 5.25 is expected to level off reaching its maximum value, but in fact it continues to rise passing this maximum value due to evaporation of the sample. Experimentally, the curve seems to be linear at high temperatures and is linearly extrapolated to lower temperatures. The deviation with the measured curve indicates the formation of cross-links and it is expected that evaporation is minimal below a temperature of 560°C. Between 560°C and 600°C the cross-linking density should be between 0.22 and 0.27, but at higher temperatures determinations of densities become unreliable. Only a quarter of the maximum cross-linking can be achieved without a significant loss of the sample.

The method of Ray [6] outlined in section 5.1.6, which is called loss on ignition, and the calculations using TGA curves are both based on mass loss measurements. The former method uses mass loss on ignition to a final state, while the latter is based on the mass loss from an initial mass. In the case of cross-link density measurements of a potassium-ammonium phosphate system, the initial mass is well defined shown by the plateau of the TGA curve between 25°C and 180°C, while a stable final mass state could not be established. The cross-link density does not necessarily have a maximum of 0.5 if the phosphate system shows azeotropic behaviour, introducing an error in the loss on ignition measurements. Furthermore, trends in mass loss like evaporation are recognised easier in TGA curves, because the mass of the sample is continuously measured. In general it can be stated that TGA curves are preferred to calculate cross-link densities, if a stable initial mass could be established. Loss on ignition could be used as an alternative if the final mass is stable and the initial mass not well defined (e.g. loosely bonded crystal water).

In order to stabilise the final mass, Ray suggested to use litharge to avoid evaporation of P_2O_5 . Litharge has a layered structure, but its counter part massicot (PbO_2) is build of chains. Cotton [27] stated that Pb_3O_4 is prepared by heating PbO or PbO_2 in air. Pb_3O_4 behaves chemically like a mixture of PbO and PbO_2 . In fact, $Pb^{IV}O_6$ octahedra share opposite edges to form chains, which are linked by bridging Pb^{II} atoms.

Such a structure indicates that the oxygen content is not fixed and it could change upon heating and/or cooling, introducing an error in the determination of cross-linking. Therefore it is concluded that a TGA analysis is the best technique to measure cross-link densities in this case.

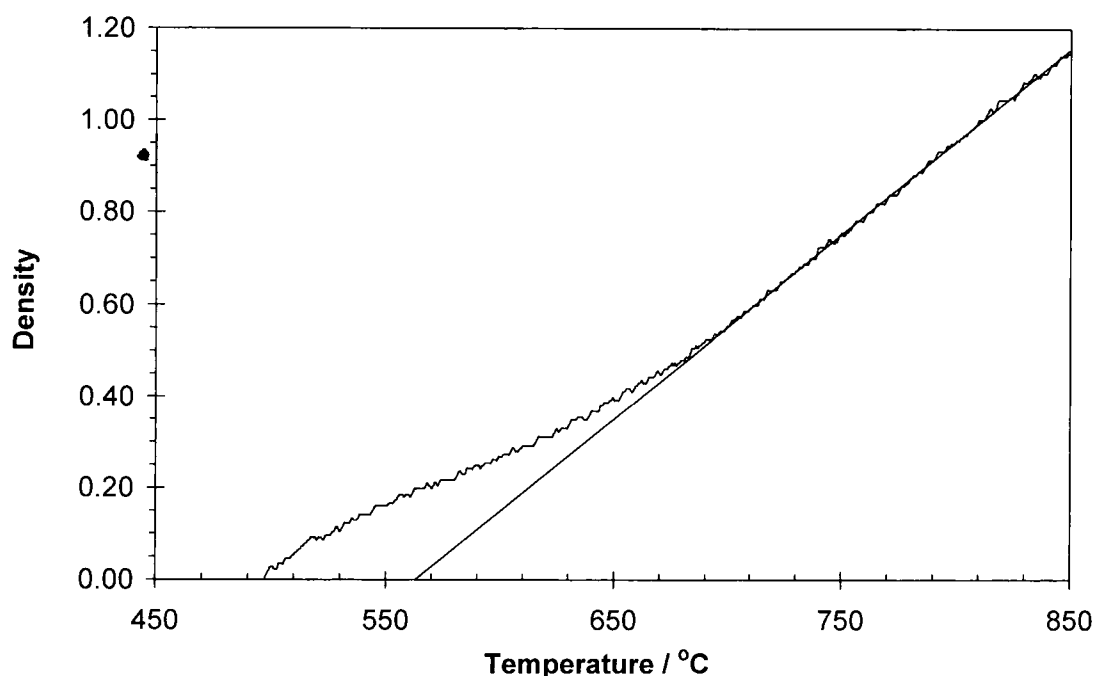


Figure 5.25 Cross-link density of a $\text{NH}_4\text{H}_2\text{PO}_4 / \text{KH}_2\text{PO}_4$ mixture versus temperature. Straight line is an extrapolation from higher to lower temperatures.

A thermogravimetric analysis of a mixture of ammonium dihydrogen phosphate and sodium dihydrogen phosphate with a ratio of 2:1 shows a similar curve (not shown), except that the curve is smoother during condensation and ammonium decomposition.

5.3.6 Concluding Remarks

The influence of additives in phosphate mixtures or different compositions of phosphates could easily be studied, extending the type of work in this chapter. It might also be possible to study other phosphate reactions at elevated temperatures, both in the liquid and the solid phase.

A major problem could be the interference from background light (luminescence) from the phosphate sample at elevated temperatures. Another practical problem could be the removal of gaseous products from the probe during heating. However, phosphates produce strong Raman bands, which are clearly visible in the spectra and useful to identify the type of phosphate.

Care should be taken in interpreting the dehydration spectra of phosphates, because the positions of P-O bands in the spectra depend on the crystal structure. Factor group analysis is necessary to understand the spectra. However a simplification is possible by identifying two distinct bands in the spectra. These bands, marked as PO_2 and P(OH)_2 , are useful for identification of the phosphate.

The P-O-P and the P-O bands are also characteristic for condensed phosphates. In addition, it is believed that the previously assigned P-O-P vibration in pyrophosphates is actually an H-O-P-O-P-O-H vibration.

Raman spectroscopy proved to be a valuable tool to study the dehydration of phosphate in-situ. The power of this technique lies in its ability to allow in-situ measurements of the phases present at a specific temperature and moment of time. Research on phosphate dehydration could not be reduced to a Raman spectroscopic study only, but Raman spectroscopy is an important technique for an integrated study.

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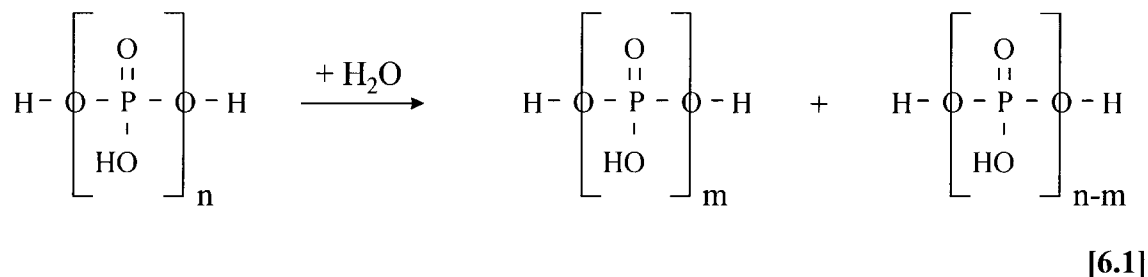
Hydrolysis of Sodium Polyphosphate

6.1 Introduction

The hydrolysis of polyphosphates has been reported in the literature, including that of polyphosphates in acidic solutions [1,2,3]. However the rate at which hydrolysis occurs is not always known. Hydrolysis of condensed phosphates is studied by ^{31}P NMR, which is a powerful and a reliable technique [4,5], but the hydrolysis of a dissolved sodium polyphosphate in an acidic medium has not been studied in such detail before. Rates of hydrolysis are determined to study the stability of the polyphosphate in an acidic medium and also to elucidate the mechanism of the reaction in general.

Linear sodium polyphosphate dissolved in acidified water is studied with Raman spectroscopy. Raman spectroscopy has not been frequently used for quantitative analysis but with developments in instrumentation it can be used effectively to monitor reactions, particularly in aqueous media. The conditions and problems encountered in the determination of reaction constants for the hydrolysis of sodium polyphosphate are also discussed.

Polyphosphates are stable in neutral solutions at room temperature. However, hydrolysis occurs in an acidic water medium. A polymer is cut into two new strings and the overall reaction of the hydrolysis can be represented as follows.



n and m are integers and represent the number of phosphate units. n has a theoretical minimum of two and m must be smaller than n with a minimum of one.

The rate of hydrolysis of a polyphosphate solution is determined by a number of factors [1]:

- The number of shared corners of PO_4 tetrahedra. Triple linked polyphosphates hydrolyse faster than those with double linkages.
- Temperature. Hydrolysis will increase with increasing temperature.
- pH. Lowering the pH increases hydrolysis.
- Concentration.
- Cation of the polyphosphate. The type of the polyphosphate cation might to a lesser extent affect the rate of hydrolysis. Polyphosphates containing alkaline earth metals make the polymer more resistant to hydrolysis.

Rates of hydrolysis are also affected by impurities in the polyphosphate. Substituting an arsenic atom for a phosphorous, for instance, results in a rapid hydrolysis of the As-O bond on dissolving. A polyphosphate in solution is thermodynamically unstable with respect to orthophosphoric acid. The reaction equation of the hydrolysis and the corresponding enthalpy is given in eq.6.2. The enthalpy in the equation has the unit kilo joule per mole P-O-P bonds severed, which is negative. The Gibbs Free Energy (ΔG) must be negative because a chain is degraded into its individual units making the entropy of the reaction positive. This means that the reaction is thermodynamically possible.



Ray, N.H., *Inorganic Polymers*, Academic Press Inc., London 1978, 63

Triphosphates are less stable towards hydrolysis than pyrophosphates and tetraphosphates are less stable than triphosphates etc. This decrease in stability continues up to 10 phosphate units, after which a progressive increase in stability occurs with increasing number of units. Before stability and mechanism can be established, all relevant species and experimental conditions must be discussed first.

6.2 Experimental

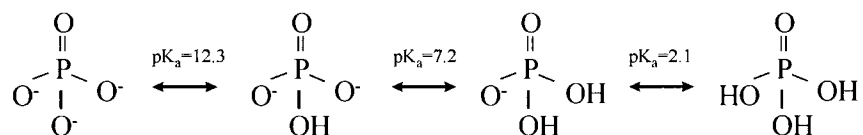
Sodium polyphosphate glasses were prepared by air quenching a melt of sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ Extra Pure Reagent Kanto Chemical Co., Inc.) from a temperature of 650°C . The glass was dissolved in water and acidified by adding concentrated hydrochloric acid (Merck) until $\text{pH}=0$ (± 0.03). The pH was monitored using a simple pH meter and pH electrode (section 2.7).

The Raman set up is similar to the description in chapter 2 (section 2.3). Raman signals were optimised by using the 459 cm^{-1} Raman line of CCl_4 to 4000-6000 cps. Samples were kept in a closed conical flask and placed in a water bath. Just before every scan a small amount was pipetted out of the flask and transferred into the sample tube, which was positioned in the macro scale chamber of the Raman spectrometer. The sample tube was in a fixed position and a spectrum of CCl_4 was recorded for normalization prior to every scan of a sample.

6.3 Results and Discussion

6.3.1 Phosphate Species

A free tribasic phosphate anion has T_d symmetry because all P-O bonds in a PO_4^{3-} species are conjugated in a tetrahedral arrangement. The irreducible representation of this phosphate anion is $\Gamma = A_1 + E + 2T_2$. Two stretch vibrations have A_1 and T_2 symmetry and the other vibrations have been identified as deformation modes with E and T_2 symmetry [1]. In solution the symmetry of the species is changed upon protonation of the phosphate anion, as shown below, and lowered due to hydrogen bonding. Therefore the spectra depends on the pH and the pK_a values of the phosphates.



Ignoring hydrogen bonding because it is an overall effect, the symmetry of a monohydrogen phosphate anion, HPO_4^{2-} , is C_{3v} . The symmetric stretch vibration of the monohydrogen phosphate species is a symmetric PO_3^{2-} stretch vibration. The irreducible representation of this vibration is A_1 in C_{3v} symmetry.

A dihydrogen phosphate anion, $H_2PO_4^-$, has C_{2v} symmetry. In dihydrogen phosphate, the symmetric stretch vibration originates from the PO_2^- species which is also A_1 .

In phosphoric acid two distinct symmetric vibrations are present i.e. the P=O (A_1) and a P(OH)₃ (A_1) stretch vibration. Both A_1 bands are the symmetric vibrations in C_{3v} symmetry.

PO_x ($x=1-4$) bonds in phosphate species differ in strength due to conjugation. This means that the A_1 bands of different species are observed at different wavenumbers [6] and therefore these spectra are highly depended on the pH and the pK_a values of phosphate. Figure 6.1 shows the relation between the concentrations of different phosphate species and the pH.

The corresponding pH at the intercept of two phosphate concentration curves equals the pK_a value of the two relevant phosphate species. According to the figure, $pK_1=2.1$, $pK_2=7.2$ and $pK_3=12.3$ [7]. Besides this, different species are present at a pH between two pK_a values giving rise to multiple bands in the spectrum.

The Raman spectrum of sodium dihydrogen phosphate in solution at pH=0 is shown in figure 6.2. The value of the pH is lower than that of the first pK_a value of phosphate in solution meaning that the main species is H_3PO_4 . The A_1 breathing vibration of the $P(OH)_3$ species is a broad intense band located at 891 cm^{-1} . The broad band at 1075 cm^{-1} could be ascribed to the degenerate stretch mode (E) of the $P(OH)_3$ species [8]. It must be noted that the complete irreducible representation of the $P(OH)_3$ stretch vibration is A_1+E . The $P=O$ (A_1) stretch vibration can be found at 1170 cm^{-1} . All bands are broad due to hydrogen bonding.

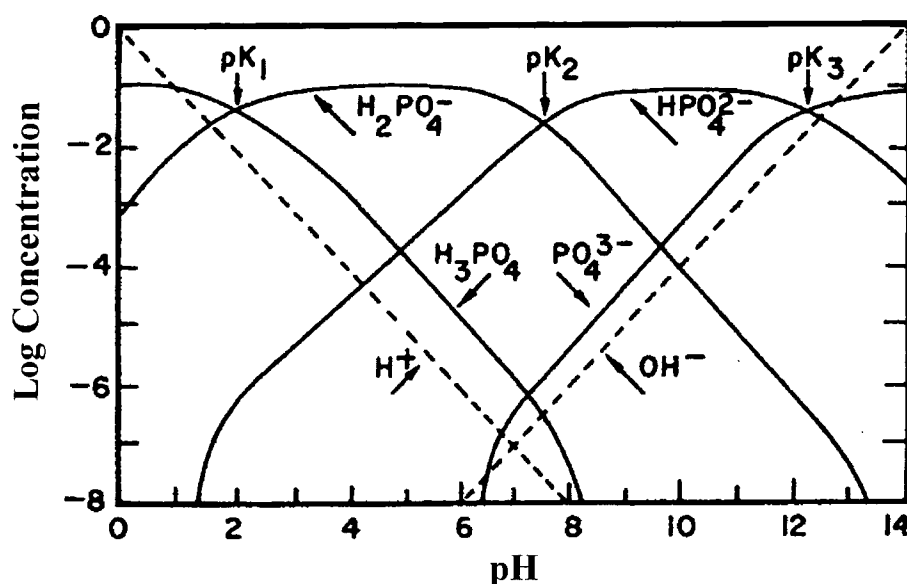


Figure 6.1 *Distribution of phosphate species for 0.1M orthophosphate solution. Analytical Chemistry of phosphorous compounds, ed. by M. Hallmann, Chemical Analysis, 37, John Wiley & Sons, New York 1972, 20.*

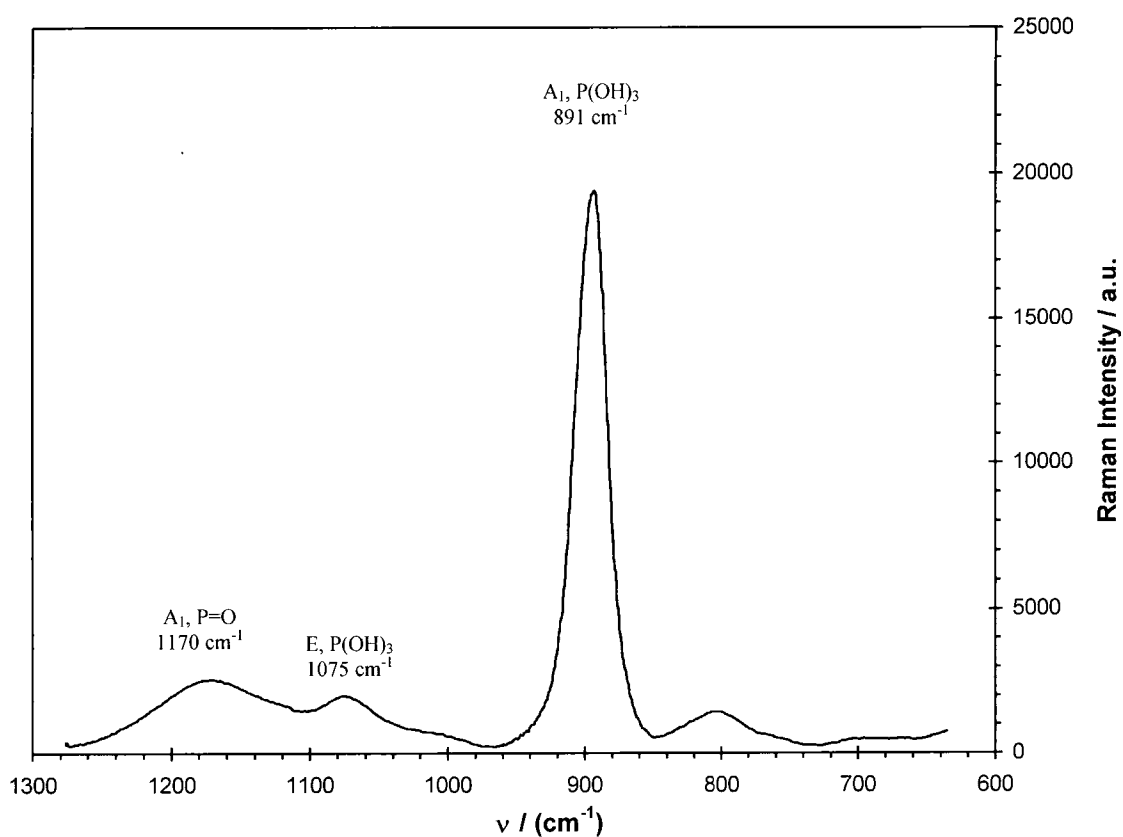


Figure 6.2 Raman spectrum of sodium dihydrogen phosphate dissolved in water ($3.5 \text{ mole}\cdot\text{l}^{-1}$) at 22°C and $\text{pH}=0$. Laser power 75mW , integration time 100s . Band positions can be found in Appendix D (Table D1).

6.3.2 Raman Spectra of Polyphosphate

Figure 6.3 shows a Raman spectrum of sodium dihydrogen phosphate glass quenched from a melt at 650°C and a spectrum of the glass dissolved in water. The spectrum of the glass shows a sharp strong peak at 1164 cm⁻¹. This is the symmetric stretch vibration of the PO₂ species [9]. Terminal oxygen atoms are not included in the backbone of the polymer chain and are conjugated.

The PO₂ vibration is usually strong and lies between 1350 cm⁻¹ and 1150 cm⁻¹. The vibration is almost independent of the type of compound in which the group occurs. Sizes of the substituents also pay a minor contribution to the position of the vibration in the spectrum. Nevertheless, the vibration is very sensitive to the electronegativity of neighbouring groups and resonance or conjugation effects [10,11].

If one of the two terminal oxygens on a phosphorous atom has a negative charge as in a sodium polyphosphate crystal, both oxygen phosphorous bonds are conjugated. In water, the vibration shows a bathochromic shift due to hydrogen bonding.

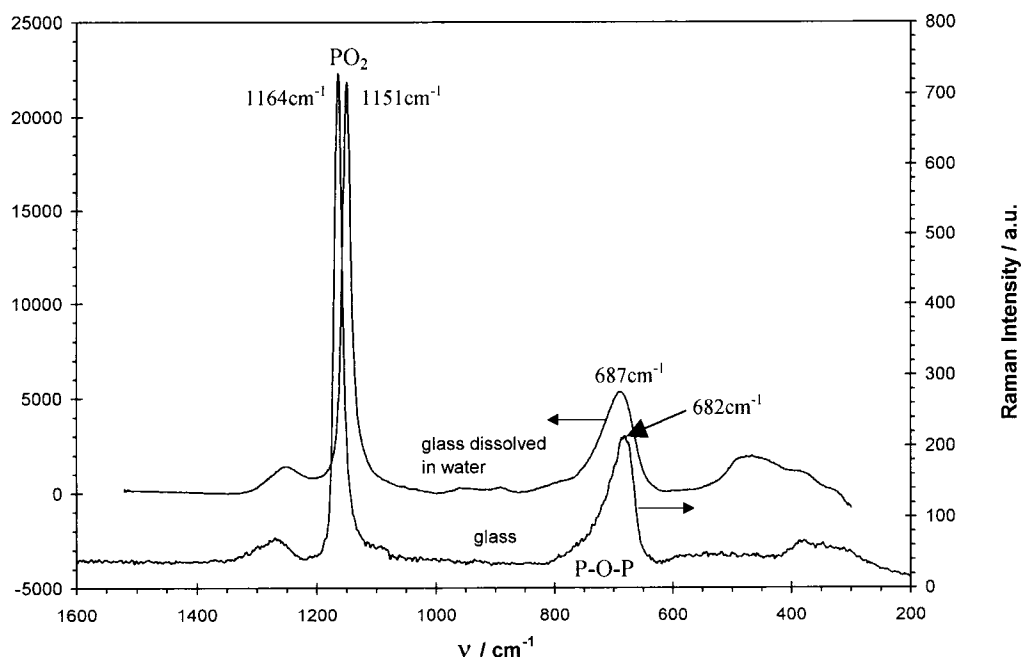


Figure 6.3 Raman spectra of sodium phosphate glass quenched from a melt at 650 °C. and a glass dissolved in water at 22°C. Laser power 75mW, integration time 100s. Band positions can be found in Appendix D (Table D2).

Although there was some debate about the unambiguous assignment of the -P-O-P-O- band in organophosphorus compounds, the -P-O-P-O- group of an inorganic polyphosphate is located at 687 cm^{-1} [9,11,12,13]. -P-O-P-O- bands shift to lower wavenumbers with increasing chain length [14] and they are very broad due to the amorphous character of the polyphosphate. P-O-P linkages form the axis of the chain, which could adopt many orientations in an amorphous state. Band shifts due to hydrogen bonding are small because the oxygen atoms are non-terminal. This is in contrast to the negatively charged terminal oxygen atoms sticking out of the chain making these atoms susceptible to hydrogen bonding with water molecules. From the spectra in figure 6.3 it can be seen that the spectrum of sodium polyphosphate glass dissolved in water is similar to that of the amorphous glass.

The polymer is stable in water. Degradation of a dissolved glass at room temperature in an alkaline medium, up to a pH of 13, could not be observed after one week.

Polyphosphate, however, is not stable in acidic medium. Sodium polyphosphate dissolved in water with a concentration of $\sim 350\text{ g}$ polyphosphate units per liter has a pH of ~ 4 . If the pH in the solution is lowered to 0, protons should exchange most of the sodium ions. Hydrolysis of a polymer to orthophosphoric acid in an acidified solution is illustrated in figure 6.4. Sodium polyphosphate is dissolved in water and hydrolysed at pH=0.

Both the PO_2 (A_1) band at 1151 cm^{-1} and the -P-O-P-O- band at 687 cm^{-1} of the polyphosphate are decreasing in intensity with time while the phosphate band at 891 cm^{-1} increases.

During hydrolysis the A_1 , P=O band at 1170 cm^{-1} and the E, $\text{P}(\text{OH})_3$ band at 1075 cm^{-1} from phosphoric acid start to overlap the PO_2 (A_1) band. At high concentrations of polyphosphate this overlap can be neglected, but at lower concentrations overlap is severe and the band can not be used directly for monitoring hydrolysis. The polyphosphate E, PO_2 band at 1247 cm^{-1} also overlaps, complicating the matter. Filtering the PO_2 (A_1) band is possible by deconvoluting the spectrum in the region of this band. The best curve fit is obtained by using a PO_2 (A_1) band, which is decomposed in a 70% Lorentzian band and a 30% Gaussian band. All remaining bands are taken as Gaussian. The result is the deconvoluted spectrum in figure 6.5.

