Solid state chemistry of the spin transition polymers 
[Fe(Htrz)$_3$](ClO$_4$)$_2$ and [Fe(NH$_2$trz)$_3$](ClO$_4$)$_2$

by
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Ekserp

Spin-oorgang verbindings ondergaan 'n oorgang tussen 'n diamagnetiese lae-spin toestand en 'n paramagnetiese hoë-spin toestand. Hierdie verbindings het moontlike toepassings in optiese skakeling, inligting stoor en vertoon, sowel as in temperatuur en druk sensors.

Die doelwit van hierdie projek was om inligting te kry oor die strukturele veranderinge wat plaasvind tydens spin-oorgang in lae-kristallynie, spin-oorgang polimere. Infrarooi spektroskopie het getoon dat die Fe-N bindings in die oktaëdries Fe-N₆ koördinasiesfeer almal verswak tydens die lae-spin na hoë-spin oorgang, maar dat twee van die verbindinge tot 'n mindere mate verswak as die ander vier.

Raman spektroskopie het getoon dat 'n moontlike verandering in die koördinasiesfeer simmetrie, tydens die oorgang, daartoe lei dat die Fe-N strekkingsvibrasie onaktief raak. Verder kan die afnemende intensiteit van die Raman band gebruik word om 'n oorgangsfunksie kurwe op te stel.

X-straal poeierdiffraksië het 'n metode uitgelig om die kristallyniteit van die spin-oorgang polimeer [Fe(Htrz)₃](ClO₄)₂ te verbeter en uit die analise van die poeier patroon is 'n seloplossing met monokliene simmetrie verkry.
Abstract

Spin-transition compounds exhibit a transition between a diamagnetic low-spin state and a paramagnetic high-spin state. These compounds have potential applications in optical switching, information storage and display, as well as in temperature and pressure sensors.

This project was aimed at obtaining information on structural changes that occur during spin-transition in poorly crystalline spin-transition polymers. Infrared spectroscopy showed that the Fe-N bonds in the octahedral Fe-N₆ coordination sphere all weaken during the low-spin to high-spin transition, with two bonds weakening to a lesser degree than the other four.

Raman spectroscopy showed that a possible change in the coordination sphere symmetry, during transition, leads to the Fe-N stretching vibration becoming inactive and that the decreasing intensity of the Raman band can be used to derive a transition function curve.

X-ray powder diffraction showed a method to increase the crystallinity of the spin-transition polymer [Fe(Htrz)₃](ClO₄)₂ and analysis of the powder pattern gave a cell solution with monoclinic symmetry.
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List of Related Achievements

Publications

Infrared Spectroscopy

Raman Spectroscopy
3. “Low-Frequency Raman Spectra Of The Spin-Transition Complexes [Fe(NH2trz)3](ClO4)2 And [Fe(Htrz)3](ClO4)2”, E. Smit, B. Manoun and D. De Waal, Journal of Raman Spectroscopy, accepted for publication.

X-ray Powder Diffraction
4. “Improvement of X-ray powder diffraction patterns of the spin transition polymer [Fe(Htrz)3](ClO4)2”, E. Smit, B. Manoun, S. M. C. Verryn and D. de Waal, Powder Diffraction, accepted for publication.

Poster Presentations
1. “Pressure-dependent FTIR of [Fe(Htrz)3](ClO4)2”, A.E. Smit, D. De Waal and A. M. Heyns, 12th International Conference in Fourier Transform Spectroscopy, Tokio, Japan.
3. “Improvement of X-ray powder diffraction patterns of the spin-transition polymer [Fe(Htrz)3](ClO4)2”, E. Smit, B. Manoun, S. M. C. Verryn and D. De Waal, SACI 2000,
Oral Presentation

1. “Pressure-dependent FTIR of [Fe(Htrz)₃](ClO₄)₂”, SACI Young Spectroscopists Symposium, 1999.
Chapter 1 – General Introduction

"Science and Technology (S and T) are recognised by both developed and developing countries as critical ingredients for socio-economic development. It seems that to survive in modern society all members of the public must possess some understanding of science and technology. As the developed world enters the information age, developing countries, no less the Southern African sub-region cannot remain a perpetual onlooker. The verdict pronounced on any community that does not give due attention to science and technology can be summed up in three words: backwardness, obsolescence and oblivion!"