Chapter 6 Hydrolysis of Sodium Polyphosphate

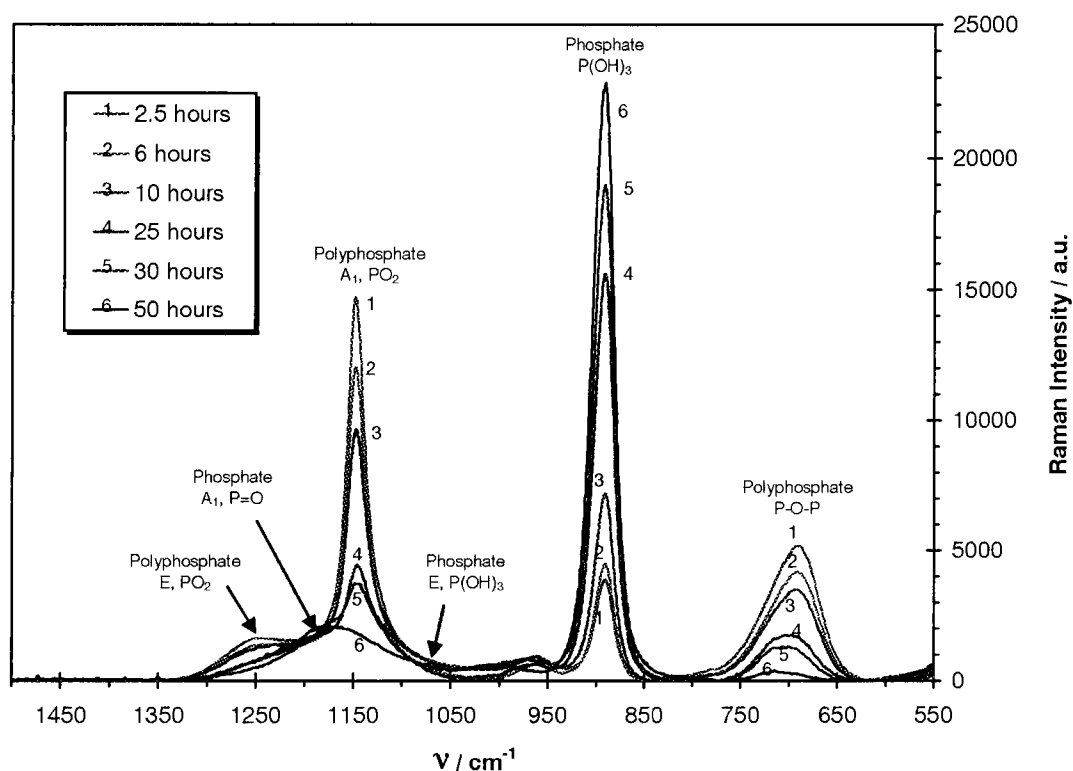


Figure 6.4 Raman spectra of sodium polyphosphate dissolved in water ($365 \text{ g}\cdot\text{l}^{-1}$) at 22°C and $\text{pH}=0$ recorded at different times. Laser power 75mW , integration time 100s .

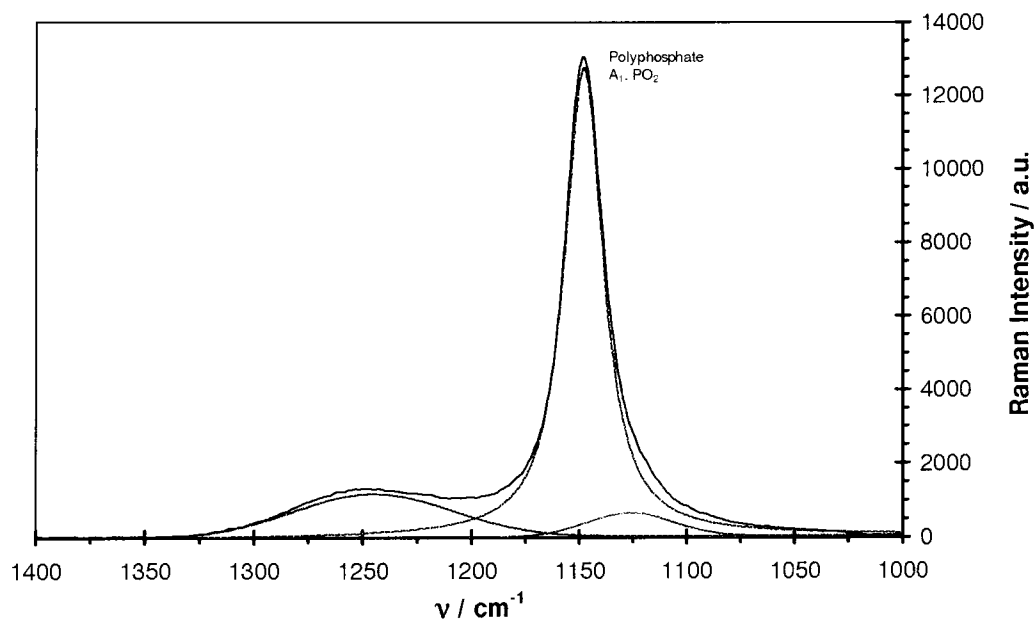


Figure 6.5 A deconvoluted spectrum of sodium polyphosphate in water.

However, during hydrolysis the concentration of orthophosphoric acid increases and this species also has a broad band at 1075 cm^{-1} (P(OH)_3 , E) and 1170 cm^{-1} (P=O , A_1). These bands grow in intensity, overlap with the PO_2 (A_1) band and deconvoluting the spectrum becomes too complex. Therefore the PO_2 (A_1) vibration is in practice not suitable for monitoring hydrolysis.

Another band inherent to polyphosphates is the -P-O-P-O- band at 687 cm^{-1} , which is the symmetric skeleton vibration. It can be used to follow degradation of the polyphosphate because orthophosphoric acid does not show bands in this region.

6.3.3 Calibration

Calibration curves of phosphate and polyphosphate need to be recorded prior to monitoring the hydrolysis of polyphosphate. Figures 6.6 and 6.7 show calibration curves of polyphosphate and phosphate respectively at pH=0. pH measurements in the vicinity of 0 are not very accurate since such a pH value lies outside the calibrated range of the pH meter. Although the pH measurement is less accurate, it is still accepted due to the absence of better alternatives. It is assumed that the error is consistent with the phosphate concentration, and therefore consistent in the analysis.

The Raman intensity is expressed in a normalised unit (n.u.), which is the area of the specific phosphate or polyphosphate band divided by an external standard. Heights instead of areas could also be used, but they are less accurate. Using an external standard excludes variations in experimental parameters like laser output, instrumental calibration, interference from scattered light, position of the focus of the laser beam in the sample and reflection at the sample tube. Carbon tetrachloride (CCl_4) is used as an external standard because it has a strong total symmetric vibration band at 459 cm^{-1} , which could be used for normalization [15,16]. Normalised areas of polyphosphate and phosphate bands depend linearly on the concentration.

Experimentally, it seems that polyphosphate calibration curves are independent of the pH between pH=-0.5 and 0.5, but phosphate calibration curves depend on the pH. This is also expected when figure 6.7 is compared with figure 6.1. An increasing in the pH will lower the concentration of H_3PO_4 species ($\text{pK}_1=2.1$), reducing the sensitivity of the Raman signal to concentration.

The polyphosphate calibration curve does not pass through the origin of the graph due to background interference. This is a systematic error, which will cancel out if all the polyphosphate bands in the spectra are similarly integrated.

The ordinate of the polyphosphate has the unit mole per litre, but this is not the concentration of the polymer strings. A polyphosphate solution consists of a distribution of strings with different lengths. Therefore monomers are chosen to quantify polyphosphate in solution. The

polymers consist of PO_3^- units with a proton or a metal cation as counter ion. NaPO_3 is a polymer unit with a mass of 102 a.u. Conversion to moles phosphate units per litre has the advantage to compare hydrolysis of polyphosphate and production of phosphate directly.

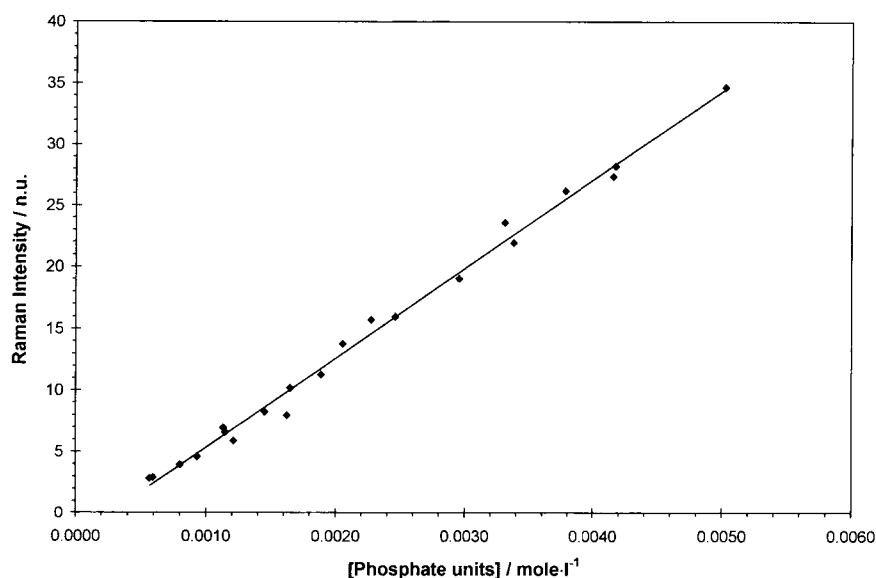


Figure 6.6 Calibration curve of polyphosphate with CCl_4 as an external standard at 22°C and $\text{pH}=-0.5$ to 0.5 . Correlation coefficient: 0.9934.

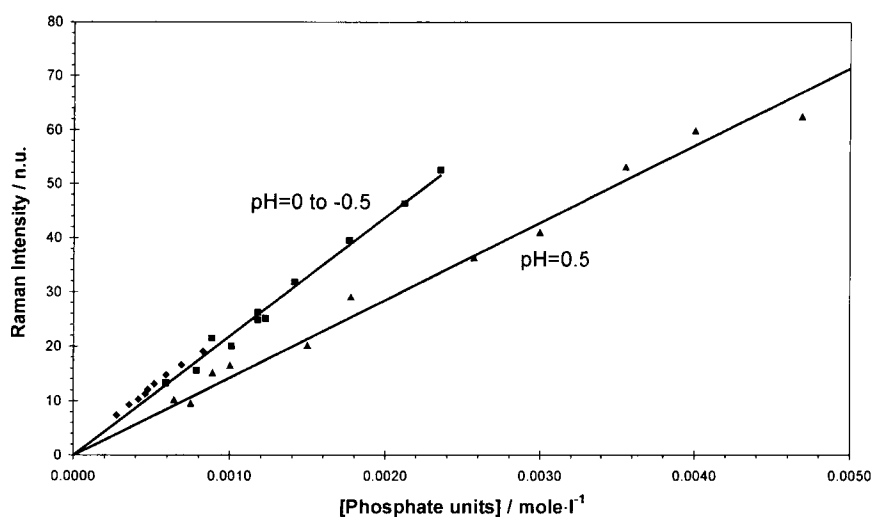


Figure 6.7 Calibration curve of phosphate with CCl_4 as an external standard at different pH and a temperature of 22°C . Correlation coefficient $\text{pH}=0$ to -0.5 : 0.9891 and $\text{pH}=0.5$: 0.9855.

6.3.4 Hydrolysis

Figure 6.8 shows the hydrolysis of a polyphosphate in solution at pH=0 and pH=0.25. A linear increase of the phosphate curve can be observed initially while the polyphosphate curve decreases correspondingly. The rates of hydrolysis and production of phosphate, defined as the initial rates, are similar but with opposite sign.

The curve of pH=0 levels off, reaching a plateau with the concentration of phosphate at the end of the hydrolysis being equal to the initial concentration of polyphosphate units.

Table I contains initial rates of different polyphosphate solutions at pH=0 and pH=0.25. Both initial rates of polyphosphate consumption and phosphoric acid production are linear.

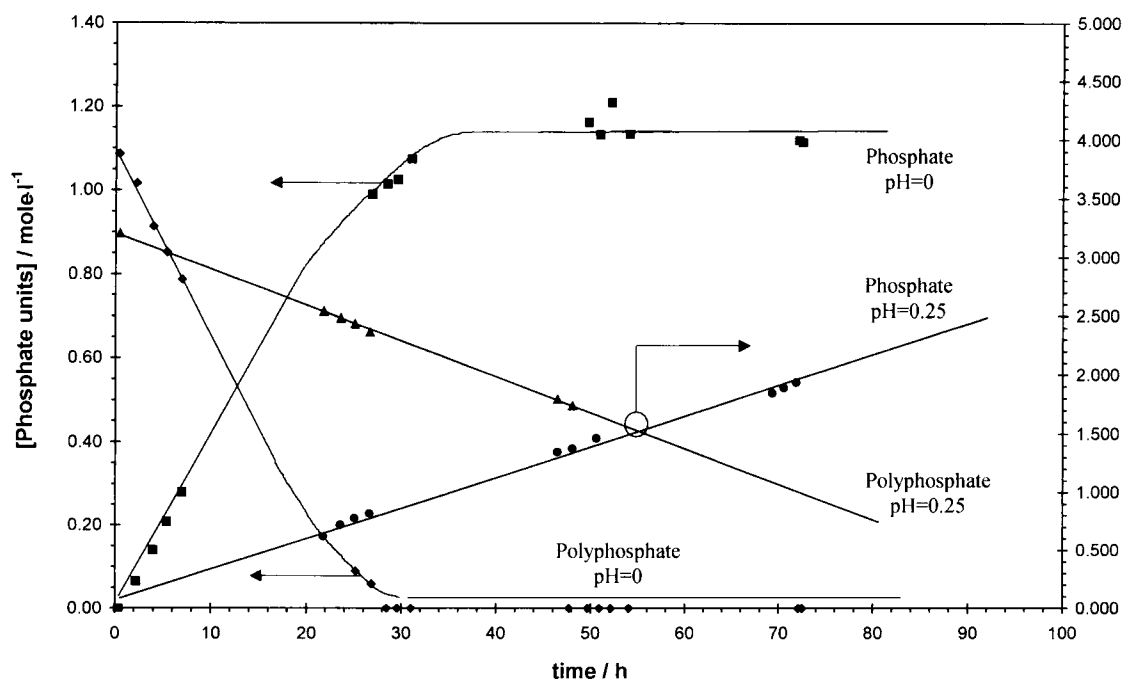


Figure 6.8 Hydrolysis of polyphosphate (pH=0: $\blacksquare$, pH=0.25: $\blacktriangle$) and the production of orthophosphoric acid (pH=0: $\blacksquare$, pH=0.25: $\bullet$) in aqueous medium at 22°C.

For solutions with pH=0, the rates of hydrolysis are similar within a concentration range of phosphate units from 3.6 mole·l⁻¹ to 0.8 mole·l⁻¹. Hydrolysis is very sensitive to variations in the pH and controlling the pH is very difficult because the reaction takes place over a long period of time. Figure 6.8 also shows the dependence of the hydrolysis on the pH. A higher pH decreases the rate of hydrolysis and phosphate production.

TABLE I Rates of hydrolysis of polyphosphates and production of phosphate monomers measured at a temperature of 22°C.

pH	initial phosphate unit concentration (mole·l ⁻¹)	V _{polyphosphate} (mole·l ⁻¹ ·h ⁻¹)	V _{phosphate} (mole·l ⁻¹ ·h ⁻¹)
0.0	3.3	0.052	0.041
0.0	1.7	0.048	0.044
0.0	1.1	0.047	0.043
0.0	0.7	0.038	0.035
0.25	3.2	0.030	0.029

Although the shape of the curve suggests a first-order reaction at first, initial rate values in Table I show an almost zeroth-order reaction. Rates, at the beginning of the hydrolysis, must be measured in order to classify the reaction by its order. Therefore, the initial concentrations of the reactants must be known. One of the reactants is water and fortunately, it is also the medium in which the reaction takes place. This means that the concentration of water can be considered as a constant during the hydrolysis. Its concentration is much larger (56 mole·l⁻¹, pure water) compared to the concentration of the total phosphate units (max. 3.5 mole·l⁻¹) present in solution. This simplifies the rate equation to:

$$V_{(\text{HPO}_3)_n} = k \cdot [(\text{NaPO}_3)_n]^a \quad [6.3]$$

in which $V_{(\text{HPO}_3)_n}$ is the rate of the hydrolysis, k the reaction constant and a the order of the reaction.

Both k and a can be determined experimentally by plotting $\ln V_{(\text{HPO}_3)_n}$ versus $\ln[(\text{NaPO}_3)_n]$. For the hydrolysis of a sodium polyphosphate solution in a concentration range of 1-3.3 mole·l⁻¹ at 22°C and pH=0, the reaction constant k is 0.046 (mole·l⁻¹·h⁻¹) with an order a of 0.09. The linearity of the plot is 0.96, which is relatively low if a linear relationship exists. Since both the hydrolysis and phosphate production curves initially show an approximate zeroth-order behaviour and a linear relation between concentration and time, the reaction advancement (ξ) must be the same to the absolute rate of change in the concentrations of polyphosphate and phosphoric acid.

$$\frac{\delta \xi}{\delta t} = -\frac{\delta [\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}]}{\delta t} = \frac{\delta [\text{H}_3\text{PO}_4]}{\delta t} \quad [6.4]$$

According to Table I the rates of hydrolysis are larger compared to the phosphate productions. Samples were measured over a period of 100 hours and the pH had to be kept constant. In order to achieve this, hydrochloric acid was added during the experiment, reducing the concentrations of polyphosphate and phosphate. This results in a higher rate of hydrolysis and a lower rate of phosphate formation.

Other phenomena must also play a role because dilution could not completely account for the differences in rates. The calibration curves of phosphate and polyphosphate are recorded separately, while both species were recorded simultaneously during hydrolysis. An interaction between phosphate and polyphosphate might affect their Raman signals. At high concentrations of polyphosphates (3 mole phosphate units per liter) the solution is viscous and its influence on the phosphoric acid band is not known.

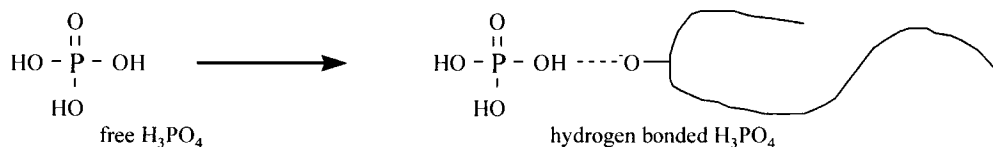
Hydroxyl groups of phosphoric acid might form hydrogen bonds with the terminal oxygen of the polymer. Such a bonding does not only affect the mobility of phosphoric acid, it also lowers the symmetry of this species. Consequently the A₁ breathing vibration is not totally symmetric anymore. The vibration could still occur, only with a lower intensity.

The calibration curves of phosphate are recorded in the absence of polyphosphate in which such an interaction could not occur. Hydrogen bonding between H₃PO₄ species could occur, but the calibration curve should automatically compensate for such an effect.

In practice, the phosphate curve in figure 6.7 is very close to linearity suggesting that Raman spectroscopy could not detect a hydrogen bonding effect or that hydrogen bonding between phosphate species is very weak or non existent. This does not mean that hydrogen bonding between phosphate and water does not exist. It is probably the dominant interaction explaining why hydrogen bonding between phosphate species could not be detected.

During hydrolysis both species are present in solution. In the beginning of the experiment the polyphosphate concentration is at its maximum, hence the effect of hydrogen bonding between phosphate and polyphosphate is most pronounced. If the area of bands were larger at this stage of the reaction, the initial rate of phosphate production should increase towards the absolute value of polyphosphate consumption.

Hydrogen bonding also tends to broaden bands in general. This is not visible in the spectra since the bands are already very large and broad due to high concentrations. On diluting the sample the discrepancies between the initial rates of phosphate production and polyphosphate consumption should be reduced since the hydrogen bonding between phosphate and polyphosphate is less in diluted samples.



Another reason for the discrepancies between the rates of hydrolysis and the phosphate productions is the accuracy of their calibration curves. The correlation coefficients of the phosphate calibration curves between a pH of -0.5 and 0.5 are lower compared to the corresponding polyphosphate curves. Therefore, rates of hydrolysis determined by monitoring the -P-O-P-O- band in the Raman spectra are more accurate.

6.3.5 Modelling of Random Hydrolysis

Random hydrolysis could not entirely be excluded. Its contribution however is expected to be very low, compared to the hydrolysis at the terminal phosphate units of the polymer. Random hydrolysis can be simulated by fitting the calculated rate of hydrolysis to the measured rate. The chance of a polymer being cut depends on the length of the polymer. Differences in stability of polymers with different lengths are not taken into account. Weighed chances for the selection of a polymer are expressed as follows:

$$P(l_i) = \frac{n(l_i) \cdot l_i}{\sum_i n(l_i) \cdot l_i} \quad [6.5]$$

in which $P(l_i)$ is the chance of a polymer with length l_i being selected. $n(l_i)$ is the concentration of polymers with length l_i .

A polymer solution can be monodisperse or polydisperse. Monodispersity is very unlikely, certainly on quenching a melt. The average polymer length of a sodium polyphosphate is 85, determined by titration of a known aliquot of polyphosphate dissolved in water with a sodium hydroxide solution. This value does not give information about the dispersity. To overcome this problem a normal distribution [17] is assumed. An expression for each polymer concentration $n(l_i)$ can now be found.

$$n(l_i) = \frac{N_0}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{1}{2} \cdot \left(\frac{l_i - \bar{l}}{\sigma}\right)^2} \quad [6.6]$$

$\bar{l}$ is the average length of the polymers. N_0 is the initial total polymer concentration, which is the concentration of phosphate units divided by the average polymer length. σ is the standard deviation, which is estimated. A normal distribution has the advantage that the initial polymer concentration is the same as the measured value if the expression of a normal distribution is multiplied by the initial total polymer concentration and summed over all the

polymer concentrations $n(l_i)$ present in solution. Phosphate curves were calculated on this basis combined with an adjustment to the experimental rate of hydrolysis (Appendix D). Only minor differences in phosphate curves were observed in the standard deviation range from $\sigma=0$ to $\sigma=20$ with $\sigma=0$ representing a monodisperse solution and $\sigma=20$ a polydisperse solution. In all cases induction times were clearly present according to figure 6.9. This process is purely statistical. If hydrolysis were at random, polymers should be cut forming smaller polymers. In the beginning of the hydrolysis, the change of a terminal polyphosphate unit being cut off is negligibly low. As the reaction proceeds, polymers are shorter thereby increasing the chance of a terminal phosphate unit being sliced off.

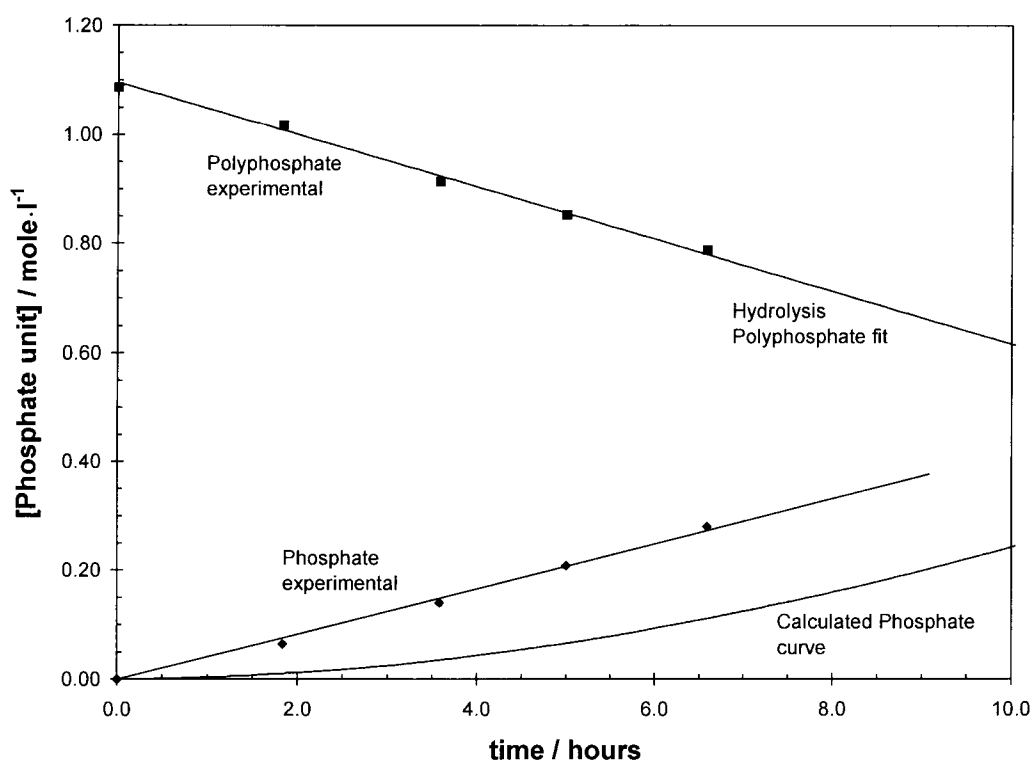


Figure 6.9 Hydrolysis and Phosphate production, experimental and calculated.

It is impossible to distinguish between longer and shorter polymer chains using Raman spectroscopy. In case of random hydrolysis an induction time, followed by a sharp increase in the phosphate concentration, would be expected with the decrease in the polyphosphate concentration.

Instead of an induction time, a linear increase in the phosphate concentration and a linear decrease in the polyphosphate concentration are measured. The rates of both processes are similar, indicating that hydrolysis mainly occurs at the terminal phosphate unit of the polymer.

6.3.6 Hydrolysis at Elevated Temperatures

Raman spectra of the hydrolysis of polyphosphate at elevated temperatures were also recorded. Since it is even more difficult to control the pH at higher temperatures, k values obtained at those temperatures are less accurate. Signal intensities of phosphoric acid are very sensitive to variations in the pH. Fortunately the -P-O-P-O- band is not, giving this band a preference for monitoring hydrolysis at elevated temperatures.

Table II shows the k values for the hydrolysis at temperatures between 22°C and 60°C assuming zeroth-order behaviour. A constant initial rate just as in the hydrolysis at room temperature is observed. Changing the initial concentration of polyphosphate does not significantly alter the rate of hydrolysis.

TABLE II *Rates of hydrolysis of polyphosphates and production of phosphate monomers at different temperatures, pH=0; initial phosphate unit concentration 1.9-2.3 mole·l⁻¹.*

Temperature (°C)	$k_{\text{polyphosphate}}$ (mole·l ⁻¹ ·h ⁻¹)	$k_{\text{phosphate}}$ (mole·l ⁻¹ ·h ⁻¹)
22	0.048	0.045
40	0.20	0.13
45	0.25	0.19
50	0.38	0.32
55	0.48	0.38
60	0.70	0.57

An example of two different initial concentrations of polyphosphate in solution with pH=0 at 50°C is shown in figure 6.10. The table shows an increase in k with the increase in temperature. k is often written in the Arrhenius equation:

$$k = A \cdot e^{-E_a/RT} \quad [6.7]$$

A is called the pre-exponential factor and involves collisions between the particles participating in the reaction, E_a is the energy of activation. The Arrhenius equation can be rewritten in the form:

$$\ln k = \ln A - E_a/RT \quad [6.8]$$

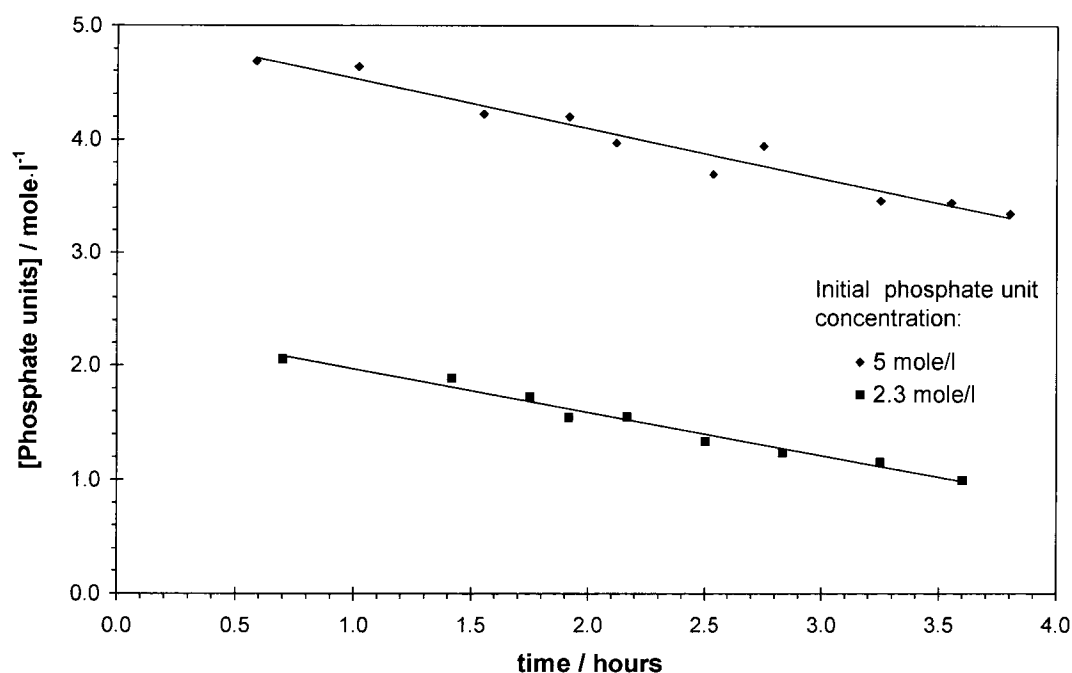


Figure 6.10 Hydrolysis of polyphosphate in aqueous medium at 50 °C, pH=0. Laser power 75mW, integration time 100s.

Figure 6.11 is a plot of $\ln k$ versus $1/T$ for two different phosphate unit concentrations. The activation energy could be determined from the slope and the pre-exponential factor can be read from the intercept of the curve with the ordinate. Their values are shown in Table III. The curve in the figure follows the Arrhenius equation suggesting that the activation energy is not a function of temperature. The reader must bear in mind that the error in the determination of E_a and A is large since the k values are measured over a small temperature range. A variation in the slope not only affects the activation energy, but also the

extrapolation of the curve to the intercept with the ordinate. Nevertheless, the correlation coefficient is 0.9988 underlining the high linearity of the curve, reducing the error in the determination.

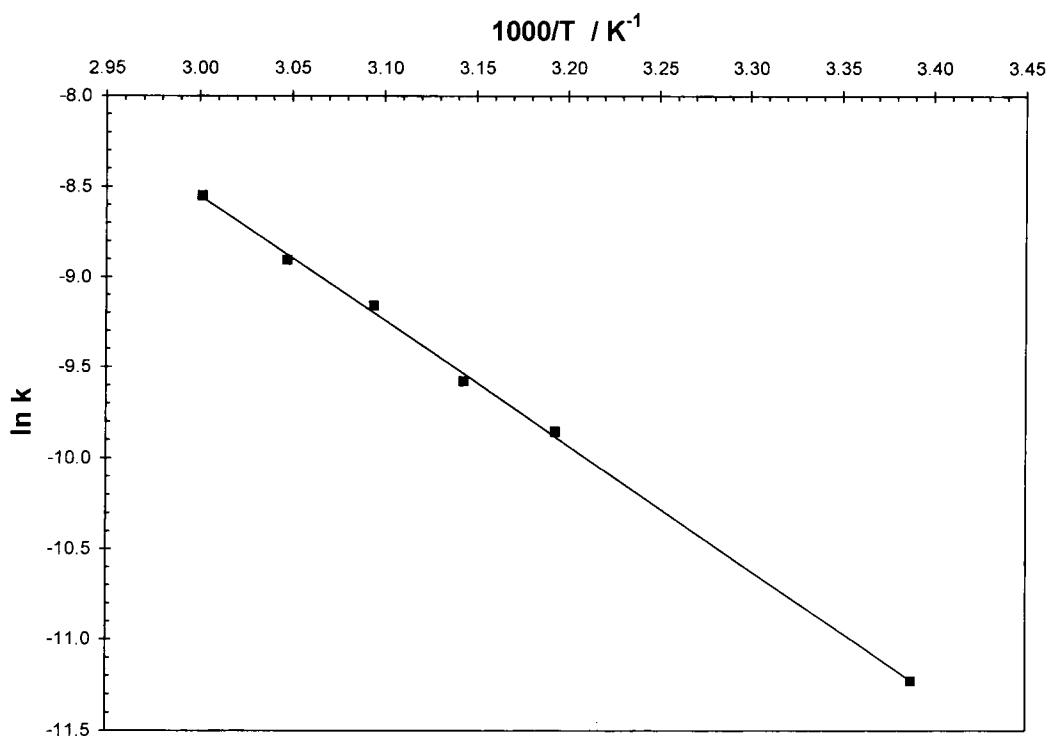


Figure 6.11 Arrhenius plot of the hydrolysis of polyphosphate in aqueous medium at pH=0.

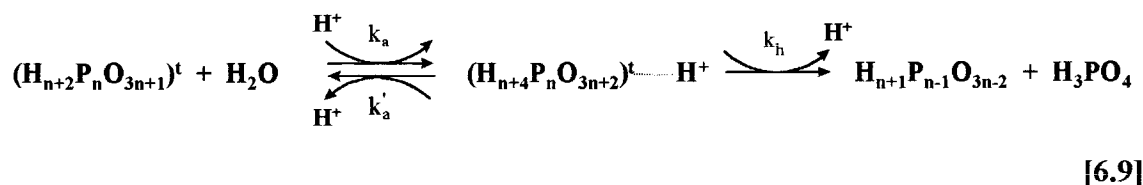
TABLE III The activation energy and pre-exponential factor of the hydrolysis of polyphosphate in acidic solution.

E_a	$57 \text{ kJ}\cdot\text{mole}^{-1}$
A	$1.89\cdot 10^5 \text{ mol}\cdot\text{l}^{-1}\cdot\text{s}^{-1}$

6.3.7 Kinetics

Combining zeroth-order behaviour of both the hydrolysis as the phosphate production plus their linear relation of concentration with time, it can be concluded that hydrolysis predominantly takes place at terminal phosphate units. Therefore terminal and non-terminal phosphate units in a polymer will be considered separately in the following discussion. Instead of using a polymer concentration, concentration of phosphate units will be used and it can be assumed that a direct relation exists between the polymer concentration and the terminal unit concentration.

Hydrolysis of a polyphosphate solution is acid catalysed. Decreasing the pH causes an increase in the rate of hydrolysis. Apparently, protonation of a polyphosphate is involved. A protonated polyphosphate is a kind of activated intermediate and/or leads to an intermediate, which makes hydrolysis possible.



n is the number of phosphate units in a chain and has a theoretical minimum of two. $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$ is the general formula of the polymers and $[\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}]$ the concentration. The relation between the two general formulae of the polyphosphate is the removal of one HPO_3 unit. Subtracting a HPO_3 unit from $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$ results in the new general formula of the polymer. It is important to note that the extra superscript t in the formula or concentration represents the terminal phosphate units in the following discussion. Also note that the polymer is activated only when terminal phosphate units are protonated and that $(\text{H}_{n+4}\text{P}_n\text{O}_{3n+2})^t$ is the intermediate. The intermediate could react back to the reactants or be hydrolysed to form the products.

k_a is the reaction constant for the formation of the intermediate, while k'_a refers to the backward reaction. k_h corresponds to the actual hydrolysis.

At this stage nothing can be said about the structure of the intermediate. The above consecutive reaction suggests a pre-equilibrium between the reactants and the intermediate if the concentrations of the intermediate and the terminal phosphate units remain constant. Under steady state conditions the intermediate concentration is constant and if a terminal phosphate unit is being hydrolysed, a new terminal unit is formed keeping the concentration of these units constant as well. The rate of hydrolysis could be written as:

$$\frac{\delta [H_{n+2}P_nO_{3n+1}]}{\delta t} = k_h \cdot [(H_{n+4}P_nO_{3n+2})^t] \quad [6.10]$$

Applying steady state conditions to the intermediate, it is possible to relate the concentration of the intermediate to the k values in eq.6.9. Water in the reaction can be considered as a constant because it is the medium of the hydrolysis.

$$\frac{\delta [(H_{n+4}P_nO_{3n+2})^t]}{\delta t} = k_a \cdot [H^+] [(H_{n+2}P_nO_{3n+1})^t] - k'_a \cdot [(H_{n+4}P_nO_{3n+2})^t] - k_h \cdot [(H_{n+4}P_nO_{3n+2})^t] = 0 \quad [6.11]$$

Solving the equation gives:

$$[(H_{n+4}P_nO_{3n+2})^t] = \frac{k_a}{(k_h + k'_a)} \cdot [H^+] [(H_{n+2}P_nO_{3n+1})^t] \quad [6.12]$$

A polymer is activated for hydrolysis after protonation. Besides terminal phosphate units, non-terminal phosphate units could also be protonated. The total concentration of protons used, defined as H_0^+ , is the concentration of H^+ (actually H_3O^+) and the concentration of protonated phosphate units, distinguishing between terminal (t) and non-terminal (nt) units:

$$[H_0^+] = [H^+] + [(H_{n+4}P_nO_{3n+2})^t] + [(H_{n+4}P_nO_{3n+2})^{nt}] \quad [6.13]$$

Now eq.6.12 can be rewritten to:

$$[(H_{n+4}P_nO_{3n+2})^t] = \frac{k_a}{(k_h + k_a')} \cdot ([H_0^+] - [(H_{n+4}P_nO_{3n+2})^t] - [(H_{n+4}P_nO_{3n+2})^{nt}]) \cdot [(H_{n+2}P_nO_{3n+1})^t] \quad [6.14]$$

which rearranges to:

$$[(H_{n+4}P_nO_{3n+2})^t] = \frac{k_a ([H_0^+] - [(H_{n+4}P_nO_{3n+2})^{nt}]) \cdot [(H_{n+2}P_nO_{3n+1})^t]}{k_h + k_a' + k_a [(H_{n+2}P_nO_{3n+1})^t]} \quad [6.15]$$

Combining eq.6.10 and eq.6.15 results in a new formulation of the hydrolysis of a polyphosphate:

$$\frac{\delta [H_{n+2}P_nO_{3n+1}]}{\delta t} = k_h \cdot [(H_{n+4}P_nO_{3n+2})^t] = \frac{k_h \cdot ([H_0^+] - [(H_{n+4}P_nO_{3n+2})^{nt}]) \cdot [(H_{n+2}P_nO_{3n+1})^t]}{K_m + [(H_{n+2}P_nO_{3n+1})^t]} \quad [6.16]$$

where $K_m = \frac{k_h + k_a'}{k_a}$

Eq.6.13 can be written in the following form:

$$[H_0^+] - [(H_{n+4}P_nO_{3n+2})^{nt}] = [H^+] + [(H_{n+4}P_nO_{3n+2})^t].$$

The left-hand side is present in eq.6.16. On the right hand side, H^+ is constant at a constant pH. Under steady state conditions the concentration of the intermediate remains constant. Since the concentration of the terminal phosphate units is also constant, the whole left-hand side must be constant. Substituting this side in eq.6.16 results in an extra constant, which will be defined as k_p :

$$\frac{\delta [H_{n+2}P_nO_{3n+1}]}{\delta t} = k_h \cdot k_p \cdot \frac{[(H_{n+2}P_nO_{3n+1})^t]}{K_m + [(H_{n+2}P_nO_{3n+1})^t]} \quad [6.17]$$

When $[(H_{n+2}P_nO_{3n+1})^4] \gg K_m$ eq.6.17 reduces to $\frac{\delta[H_{n+2}P_nO_{3n+1}]}{\delta t} = k_h \cdot k_p$, which is initially zeroth-order.

The concentration range of the polyphosphate samples in which zeroth-order is observed ranges from 0.8 to 3.6 mole phosphate units per liter. If the average chain length of a polymer is 85, the concentration of terminal phosphate units ranges from 0.019 to 0.085 mole·l⁻¹. K_p depends on the concentration of the intermediate and therefore slightly depends on the polyphosphate concentration accounting for the small increase in the rate of hydrolysis with concentration. This dependency however is negligibly low.

Eq.6.17 explains the approximate zeroth-order behaviour at high polymer concentrations (1-3.3 mole·l⁻¹·h⁻¹). It also explains the behaviour at lower concentrations. As the polyphosphate concentration is low, the number of terminal phosphate units is also low. K_m can not be neglected anymore and the rate of hydrolysis depends on both the pH and the polymer concentration. This results in a lower rate of hydrolysis.

The equation also explains the shape of the hydrolysis curve in figure 6.8. A polyphosphate solution has a distribution of chain lengths. During hydrolysis polymers are shortened, but the rate is constant as long as the number of terminal phosphate units remains constant. Once a chain is completely hydrolysed, the terminal units of the chain are destroyed. Short units are completely hydrolysed in a shorter time and the concentration of terminal units decreases, affecting the rate of hydrolysis. As a consequence, the polyphosphate curve levels off, and a plateau is reached when all polymers are completely hydrolysed.

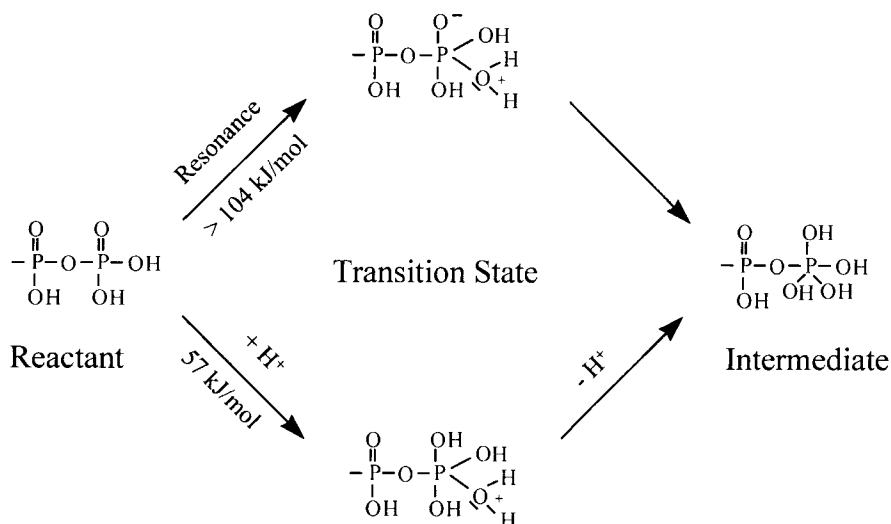
6.3.8 Mechanism

Strauss et. al. studied hydrolysis of branched sodium polyphosphate solutions [3]. They found first-order dependence on concentration based on viscosity measurements. Ray [18] also mentioned first-order hydrolytic degradation with an activation energy of 104 ± 8 kJ/mole determined by viscosity measurements in a temperature range of 25-90°C.

The order seems to contrast the results obtained by Raman spectroscopy, but the two processes are of a different nature. Strauss et. al. and Ray studied the hydrolysis of branched polymer solutions. The -P-O-P-O- bonds at branch points are much weaker compared to nonbranched bonds, meaning that the former bond type hydrolyses first, decreasing the viscosity accordingly. When this type of hydrolysis is completed, linear chains are present in solution [19], and this is the starting solution of the acid-catalysed hydrolysis in this study. Before the pH was lowered, the neutral polyphosphate solution had been standing for 24 hours to ensure that all branched points were hydrolysed. In this way hydrolysis of these points does not interfere with the hydrolysis process in acidic medium.

Ray presented an enthalpy expressed in kilojoules per mole P-O-P bonds severed (eq.6.2), implying that all these bonds are identical, which is in practice not the case. P-O-P bonds at branches hydrolyse in neutral solutions, but the remaining bonds stay intact indicating that the latter are more stable. Therefore, the energy of activation for the hydrolysis of nonbranched P-O-P bonds in neutral solutions should be higher than 104 kJ/mole. The activation energy of acid catalysed hydrolysis is 57 kJ/mole.

Before a polyphosphate is to be hydrolysed, it must first be made susceptible to nucleophilic attack of water. In neutral solutions this can be accomplished by the resonance structure of a phosphate unit, which could be interpreted as the Transition State. In an acidic solution, protonation of the double-bond oxygen on the terminal phosphate unit in a polymer also activates the polymer for nucleophilic attack of water. In this case a hydrated species represents the Transition State. Protonation/deprotonation is instantaneous, but the nucleophilic attack of water to form the intermediate is a kinetic step in the process.



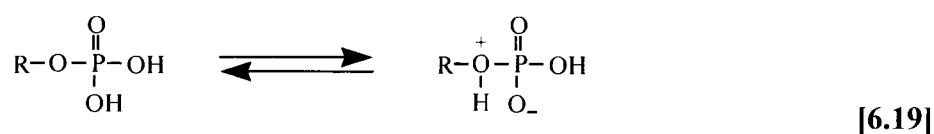
[6.18]

The pathway in which terminal phosphate units are activated by protonation has a lower activation energy compared to the non-catalysed pathway. This is exactly the function of a catalyst. It does not change the thermodynamic states of the reactants and intermediate, but it lowers the activation energy. It must be noted that the hydrolysis of branched points in a polymer does not necessarily follow the mechanism in eq.6.18. The value of its activation energy is used and extrapolated to the reaction profile in the case of the hydrolysis of terminal phosphate units in neutral solutions.

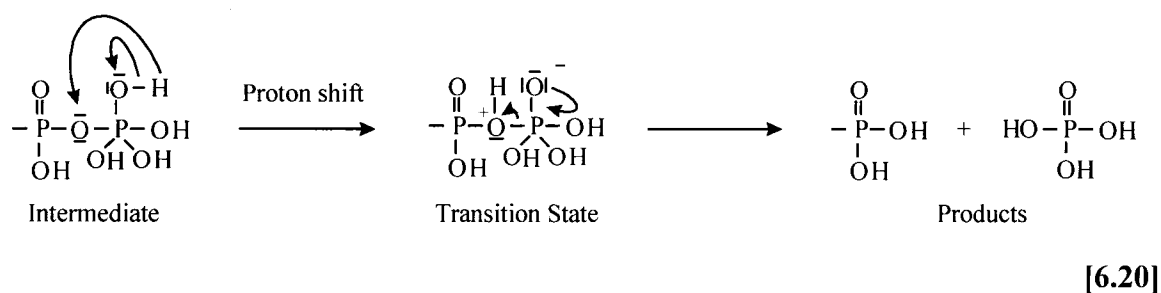
After nucleophilic attack, constitutional water is added to the terminal phosphate unit in both processes resulting in a five-coordinated terminal phosphorous atom. According to the literature, the mechanism of the hydrolysis of di-esters also involves a five coordination of phosphorous by oxygen atoms [20,21,22]. Lowering the activation energy results in a higher concentration of intermediate and by recalling eq.6.10 it can be seen that this leads to an increase in the rate of hydrolysis.

From the intermediate onwards, the reaction profiles of acid-catalysed and non-catalysed hydrolysis are the same. The polyphosphate structure in the second Transition State in the reaction energy diagram is not well known. If the hydrolysis is analogous to acid-catalysed hydrolysis of esters, a transfer of a proton from one oxygen atom to another is involved to break a P-O-P bond [23]. Proton transfer is not uncommon in phosphates. It occurs in

sodium phosphor amidate ($\text{NaHPO}_3\text{NH}_2$) and acid mono-esters of phosphates [24]. The formula of the former compound differs slightly from sodium dihydrogen phosphate. An amino group replaces an oxygen atom and a proton is removed to balance the charge. More important are proton shifts in acid mono-esters. These types of phosphates have a very close resemblance to phosphate polymers. The oxygen in the P-O-R bond is protonated by an OH group of an adjacent terminal phosphate group resulting in a sort of zwitterion (eq.6.19).



If R represents the rest of a polyphosphate polymer, the bond-breaking process can be explained in terms of a proton transfer. On this basis the second part of the hydrolysis could be explained as follows:



A non-terminal phosphate could also be protonated just like a terminal phosphate, but hydrolysis takes place at a terminal phosphate after protonation of its double-bond oxygen. Proton transfer from a terminal phosphate unit might be easier because of the presence of four OH groups instead of two in a non-terminal unit. Compare the difference in acidity between orthophosphoric acid, monobasic phosphate and dibasic phosphate. The acid form with three OH groups is a better proton donor ($\text{pK}_a=2.1$) than monobasic ($\text{pK}_a=7.2$) with two groups or dibasic phosphate ($\text{pK}_a=12.3$) with one OH group.

Inductive stabilization of a negative charged oxygen in a terminal phosphate unit is expected to be higher than in a non-terminal unit. Chandler and Kirby [20] accepted the idea that the hydrolysis proceeds by way of a penta covalent intermediate in which a neighbouring nucleophilic OH group could act as a general acid and/or base depending on its pK_a . They also reported that the breakdown of a penta covalent intermediate should be rapid and its formation rate determining. This is in line with the mechanism presented here. Formation of an intermediate in the hydrolysis of a polyphosphate is an assumption made to explain the order of the reaction. Furthermore, if the rate of formation is rate determining and the actual breakdown is rapid, the measured activation energy determined in this paper is confined to the first step of the hydrolysis, and the activation energy for the second step must be much lower. The height of the second Transition State is not important because it remains the same in both processes. Once the intermediate is formed, the reaction does not depend on the acidity of the medium anymore, only on the acidity of the terminal phosphate group.