These strong words, from reference [1], can not, in all fairness, be applied to the academic research departments in South Africa. The Current Reality of SET (Science, Engineering and Technology) in South Africa, as taken from South Africa’s Green Paper on Science and Technology (1996)[2], shows that our output of scientific publications amounts to 50% of the sub-Saharan total. These however, have shown a slow but steady decline in the past few years, and are mainly concentrated in plant and animal science, geosciences, ecology and environmental science.

We are lagging behind in many high-technology fields that are quickly becoming the basic building blocks of the global village of tomorrow. One obvious example is the field of solid-state electronics i.e. the heart of computers. It is often difficult if not impossible to “reinvent the wheel” when taking financial and/or legislative aspects into consideration, but it seems that we have started to depend on countries like Germany, the USA and Japan to generate most, if not all, of the new technologies that we use. By avoiding such fields of research, we are becoming slaves to the creators of the technologies on which we depend. This kind of attitude is not only detrimental to the growth of SET in our country, but actually limits the progress of all humankind!
In our approach to research, as a developing country, it is important to realise that it is impossible to compete with the creators of today's high technologies. We should rather be predicting what the technologies of tomorrow will be, and start developing them today. Successful technologies are those that solve problems efficiently and many of tomorrow's problems can be deduced by observing current trends. One instance of a current trend, and the problems that arise from this, serves as an example:

The world population is growing at an alarming rate; this is the current trend.

Problems that can easily be deduced from this are shortages of food, housing, employment etc. By identifying such problems, we can start working toward solutions to alleviate, or even eliminate the impact that they will have on tomorrow's society.

There are thousands of observable trends, and millions of possible solutions to the problems related to them. The sensible choice is to identify a foreseeable trend-related problem that will, in the near future, have a marked effect on life in South Africa. This effect can be social, economic, or even environmental. Once such a problem has been identified, possible solutions can be suggested and research can begin.

The whole world, including South Africa, is moving into the Information Age. One of the current trends emanating from the Information Age is a rapid increase in the volume of information. We, along with the rest of the world, are faced with numerous problems in this regard:

- Increased computing power is required to manipulate the information.
- Huge volumes of information must be stored and retrieved fast, accurately, and without omissions.
- Large numbers of computers, that become redundant due to technological demand surpassing their ability, need to be recycled.
New technologies need to be developed to solve some of these problems. Developing new technologies often require new materials that make them possible. One group of materials, which has been identified for application in optical computing, information storage and information display, is spin-transition polymers.

In the last forty years the bit length (physical length of one binary digit in passive information storage devices) has decreased from
- 250 μm (the first hard disk from IBM in 1950) to
- 1 μm in audio compact disks and even
- 0.6 μm (through the use of frequency doubling techniques).

To further increase the achievable capacity, there is a crucial need for new materials. Spin-transition polymers offer many interesting capabilities and one of these is very small bit size. The predicted storage density limit for optical writing is 100 bits/μm². Conservative estimates of the potential storage density with spin-transition polymers gives a staggering 22 500 bits/μm²! In other words, if an ordinary data compact disk has a capacity of ±600 megabytes, the spin-transition polymer analogue of similar size will have a capacity of ±132 gigabytes. Another way of putting it would be to say that one spin-transition polymer disk could contain data that would require approximately 220 compact disks for storage!

It is obvious that spin-transition polymers have the potential to be a very important group of materials in the near future. Since research on spin-transition polymers is still in its infancy, it is possible and in fact imperative that we start research in this field, or face the possibility of once more falling out of the race.

The aim of this research project was
- to study/review the existing knowledge on spin-transition;
- to identify unknowns or inconclusive theories about spin-transition polymers;
to investigate one or more of these unknowns in order to obtain a better understanding of spin-transition materials in general and polymeric spin-transition compounds in particular, and

• to add to the pool of knowledge on the subject.

From the study/review of spin-transition (Chapter 2) the two spin-transition polymers \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) and \([\text{Fe(NH}_2\text{trz)}_3](\text{ClO}_4)_2\) were identified as good subjects for further investigation. It was determined that more information was needed on the structures of these compounds and on the changes that occur in the structures during spin-transition.

For reasons to be discussed in Chapter 2, three studies were undertaken (Infrared, Raman, and X-ray powder diffraction). The experimental details and special considerations of the three studies are given in Chapter 3. The results obtained from the Infrared, Raman, and X-ray powder diffraction studies are given and discussed in Chapters 4, 5, and 6 respectively.