In the intermediate the relevant phosphorous atom is fivefold coordinated and steric hindrance could also play a role. If a non-terminal phosphate is protonated, two groups form the rest of the polymer and can be regarded as bulky ligands inhibiting a large coordination number of the intermediate. Steric hindrance increases the barrier of the Transition State reducing the rate constant of the hydrolysis.

Finally, a reaction energy diagram could be constructed and is shown in figure 6.12. The rate of hydrolysis does not depend on the activation energy only. According to the Arrhenius equation (eq.6.7) a pre-exponential factor is also involved. Hydrolysis at a higher pH is slower. In a polyphosphate solution with a pH of 0.25, the reaction constant of the hydrolysis is $0.029 \text{ mole} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$. Since the reaction energy diagram remains the same because it is based on thermodynamic properties, the pre-exponential factor must be lower. Using a single-point determination, the pre-exponential factor is $9.9 \cdot 10^4 \text{ mole} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$ at a temperature of 22°C . Strauss et. al. found a reaction coefficient of $0.48 (\pm 0.24) \text{ h}^{-1}$ for the hydrolysis of branched P-O-P bonds at 25°C [3].

Combining this with the activation energy given by Ray results in a pre-exponential factor of $2.2 \cdot 10^{14} \text{ s}^{-1}$, which is appreciably higher compared to the factor in acid-catalysed hydrolysis ($1.89 \cdot 10^5 \text{ mole} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$). The pre-exponential factor of acid-catalysed hydrolysis decreases with an increasing pH, but in the non-catalysed process, which is in neutral solutions, it is much higher. This can be explained as follows. A pre-exponential factor in acid-catalysed hydrolysis involves collisions between three types of particles i.e. a polyphosphate, H^+ , and H_2O . As the pH increases, the concentration of H^+ decreases, lowering the chance of a collision between the three participating particles simultaneously. The pH dependence could be seen in eq.6.16 since k_p is related to the concentration of H^+ . In non-catalysed hydrolysis, only two reactants are involved and the chance of a collision between two particles is much higher, reflected in the corresponding pre-exponential factor.

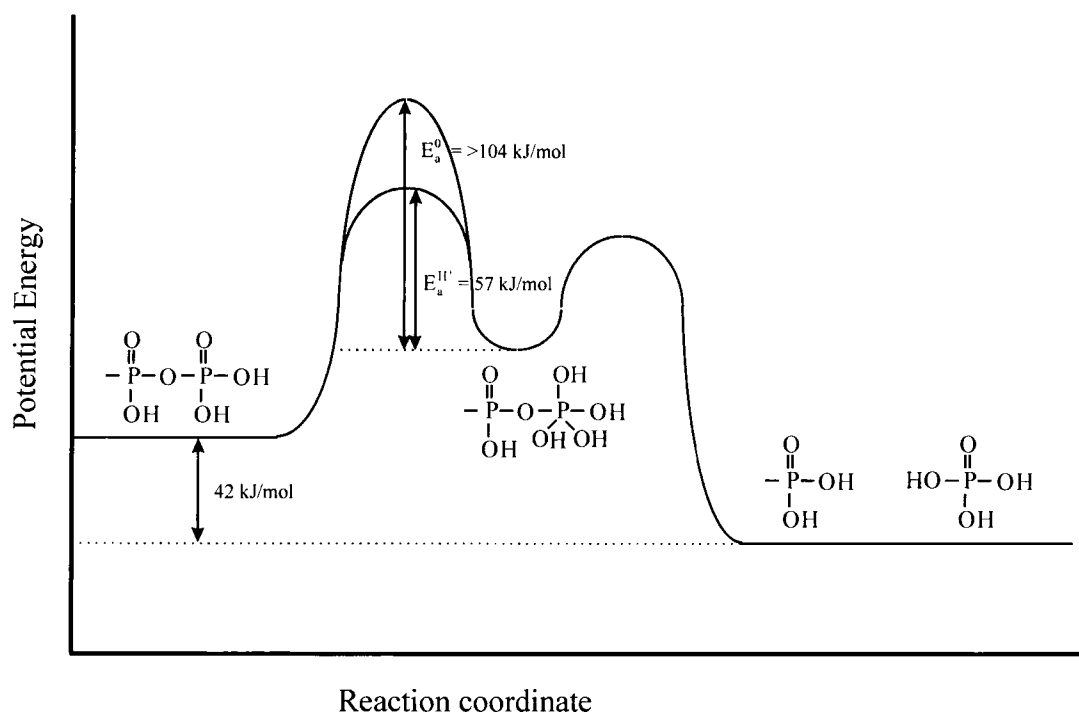


Figure 6.12 Reaction energy diagram of the hydrolysis of a sodium polyphosphate solution with and without an acid catalyst.

6.3.9 Concluding Remarks

Polyphosphates are stable in neutral aqueous solutions but hydrolyses in acidic medium which is catalysed by H^+ . The reaction can be followed with Raman spectroscopy by monitoring the -P-O-P-O- band of the polyphosphate and the $P(OH)_3$ band of orthophosphoric acid. Intensities of the bands must be normalised by an external standard to exclude variations in experimental conditions. The intensities are transformed to phosphate units to quantify the polyphosphate in solution.

Hydrolysis shows zeroth-order behaviour, which differ from the first-order in branched polymer solutions [3]. Although the branched and the non-branched solutions are two different systems, it must be noted that a zero-order reaction could be the result of limited kinetics in viscous solutions. It might mask a different reaction order in more dilute phosphate solutions. If limited kinetics is due to a particular mechanism occurring at high concentrations, then the mechanism is inherent to the process described in this chapter and the mathematical model in section 6.3.7 is still valid. However, it is recommended to verify the phenomenon of limited kinetics by viscosity measurements of both viscous and dilute polyphosphate solutions during the hydrolysis process.

The mathematical expression for the rate of hydrolysis explaining zeroth-order behaviour is developed assuming an intermediate is involved in the process. Hydrolysis is mainly limited to terminal phosphate units. Random hydrolysis might be involved in the hydrolysis. Its contribution however is very low since the phosphate production also shows a zeroth-order dependence on the polyphosphate concentration. This concentration increases linearly with time and no induction time is present in the beginning of the reaction.

The temperature dependence of the reaction predicted by the literature is confirmed [17]. Hydrolysis at elevated temperature follows Arrhenius behaviour. The activation energy plus the corresponding pre-exponential factor can be determined using Raman spectroscopy. The literature stated that the rate of hydrolysis depends on the concentration of polyphosphate [1,3,18]. This is the case for non-catalysed hydrolysis, but not for acid-catalysed reactions.

Stability of linear polyphosphates in neutral solutions can be explained in terms of activation energies using the activation energy for the hydrolysis of branched phosphate polymers.

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Industrial Evaluation

18,000 tonnes of basic zirconium carbonate is produced per annum world wide at a price of US\$3.00/kg. Basic zirconium carbonate is mainly used to prepare zirconium octovate. The high price of the carbonate is due to the extensive procedure to make this product. Baddeleyite must be digested in sulphuric acid to form acidic zirconium sulphate tetrahydrate (AZST). It is precipitated to zirconium oxy hydroxide by a base and redissolved in hydrochloric acid, forming zirconium oxy chloride. Sulphate groups replace the chlorides to produce basic zirconium sulphate (BZS), which is finally converted to basic zirconium carbonate (BZC). The route is schematically shown below.

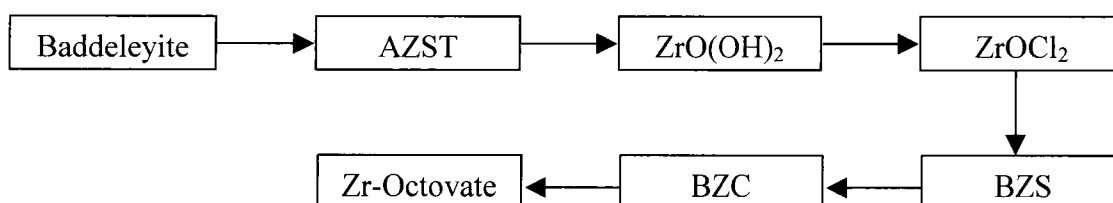


Figure 7.1 Schematic route of the production of Basic Zirconium Carbonate and Zirconium Octovate.

The reaction of ammonium zirconium sulphate with DMSO was an attempt to produce an organic zirconium complex directly from AZST, skipping several intermediates. Note that ammonium zirconium sulphate is obtained by mixing the appropriate amounts of AZST and ammonia.

However, the compound obtained is not soluble in an organic medium. It might still be possible to replace the sulphate groups of the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ compound by carbonate without hydrolysing the zirconium complex. The ligands are strongly bonded to the zirconium atom, donating non-bonding electrons in vacant d orbitals of zirconium and therefore stabilising the atom towards hydrolysis. The use of strongly donating ligands imposes a problem to the production of basic zirconium carbonate, because of the difficulty in removing the ligands afterwards. The DMSO ligands in $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ can be removed by a thermal treatment, but this is accompanied by the decomposition to zirconia. It is expected that basic zirconium carbonate might decompose at even lower temperatures.

The concept of an organic coupling with zirconium is described, which might lead to more suitable organometallic zirconium compounds. The use of other types of ligands is a possibility, but additional research is required to investigate a shorter and cheaper route to produce zirconium octovate.

Ammonium zirconium sulphate is successfully used in a new crystallisation method to purify baddeleyite. The advantages of this process are:

- Removal of radioactive elements
- Removal of transition metal impurities
- Eliminating the large volume of sulphuric acid (45 wt%) waste
- Shift from a chemical intensive process to an energy intensive process

The latter is an advantage since electricity as a commodity in South Africa is very cheap with respect to chemicals. A disadvantage is the ammonia waste during the fusion of baddeleyite and ammonium sulphate, but it is possible to neutralise the ammonia fumes by a scrubber. If these fumes could be flowed through an aqueous solution of sulphuric acid, ammonium sulphate is regenerated, which could be recycled in to the process.

The chemistry of the ammonium zirconium sulphate compound is similar to AZST, although it is less acidic in nature. The compound is very pure and can serve as a starting material for basic zirconium carbonate, zirconium octovate or zirconium phosphate.

The next step of the project was to study the behaviour of phosphate at elevated temperatures. Dehydration is simple, but different types of phosphates show different behaviour upon dehydration. Important parameters are the temperatures of condensation and cross-linking between phosphate units. Raman spectroscopy has been successfully applied to dehydration processes of monobasic phosphates, which can be extended to study similar processes for other phosphate systems, including zirconium phosphate.

The reverse reaction of the dehydration is the hydrolysis of a condensed phosphate and Raman spectroscopy is a valuable tool in determining reaction rates. Raman spectroscopy could be used to monitor the hydrolysis of condensed phosphates and a basis is established to study the stability of zirconium phosphate esters in acidic aqueous media.

The research in this study is conducted in the context of the development of zirconium phosphate flame-retardants and catalysts, of which the former is currently being continued at the INSTITUTE OF APPLIED MATERIALS. No actual work on zirconium phosphates has been conducted since preparatory work turned out to be very comprehensive and only zirconium phosphate related topics could be covered. A process to purify zirconia has been developed successfully and several techniques have been established which can be used to study the chemistry of phosphates in general. It is therefore recommended that these techniques will be employed to study the synthesis of zirconium phosphate compounds.

Appendix

Appendix A

X-ray and Spectroscopic Data of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$

Monoclinic Unit Cell. Space Group Cc (No.9).

Cell Parameters (Å): $a = 16.1956(18)$; $b = 9.7844(14)$; $c = 14.6308(18)$;

$\alpha = 90^\circ$, $\beta = 104.243(9)^\circ$, $\gamma = 90^\circ$

Table A1 Atomic co-ordinates of $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$

Atom	Fractional Coordinates			Coordinates in Å along Basis Vectors in Å			Normalized Real Space Coordinates (Å) in Orthogonal System with respect to Zr		
	x	y	z	x	y	z	x	y	z
Zr	0.00000	0.81892	0.25000	0.00000	8.01264	3.65770	0.00000	0.00000	0.00000
O11	-0.05871	0.96289	0.13862	-0.95084	9.42130	2.02812	-0.54991	1.40866	-1.57949
O12	-0.11754	0.92493	0.26275	-1.90363	9.04989	3.84424	-1.94953	1.03724	0.18081
O21	0.05326	0.96512	0.35818	0.86258	9.44312	5.24046	0.47316	1.43048	1.53411
O22	0.11990	0.92693	0.23870	1.94185	9.06945	3.49237	1.98253	1.05681	-0.16025
O3	-0.09399	0.66282	0.18957	-1.52222	6.48530	2.77356	-1.30470	-1.52734	-0.85696
O4	0.09223	0.66497	0.30994	1.49372	6.50633	4.53467	1.27795	-1.50631	0.85001
O5	-0.03592	0.73427	0.37572	-0.58175	7.18439	5.49708	-1.03430	-0.82825	1.78284
O6	0.03446	0.73018	0.12722	0.55810	7.14437	1.86133	1.00007	-0.86827	-1.74115
S1	-0.13182	1.00893	0.17426	-2.13490	9.87177	2.54956	-1.86226	1.85913	-1.07407
S2	0.13500	1.00883	0.32801	2.18641	9.87080	4.79905	1.90559	1.85816	1.10626
S3	-0.17115	0.62347	0.22430	-2.77188	6.10028	3.28169	-2.67936	-1.91236	-0.36445
S4	0.17354	0.62391	0.27835	2.81058	6.10459	4.07248	2.70853	-1.90806	0.40203
S5	-0.05675	0.81102	0.45711	-0.91910	7.93534	6.68788	-1.66463	-0.07730	2.93704
S6	0.05825	0.80955	0.04541	0.94339	7.92096	0.66438	1.67985	-0.09168	-2.90130
O13	-0.20639	0.96129	0.10745	-3.34261	9.40565	1.57208	-2.82947	1.39301	-2.02151
O14	-0.12723	1.15077	0.19439	-2.06057	11.25959	2.84408	-1.86039	3.24695	-0.78861
O23	0.13335	1.15396	0.30892	2.15968	11.29081	4.51975	1.94759	3.27817	0.83555
O24	0.21355	0.97125	0.39312	3.45857	9.50310	5.75166	2.94338	1.49046	2.02959
C31	-0.15327	0.43475	0.25927	-2.48230	4.25377	3.79333	-2.51567	-3.75887	0.13146
H31a	-0.16410	0.37702	0.20112	-2.65770	3.68891	2.94255	-2.48175	-4.32373	-0.69317
H31b	-0.19322	0.40743	0.29840	-3.12931	3.98646	4.36583	-3.30354	-4.02618	0.68636
H31c	-0.09318	0.42144	0.29651	-1.50911	4.12354	4.33818	-1.67653	-3.88910	0.65956

Appendix A

Atom	Fractional Coordinates			Coordinates in Å along Basis Vectors in Å			Normalized Real Space Coordinates (Å) in Orthogonal System with respect to Zr		
	x	y	z	x	y	z	x	y	z
C32	-0.25126	0.60717	0.11862	-4.06931	5.94079	1.73551	-3.59638	-2.07185	-1.86311
H32a	-0.25920	0.69674	0.08465	-4.19790	6.81718	1.23850	-3.60269	-1.19546	-2.34484
H32b	-0.30594	0.57947	0.13351	-4.95488	5.66977	1.95336	-4.53555	-2.34287	-1.65195
H32c	-0.23405	0.53607	0.07780	-3.79058	5.24512	1.13828	-3.17071	-2.76752	-2.44198
C41	0.15912	0.46279	0.25915	2.57704	4.52812	3.79157	2.54411	-3.48452	0.12976
H41a	0.13328	0.42207	0.30834	2.15855	4.12970	4.51126	1.94854	-3.88294	0.82732
H41b	0.21511	0.41782	0.26176	3.48384	4.08812	3.82976	3.44150	-3.92452	0.16677
H41c	0.12002	0.44829	0.19541	1.94380	4.38625	2.85900	2.14030	-3.62639	-0.77414
C42	0.25151	0.61413	0.38389	4.07336	6.00889	5.61662	3.59139	-2.00375	1.89870
H42a	0.27666	0.70680	0.40092	4.48067	6.91561	5.86578	3.93741	-1.09703	2.14021
H42b	0.29725	0.54950	0.37644	4.81414	5.37653	5.50762	4.35900	-2.63611	1.79305
H42c	0.22544	0.58047	0.43495	3.65114	5.67955	6.36367	2.98537	-2.33309	2.62279
C51	0.03105	0.77147	0.55899	0.50287	7.54837	8.17847	-0.60939	-0.46427	4.38181
H51a	0.05478	0.67934	0.55036	0.88719	6.64693	8.05221	-0.19401	-1.36571	4.25942
H51b	0.00961	0.77147	0.61752	0.15564	7.54837	9.03481	-1.16732	-0.46427	5.21182
H51c	0.07675	0.84199	0.56477	1.24301	8.23837	8.26304	0.10994	0.22573	4.46377
C52	-0.13797	0.70085	0.48238	-2.23451	6.85740	7.05761	-3.07100	-1.15524	3.29540
H52a	-0.18362	0.68556	0.42338	-2.97384	6.70779	6.19439	-3.59795	-1.30485	2.45871
H52b	-0.16318	0.74487	0.53095	-2.64280	7.28811	7.76822	-3.65413	-0.72453	3.98417
H52c	-0.11203	0.61116	0.50678	-1.81439	5.97983	7.41460	-2.73872	-2.03281	3.64141
C61	0.14542	0.72735	0.02668	2.35516	7.11668	0.39035	3.15905	-0.89596	-3.16692
H61a	0.19673	0.75270	0.07745	3.18616	7.36472	1.13316	3.80729	-0.64792	-2.44694
H61b	0.15436	0.75479	-0.03602	2.49995	7.38517	-0.52700	3.52954	-0.62747	-4.05607
H61c	0.13631	0.62632	0.02763	2.20762	6.12817	0.40425	3.00808	-1.88448	-3.15344
C62	-0.01451	0.75892	-0.05072	-0.23500	7.42558	-0.74207	0.84750	-0.58706	-4.26453
H62a	-0.01171	0.65735	-0.05702	-0.18965	6.43178	-0.83425	0.91553	-1.58087	-4.35387
H62b	-0.00275	0.80340	-0.10775	-0.04454	7.86079	-1.57647	1.24325	-0.15185	-5.07328
H62c	-0.07258	0.78571	-0.04487	-1.17548	7.68770	-0.65648	-0.11404	-0.32494	-4.18157

Figure A1 XRD spectrum of a $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ powder

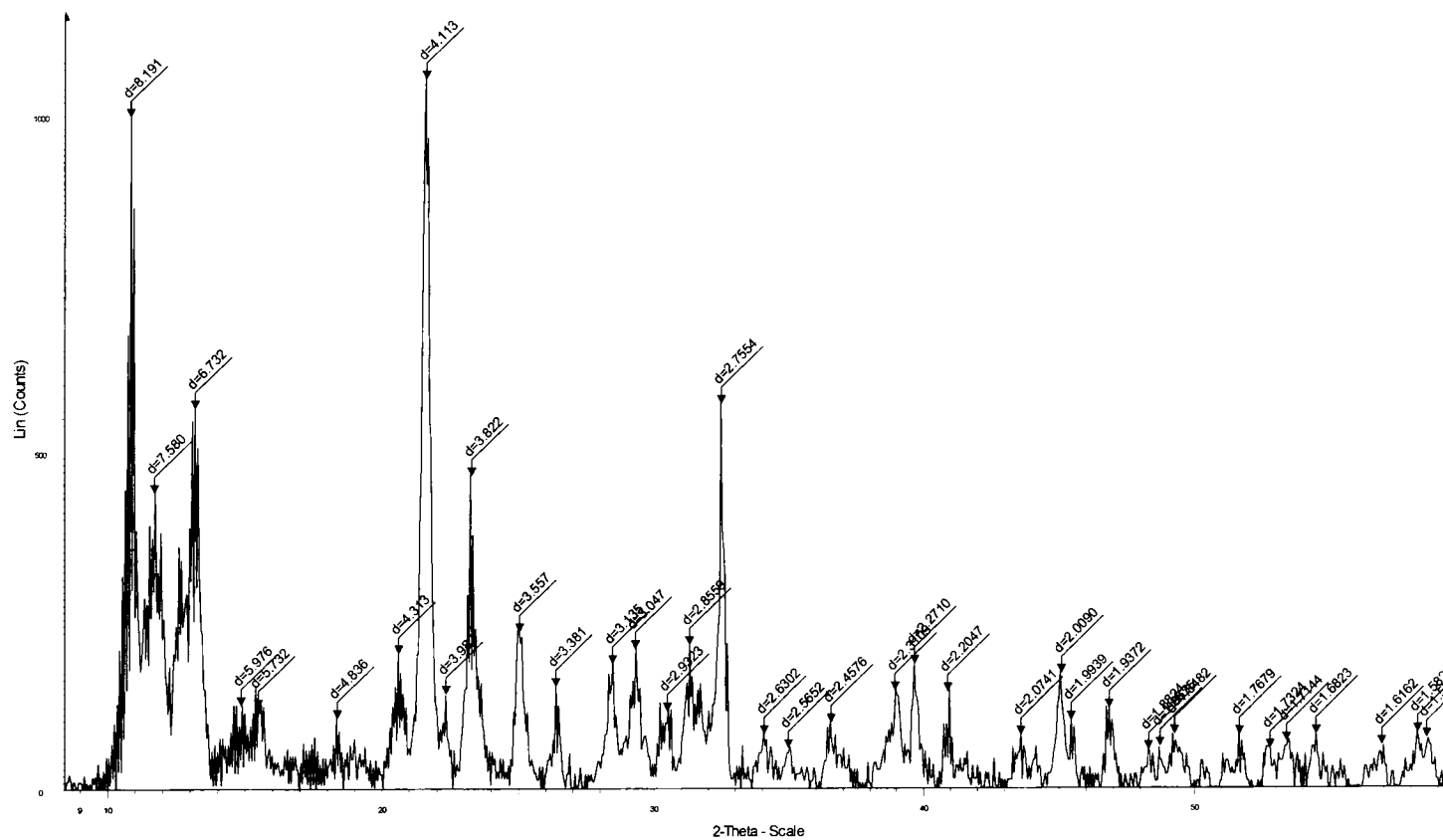


Table A2 XRD Peak Intensities of the $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ powder

Angle $2\theta^\circ$	d value $\text{\AA}$	Intensity Count	Intensity %
10.792	8.191	1001	94.7
11.665	7.580	440	41.6
13.141	6.732	566	53.5
14.813	5.976	123	11.6
15.446	5.732	120	11.3
18.332	4.836	104	9.8
20.579	4.313	199	18.9
21.588	4.113	1058	100.0
22.309	3.982	140	13.2
23.254	3.822	465	44.0
25.016	3.557	233	22.0
26.339	3.381	151	14.3
28.447	3.135	185	17.5
29.287	3.047	207	19.6
30.460	2.932	115	10.9
31.295	2.856	213	20.1
32.468	2.755	573	54.2
34.060	2.630	81	7.7
34.950	2.565	60	5.7
36.533	2.458	98	9.3
38.942	2.311	145	13.7
39.655	2.271	185	17.5
40.900	2.205	143	13.5
43.604	2.074	79	7.5
45.091	2.009	170	16.1
45.453	1.994	102	9.6
46.861	1.937	119	11.3
48.310	1.882	57	5.4
48.722	1.868	62	5.9
49.263	1.848	81	7.6
51.662	1.768	79	7.5
52.800	1.732	59	5.6
53.400	1.714	69	6.6
54.500	1.682	80	7.5
56.929	1.616	63	6.0
58.259	1.582	82	7.8
58.601	1.574	75	7.0

Table A3 Infrared Spectrum $\text{Zr}(\text{SO}_4)_2(\text{DMSO})_4$ between 100 cm^{-1} – 4000 cm^{-1}

Figure 3.15 and 3.16

FIR		MIR	
ν / cm^{-1}	Intensity	ν / cm^{-1}	Intensity
159	vw	721	s
172	w	950	s $\text{SO}_4 + \text{DMSO}$
190	vw	1040	w DMSO S=O
213	m	1140	m
282	vs	1180	m
326	s	1252	m
355	s	1325	w $\text{DMSO } \delta_s(\text{CH}_3)$
366	vs	1430	s $\text{DMSO } \delta_{as}(\text{CH}_3)$
432	vs	1635	m $\delta \text{ H}_2\text{O}$
453	vs	2920	s $\text{DMSO } \nu_s(\text{CH}_3)$
462	vs	3009	s $\text{DMSO } \nu_{as}(\text{CH}_3)$
511	m	3480	m $\text{H}_2\text{O } \nu_s$
583	vs	3564	m $\text{H}_2\text{O } \nu_{as}$
594	s		
624	s		
657	s		
674	s		

vs=very strong, s=strong, m=medium, w=weak, vw=very weak
subscript s=symmetric, subscript as=antisymmetric

Table A4 Raman Spectrum 40 cm⁻¹ – 1500 cm⁻¹

Figure 3.17 and 3.18

ν / cm ⁻¹	Intensity	ν / cm ⁻¹	Intensity
44	w	732	s
104	w	932	vw
188	m	944	m
278	m	961	m
314	m	981	w
358	m	997	vw
364	m	1003 s	s
409	m	1033	vw
443	w	1165	vw
454	w	1174	m
529	m	1250	m
587	Vw	1323	vw
618	Vw	1425	s
624	Vw	2920	s
670	Vs	2936	s
694	Vs	3007	s
726	S	3025	s

vs=very strong, s=strong, m=medium, w=weak, vw=very weak

Appendix B

Ammonium Zirconium Sulphate

Chemical Analysis

The analyses of the $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ powder were out-sourced to the Anglovaal Mining Research Laboratory (AVMIN), Avtech Park, Main Road, Florida 2001, South Africa, telephone: +27 (0)11-472 1622. The results were published in the Certificate of Analysis, reference no. HJD0402. Below is a description of the analysis, including the equipment.

1 ICP

1.1 Equipment

Samples were analysed on a ICAP 9000 consisting of a Jarrell-Ash Spectrometer with a 2.5 kW radio frequency generator, operating at 27.12MHz, and a inductively coupled argon plasma excitation source. The system was operated by an Apple II-plus Data Acquisition System (microcomputer) for all special and routine functions. Liquid samples were nebulised into a spray chamber, where a stream of argon gas carried the sample into the plasma of ionised argon gas. The atoms and ions in the sample emitted electromagnetic radiation, which are characteristic for the element. This radiation was directed through an entrance slit and diffracted by a grating (Rowland Circle with 1510 grooves/mm). The wavelength range was 190-800nm for the air spectrometer and 170-800nm for the vacuum spectrometer. It was refocused on the exit slits and projected on the photo-multiplier tubes to convert the radiation into electrical signals. These signals were processed by the microcomputer.

1.2 Analysis of Zirconium

0.2g of the sample was mixed with 1.5g of lithium metaborate and 0.5g of silica (glass forming agent). The mixture was fused at 1000°C in a platinum crucible and leached in a 5% nitric acid in water with indium as an internal standard. The solution was made up to 500ml and analysed on the ICP spectrometer at a wavelength of zirconium is 339.198nm.

1.3 Analysis of Sulphur

1g of the sample was dissolved in 100ml water and analysed on the ICP spectrometer at a wavelength of 180.731nm. Note that the spectrometer had to be evacuated for the analysis. A 333ppm solution of S was used as a standard.

2 Analysis of Ammonium

0.5g of sample was dissolved in water and made up to 500ml. The sample was then analysed on a CADAS 100 UV/VIS Spectrophotometer using a 10mm round glass cuvet and measured at a wavelength of 694nm. A 20ppm ammonia aqueous solution was used as a standard.

Spectroscopic Data

Table B1 Infrared Spectrum of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ Powder between 300 cm^{-1} – 4000 cm^{-1}

Figure 4.2 and 4.3

FIR		MIR	
ν / cm^{-1}	Intensity	ν / cm^{-1}	Intensity
274	vs	998	s SO_4
304	s	1055	s “
362	s	1122	s “
445	s	1175	s “
470	m	1248	s “
510	w	1399	s NH_4
541	m	1433	s NH_4
584	s	1652	s $\delta \text{H}_2\text{O}$
594	s	3000- 4000	broad vs $\text{NH}_4/\text{H}_2\text{O}$

vs=very strong, s=strong, m=medium

Table B2 Raman Spectrum of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ Powder between 40 cm^{-1} – 1600 cm^{-1}

Figure 4.38

ν / cm^{-1}	Intensity	ν / cm^{-1}	Intensity
133	m	737	m
222	s	1033	vs
321	w	1109	w
424	m	1138	w
469	m	1158	w
495	w	1221	w
602	w	1293	w
621	m	1428	vw
666	m	1685	m

s=strong, m=medium, w=weak, vw=very weak

XRD

Table B3 XRD Peaks of $\text{NH}_4\text{HZrO}(\text{SO}_4)_2$ Powder

Figure 4.5

Angle $2\theta^\circ$	d value $\text{\AA}$	Intensity Count	Intensity %
7.824	11.291	927	61.5
10.021	8.820	1506	100.0
10.950	8.073	728	48.3
12.435	7.112	129	8.6
13.395	6.605	139	9.2
14.300	6.189	146	9.7
15.281	5.794	115	7.6
15.643	5.660	246	16.3
16.125	5.492	160	10.6
16.455	5.383	79	5.3
17.887	4.955	130	8.6
19.415	4.568	370	24.6
20.124	4.409	167	11.1
22.431	3.960	288	19.1
23.478	3.786	187	12.4
24.124	3.686	174	11.5
24.770	3.591	83	5.5
25.166	3.536	285	18.9
26.039	3.419	598	39.7
26.629	3.345	1147	76.1
26.874	3.315	687	45.6
27.750	3.212	500	33.2
27.995	3.185	222	14.7
28.791	3.098	257	17.1
29.166	3.059	132	8.8
30.060	2.970	482	32.0

Angle $2\theta^\circ$	d value $\text{\AA}$	Intensity Count	Intensity %
31.270	2.858	208	13.8
32.103	2.786	305	20.3
32.787	2.729	107	7.1
33.496	2.673	67	4.5
34.093	2.628	146	9.7
34.694	2.584	83	5.5
35.183	2.549	91	6.0
35.916	2.498	147	9.7
36.332	2.471	147	9.7
36.845	2.438	95	6.3
38.135	2.358	88	5.9
39.326	2.289	68	4.5
41.085	2.195	52	3.5
42.837	2.109	116	7.7
43.950	2.059	65	4.3
45.841	1.978	182	12.1
48.883	1.862	131	8.7
50.800	1.796	91	6.0
53.010	1.726	89	5.9
54.498	1.682	99	6.6
57.213	1.609	101	6.7

Single Crystal XRD Data

Hexagonal Unit Cell. Space group $P6_3/m$.

Cell parameters (Å): $a = 34.891(3)$; $b = 34.891(3)$; $c = 18.8022(16)$;

$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$

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Crystal Data

=====

Input Cell (Lattice Type: P)

Reduced Cell (Acta Cryst. (1976), A32, 297)

a = 34.891(3) Angstrom
b = 34.891(3)
c = 18.8022(16)
V = 19823(3) Cubic-Angstrom
alpha = 90 Degree
beta = 90
gamma = 120
Lambda(MoKa) = 0.71073 Angstrom

a = 18.802 alpha = 120.00 V = 19823.0
b = 34.891 beta = 90.00
c = 34.891 gamma = 90.00

Niggli Values

353.520 1217.380 1217.380
-608.690 0.000 0.000

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Orthogonalization Matrices

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(See e.g. J.D.Dunitz, Xray Analysis and Structure determination of Organic Molecules, Cornell Univ. Press, 1979, P236)

(XO) (34.89100 -17.44550 0) (X) , (X) (0.02866 0.01655 0) (XO) Orthogonal Axes AO, BO and CO
(YO) = (0 30.21649 0)*(Y) , (Y) = (0 0.03309 0)*(YO) are defined as:
(ZO) (0 0 18.80220) (Z) , (Z) (0 0 0.05319) (ZO) AO // A, CO // C*, BO // CO X AO

=====

Space Group Symmetry

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(See e.g. G. Burns & A.M. Glazer, Space Groups for Solid State Scientists, Academic Press, 1990 or Int. Tables A)

Space Group P63/m No: 176, Laue: 6/m [Hall: -P 6c]

Lattice Type hP, Centric, Hexagonal, Order 12(6) [Shoenflies: C6h^2]

Nr ***** Symmetry Operation(s) *****

1	X ,	Y ,	Z
2	X - Y ,	X ,	1/2 + Z
3	- Y ,	X - Y ,	Z
4	- X ,	- Y ,	1/2 + Z
5	- X + Y ,	- X ,	Z
6	Y ,	- X + Y ,	1/2 + Z
7	- X ,	- Y ,	- Z
8	- X + Y ,	- X ,	1/2 - Z
9	Y ,	- X + Y ,	- Z
10	X ,	Y ,	1/2 - Z
11	X - Y ,	X ,	- Z
12	- Y ,	X - Y ,	1/2 - Z

=====
(1:19-Rounded) Coordinates of Unique Residue(s) Identified. Standard Deviations in the Last Digit are in Parentheses.

Site = Site Symmetry; SSN = Site Symmetry Number; SSOF = SHELX Site Occupation Factor (= S.O.F / SSN).
***** Move = Transformation on Input Data: N.IJK (N = SymOp, IJK = Translation) i.e. 1.555 = nomove
SYMBOLS: Type = D/A = Potential Donor or Acceptor atom, D-H = H on Donor atom, MET = Metal.
***** El Type = AK = Alkali Metal, AE = Alkaline Earth, HL = Halogen, AN = Actinide, LN = Lanthanide, TR = Transition Element.
ARU = Asymmetric Residue Unit encoded as sklm.nn, with s = symmetry op, klm = translation, nn = residue #.
RESIDUE = collection of ARU's constituting an isolated unit (= molecule, ion).

Atom Types : H N O S Zr
Cov.Rad(Ang): 0.23 0.68 0.68 1.02 1.56
Atom Number : 1 7 8 16 40
Atom Weight : 1.008 14.010 16.00 32.07 91.22
Scat.Fact.f0: 1.000 6.995 7.999 16.000 39.968
Scat.Fact.f': 0.000 0.006 0.011 0.125 -2.967
Scat.Fact.f'': 0.000 0.003 0.006 0.123 0.560
Mu/Rho(MoKa): 0.37 0.84 1.22 9.99 16.31
Elem. Type : -- -- -- -- TR

Sources - Cov. Radii : Manual Cambridge Cryst. Data Base
- Atomic Wt. : IUPAC 1993
- mu/rho : International Tables C, table 4.2.4.2, p193-199

RESIDUE = 1

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site	SSN*SSOF =	S.O.F	Move	Type
1.	Zr(1)	0.43639(4)	0.16814(5)	1/4	12.293(2)	5.081(2)	4.701	..m 2	1/2	1	-	Met
2	Zr(2)	0.29792(4)	0.09698(4)	1/4	8.703(2)	2.930(1)	4.701	..m 2	1/2	1	-	Met
3	Zr(3)	0.16182(4)	-0.00367(4)	1/4	5.710(2)	-0.111(1)	4.701	..m 2	1/2	1	-	Met
4	Zr(4)	0.48528(3)	0.11809(3)	0.34777(5)	14.872(1)	3.568(1)	6.539(1)	1	1	1	10.555	Met
5	Zr(5)	0.36803(3)	0.07445(3)	0.15661(5)	11.542(1)	2.250(1)	2.945(1)	1	1	1	-	Met
6	Zr(6)	0.24929(3)	-0.00040(3)	0.34301(5)	8.705(1)	-0.012(1)	6.449(1)	1	1	1	-	Met
7	Zr(7)	0.14410(3)	-0.09834(3)	0.34801(5)	6.743(1)	-2.971(1)	6.543(1)	1	1	1	10.555	Met
8	Zr(8)	0.32101(4)	-0.02708(4)	1/4	11.673(2)	-0.818(1)	4.701	..m 2	1/2	1	-	Met
9	Zr(9)	0.41641(3)	0.04724(3)	0.49160(5)	13.705(1)	1.427(1)	9.243(1)	1	1	1	10.555	Met
10	Zr(10)	0.32998(3)	-0.06011(3)	0.54236(5)	12.562(1)	-1.816(1)	10.198(1)	1	1	1	10.555	Met
11	Zr(11)	0.22321(3)	-0.07647(3)	0.49206(5)	9.122(1)	-2.311(1)	9.252(1)	1	1	1	10.555	Met
12	S(1)	0.36715(11)	0.21248(11)	1/4	9.103(4)	6.420(3)	4.701	..m 2	1/2	1	-	-
13	S(2)	0.21899(8)	0.07799(8)	0.37035(13)	6.280(3)	2.357(2)	6.963(2)	1	1	1	-	-
14	S(3)	0.49424(11)	0.21596(11)	0.39904(19)	13.477(4)	6.526(3)	7.503(4)	1	1	1	10.555	-
15	*S(4A)	0.0896(3)	-0.0426(3)	0.1067(5)	3.869(12)	-1.287(9)	2.006(9)	1	1/2	1/2	-	-
16	*S(4B)	0.0754(3)	-0.0547(3)	0.1323(4)	3.585(12)	-1.653(9)	2.488(8)	1	1/2	1/2	-	-
17	S(5)	0.39889(12)	-0.03889(13)	1/4	14.596(5)	-1.175(4)	4.701	..m 2	1/2	1	-	-
18	S(6)	0.26521(13)	-0.12432(12)	1/4	11.422(5)	-3.757(4)	4.701	..m 2	1/2	1	-	-
19	S(7)	0.50225(9)	0.03736(10)	0.42267(14)	16.872(4)	1.129(3)	7.947(3)	1	1	1	10.555	-
20	S(8)	0.16000(11)	-0.17959(10)	0.42660(17)	8.716(4)	-5.427(3)	8.021(3)	1	1	1	10.555	-
21	O(1)	0.4069(3)	0.2084(3)	1/4	10.562(12)	6.297(9)	4.701	..m 2	1/2	1	-	D/A
22	O(2)	0.3268(3)	0.1678(3)	1/4	8.475(12)	5.070(9)	4.701	..m 2	1/2	1	-	D/A
23	O(3)	0.3664(3)	0.2356(3)	0.3131(4)	8.674(12)	7.119(9)	5.887(8)	1	1	1	-	D/A
24	O(4)	0.2582(2)	0.1108(2)	0.3277(4)	7.076(8)	3.348(6)	6.161(8)	1	1	1	-	D/A
25	O(5)	0.1809(2)	0.0543(2)	0.3220(4)	5.364(8)	1.641(6)	6.054(8)	1	1	1	-	D/A
26	O(6)	0.2298(2)	0.0461(2)	0.4029(3)	7.214(8)	1.393(6)	7.575(6)	1	1	1	-	D/A
27	O(7)	0.2090(2)	0.1013(2)	0.4248(4)	5.525(8)	3.061(6)	7.987(8)	1	1	1	-	D/A

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28	O(8)	0.4774(2)	0.2194(2)	0.3276(4)	12.829(8)	6.629(6)	6.160(8)	1	1	1	10.555 D/A
29	O(9)	0.5131(2)	0.1861(2)	0.3925(4)	14.656(8)	5.623(6)	7.380(8)	1	1	1	10.555 D/A
30	O(10)	0.5282(3)	0.2589(3)	0.4227(6)	13.913(12)	7.823(9)	7.948(11)	1	1	1	10.555 D/A
31	O(11)	0.4566(3)	0.1976(3)	0.4503(5)	12.484(12)	5.971(9)	8.467(9)	1	1	1	10.555 D/A
32	O(12)	0.1048(2)	-0.0188(2)	0.1784(4)	3.985(8)	-0.568(6)	3.354(8)	1	1	1	- D/A
33	O(13)	0.0985(2)	-0.0784(2)	0.3964(4)	4.804(8)	-2.369(6)	7.453(8)	1	1	1	10.555 D/A
34	O(14)	0.0525(5)	-0.0474(5)	0.0849(8)	2.659(20)	-1.432(15)	1.596(15)	1	1	1	- D/A
35	*O(15A)	0.1151(8)	-0.0117(6)	0.0504(9)	4.220(30)	-0.354(18)	0.948(17)	1	1/2	1/2	- D/A
36	*O(15B)	0.0389(5)	-0.0875(6)	0.1731(11)	2.884(20)	-2.644(18)	3.255(21)	1	1/2	1/2	- D/A
37	O(16)	0.3739(3)	-0.0346(3)	0.3104(4)	13.649(12)	-1.045(9)	5.836(8)	1	1	1	- D/A
38	O(17)	0.3974(4)	-0.0806(4)	1/4	15.272(16)	-2.435(12)	4.701	.m	2	1/2	1 - D/A
39	O(18)	0.4436(4)	-0.0030(4)	1/4	15.530(16)	-0.091(12)	4.701	.m	2	1/2	1 - D/A
40	O(19)	0.2823(3)	-0.0922(2)	0.3108(4)	11.458(11)	-2.786(6)	5.844(8)	1	1	1	- D/A
41	O(20)	0.2823(4)	-0.1543(4)	1/4	12.542(16)	-4.662(12)	4.701	.m	2	1/2	1 - D/A
42	O(21)	0.2182(4)	-0.1479(4)	1/4	10.193(16)	-4.469(12)	4.701	.m	2	1/2	1 - D/A
43	O(22)	0.5043(2)	0.0665(3)	0.3635(4)	16.435(9)	2.009(9)	6.835(8)	1	1	1	10.555 D/A
44	O(23)	0.4589(2)	0.0198(3)	0.4589(4)	15.666(9)	0.598(9)	8.628(8)	1	1	1	10.555 D/A
45	O(24)	0.5040(3)	-0.0001(3)	0.3925(4)	17.587(12)	-0.003(9)	7.380(8)	1	1	1	10.555 D/A
46	O(25)	0.5387(3)	0.0627(3)	0.4725(4)	17.702(12)	1.895(9)	8.884(8)	1	1	1	10.555 D/A
47	O(26)	0.1448(2)	-0.1620(2)	0.3671(4)	7.878(8)	-4.895(6)	6.902(8)	1	1	1	10.555 D/A
48	O(27)	0.2037(2)	-0.1444(2)	0.4524(4)	9.626(8)	-4.363(6)	8.506(8)	1	1	1	10.555 D/A
49	O(28)	0.1277(3)	-0.1915(4)	0.4866(5)	7.796(13)	-5.786(12)	9.149(9)	1	1	1	10.555 D/A
50	O(29)	0.1633(4)	-0.2166(3)	0.4019(6)	9.476(15)	-6.545(9)	7.557(11)	1	1	1	10.555 D/A
51	O(30)	0.3675(3)	0.1161(3)	1/4	10.797(12)	3.508(9)	4.701	.m	2	1/2	1 - D/A
52	O(31)	0.4995(3)	0.1630(3)	1/4	14.584(12)	4.925(9)	4.701	.m	2	1/2	1 - D/A
53	O(32)	0.4322(2)	0.1275(2)	0.1685(3)	12.856(8)	3.853(6)	3.168(6)	1	1	1	10.555 D/A
54	O(33)	0.2362(3)	0.0323(3)	1/4	7.678(12)	0.976(9)	4.701	.m	2	1/2	1 - D/A
55	O(34)	0.3043(2)	0.0635(2)	0.3338(3)	9.510(8)	1.919(6)	6.276(6)	1	1	1	10.555 D/A
56	O(35)	0.1807(2)	-0.0314(2)	0.3297(3)	6.853(8)	-0.949(6)	6.199(6)	1	1	1	10.555 D/A
57	O(36)	0.1167(3)	-0.0809(3)	1/4	5.483(12)	-2.445(9)	4.701	.m	2	1/2	1 - D/A
58	O(37)	0.4738(3)	0.0845(3)	1/4	15.057(12)	2.553(9)	4.701	.m	2	1/2	1 - D/A
59	O(38)	0.4190(2)	0.0539(2)	0.3724(3)	13.679(8)	1.629(6)	7.002(6)	1	1	1	10.555 D/A
60	O(39)	0.4730(2)	0.1073(2)	0.4588(4)	14.632(8)	3.242(6)	8.626(8)	1	1	1	10.555 D/A
61	O(40)	0.3654(3)	0.0406(3)	1/4	12.041(12)	1.227(9)	4.701	.m	2	1/2	1 - D/A
62	O(41)	0.3163(2)	-0.0024(2)	0.1454(3)	11.078(8)	-0.073(6)	2.734(6)	1	1	1	- D/A
63	O(42)	0.3691(2)	0.0635(2)	0.4549(3)	11.770(8)	1.919(6)	8.553(6)	1	1	1	10.555 D/A
64	O(43)	0.2632(3)	-0.0246(3)	1/4	9.612(12)	-0.743(9)	4.701	.m	2	1/2	1 - D/A
65	O(44)	0.2172(2)	-0.0741(2)	0.3715(3)	8.871(8)	-2.239(6)	6.985(6)	1	1	1	10.555 D/A
66	O(45)	0.2524(2)	-0.0108(2)	0.4548(3)	8.995(8)	-0.326(6)	8.551(6)	1	1	1	10.555 D/A
67	O(46)	0.1629(3)	-0.1139(3)	1/4	7.671(12)	-3.442(9)	4.701	.m	2	1/2	1 - D/A
68	O(47)	0.1582(2)	-0.0939(2)	0.4597(4)	7.158(8)	-2.837(6)	8.643(8)	1	1	1	10.555 D/A
69	O(48)	0.3735(2)	-0.0206(2)	0.4605(3)	13.391(8)	-0.622(6)	8.658(6)	1	1	1	10.555 D/A
70	O(49)	0.3647(2)	0.0080(2)	0.5667(4)	12.585(8)	0.242(6)	10.655(8)	1	1	1	10.555 D/A
71	O(50)	0.2834(2)	-0.0748(2)	0.4583(3)	11.193(8)	-2.260(6)	8.617(6)	1	1	1	10.555 D/A
72	O(51)	0.2731(2)	-0.0565(3)	0.5732(4)	10.514(9)	-1.707(9)	10.777(8)	1	1	1	10.555 D/A
73	O(52)	0.5580(2)	0.1499(3)	0.3449(4)	16.854(9)	4.529(9)	6.485(8)	1	1	1	10.555 D/A
74	O(53)	0.3711(2)	0.1379(2)	0.1029(4)	10.542(8)	4.167(6)	1.935(8)	1	1	1	- D/A
75	O(54)	0.0745(2)	-0.1555(2)	0.3393(4)	5.312(8)	-4.699(6)	6.380(8)	1	1	1	10.555 D/A
76	O(55)	0.4567(3)	0.0487(3)	0.5841(4)	15.085(12)	1.472(9)	10.982(8)	1	1	1	10.555 D/A
77	O(56)	0.4186(3)	0.0994(3)	0.5699(4)	12.871(12)	3.004(9)	10.715(8)	1	1	1	10.555 D/A
78	O(57)	0.3369(3)	-0.1086(2)	0.4666(4)	13.649(11)	-3.282(6)	8.773(8)	1	1	1	10.555 D/A
79	O(58)	0.3894(2)	-0.0624(3)	0.5797(4)	14.675(9)	-1.886(9)	10.900(8)	1	1	1	10.555 D/A
80	O(59)	0.2910(3)	-0.1283(3)	0.5848(4)	12.392(12)	-3.877(9)	10.996(8)	1	1	1	10.555 D/A
81	O(60)	0.3335(2)	-0.0531(3)	0.6653(4)	12.563(9)	-1.604(9)	12.509(8)	1	1	1	10.555 D/A
82	O(61)	0.1870(3)	-0.1231(3)	0.5825(4)	8.672(12)	-3.720(9)	10.952(8)	1	1	1	10.555 D/A
83	O(62)	0.2038(2)	-0.0411(3)	0.5735(4)	7.828(9)	-1.242(9)	10.783(8)	1	1	1	10.555 D/A