The conclusions that were drawn from the three studies, together with suggested applications and procedures that could be derived therefrom, are given in Chapter 7.
Chapter 2 – Spin-transition uncovered

2.1 The Spin-Transition Phenomenon

Certain $3d^n$ ($4 \leq n \leq 7$) transition metal compounds, with octahedral ligand-field symmetry, show a transition between a diamagnetic low-spin state and a paramagnetic high-spin state. This is known as spin-transition, also sometimes referred to as spin crossover, magnetic crossover, spin equilibrium or spin isomerism. The transition can be brought about by a change in temperature ($\Delta T$), a change in pressure ($\Delta P$), or by irradiation ($h\nu$). The transition is often accompanied by a pronounced change in the colour of the compound: from purple in the low-spin state to white in the high-spin state. The phenomenon is observed in the solid state as well as in solution.

A substantial amount of research has been done on spin-transition compounds involving Fe$^{2+}$ with the $3d^6$ configuration. In octahedral symmetry the orbital degeneracy is lowered and the 3d metal orbitals are split into the low-lying $t_{2g}$ orbitals and high-lying $e_g$ orbitals (see Figure 1). The double-occupation of the anti-bonding $e_g^*$ orbitals in the high-spin state leads to a weakening (and lengthening) of the Fe-ligand bonds.

$\Delta t_{2g}$ $\Delta e_g$ $\Delta P$ or $h\nu$

Diamagnetic
Low-spin $^1A_{1g}$ Purple

Paramagnetic
High-spin $^3T_{2g}$ White

Figure 1 Schematic representation of spin-transition for a $3d^6$ system such as Fe(II)
To a first approximation, the crossover occurs when the enthalpy of the low-spin state is slightly lower than that of the high-spin state. At low temperature, the thermodynamically stable state is the low-spin state. On the other hand, when the temperature is higher than a certain temperature, denoted $T_{1/2}$, the high-spin state becomes the thermodynamically stable state, because the entropy associated with the high-spin state is much larger than the entropy associated with the low-spin state, and the $T\Delta S$ (temperature multiplied by entropy) gain overcomes the enthalpy loss. $T_{1/2}$, also known as the critical temperature $T_c$, is the temperature for which there is coexistence of 50% of low-spin and 50% of high-spin molecules.

The transition can be characterised by an $x_{HS} = f($Perturbation$)$ curve (see Figure 2), where $x_{HS}$ is the molar fraction of high-spin molecules and the perturbation is temperature- or pressure change or irradiation.

Any technique that gives a response that can be related to $x_{HS}$ as a function of the perturbation can be used to construct such a curve. Techniques that have been used in this regard include: optical observation with UV-vis spectroscopy, magnetic susceptibility measurements, Mössbauer spectroscopy, electron
paramagnetic resonance (EPR) spectroscopy\textsuperscript{39,40}, single crystal\textsuperscript{41-50} and powder\textsuperscript{51,52} X-ray diffraction, infrared\textsuperscript{53-60} and Raman\textsuperscript{61-64} spectroscopy and other techniques including NMR, EXAFS, LAXS\textsuperscript{65-67} and heat capacity measurements\textsuperscript{68}. Section 2 gives a brief review of the application of these techniques in the study of spin-transition compounds.

2.2 Application of various techniques in the study of spin-transition

2.2.1 Optical Observation (UV-vis or electronic absorption spectroscopy)
According to the Tanabe-Sugano (TS) diagram for an ion with a d\textsuperscript{6} electronic configuration in an octahedral ligand field (see Figure 3), one can expect quite different absorption spectra for high-spin or low-spin complexes\textsuperscript{69}.

![Figure 3 Tanabe-Sugano diagram for an octahedral d\textsuperscript{6} complex calculated with the Racah parameters of the free iron(II) ion.](image)

In an Fe\textsuperscript{2+}, d\textsuperscript{6}, O\textsubscript{6} system the purple (low-spin) colour results from the spin-allowed \( ^{1}A_{1g} \rightarrow ^{1}T_{1g} \) d-d transition occurring at ±520nm. The white (high-spin) colour arises from the fact that the spin-allowed d-d transition of lowest energy in the high-spin state, \( ^{5}T_{2g} \rightarrow ^{5}E_{g} \), occurs in the near-infrared (±850nm).

Since the intensity of the 520nm band is proportional to the molar fraction of high-spin molecules, recording the transmittance of the material at 520nm
wavelength, as a function of temperature, gives a transition function curve (see Figure 4).

Optical observation is of particular relevance for Fe(II) compounds in which the d-d bands are not obscured by intraligand or charge-transfer bands.

Electronic absorption spectroscopy can also be used to obtain ligand-field information on the compound.