" shelxl "										PLATON-INTRA	Page	4	
84	H(31)	0.52830	0.19160	1/4	15.090	5.789	4.701	.m	2	1/2	1	-	D-H
85	H(36)	0.08400	-0.09240	1/4	4.543	-2.792	4.701	.m	2	1/2	1	-	D-H
86	H(37)	0.46330	0.05360	1/4	15.230	1.620	4.701	.m	2	1/2	1	-	D-H
87	H(38)	0.41510	0.02710	0.34650	14.010	0.819	6.515		1	1	1	10.555	D-H
88	H(39)	0.49210	0.12860	0.49260	14.926	3.886	9.262		1	1	1	10.555	D-H
89	H(41)	0.31930	-0.01790	0.10280	11.453	-0.541	1.933		1	1	1	-	D-H
90	H(42)	0.34910	0.06580	0.48660	11.033	1.988	9.149		1	1	1	10.555	D-H
91	H(44)	0.22960	-0.09020	0.34470	9.585	-2.726	6.481		1	1	1	10.555	D-H
92	H(46) ← H45	0.18010	-0.12810	1/4	8.519	-3.871	4.701	.m	2	1/2	1	-	D-H
93	H(47)	0.13590	-0.09960	0.49390	6.479	-3.010	9.286		1	1	1	10.555	D-H
94	H(48)	0.37410	-0.03160	0.41460	13.604	-0.955	7.795		1	1	1	10.555	D-H
95	H(49)	0.35820	0.02020	0.60690	12.146	0.610	11.411		1	1	1	10.555	D-H
96	H(50)	0.28860	-0.08010	0.41070	11.467	-2.420	7.722		1	1	1	10.555	D-H
97	H(51)	0.27010	-0.04690	0.61900	10.242	-1.417	11.639		1	1	1	10.555	D-H
98	H(52A)	0.56670	0.13710	0.30600	17.381	4.143	5.753		1	1	1	10.555	D-H
99	H(52B)	0.57090	0.18170	0.33710	16.749	5.490	6.338		1	1	1	10.555	D-H
100	H(53A)	0.34700	0.12820	0.06840	9.871	3.874	1.286		1	1	1	-	D-H
101	H(53B)	0.39960	0.15510	0.07850	11.237	4.687	1.476		1	1	1	-	D-H
102	H(54A)	0.07550	-0.18210	0.32540	5.811	-5.502	6.118		1	1	1	10.555	D-H
103	H(54B)	0.05970	-0.16050	0.38550	4.883	-4.850	7.248		1	1	1	10.555	D-H
104	H(55A)	0.46350	0.07440	0.61370	14.874	2.248	11.539		1	1	1	10.555	D-H
105	H(55B)	0.48430	0.05100	0.56700	16.008	1.541	10.661		1	1	1	10.555	D-H
106	H(56A)	0.44860	0.11670	0.58960	13.616	3.526	11.086		1	1	1	10.555	D-H
107	H(56B)	0.39750	0.08450	0.60860	12.395	2.553	11.443		1	1	1	10.555	D-H
108	H(57A)	0.30750	-0.13160	0.45100	13.025	-3.976	8.480		1	1	1	10.555	D-H
109	H(57B)	0.35150	-0.12240	0.49170	14.400	-3.699	9.245		1	1	1	10.555	D-H
110	H(58A)	0.38160	-0.09330	0.58700	14.942	-2.819	11.037		1	1	1	10.555	D-H
111	H(58B)	0.41270	-0.04890	0.54370	15.253	-1.478	10.223		1	1	1	10.555	D-H
112	H(59A)	0.31070	-0.14030	0.59300	13.288	-4.239	11.150		1	1	1	10.555	D-H
113	H(59B)	0.27710	-0.12770	0.62980	11.896	-3.859	11.842		1	1	1	10.555	D-H
114	H(60A)	0.32850	-0.08090	0.68660	12.873	-2.445	12.910		1	1	1	10.555	D-H
115	H(60B)	0.36290	-0.02910	0.67920	13.170	-0.879	12.770		1	1	1	10.555	D-H
116	H(61A)	0.20860	-0.12380	0.61500	9.438	-3.741	11.563		1	1	1	10.555	D-H
117	H(61B)	0.16740	-0.15290	0.56390	8.508	-4.620	10.603		1	1	1	10.555	D-H
118	H(62A)	0.20150	-0.01730	0.55000	7.332	-0.523	10.341		1	1	1	10.555	D-H
119	H(62B)	0.22660	-0.02850	0.61060	8.403	-0.861	11.481		1	1	1	10.555	D-H
120	Zr(4)a	0.48528(3)	0.11809(3)	0.15223(5)	14.872(1)	3.568(1)	2.862(1)		1	1	1	-	Met
121	Zr(5)a	0.36803(3)	0.07445(3)	0.34339(5)	11.542(1)	2.250(1)	6.456(1)		1	1	1	10.555	Met
122	Zr(6)a	0.24929(3)	-0.00040(3)	0.15699(5)	8.705(1)	-0.012(1)	2.952(1)		1	1	1	10.555	Met
123	Zr(7)a	0.14410(3)	-0.09834(3)	0.15199(5)	6.743(1)	-2.971(1)	2.858(1)		1	1	1	-	Met
124	Zr(9)a	0.41641(3)	0.04724(3)	0.00840(5)	13.705(1)	1.427(1)	0.158(1)		1	1	1	-	Met
125	Zr(10)a	0.32998(3)	-0.06011(3)	-0.04236(5)	12.562(1)	-1.816(1)	-0.796(1)		1	1	1	-	Met
126	Zr(11)a	0.22321(3)	-0.07647(3)	0.00794(5)	9.122(1)	-2.311(1)	0.149(1)		1	1	1	-	Met
127	S(2)a	0.21899(8)	0.07799(8)	0.12965(13)	6.280(3)	2.357(2)	2.438(2)		1	1	1	10.555	-
128	S(3)a	0.49424(11)	0.21596(11)	0.10096(19)	13.477(4)	6.526(3)	1.898(4)		1	1	1	-	-
129	*S(4A)a	0.0896(3)	-0.0426(3)	0.3933(5)	3.869(12)	-1.287(9)	7.395(9)		1	1/2	1/2	10.555	-
130	*S(4B)a	0.0754(3)	-0.0547(3)	0.3677(4)	3.585(12)	-1.653(9)	6.914(8)		1	1/2	1/2	10.555	-
131	S(7)a	0.50225(9)	0.03736(10)	0.07733(14)	16.872(4)	1.129(3)	1.454(3)		1	1	1	-	-
132	S(8)a	0.16000(11)	-0.17959(10)	0.07340(17)	8.716(4)	-5.427(3)	1.380(3)		1	1	1	-	-
133	O(3)a	0.3664(3)	0.2356(3)	0.1869(4)	8.674(12)	7.119(9)	3.514(8)		1	1	1	10.555	D/A
134	O(4)a	0.2582(2)	0.1108(2)	0.1723(4)	7.076(8)	3.348(6)	3.240(8)		1	1	1	10.555	D/A
135	O(5)a	0.1809(2)	0.0543(2)	0.1780(4)	5.364(8)	1.641(6)	3.347(8)		1	1	1	10.555	D/A
136	O(6)a	0.2298(2)	0.0461(2)	0.0971(3)	7.214(8)	1.393(6)	1.826(6)		1	1	1	10.555	D/A
137	O(7)a	0.2090(2)	0.1013(2)	0.0752(4)	5.525(8)	3.061(6)	1.414(8)		1	1	1	10.555	D/A
138	O(8)a	0.4774(2)	0.2194(2)	0.1724(4)	12.829(8)	6.629(6)	3.241(8)		1	1	1	-	D/A
139	O(9)a	0.5131(2)	0.1861(2)	0.1075(4)	14.656(8)	5.623(6)	2.021(8)		1	1	1	-	D/A

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140	O(10)a	0.5282(3)	0.2589(3)	0.0773(6)	13.913(12)	7.823(9)	1.453(11)	1	1	1	-	D/A
141	O(11)a	0.4566(3)	0.1976(3)	0.0497(5)	12.484(12)	5.971(9)	0.934(9)	1	1	1	-	D/A
142	O(12)a	0.1048(2)	-0.0188(2)	0.3216(4)	3.985(8)	-0.568(6)	6.047(8)	1	1	1	10.555	D/A
143	O(13)a	0.0985(2)	-0.0784(2)	0.1036(4)	4.804(8)	-2.369(6)	1.948(8)	1	1	1	-	D/A
144	O(14)a	0.0525(5)	-0.0474(5)	0.4151(8)	2.659(20)	-1.432(15)	7.805(15)	1	1	1	10.555	D/A
145	*O(15A)a	0.1151(8)	-0.0117(6)	0.4496(9)	4.220(30)	-0.354(18)	8.453(17)	1	1/2	1/2	10.555	D/A
146	*O(15B)a	0.0389(5)	-0.0875(6)	0.3269(11)	2.884(20)	-2.644(18)	6.146(21)	1	1/2	1/2	10.555	D/A
147	O(16)a	0.3739(3)	-0.0346(3)	0.1896(4)	13.649(12)	-1.045(9)	3.565(8)	1	1	1	10.555	D/A
148	O(19)a	0.2823(3)	-0.0922(2)	0.1892(4)	11.458(11)	-2.786(6)	3.557(8)	1	1	1	10.555	D/A
149	O(22)a	0.5043(2)	0.0665(3)	0.1365(4)	16.435(9)	2.009(9)	2.567(8)	1	1	1	-	D/A
150	O(23)a	0.4589(2)	0.0198(3)	0.0411(4)	15.666(9)	0.598(9)	0.773(8)	1	1	1	-	D/A
151	O(24)a	0.5040(3)	-0.0001(3)	0.1075(4)	17.587(12)	-0.003(9)	2.021(8)	1	1	1	-	D/A
152	O(25)a	0.5387(3)	0.0627(3)	0.0275(4)	17.702(12)	1.895(9)	0.517(8)	1	1	1	-	D/A
153	O(26)a	0.1448(2)	-0.1620(2)	0.1329(4)	7.878(8)	-4.895(6)	2.499(8)	1	1	1	-	D/A
154	O(27)a	0.2037(2)	-0.1444(2)	0.0476(4)	9.626(8)	-4.363(6)	0.895(8)	1	1	1	-	D/A
155	O(28)a	0.1277(3)	-0.1915(4)	0.0134(5)	7.796(13)	-5.786(12)	0.252(9)	1	1	1	-	D/A
156	O(29)a	0.1633(4)	-0.2166(3)	0.0981(6)	9.476(15)	-6.545(9)	1.844(11)	1	1	1	-	D/A
157	O(32)a	0.4322(2)	0.1275(2)	0.3315(3)	12.856(8)	3.853(6)	6.233(6)	1	1	1	-	D/A
158	O(34)a	0.3043(2)	0.0635(2)	0.1662(3)	9.510(8)	1.919(6)	3.125(6)	1	1	1	-	D/A
159	O(35)a	0.1807(2)	-0.0314(2)	0.1703(3)	6.853(8)	-0.949(6)	3.202(6)	1	1	1	-	D/A
160	O(38)a	0.4190(2)	0.0539(2)	0.1276(3)	13.679(8)	1.629(6)	2.399(6)	1	1	1	-	D/A
161	O(39)a	0.4730(2)	0.1073(2)	0.0412(4)	14.632(8)	3.242(6)	0.775(8)	1	1	1	-	D/A
162	O(41)a	0.3163(2)	-0.0024(2)	0.3546(3)	11.078(8)	-0.073(6)	6.667(6)	1	1	1	10.555	D/A
163	O(42)a	0.3691(2)	0.0635(2)	0.0451(3)	11.770(8)	1.919(6)	0.848(6)	1	1	1	-	D/A
164	O(44)a	0.2172(2)	-0.0741(2)	0.1285(3)	8.871(8)	-2.239(6)	2.416(6)	1	1	1	-	D/A
165	O(45)a	0.2524(2)	-0.0108(2)	0.0452(3)	8.995(8)	-0.326(6)	0.850(6)	1	1	1	-	D/A
166	O(47)a	0.1582(2)	-0.0939(2)	0.0403(4)	7.158(8)	-2.837(6)	0.758(8)	1	1	1	-	D/A
167	O(48)a	0.3735(2)	-0.0206(2)	0.0395(3)	13.391(8)	-0.622(6)	0.743(6)	1	1	1	-	D/A
168	O(49)a	0.3647(2)	0.0080(2)	-0.0667(4)	12.585(8)	0.242(6)	-1.254(8)	1	1	1	-	D/A
169	O(50)a	0.2834(2)	-0.0748(2)	0.0417(3)	11.193(8)	-2.260(6)	0.784(6)	1	1	1	-	D/A
170	O(51)a	0.2731(2)	-0.0565(3)	-0.0732(4)	10.514(9)	-1.707(9)	-1.376(8)	1	1	1	-	D/A
171	O(52)a	0.5580(2)	0.1499(3)	0.1551(4)	16.854(9)	4.529(9)	2.916(8)	1	1	1	-	D/A
172	O(53)a	0.3711(2)	0.1379(2)	0.3971(4)	10.542(8)	4.167(6)	7.466(8)	1	1	1	10.555	D/A
173	O(54)a	0.0745(2)	-0.1555(2)	0.1607(4)	5.312(8)	-4.699(6)	3.022(8)	1	1	1	-	D/A
174	O(55)a	0.4567(3)	0.0487(3)	-0.0841(4)	15.085(12)	1.472(9)	-1.581(8)	1	1	1	-	D/A
175	O(56)a	0.4186(3)	0.0994(3)	-0.0699(4)	12.871(12)	3.004(9)	-1.314(8)	1	1	1	-	D/A
176	O(57)a	0.3369(3)	-0.1086(2)	0.0334(4)	13.649(11)	-3.282(6)	0.628(8)	1	1	1	-	D/A
177	O(58)a	0.3894(2)	-0.0624(3)	-0.0797(4)	14.675(9)	-1.886(9)	-1.499(8)	1	1	1	-	D/A
178	O(59)a	0.2910(3)	-0.1283(3)	-0.0848(4)	12.392(12)	-3.877(9)	-1.594(8)	1	1	1	-	D/A
179	O(60)a	0.3335(2)	-0.0531(3)	-0.1653(4)	12.563(9)	-1.604(9)	-3.108(8)	1	1	1	-	D/A
180	O(61)a	0.1870(3)	-0.1231(3)	-0.0825(4)	8.672(12)	-3.720(9)	-1.551(8)	1	1	1	-	D/A
181	O(62)a	0.2038(2)	-0.0411(3)	-0.0735(4)	7.828(9)	-1.242(9)	-1.382(8)	1	1	1	-	D/A
182	H(38)a	0.41510	0.02710	0.15350	14.010	0.819	2.886	1	1	1	-	D-H
183	H(39)a	0.49210	0.12860	0.00740	14.926	3.886	0.139	1	1	1	-	D-H
184	H(41)a	0.31930	-0.01790	0.39720	11.453	-0.541	7.468	1	1	1	10.555	D-H
185	H(42)a	0.34910	0.06580	0.01340	11.033	1.988	0.252	1	1	1	-	D-H
186	H(44)a	0.22960	-0.09020	0.15530	9.585	-2.726	2.920	1	1	1	-	D-H
187	H(47)a	0.13590	-0.09960	0.00610	6.479	-3.010	0.115	1	1	1	-	D-H
188	H(48)a	0.37410	-0.03160	0.08540	13.604	-0.955	1.606	1	1	1	-	D-H
189	H(49)a	0.35820	0.02020	-0.10690	12.146	0.610	-2.010	1	1	1	-	D-H
190	H(50)a	0.28860	-0.08010	0.08930	11.467	-2.420	1.679	1	1	1	-	D-H
191	H(51)a	0.27010	-0.04690	-0.11900	10.242	-1.417	-2.237	1	1	1	-	D-H
192	H(52A)a	0.56670	0.13710	0.19400	17.381	4.143	3.648	1	1	1	-	D-H
193	H(52B)a	0.57090	0.18170	0.16290	16.749	5.490	3.063	1	1	1	-	D-H
194	H(53A)a	0.34700	0.12820	0.43160	9.871	3.874	8.115	1	1	1	10.555	D-H
195	H(53B)a	0.39960	0.15510	0.42150	11.237	4.687	7.925	1	1	1	10.555	D-H

Atom	Label	Fractional Coordinates (x,y,z)	Orthogonal Coordinates (XO,YO,ZO)	Site SSN*SSOF =	S.O.F	Move Type
196	H(54A)a	0.07550 -0.18210 0.17460	5.811 -5.502 3.283	1 1 1	-	D-H
197	H(54B)a	0.05970 -0.16050 0.11450	4.883 -4.850 2.153	1 1 1	-	D-H
198	H(55A)a	0.46350 0.07440 -0.11370	14.874 2.248 -2.138	1 1 1	-	D-H
199	H(55B)a	0.48430 0.05100 -0.06700	16.008 1.541 -1.260	1 1 1	-	D-H
200	H(56A)a	0.44860 0.11670 -0.08960	13.616 3.526 -1.685	1 1 1	-	D-H
201	H(56B)a	0.39750 0.08450 -0.10860	12.395 2.553 -2.042	1 1 1	-	D-H
202	H(57A)a	0.30750 -0.13160 0.04900	13.025 -3.976 0.921	1 1 1	-	D-H
203	H(57B)a	0.35150 -0.12240 0.00830	14.400 -3.698 0.156	1 1 1	-	D-H
204	H(58A)a	0.38160 -0.09330 -0.08700	14.942 -2.819 -1.636	1 1 1	-	D-H
205	H(58B)a	0.41270 -0.04890 -0.04370	15.253 -1.478 -0.822	1 1 1	-	D-H
206	H(59A)a	0.31070 -0.14030 -0.09300	13.288 -4.239 -1.749	1 1 1	-	D-H
207	H(59B)a	0.27710 -0.12770 -0.12980	11.896 -3.859 -2.441	1 1 1	-	D-H
208	H(60A)a	0.32850 -0.08090 -0.18660	12.873 -2.445 -3.508	1 1 1	-	D-H
209	H(60B)a	0.36290 -0.02910 -0.17920	13.170 -0.879 -3.369	1 1 1	-	D-H
210	H(61A)a	0.20860 -0.12380 -0.11500	9.438 -3.741 -2.162	1 1 1	-	D-H
211	H(61B)a	0.16740 -0.15290 -0.06390	8.508 -4.620 -1.201	1 1 1	-	D-H
212	H(62A)a	0.20150 -0.01730 -0.05000	7.332 -0.523 -0.940	1 1 1	-	D-H
213	H(62B)a	0.22660 -0.02850 -0.11060	8.403 -0.861 -2.080	1 1 1	-	D-H

***** RESIDUE = 2 *****

Atom	Label	Fractional Coordinates (x,y,z)	Orthogonal Coordinates (XO,YO,ZO)	Site SSN*SSOF =	S.O.F	Move Type
1	S(100)	0.35895(17) 0.42735(18) 1/4	5.069(7) 12.913(5) 4.701	..m 2 1/2	1	-
2	*O(101)	0.3307(6) 0.3941(6) 0.1946(8)	4.663(23) 11.908(18) 3.659(15)	1 1/2	1/2	- D/A
3	*O(102)	0.3848(6) 0.4112(6) 0.2113(8)	6.252(23) 12.425(18) 3.973(15)	1 1/2	1/2	- D/A
4	*O(103)	0.3908(6) 0.4695(6) 0.2142(8)	5.445(23) 14.187(18) 4.027(15)	1 1/2	1/2	- D/A
5	*O(104)	0.3293(6) 0.4359(7) 0.2062(9)	3.885(24) 13.171(21) 3.877(17)	1 1/2	1/2	- D/A
6	*O(101)b	0.3307(6) 0.3941(6) 0.3054(8)	4.663(23) 11.908(18) 5.742(15)	1 1/2	1/2	10.555 D/A
7	*O(102)b	0.3848(6) 0.4112(6) 0.2887(8)	6.252(23) 12.425(18) 5.428(15)	1 1/2	1/2	10.555 D/A
8	*O(103)b	0.3908(6) 0.4695(6) 0.2858(8)	5.445(23) 14.187(18) 5.374(15)	1 1/2	1/2	10.555 D/A
9	*O(104)b	0.3293(6) 0.4359(7) 0.2938(9)	3.885(24) 13.171(21) 5.524(17)	1 1/2	1/2	10.555 D/A

***** RESIDUE = 3 *****

Atom	Label	Fractional Coordinates (x,y,z)	Orthogonal Coordinates (XO,YO,ZO)	Site SSN*SSOF =	S.O.F	Move Type
1	*S(300)	0.2723(2) 0.2875(2) 0.2702(3)	4.485(8) 8.687(6) 5.080(6)	1 1/2	1/2	-
2	O(301)	0.2275(4) 0.2782(4) 1/4	3.084(16) 8.406(12) 4.701	..m 2 1/2	1	- D/A
3	*O(302)	0.2920(6) 0.3236(7) 0.3199(9)	4.543(24) 9.778(21) 6.015(17)	1 1/2	1/2	- D/A
4	*O(303)	0.2723(7) 0.2487(7) 0.3010(8)	5.162(27) 7.515(21) 5.659(15)	1 1/2	1/2	- D/A
5	*O(304)	0.2980(6) 0.2972(7) 0.1993(10)	5.213(24) 8.980(21) 3.747(19)	1 1/2	1/2	- D/A
6	*S(300)d	0.2723(2) 0.2875(2) 0.2298(3)	4.485(8) 8.687(6) 4.321(6)	1 1/2	1/2	10.555 -
7	*O(302)d	0.2920(6) 0.3236(7) 0.1801(9)	4.543(24) 9.778(21) 3.386(17)	1 1/2	1/2	10.555 D/A
8	*O(303)d	0.2723(7) 0.2487(7) 0.1990(8)	5.162(27) 7.515(21) 3.742(15)	1 1/2	1/2	10.555 D/A
9	*O(304)d	0.2980(6) 0.2972(7) 0.3007(10)	5.213(24) 8.980(21) 5.654(19)	1 1/2	1/2	10.555 D/A

=====

RESIDUE = 4 *****

=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site SSN*SSOF =		S.O.F	Move Type	
1	S(200)	0.49240(15)	0.36799(16)	1/4	10.761(6)	11.119(5)	4.701	.m	2 1/2	1	-	-
2	O(201)	0.4476(4)	0.3306(4)	1/4	9.850(16)	9.990(12)	4.701	.m	2 1/2	1	-	D/A
3	O(202)	0.5011(4)	0.3952(4)	0.1892(6)	10.589(16)	11.942(12)	3.557(11)	1	1	1	-	D/A
4	O(203)	0.5231(6)	0.3496(8)	1/4	12.153(25)	10.564(24)	4.701	.m	2 1/2	1	-	D/A
5	O(202)c	0.5011(4)	0.3952(4)	0.3108(6)	10.589(16)	11.942(12)	5.844(11)	1	1	1	10.555	D/A

=====

RESIDUE = 5 *****

=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site SSN*SSOF =		S.O.F	Move Type	
1	N(401)	0.0486(3)	-0.2529(3)	0.0510(5)	6.108(12)	-7.642(9)	0.959(9)	1	1	1	-	D/A

=====

RESIDUE = 6 *****

=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site SSN*SSOF =		S.O.F	Move Type	
1	N(402)	0.2355(5)	0.3676(5)	1/4	1.804(20)	11.108(15)	4.701	.m	2 1/2	1	-	D/A

=====

RESIDUE = 7 *****

=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site SSN*SSOF =		S.O.F	Move Type	
1	N(403)	0.4135(3)	-0.0888(3)	0.0988(5)	15.977(12)	-2.683(9)	1.858(9)	1	1	1	-	D/A

=====

RESIDUE = 8 *****

=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site SSN*SSOF =		S.O.F	Move Type	
1	N(404)	0.3233(3)	-0.1826(3)	-0.0838(6)	14.466(12)	-5.518(9)	-1.576(11)	1	1	1	-	D/A

=====

RESIDUE = 9 *****

=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site SSN*SSOF =		S.O.F	Move Type	
------	-------	--------------------------------	--	--	-----------------------------------	--	--	-----------------	--	-------	-----------	--

```
=====
1 N(405) 0.1804(3) 0.0176(3) -0.0329(6) 5.987(12) 0.532(9) -0.619(11) 1 1 1 - D/A
=====
```

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*****
RESIDUE = 10
*****
```

```
-----
Atom Label Fractional Coordinates (x,y,z) Orthogonal Coordinates (XO,YO,ZO) Site SSN*SSOF = S.O.F Move Type
-----
1 N(406) 0.5318(5) 0.0109(5) 1/4 18.365(20) 0.329(15) 4.701 .m 2 1/2 1 - D/A
-----
```

```
*****
RESIDUE = 11
*****
```

```
-----
Atom Label Fractional Coordinates (x,y,z) Orthogonal Coordinates (XO,YO,ZO) Site SSN*SSOF = S.O.F Move Type
-----
1 N(407) 0.0719(5) -0.0439(5) -0.0820(8) 3.275(20) -1.327(15) -1.542(15) 1 1 1 - D/A
-----
```

```
*****
RESIDUE = 12
*****
```

```
-----
Atom Label Fractional Coordinates (x,y,z) Orthogonal Coordinates (XO,YO,ZO) Site SSN*SSOF = S.O.F Move Type
-----
1 N(408) 0.2584(5) -0.1886(5) 0.0587(8) 12.306(20) -5.699(15) 1.104(15) 1 1 1 - D/A
-----
```

```
*****
RESIDUE = 13
*****
```

```
-----
Atom Label Fractional Coordinates (x,y,z) Orthogonal Coordinates (XO,YO,ZO) Site SSN*SSOF = S.O.F Move Type
-----
1 *N(410) 0.1778(5) -0.0602(5) -0.2136(9) 7.254(20) -1.819(15) -4.016(17) 1 1/2 1/2 - D/A
-----
```

```
*****
RESIDUE = 14
*****
```

```
-----
Atom Label Fractional Coordinates (x,y,z) Orthogonal Coordinates (XO,YO,ZO) Site SSN*SSOF = S.O.F Move Type
-----
1 N(411) 0.6210(7) 0.2364(7) 0.1443(11) 17.543(27) 7.143(21) 2.713(21) 1 1 1 - D/A
-----
```