![Graph](image)

**Figure 4** Spin-transition function curve constructed from the recording of the transmittance of the material at 520nm.

### 2.2.2 Magnetic susceptibility

One of the simplest methods of obtaining a transition function curve consists of measuring the molar magnetic susceptibility ($\chi_M$) as a function of temperature. According to Kahn et al.\[70], $\chi_M$ obeys the Curie law in the temperature range where all molecules are in the same spin-state, with ($\chi_M T)_{LS}$ and ($\chi_M T)_{HS}$ constant. This is valid if the orbital degeneracy in a strictly octahedral environment is totally removed by symmetry lowering. $\chi_{HS} = f(T)$ can then be deduced from the experimental $\chi_M T = f(T)$ curve (Figure 5) according to Equation 1. In the case of iron(II) compounds, the low-spin state is diamagnetic and thus ($\chi_M T)_{LS} = 0$ and Equation 1 reduces to Equation 2.
2.2.3 Mössbauer spectroscopy

Mössbauer spectroscopy utilises the Mössbauer effect to study the magnetic fields inside ions. Further information on Mössbauer spectroscopy and the use thereof in transition metals chemistry can be found in reference [71]. This technique is especially useful for the study of iron compounds, since the $^{57}\text{Fe}$ nuclide is Mössbauer-active. Distinct signals can, in principle, be obtained when the spin-flipping frequency is lower than the technique frequency scale. Otherwise, a single average signal is obtained. In the case of Fe spin-transition compounds, Mössbauer spectra show two well-resolved quadrupole doublets with variable intensity as a function of temperature. This holds, if the coexisting spin-isomers have lifetimes larger than $10^{-7}$s. One of these doublets is associated with low-spin ions and the other with high-spin ions. The high-spin molar fraction can then be deduced from

\[ x_{HS} = \frac{\chi_M T - (\chi_M T)_{LS}}{(\chi_M T)_{HS} - (\chi_M T)_{LS}} \]  

(1)

\[ x_{HS} = \frac{\chi_M T}{(\chi_M T)_{HS}} \]  

(2)

![Figure 5 Typical experimental $\chi_M T = f(T)$ curve](image)

**Figure 5** Typical experimental $\chi_M T = f(T)$ curve
the relative intensities of these quadrupole doublets.\cite{71} The Mössbauer effect can also provide information on the microscopic environments of the $^{57}$Fe nuclei and spin-state interconversion rates but these applications are not discussed here.

2.2.4 **Electron Paramagnetic Resonance (EPR; or Electron Spin Resonance, ESR).**

EPR is the study of molecules containing unpaired electrons by observing the magnetic fields at which they come into resonance with monochromatic microwave radiation\cite{72}

Distinct low-spin and high-spin EPR-signals are obtained when the spin-state interconversion rate is slower than $10^{-9}$s$^{-1}$ (the EPR spectra time scale). If this holds, $x_{HS}$ can be deduced from the relative intensities of the low-spin and high-spin signals. EPR can also provide information on the microscopic environment of the molecular orbitals and on spin-state interconversion rates.

2.2.5 **Single crystal and powder X-ray diffraction**

As stated in section 1 of this chapter, the excitation of two electrons, from the $t_{2g}$ orbitals to the anti-bonding $e_g^*$ orbitals in Fe(II) complexes, leads to a weakening and lengthening of the Fe-ligand bonds. This change in the metal-ligand bond length can be observed in crystalline samples with the aid of single crystal X-ray diffraction. One example, from reference [4], shows a single crystal diffraction study of the $[\text{Fe}_3(4-\text{Ettrz})_6(\text{H}_2\text{O})_6]^{3+}$ cation (with 4-Ettrz = 4-Ethyltriazole) at 300K and 105K. The crystal structures are essentially the same, except for a significant shortening of the Fe-N bond in the low-temperature, low-spin state. Metal-ligand bond lengths typically increase by 0.14Å to 0.24Å during the transition from the low-spin state to the high-spin state.\cite{7}

Some spin-transition compounds such as the spin-transition polymers studied here, crystallize poorly. This makes single crystal studies on such compounds difficult, even impossible. In such cases powder X-ray diffraction has been used to derive
structural information on spin-transition. In one example[9] the powder diffraction pattern shows broad diffraction peaks for the compound in the low-spin state. Upon heating the sample to the L.S→HS transition temperature, a giant enhancement of one of the peaks is observed. This suggests a long-range order along one of the directions in the high-spin state.