```
*****
RESIDUE = 15
*****
```

```
-----
Atom Label Fractional Coordinates (x,y,z) Orthogonal Coordinates (XO,YO,ZO) Site SSN*SSOF = S.O.F Move Type
-----
1 N(412) 0.5833(11) 0.2429(11) 1/4 16.114(43) 7.340(33) 4.701 .m 2 1/2 1 - D/A
-----
```

===== RESIDUE = 16 *****
=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site	SSN*SSOF =	S.O.F	Move Type
1	*N(413)	0.0030(8)	-0.1508(8)	0.2105(13)	2.735(31)	-4.557(24)	3.958(24)	1	1/2	1/2	- D/A

===== RESIDUE = 17 *****
=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site	SSN*SSOF =	S.O.F	Move Type
1	N(414)	0.5287(8)	0.1650(8)	-0.0665(14)	15.568(31)	4.986(24)	-1.250(26)	1	1	1	- D/A

===== RESIDUE = 18 *****
=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site	SSN*SSOF =	S.O.F	Move Type
1	N(415)	0.2126(14)	-0.2506(13)	1/4	11.790(54)	-7.572(39)	4.701	.m 2	1/2	1	- D/A

===== RESIDUE = 19 *****
=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site	SSN*SSOF =	S.O.F	Move Type
1	N(416)	-0.027(2)	-0.0760(19)	1/4	0.384(77)	-2.296(57)	4.701	.m 2	1/2	1	- D/A

===== RESIDUE = 20 *****
=====

Atom	Label	Fractional Coordinates (x,y,z)			Orthogonal Coordinates (XO,YO,ZO)			Site	SSN*SSOF =	S.O.F	Move Type
1	N(417)	0.6074(11)	0.1685(11)	-0.0155(18)	18.253(43)	5.091(33)	-0.291(34)	1	1	1	- D/A

NOTE: Atoms preceded by > * or < indicate disordered positions (SOF : < 50%, 50%, > 50%)

DisOrdered Structure					Unit Cell Contents (Based on Contents of Atom List, that may be Incomplete)						
Resd Site	X(cen)	Y(cen)	Z(cen)	Res.Mol.Wt.	Z	H	N	O	S	Zr	
1	.m	0.307	0.010	1/4	3887.42	6	10	110	13	18	$18 \times 4 + 13 \times 6 + 7 \times 0 - 110 \times 2 = 0$
2	.m	0.359	0.428	1/4	96.07	6	-	4	1	-	
3	.m	0.276	0.288	1/4	96.07	6	-	4	1	-	
4	.m	0.493	0.368	1/4	96.07	6	-	4	1	-	
5	1	0.049	-0.253	0.051	14.01	12	-	1	-	-	
6	.m	0.235	0.368	1/4	14.01	6	-	1	-	-	
7	1	0.414	-0.089	0.099	14.01	12	-	1	-	-	
8	1	0.323	-0.183	-0.084	14.01	12	-	1	-	-	
9	1	0.180	0.018	-0.033	14.01	12	-	1	-	-	
10	.m	0.532	0.011	1/4	14.01	6	-	1	-	-	
11	1	0.072	-0.044	-0.082	14.01	12	-	1	-	-	
12	1	0.258	-0.189	0.059	14.01	12	-	1	-	-	
13	1	0.178	-0.060	-0.214	14.01	6	-	1	-	-	
14	1	0.621	0.236	0.144	14.01	12	-	1	-	-	
15	.m	0.583	0.243	1/4	14.01	6	-	1	-	-	
16	1	0.003	-0.151	0.211	14.01	6	-	1	-	-	
17	1	0.529	0.165	-0.067	14.01	12	-	1	-	-	
18	.m	0.213	-0.251	1/4	14.01	6	-	1	-	-	
19	.m	-0.027	-0.076	1/4	14.01	6	-	1	-	-	
20	1	0.607	0.169	-0.015	14.01	12	-	1	-	-	

Unit Cell Weight = 27155.26
 Calculated Analysis (Percent) =
 Moiety_Formula = $H_{10}O_{110}S_{13}Zr_{18}, 3(O_4S), 25(N)$
 Sum_Formula = $H_{58}N_{25}O_{122}S_{16}Zr_{18}$
 Formula_Weight = 4525.88
 Formula_Z = 6
 SpaceGroup_Z = 12 ==> Z' = 6 / 12 = 0.500
 Calculated Density = 2.2748(3) g cm⁻³ [= Mg m⁻³]
 F(000) = 13170.0 [12865.69]
 mu(MoKa) = 17.4 cm⁻¹ = 1.74 mm⁻¹

** WARNING **
 Please Check the Derived Crystal Data.
 They may be Incorrect for Disordered,
 Incomplete or Polymeric Structures.

Note on F000: The first number is a pure electron count, the second number between [] is calculated from f, f' & f''

Asymmetric Residue Unit (= ARU) Code List

ARU-CODE	Symmetry-Code	sym TX TY TZ Ires	x(cen)	y(cen)	z(cen)
a = [10555.01]	= x,y,1/2-z	= [10 0 0 0 1]	0.307	0.010	1/4
b = [10555.02]	= x,y,1/2-z	= [10 0 0 0 2]	0.359	0.428	1/4
c = [10555.04]	= x,y,1/2-z	= [10 0 0 0 4]	0.493	0.368	1/4

=====

d = [10555.03] = x,y,1/2-z = [10 0 0 0 3] 0.276 0.288 1/4

=====

Note: Symmetry Operations Refer to the Coordinates listed in the Fractional Coordinate Table given above

X(J) = X(sym) + TX , Y(J) = Y(sym) + TY , Z(J) = Z(sym) + TZ,

SYM - Number of the Symmetry Operator.
Ires - Residue Number.
TX, TY, TZ - Unit Cell Translations.

=====
(An)isotropic (Oblique/Cartesian), Equivalent and Main Axes Thermal Parameters - Unusual Values Marked with a #
=====*****
Residue = 1 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	Zr(1)	0.0206(7)	0.0250(7)	0.0273(7)	0	0	0.0107(6)	0.0246(4)	0.0206	0.0260	0.0273	1.33
2	Zr(2)	0.0194(7)	0.0190(7)	0.0166(6)	0	0	0.0091(6)	0.0186(4)	0.0166	0.0188	0.0202	1.22
3	Zr(3)	0.0183(7)	0.0212(7)	0.0249(7)	0	0	0.0081(6)	0.0223(4)	0.0180	0.0238	0.0249	1.38
4	Zr(4)	0.0211(5)	0.0339(5)	0.0198(5)	-0.0017(4)	-0.0019(4)	0.0132(4)	0.0252(3)	0.0184	0.0218	0.0354	1.93
5	Zr(5)	0.0212(5)	0.0254(5)	0.0143(4)	0.0011(4)	0.0010(4)	0.0123(4)	0.0200(3)	0.0141	0.0204	0.0255	1.81
6	Zr(6)	0.0209(5)	0.0223(5)	0.0155(4)	0.0009(4)	0.0016(4)	0.0100(4)	0.0199(3)	0.0151	0.0212	0.0235	1.56
7	Zr(7)	0.0219(5)	0.0218(5)	0.0232(5)	0.0030(4)	0.0027(4)	0.0084(4)	0.0234(3)	0.0181	0.0253	0.0269	1.49
8	Zr(8)	0.0248(7)	0.0230(7)	0.0135(6)	0	0	0.0124(6)	0.0202(4)	0.0135	0.0224	0.0248	1.84
9	Zr(9)	0.0265(5)	0.0334(5)	0.0121(4)	0.0004(4)	-0.0006(4)	0.0165(4)	0.0233(3)	0.0120	0.0245	0.0334	2.78
10	Zr(10)	0.0264(5)	0.0366(6)	0.0143(4)	0.0065(4)	0.0036(4)	0.0183(5)	0.0246(3)	0.0125	0.0230	0.0384	3.06
11	Zr(11)	0.0231(5)	0.0312(5)	0.0160(5)	0.0060(4)	0.0042(4)	0.0137(4)	0.0234(3)	0.0135	0.0231	0.0335	2.49
12	S(1)	0.0250(18)	0.0187(17)	0.0151(16)	0	0	0.0092(15)	0.0204(10)	0.0151	0.0187	0.0273	1.81
13	S(2)	0.0228(12)	0.0236(13)	0.0261(13)	-0.0019(10)	0.0036(10)	0.0100(11)	0.0249(7)	0.0202	0.0227	0.0318	1.57
14	S(3)	0.0437(18)	0.0497(19)	0.059(2)	-0.0251(17)	-0.0207(16)	0.0254(16)	0.0499(11)	0.0265	0.0418	0.0813	3.07
15	*S(4A)	0.035(5)	0.028(4)	0.044(5)	-0.002(3)	-0.016(4)	0.015(4)	0.036(3)	0.0222	0.0278	0.0580	2.61
16	*S(4B)	0.021(4)	0.039(5)	0.033(5)	0.000(3)	-0.003(3)	0.012(4)	0.032(3)	0.0201	0.0335	0.0434	2.16
17	S(5)	0.031(2)	0.034(2)	0.0297(19)	0	0	0.0219(18)	0.0291(11)	0.0210	0.0297	0.0365	1.74
18	S(6)	0.030(2)	0.0239(19)	0.040(2)	0	0	0.0151(17)	0.0306(11)	0.0217	0.0300	0.0400	1.84
19	S(7)	0.0361(15)	0.0566(19)	0.0257(14)	0.0080(13)	0.0039(12)	0.0328(15)	0.0352(9)	0.0217	0.0246	0.0593	2.73
20	S(8)	0.0484(18)	0.0314(16)	0.0469(18)	0.0127(14)	-0.0076(15)	0.0139(14)	0.0449(10)	0.0229	0.0411	0.0708	3.10
21	O(1)	0.024(6)	0.022(5)	0.071(8)	0	0	0.011(5)	0.039(4)	0.0220	0.0247	0.0710	3.23
22	O(2)	0.031(5)	0.020(5)	0.022(5)	0	0	0.013(4)	0.024(3)	0.0190	0.0220	0.0317	1.67
23	O(3)	0.040(5)	0.037(4)	0.035(4)	-0.015(4)	0.010(4)	0.003(4)	0.045(3)	0.0206	0.0293	0.0838	4.07
24	O(4)	0.024(4)	0.024(4)	0.030(4)	0.000(3)	0.005(3)	0.012(3)	0.026(2)	0.0205	0.0240	0.0335	1.63
25	O(5)	0.021(4)	0.025(4)	0.031(4)	-0.004(3)	0.000(3)	0.011(3)	0.026(2)	0.0209	0.0231	0.0337	1.61
26	O(6)	0.028(4)	0.022(4)	0.024(4)	-0.001(3)	0.001(3)	0.009(3)	0.026(2)	0.0214	0.0238	0.0335	1.57
27	O(7)	0.028(4)	0.029(4)	0.029(4)	-0.009(3)	0.004(3)	0.012(3)	0.030(2)	0.0175	0.0270	0.0445	2.54
28	O(8)	0.035(4)	0.032(4)	0.055(5)	-0.012(4)	-0.012(4)	0.016(4)	0.041(3)	0.0260	0.0353	0.0617	2.37
29	O(9)	0.028(4)	0.037(4)	0.035(4)	-0.010(3)	-0.008(3)	0.014(3)	0.034(2)	0.0219	0.0349	0.0462	2.11
30	O(10)	0.057(6)	0.055(6)	0.092(8)	-0.043(6)	-0.040(6)	0.034(5)	0.065(4)	0.0251	0.0443	0.1266	5.04
31	O(11)	0.047(6)	0.087(7)	0.063(6)	-0.035(6)	-0.011(5)	0.034(5)	0.065(4)	0.0380	0.0438	0.1146	3.02
32	O(12)	0.025(4)	0.032(4)	0.046(5)	-0.004(4)	-0.006(3)	0.016(3)	0.034(3)	0.0217	0.0311	0.0479	2.20
33	O(13)	0.033(4)	0.039(4)	0.041(5)	0.007(4)	0.011(4)	0.021(4)	0.036(3)	0.0242	0.0347	0.0500	2.06
34	O(14)	0.135(12)	0.187(15)	0.154(13)	-0.117(12)	-0.104(11)	0.140(12)	0.132(8)	0.0327	0.0533	0.3107	9.50#
35	*O(15A)	0.131(19)	0.039(10)	0.037(10)	0.007(8)	-0.029(11)	0.041(12)	0.070(8)	0.0140	0.0449	0.1500	10.69#
36	*O(15B)	0.029(9)	0.046(11)	0.080(14)	-0.014(10)	0.017(9)	-0.001(8)	0.060(7)	0.0213	0.0501	0.1099	5.15#
37	O(16)	0.066(6)	0.077(6)	0.018(4)	-0.003(4)	-0.005(4)	0.061(5)	0.042(3)	0.0163	0.0218	0.0892	5.47#
38	O(17)	0.042(7)	0.038(6)	0.036(6)	0	0	0.025(5)	0.036(4)	0.0296	0.0360	0.0437	1.48
39	O(18)	0.031(7)	0.043(8)	0.184(18)	0	0	0.019(7)	0.086(7)	0.0297	0.0436	0.1840	6.19
40	O(19)	0.075(6)	0.028(4)	0.022(4)	0.007(3)	0.009(4)	0.026(4)	0.042(3)	0.0173	0.0278	0.0796	4.61
41	O(20)	0.043(7)	0.039(6)	0.047(7)	0	0	0.025(6)	0.041(4)	0.0316	0.0444	0.0470	1.49
42	O(21)	0.031(7)	0.029(7)	0.188(18)	0	0	0.016(6)	0.082(7)	0.0276	0.0311	0.1880	6.82
43	O(22)	0.035(4)	0.055(5)	0.029(4)	0.009(4)	0.006(3)	0.032(4)	0.035(3)	0.0215	0.0262	0.0586	2.73
44	O(23)	0.037(4)	0.051(5)	0.022(4)	0.010(3)	0.003(3)	0.028(4)	0.034(3)	0.0180	0.0297	0.0543	3.01
45	O(24)	0.057(5)	0.067(6)	0.030(4)	0.008(4)	0.007(4)	0.048(5)	0.044(3)	0.0273	0.0283	0.0757	2.78

46	O(25)	0.036(4)	0.064(6)	0.036(4)	0.006(4)	-0.003(4)	0.029(4)	0.044(3)	0.0259	0.0389	0.0659	2.54
47	O(26)	0.038(4)	0.026(4)	0.032(4)	0.004(3)	-0.003(3)	0.013(3)	0.033(2)	0.0236	0.0316	0.0448	1.90
48	O(27)	0.034(4)	0.031(4)	0.029(4)	0.004(3)	0.003(3)	0.016(3)	0.031(2)	0.0258	0.0331	0.0354	1.37
49	O(28)	0.048(6)	0.098(8)	0.061(6)	0.054(6)	0.012(5)	0.015(6)	0.079(4)	0.0206	0.0568	0.1583	7.70
50	O(29)	0.130(10)	0.045(6)	0.104(9)	-0.022(6)	-0.055(8)	0.059(7)	0.086(5)	0.0241	0.0605	0.1741	7.23
51	O(30)	0.018(5)	0.021(5)	0.017(5)	0	0	0.007(4)	0.020(3)	0.0170	0.0173	0.0254	1.49
52	O(31)	0.023(5)	0.033(6)	0.027(5)	0	0	0.011(5)	0.029(3)	0.0230	0.0270	0.0370	1.61
53	O(32)	0.020(3)	0.026(4)	0.019(3)	0.001(3)	0.000(3)	0.011(3)	0.0219(19)	0.0188	0.0198	0.0270	1.44
54	O(33)	0.018(5)	0.015(5)	0.026(5)	0	0	0.005(4)	0.021(3)	0.0140	0.0233	0.0260	1.86
55	O(34)	0.020(3)	0.023(3)	0.017(3)	0.000(3)	-0.001(3)	0.011(3)	0.0199(17)	0.0166	0.0200	0.0231	1.39
56	O(35)	0.019(3)	0.023(3)	0.025(4)	0.003(3)	0.003(3)	0.010(3)	0.0226(19)	0.0178	0.0227	0.0272	1.53
57	O(36)	0.017(5)	0.025(5)	0.028(5)	0	0	0.006(4)	0.025(3)	0.0164	0.0280	0.0316	1.92
58	O(37)	0.022(5)	0.037(6)	0.025(5)	0	0	0.018(5)	0.027(3)	0.0176	0.0250	0.0370	2.10
59	O(38)	0.024(4)	0.031(4)	0.016(3)	-0.003(3)	-0.001(3)	0.014(3)	0.024(2)	0.0154	0.0233	0.0320	2.07
60	O(39)	0.024(4)	0.037(4)	0.024(4)	-0.001(3)	-0.004(3)	0.010(3)	0.031(2)	0.0200	0.0276	0.0444	2.22
61	O(40)	0.024(5)	0.024(5)	0.015(4)	0	0	0.016(4)	0.019(3)	0.0150	0.0160	0.0267	1.78
62	O(41)	0.028(4)	0.024(3)	0.017(3)	-0.004(3)	0.001(3)	0.013(3)	0.0230(19)	0.0142	0.0258	0.0290	2.04
63	O(42)	0.033(4)	0.042(4)	0.015(3)	-0.001(3)	0.001(3)	0.025(4)	0.027(2)	0.0146	0.0239	0.0432	2.96
64	O(43)	0.021(5)	0.026(5)	0.019(5)	0	0	0.015(4)	0.021(3)	0.0161	0.0190	0.0265	1.65
65	O(44)	0.028(4)	0.029(4)	0.021(3)	0.004(3)	0.005(3)	0.014(3)	0.026(2)	0.0182	0.0291	0.0310	1.71
66	O(45)	0.026(4)	0.034(4)	0.019(3)	0.002(3)	0.005(3)	0.015(3)	0.026(2)	0.0163	0.0281	0.0347	2.13
67	O(46)	0.031(5)	0.023(5)	0.020(5)	0	0	0.014(4)	0.024(3)	0.0200	0.0220	0.0313	1.57
68	O(47)	0.030(4)	0.033(4)	0.022(4)	0.002(3)	0.005(3)	0.013(3)	0.030(2)	0.0196	0.0314	0.0377	1.93
69	O(48)	0.034(4)	0.040(4)	0.014(3)	0.001(3)	0.002(3)	0.018(4)	0.030(2)	0.0138	0.0340	0.0409	2.96
70	O(49)	0.048(5)	0.043(4)	0.018(4)	0.002(3)	0.009(3)	0.029(4)	0.034(3)	0.0145	0.0342	0.0519	3.57
71	O(50)	0.029(4)	0.046(4)	0.016(3)	0.002(3)	0.004(3)	0.021(4)	0.029(2)	0.0147	0.0270	0.0463	3.15
72	O(51)	0.037(4)	0.059(5)	0.018(4)	-0.002(4)	-0.002(3)	0.029(4)	0.036(3)	0.0178	0.0304	0.0591	3.32
73	O(52)	0.029(4)	0.050(5)	0.039(4)	-0.003(4)	-0.001(4)	0.021(4)	0.039(3)	0.0264	0.0383	0.0516	1.95
74	O(53)	0.027(4)	0.032(4)	0.025(4)	0.005(3)	-0.001(3)	0.014(3)	0.028(2)	0.0213	0.0272	0.0365	1.72
75	O(54)	0.029(4)	0.028(4)	0.049(5)	0.007(4)	0.008(4)	0.010(3)	0.037(3)	0.0228	0.0369	0.0519	2.28
76	O(55)	0.059(5)	0.067(6)	0.024(4)	-0.008(4)	-0.015(4)	0.043(5)	0.045(3)	0.0176	0.0426	0.0744	4.22
77	O(56)	0.047(5)	0.044(5)	0.022(4)	-0.004(3)	-0.005(3)	0.025(4)	0.037(3)	0.0209	0.0405	0.0485	2.32
78	O(57)	0.051(5)	0.040(4)	0.032(4)	0.002(4)	-0.004(4)	0.028(4)	0.039(3)	0.0269	0.0371	0.0520	1.94
79	O(58)	0.036(4)	0.052(5)	0.031(4)	0.010(4)	0.007(3)	0.027(4)	0.037(3)	0.0261	0.0301	0.0561	2.15
80	O(59)	0.043(5)	0.053(5)	0.032(4)	0.011(4)	0.009(4)	0.028(4)	0.041(3)	0.0264	0.0380	0.0582	2.20
81	O(60)	0.035(4)	0.054(5)	0.024(4)	0.008(4)	0.004(3)	0.023(4)	0.037(3)	0.0219	0.0332	0.0569	2.60
82	O(61)	0.041(5)	0.045(5)	0.029(4)	0.009(4)	0.005(4)	0.020(4)	0.039(3)	0.0248	0.0423	0.0499	2.01
83	O(62)	0.035(4)	0.046(5)	0.022(4)	0.001(3)	0.003(3)	0.019(4)	0.035(3)	0.0213	0.0355	0.0479	2.25
84	H(31)	0.0350						0.0350				
85	H(36)	0.0300						0.0300				
86	H(37)	0.0320						0.0320				
87	H(38)	0.0280						0.0280				
88	H(39)	0.0370						0.0370				
89	H(41)	0.0270						0.0270				
90	H(42)	0.0330						0.0330				
91	H(44)	0.0310						0.0310				
92	H(46)	0.0290						0.0290				
93	H(47)	0.0360						0.0360				
94	H(48)	0.0350						0.0350				
95	H(49)	0.0400						0.0400				
96	H(50)	0.0350						0.0350				
97	H(51)	0.0430						0.0430				
98	H(52A)	0.0580						0.0580				
99	H(52B)	0.0580						0.0580				
100	H(53A)	0.0430						0.0430				
101	H(53B)	0.0430						0.0430				
102	H(54A)	0.0560						0.0560				

103	H(54B)	0.0560	0.0560
104	H(55A)	0.0670	0.0670
105	H(55B)	0.0670	0.0670
106	H(56A)	0.0550	0.0550
107	H(56B)	0.0550	0.0550
108	H(57A)	0.0580	0.0580
109	H(57B)	0.0580	0.0580
110	H(58A)	0.0560	0.0560
111	H(58B)	0.0560	0.0560
112	H(59A)	0.0610	0.0610
113	H(59B)	0.0610	0.0610
114	H(60A)	0.0550	0.0550
115	H(60B)	0.0550	0.0550
116	H(61A)	0.0580	0.0580
117	H(61B)	0.0580	0.0580
118	H(62A)	0.0530	0.0530
119	H(62B)	0.0530	0.0530

Residue = 2 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	S(100)	0.053(3)	0.065(3)	0.034(2)	0	0	0.027(3)	0.0518(16)	0.0340	0.0530	0.0684	2.01
2	*O(101)	0.060(12)	0.078(13)	0.025(8)	-0.005(9)	-0.014(8)	0.034(11)	0.055(6)	0.0199	0.0640	0.0798	4.02
3	*O(102)	0.062(12)	0.055(11)	0.036(9)	-0.010(8)	0.012(8)	0.031(10)	0.050(6)	0.0215	0.0583	0.0709	3.30
4	*O(103)	0.061(12)	0.056(11)	0.030(9)	0.008(8)	0.004(8)	0.002(10)	0.061(6)	0.0263	0.0438	0.1133	4.32
5	*O(104)	0.056(11)	0.103(16)	0.034(10)	-0.018(10)	-0.019(8)	0.054(12)	0.058(7)	0.0220	0.0441	0.1079	4.90

Residue = 3 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	*S(300)	0.037(3)	0.044(3)	0.037(5)	0.005(2)	0.005(2)	0.021(3)	0.039(2)	0.0320	0.0384	0.0466	1.46
2	O(301)	0.021(6)	0.037(8)	0.049(8)	0	0	0.011(6)	0.037(4)	0.0210	0.0417	0.0490	2.34
3	*O(302)	0.036(10)	0.048(9)	0.024(8)	-0.009(7)	-0.007(7)	0.027(9)	0.033(5)	0.0206	0.0277	0.0517	2.51
4	*O(303)	0.055(12)	0.055(9)	0.011(8)	-0.006(7)	-0.003(7)	0.038(10)	0.036(6)	0.0101	0.0344	0.0625	6.19
5	*O(304)	0.025(9)	0.057(13)	0.023(8)	-0.004(7)	0.010(7)	0.014(10)	0.038(6)	0.0124	0.0332	0.0681	5.48

Residue = 4 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
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1	S(200)	0.038(2)	0.050(3)	0.029(2)	0	0	0.008(2)	0.0452(14)	0.0290	0.0334	0.0732	2.53
2	O(201)	0.035(5)	0.040(6)	0.040(6)	0	0	0.010(5)	0.042(3)	0.0313	0.0400	0.0554	1.77
3	O(202)	0.078(8)	0.111(9)	0.074(8)	0.050(7)	-0.043(7)	-0.033(6)	0.123(5)	0.0327	0.0415	0.2957	9.03#
4	O(203)	0.064(10)	0.15(2)	0.29(3)	0	0	0.068(13)	0.162(12)	0.0441	0.1506	0.2900	6.58#

Residue = 5 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(401)	0.035(2)						0.035(2)				

Residue = 6 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(402)	0.041(3)						0.041(3)				

Residue = 7 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(403)	0.042(2)						0.042(2)				

Residue = 8 *****

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(404)	0.047(3)						0.047(3)				

=====

Residue = 9 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(405)	0.048(3)						0.048(3)				

Residue = 10 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(406)	0.050(4)						0.050(4)				

Residue = 11 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(407)	0.083(4)						0.083(4)				

Residue = 12 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(408)	0.091(5)						0.091(5)				

Residue = 13 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	*N(410)	0.029(4)						0.029(4)				

=====

Residue = 14 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(411)	0.130(7)						0.130(7)				

Residue = 15 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(412)	0.148(11)						0.148(11)				

Residue = 16 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	*N(413)	0.066(7)						0.066(7)				

Residue = 17 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(414)	0.165(9)						0.165(9)				

Residue = 18 *****
=====

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(415)	0.197(16)						0.197(16)				

Residue = 19

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(416)	0.30(3)						0.30(3)				

Residue = 20

Atom	Label	U11 or Uiso	U22	U33	U23	U13	U12	Ueq(sUeq)	U1	U2	U3	U3/U1
1	N(417)	0.240(14)						0.240(14)				

=====
The Temperature Factor has the Form of $\text{Exp}(-T)$

where

$T = 8 * (\pi^2) * U_{iso} * \sin(\theta / \lambda)^2$, for Isotropic Atoms,

$T = 2 * (\pi^2) * (U_{11} * (h^2 a^2) + U_{22} * (k^2 b^2) + U_{33} * (l^2 c^2) + 2 * U_{23} * k * l * b * c + 2 * U_{13} * h * l * a * c + 2 * U_{12} * h * k * a * b)$, for Anisotr. Atoms

$U_{eq} = 1/3 \text{ Sum}(i,j) (U_{ij} * a(i) * a(j) * a(i) . a(j))$

U1, U2, U3 are the three Main Axes Components of U_{ij}

Reference U_{eq} : R.X. Fischer & E. Tillmanns, Acta Cryst. (1988). C44, 775-776

U_{eq} [or U_{iso}] Averages per Element

	Non-H	H	N	O	S	Zr
Average	0.0490	0.0475	0.1070	0.0425	0.0366	0.0223
Minimum	0.0186	0.0270	0.0290	0.0190	0.0204	0.0186
Maximum	0.3000	0.0670	0.3000	0.1620	0.0518	0.0252
Ratio	9.9999	2.4815	9.9999	8.5263	2.5392	1.3548
Number	113	36	16	74	12	11

Appendix C

X-ray and Spectroscopic Data of Phosphates

XRD Patterns of Sodium Phosphates

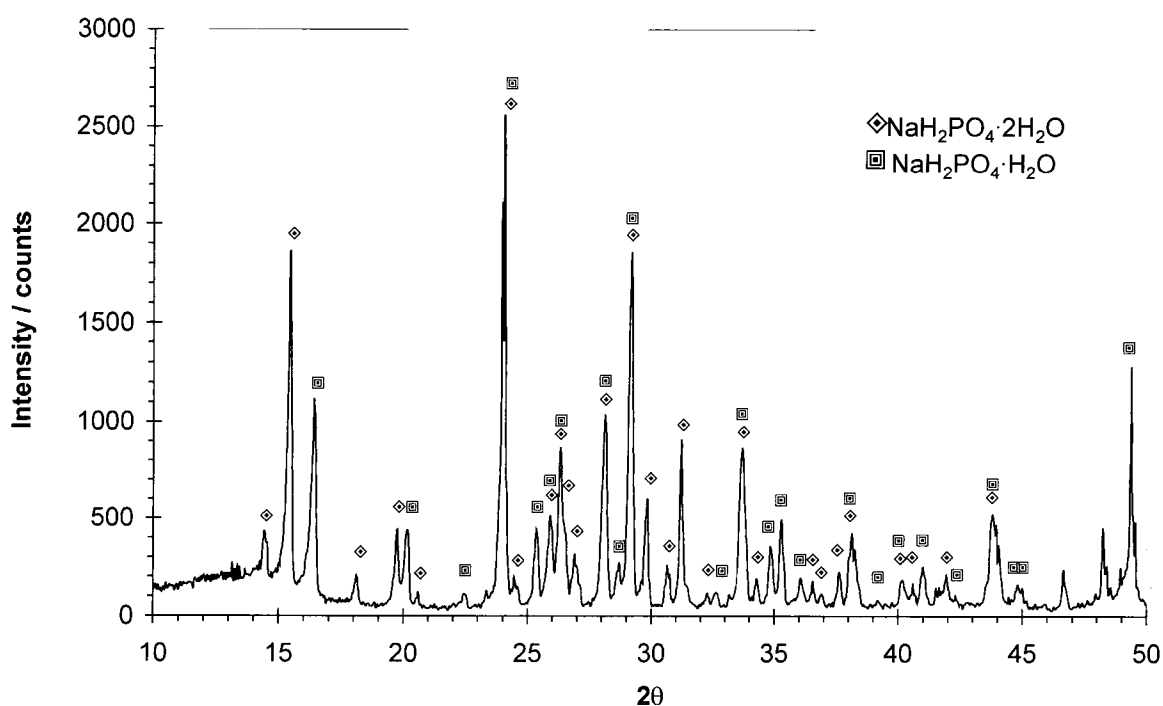


Figure C1 XRD spectra of sodium dihydrogen phosphate dihydrate at room temperature.

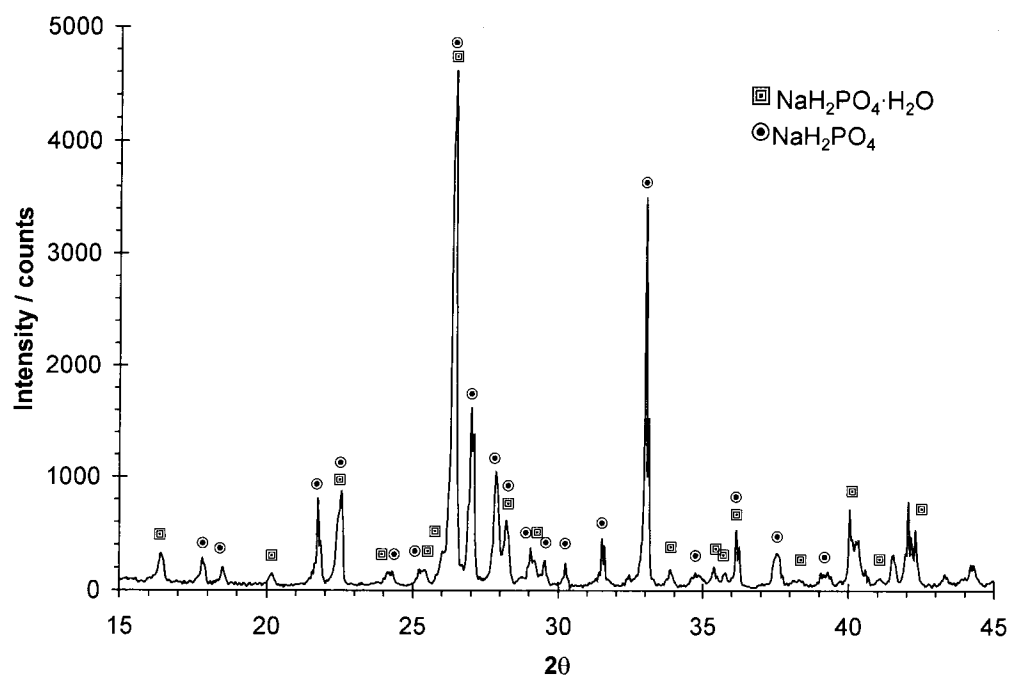


Figure C2 XRD spectra of sodium dihydrogen phosphate dihydrate dehydrated at 60°C overnight.

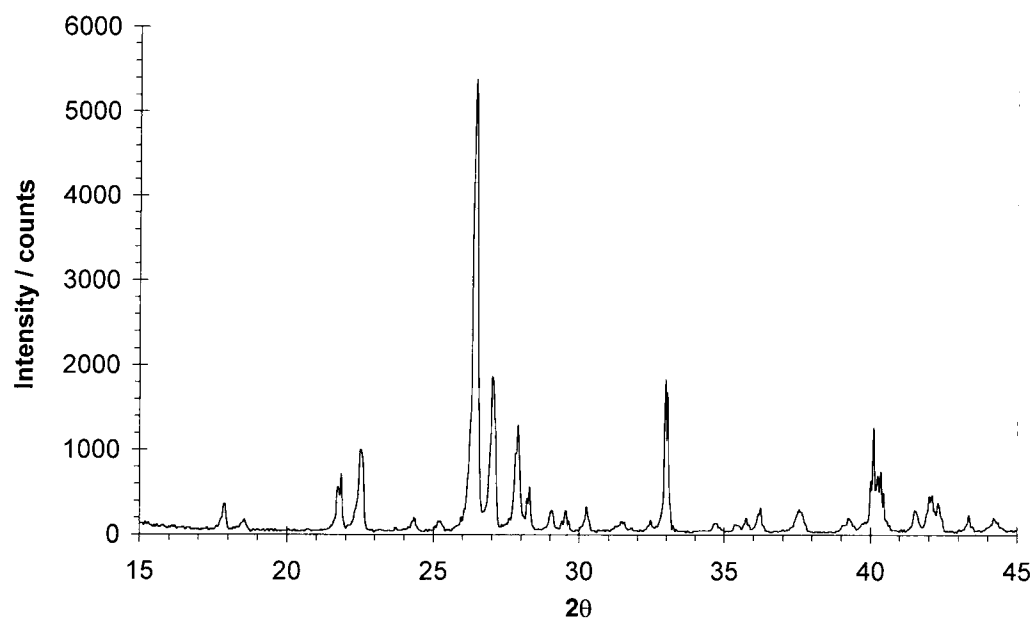


Figure C3 XRD spectra of sodium dihydrogen phosphate dehydrated at 180°C for 3h.

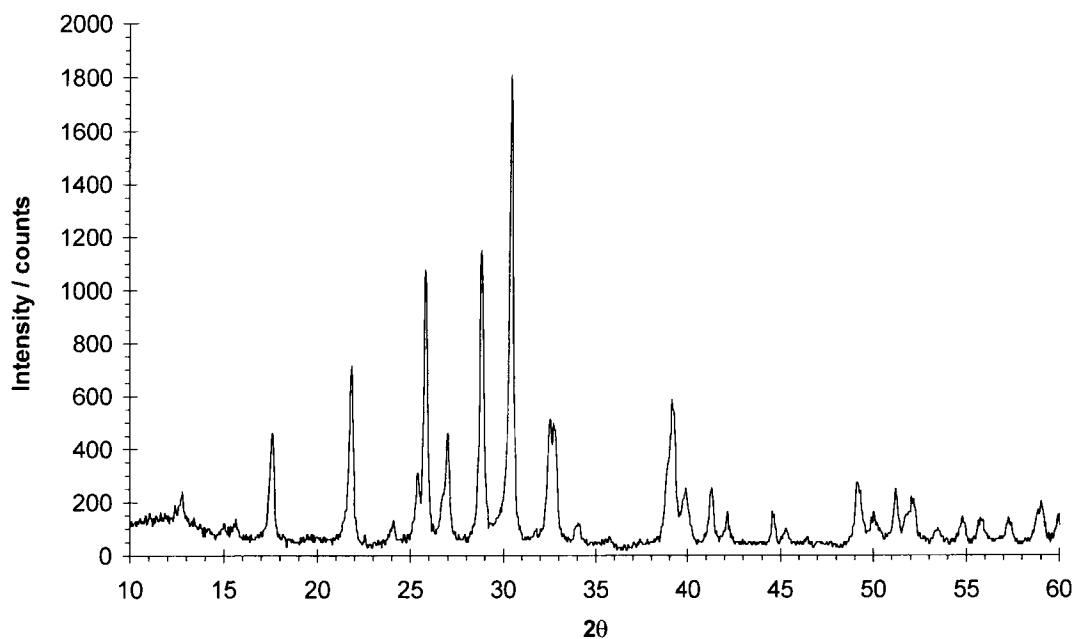


Figure C4 XRD spectra of sodium dihydrogen pyrophosphate dehydrated at 230°C for 3h.

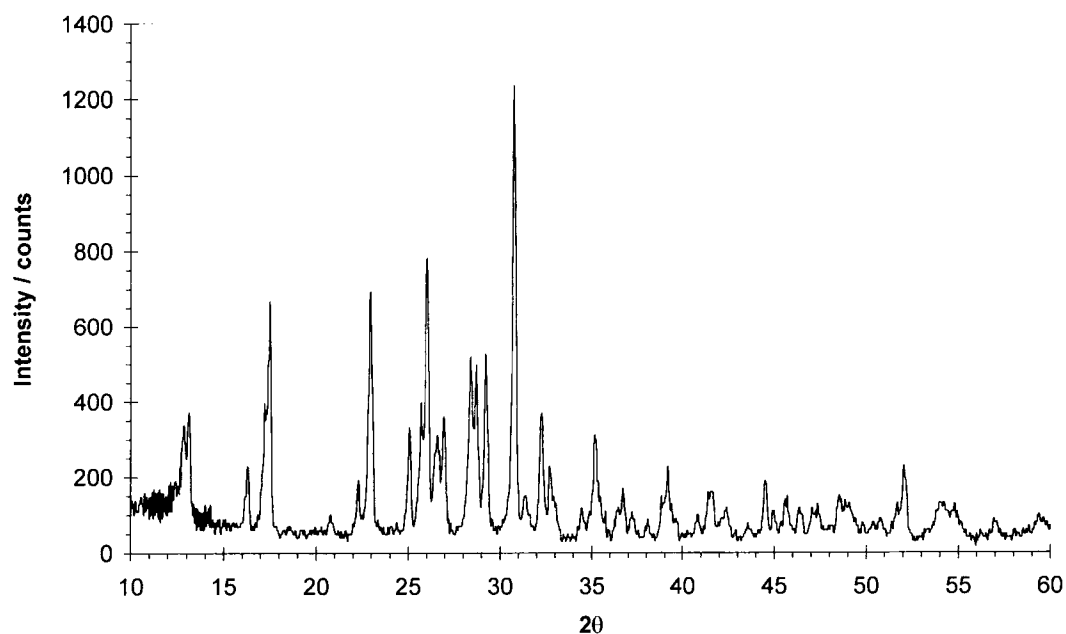


Figure C5 XRD spectra of sodium metaphosphate dehydrated at 400°C for 3h.

Band Positions in the Raman Spectra of Sodium Phosphates

Table C1 Band Positions in the Raman Spectra of KH_2PO_4 between 300 and 2000 cm^{-1} at room temperature

Figure 5.5A crystal		Figure 5.5B solution	
ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity
359	w	390	m
390	m	525	m
468	w		
528	w		
914	vs	879	vs
		939	vw
		1073	vs
		1151	w
1320	vw	1643	m

vs=very strong, m=medium, w=weak, vw=very weak

Table C2 Band Positions in the Raman Spectra of KH_2PO_4 between 300 and 1400 cm^{-1} at room temperature

Figure 5.7A 230°C		Figure 5.7B 360°C	
ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity
		284	m
		393	m
		425	vw
		499	w
		553	vw
		603	vw
705	m	678	m
914	vs		
1120	w	1149	vs
		1255	w
		1302	w

vs=very strong, m=medium, w=weak, vw=very weak

Table C5 Band Positions in the Raman Spectra of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ between 300 and 4000 cm^{-1}

Figure 5.14

Figure 5.15

$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

ν/cm^{-1}	Intensity
383	m
422	vw
525	m
912	vs
977	vs
1060	vw
1174	m
3451	m
3524	m

vs=very strong, m=medium, vw=very weak

Table C6 Band Positions in the Raman Spectra of NaH_2PO_4 and NaD_2PO_4 between 300 and 1400 cm^{-1}

Figure 5.17A

NaH_2PO_4

ν/cm^{-1}	Intensity
365	m
426	m
504	w
530	w
546	w
557	w
874	vs
924	vs
1004	s
1075	w
1177	w
1300	vw

Figure 5.17B

NaD_2PO_4

ν/cm^{-1}	Intensity
354	m
416	m
491	w
526	w
544	w
857	s
903	s
932	vw
1022	s
1075	vw
1198	w

vs=very strong, s=strong, m=medium, w=weak, vw=very weak

Table C7 Band Positions in the Raman Spectra of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and $\text{Na}_2\text{D}_2\text{P}_2\text{O}_7$ between 300 and 1400 cm^{-1}

Figure 5.18A

$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$

ν/cm^{-1}	Intensity
301	vw
359	vw
416	vw
458	vw
475	vw
737	vs
1023	s
1115	vw
1160	vw
1205	vw

Figure 5.18B

$\text{Na}_2\text{D}_2\text{P}_2\text{O}_7$

ν/cm^{-1}	Intensity
320	w
360	vw
386	vw
405	vw
450	vw
483	vw
534	vw
715	vs
800	w
955	w
992	w
1065	s
1110	m
1173	w
1227	vw

vs=very strong, s=strong, m=medium, w=weak, vw=very weak

Table C8 Band Positions in the Raman Spectra of NaPO_3 between 300 and 1400 cm^{-1}

Figure 5.20A from NaH_2PO_4		Figure 5.20B from NaD_2PO_4	
ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity
280	vw	275	vw
332	w	314	w
389	m	381	w
428	w	421	vw
475	w	467	vw
538	vw		
602	vw		
694	s	690	s
741	m	738	w
1092	m	1088	w
1151	vs	1148	vs
1262	m	1258	w
1286	m	1283	w

vs=very strong, s=strong, m=medium, w=weak, vw=very weak

Table C9 Band Positions in the Raman Spectra of a $(\text{NH}_4)\text{H}_2\text{PO}_4/\text{KH}_2\text{PO}_4$ mixture between 200 and 2000 cm^{-1}

Figure 5.24A 22°C		Figure 5.24B 350°C	
ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity
		245	w
		294	vw
358	w	323	vw
392	w	368	vw
475	w	490	vw
530	w		
		700	s
916	vs	878	m
		1155	s
		1250	w
1660	m		

vs=very strong, s=strong, m=medium, w=weak, vw=very weak

Table C10 Band Positions in the Infrared Spectra of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ between 200 and 4000 cm^{-1} after heating

Figure 5.24B

22°C		65°C		170°C	
ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity
				865	m
955	m	945	w	930	s
				990	m
1075	m	1075	w	1055	m
				1125	m
1150	m	1155	w	1170	m
1250	m				
1280	m			1300	s
1650	m	1630	s		
3450	vs	3450	vs		
3570	m				

vs=very strong, s=strong, m=medium, w=weak

APPENDIX D

Spectroscopic Data and Random Hydrolysis of Sodium Phosphates

Band Positions in the Raman Spectra of Sodium Phosphates solutions

Table D1 NaH_2PO_4 in water

Figure 6.2

ν/cm^{-1}	Intensity
804	w
891	vs
1075	w
1170	m

vs=very strong, m=medium, w=weak

Table D2 Sodium Polyphosphate glass

Figure 6.3

Dissolved in water		glass	
ν/cm^{-1}	Intensity	ν/cm^{-1}	Intensity
690	s	682	s
1151	vs	1164	vs
1246	w	1268	w

vs=very strong, s=strong, w=weak

Simulation of Random Hydrolysis of a Polyphosphate in Solution

Hydrolysis can be simulated by a computer program written in PASCAL. In this program the rate of hydrolysis is constant and fit to the initial experimental values. The corresponding production of orthophosphoric acid is then calculated.

CONC is the concentration of phosphate units and since the average length of a polyphosphate is 85 (variable L), the number of polymers in solution is CONC/L .

k is the reaction rate which is taken as a constant. It means that one mol of bonds are broken after a time interval $1/k$. A factor of $1 \cdot 10^{-5}$ is therefore introduced to shorten this interval making calculations more accurate.

It is possible to distribute the chains in an array (named PP) because each polyphosphate string contains a discrete number of units. The number in brackets (Li) represents the length of the polymer. It's value (PP[Li]) is the number of chains with length Li.

TOTALPOP represents the number of total P-O-P bonds and TOTALP the total of phosphate units.

The program gives the user an option to choose between a monodisperse and a polydisperse distribution. In the former just the polyphosphate concentration is put in the array element of PP with Li as the number of the average polymer length. All other elements are set to zero. Eqn. 16 is used for the polydisperse distribution with SIGMA set to 20 as default. SIGMA can be changed in the declaration part of the program.

In the procedure SELECT_POLYMER a weighed chance is applied to select a certain polymer. Procedure CUT selects a bond in the selected polymer on a random basis. It cuts the polymer and re-establishes the distribution of polymers.

The program just stores time, concentration of orthophosphoric acid and the total of P-O-P bonds. The latter is multiplied by the interval factor $1 \cdot 10^{-5}$. Furthermore it is also multiplied by a calibration factor (CAL) to fit to the experimental values. This is already done in the declaration of constants.

PROGRAM HYDROLYSIS;

USES CRT;

CONST k = 0.048;
 dt = 1/k*1E-5;
 CAL = 1.11;
 CONC = 1E5*CAL;
 L = 85;
 No = CONC / L;
 SIGMA= 20;

VAR Hydrol : text;
 CHOICE1 : char;
 PP : array[1..150] of longint;
 t : real;
 Li, SELECTED_PP : integer;
 TOTALPOP, TOTALP, TOTAL, CHOICE, X : longint;
 STOP : boolean;

PROCEDURE INITIATION;

begin
 t := 0;
 TOTALPOP := 0;
 TOTALP := 0;
 STOP := False;
 CHOICE1 := '0';
end;

PROCEDURE MONODISPERSE;

begin
 For Li := 1 TO 150 do PP[Li] := 0;
 PP[L] := round(No);
end;

PROCEDURE POLYDISPERSE;

begin
 For Li := 1 TO 150 do
 PP[Li] := Round(No/(SIGMA*sqrt(2*PI))*exp(-0.5*sqr((Li-L)/SIGMA)));
 end;

PROCEDURE DISPERSITY;

begin

```
writeln; writeln; writeln;
writeln('Modelling Random Hydrolysis of a polyphosphate solution');
writeln; writeln; writeln;
writeln('1) Monodisperse distribution');
writeln('2) Polydisperse distribution'); writeln; writeln; writeln;
repeat CHOICE1 := readkey until (CHOICE1 in ['1','2']);
if CHOICE1 = '1' then MONODISPERSE else POLYDISPERSE;
writeln('1) Show Process on Screen');
writeln('2) Do not Show Process on Screen'); writeln;
repeat CHOICE1 := readkey until (CHOICE1 in ['1','2']);
if (CHOICE1 = '2') then writeln ('Calculation in Progress');
```

end;

PROCEDURE SETTING;

begin

```
for Li := 1 to 150 do
begin
TOTALPOP := TOTALPOP + PP[Li] * (Li-1);
TOTALP := TOTALP + PP[Li] * Li;
```

end;

end;

PROCEDURE SHOW;

begin

```
CLRSCR;
for Li := 1 to 150 do
begin
Write('PP[',Li:3,']= ',PP[Li]:6,' ':6);
if Li=75 then begin Readln; CLRSCR end;
end;
readln;
```

end;

```
PROCEDURE SELECT_POLYMER;
```

```
begin
    TOTAL    := 0;
    Li       := 0;
    CHOICE   := round(random*(TOTALP-PP[1]))+PP[1];
    if (CHOICE = PP[1]) then CHOICE := TOTALP;
    if (TOTALP > PP[1]) then
        begin
            while CHOICE > TOTAL do
                begin
                    Li := Li + 1;
                    TOTAL := TOTAL + PP[Li] * Li;
                end;
            SELECTED_PP := Li;
        end
    else STOP := true;
end;
```

```
PROCEDURE CUT;
```

```
Var PART1, PART2 : integer;
begin
    PART1 := random(SELECTED_PP-1)+1;
    PART2 := SELECTED_PP - PART1;
    PP[PART1] := PP[PART1] + 1;
    PP[PART2] := PP[PART2] + 1;
    PP[SELECTED_PP] := PP[SELECTED_PP] - 1;
    if PP[1] = TOTALP then STOP := true;
end;
```

```
PROCEDURE STORAGE;
```

```
begin
    TOTALPOP := 0;
    for Li := 2 to 150 do TOTALPOP := TOTALPOP + PP[Li] * (Li-1);
    writeln(HYDROL,t,' ',PP[1]*1E-5,' ',TOTALPOP*1E-5);
end;
```

```
BEGIN      {Main Program}
  CLRSCR;
  Randomize;
  INITIATION;
  DISPERSITY;
  SETTING;
  assign (HYDROL,'HYDR.dat');
  rewrite (HYDROL);
  if (CHOICE1 = '1') then SHOW;
  STORAGE;
  repeat
    t := t + dt;
    X := X + 1;
    SELECT_POLYMER;
    CUT;
    If (X mod 500 = 0) then
      begin
        if (CHOICE1 = '1') and (X mod 5000 =0) then SHOW;
        STORAGE;
      end;
  until STOP;
  if (CHOICE1 = '1') then SHOW;
  STORAGE;
  writeln('End');
  close(HYDROL);
  readln;
END.
```