2.2.6 Infrared and Raman spectroscopy

Vibrational spectroscopy (i.e. Infrared and Raman) gives information on the vibrational frequencies and force constants of chemical bonds. Since the metal-ligand bondlengths and -strengths of spin-transition compounds change during spin-transition, a lot of useful information can be obtained from their vibrational spectra.

In infrared spectroscopy, the metal ligand bands are systematically lower in energy in the high-spin state than in the low-spin state. This is due to the weakening of the metal-ligand bonds in the high-spin state. Other stretching vibrations, which are, for instance, strongly affected by π-backbonding between the metal and the ligand, can also be strongly affected by spin-transition.

Raman spectroscopy, particularly Resonance Raman, has been used extensively in the investigation of biological spin-transition systems with iron-porphyrins. Raman spectroscopy, in combination with infrared spectroscopy, can be used to investigate changes in the symmetry of the compounds during spin-transition.

2.2.7 Other techniques

Proton Nuclear Magnetic Resonance (NMR) has been used to study spin-transition. The line widths of Fe(II) complexes are constant in the diamagnetic temperature region but increase markedly in the spin-transition region. At higher temperatures, the line width follows a T⁻¹ dependence.[65]
Extended X-ray Absorption fine structure (EXAFS) and Large angle X-ray scattering (LAXS) are two other techniques that have been used to obtain structural information from poorly crystalline spin-transition compounds.\textsuperscript{[66,57]} In Chapter 4, reference is specifically made to the results obtained from these studies.

Heat capacity (C\textsubscript{p}) measurements have been used to characterise the spin-transition phenomenon and to determine thermodynamic values, such as mixing entropies, of the transition.\textsuperscript{[24]}

2.3 Spin-transition compounds and transition curves

With the possible exception of the cluster compounds HNb\textsubscript{6}I\textsubscript{11} and Nb\textsubscript{6}I\textsubscript{11}, which are also thought to exhibit spin-transition, spin-transition compounds are generally transition metal complexes. These complex materials generically consist of ligands, coordinated to one or more transition metal ions, with non-coordinating counter ions, non-coordinating solvent molecules and, sometimes, non-coordinating water molecules. The compounds can consist of polymeric or singular molecules. In the solid state the different combinations of ligands, metal ions, counter ions and solvents have a marked effect on the long-range cooperative interactions in the material, and therefore lead to differences in the spin-transition behaviour of the material.

Thermally induced spin-transitions in solution are always gradual, because the \( x_{\text{HS}} = f(T) \) function obeys a simple Boltzmann Law. On the other hand, solid state \( x_{\text{HS}}(T) \) curves show a much larger variety and can be classified according to the \( x_{\text{HS}}(T) \) curve shapes. Figure 6 shows schematic representations of the curve shapes of different spin-transition types.\textsuperscript{[7,24]}

- The transition may be smooth, occurring gradually over a large temperature range, similar to spin-transition in solution (Figure 6.a).
- The transition may be abrupt, occurring within a few Kelvin (Figure 6.b).
- The transition may occur with two discernible steps (gradual or abrupt) and a step or plateau along the $x_{\text{HS}}(T)$ curve (Figure 6.c).
- The transition may be incomplete at low temperature ($x_{\text{HS}} \neq 0$) and/or high-temperature ($x_{\text{HS}} \neq 1$), the former situation being observed more often (Figure 6.d).
- The transition curves may be strictly identical in the cooling and heating modes or exhibit a hysteresis effect (Figure 6.e). In the latter case, the temperature of the LS→HS transition in the heating mode, $T_{y,\uparrow}$, is higher than the temperature of the HS→LS transition in the cooling mode, $T_{y,\downarrow}$. Both $T_{y,\uparrow}$ and $T_{y,\downarrow}$ are defined as the temperatures for which the high-spin molar fraction $x_{\text{HS}} = 0.5$.

![Figure 6](image-url)

Figure 6: Schematic representations of spin-transition types. $T_{y,\downarrow}$ is defined as the temperature value for which $x_{\text{HS}} = 0.5$. 
Chapter 2 – Spin-transition uncovered

2.4 Cooperativity and the effect of chemical and physical factors on the behaviour of spin-transition compounds.

More or less strong long-range molecular interactions in the solid state result in a more or less pronounced cooperative effect. In strongly cooperative transitions, the spin conversion of one molecule induces the transition of the neighbouring molecules through electron-phonon coupling.[73,74] The cooperativity, and thus the behaviour of any spin-transition material, is strongly dependent on the ligand-field strength of coordinating ligands and non-coordinating counter ions. It is also dependent on ion size, ligand size, hydrogen bonding and all other components of the material that affect the electronic and/or vibrational functions within the material. Variation of these factors can lead to changes in T_yg gradual transitions becoming abrupt, or it can even lead to the suppression of the transition altogether.

The existence of hydrogen bonds generally favours the cooperative character of the transition. A steric hindrance generally has the opposite effect[72]. Exchange of non-coordinating counter anions can lead to an increase in the residual high-spin molecules at low temperatures (see Figure 6.d), as well as a complete suppression of the transition[75]. Molecular alloying, a technique where two or more similar ligands are added to the complex in different ratios, has been used very successfully to alter the critical temperature (T_yg) of transition[6]. Metal dilution, another technique in which the spin-transition–active metal is exchanged for another spin-transition–inactive metal (Mn, Co or Zn), causes the x_HS = f(T) curve to become more gradual. Concurrently T_yg is shifted to lower temperatures[24].

It is generally observed that the preparation technique of spin-transition complexes affects the spin-transition behaviour of the compounds. Crystal defects, as obtained for example by grinding the samples, make the transition less abrupt.[73] When the grain size is smaller, the critical temperatures are lower, the hysteresis loop is less square shaped, and the colour contrast is more, or in some cases less, pronounced.[7]
The lengthening of the metal-ligand bonds in the LS→HS transition cause the spin-transition molecules to be bigger in the high-spin state than in the low-spin state (an observed fact from crystal structure analyses). From this, it can be expected that an increase in pressure will favour the low-spin state. In other words, at elevated pressure the spin transition will occur at higher temperatures than at ambient pressure. High-pressure experiments on iron(II) spin-transition complexes in the solid have always confirmed this.[24]

2.5 Application of spin-transition compounds

The recent appearance, in popular language, of buzzwords such as nanotechnology and micromachines, gives an indication of the increasing scientific and public interest in miniaturisation. Molecular electronics is another term that stems from the miniaturisation trend and refers to molecular-based compounds exhibiting a property, or set of properties, which can be used in devices.[7] Spin-transition compounds have been cited as a potential group of materials for use in molecular electronics. Technological fields where spin-transition may find application include information storage, signal processing, optical switching, optical display, as well as temperature and pressure sensors.

At molecular level, spin-transition corresponds to an intra-ionic electron transfer accompanied by the spin flip of the transferred electrons. The word “intra-ionic” means that the electrons are transferred from the $t_{2g}$ to the $e_g$ orbitals but remain in the immediate environment of the metal ion. There is no electron displacement between sites far apart from each other as it occurs in mixed valence compounds, and no bond displacement as it occurs in photoisomerization. Because of this, the spin-transition compounds do not present any kind of fatigability. The transition may be reproduced as many times as one wants, without altering its characteristics.[73]. This gives spin-transition compounds an obvious advantage over competing materials.
Application of a molecular species in information storage or signal processing requires it to have the ability to change electronic ground state as a function of external perturbation. In addition, information storage requires the transition between the two states:

- to present a hysteresis
- to be abrupt
- to have $T_c$ near room temperature
- to be associated with a colour change, and
- to be chemically stable.\(^{[7,73]}\)

The chemical stability of spin-transition compounds is generally acceptable and technical preparative methods, such as hermitic encapsulation of granules in resins, lead to even better stability.\(^{[3,7]}\)

The requirement of colour change to be associated with the transition is virtually guaranteed for Fe(II) spin-transition compounds since, as stated earlier, the d-d transitions are not obscured by intraligand or charge-transfer bands.

It then remains to define, as accurately as possible, the factors that control the abruptness, hysteresis, and critical temperatures of spin-transition compounds. This has been the object of most recent research on spin-transition. In the previous section, it was shown that abruptness and hysteresis are dependent on the cooperative character in the material. It was shown that increased cooperativity is obtained by use of polymeric spin-transition compounds instead of non-polymeric compounds.

Kröber et al.\(^{[6]}\) used the technique of molecular alloying to design a polymeric spin-transition compound with room temperature in the hysteresis loop. The basic
compound is \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\), (where Htrz = 1H-1,2,4-Triazole) with the chain structure shown in Figure 7:

![Chain structure of the \([\text{Fe(Htrz)}_3]\text{Cl}^+\) cation (Hydrogens removed for clarity)](image)

The hysteresis loop of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) is just above room temperature. \(T_c^{\uparrow}\) and \(T_c^{\downarrow}\) were shifted to lower temperatures by replacing Htrz with a mixture of Htrz and 4-NH\(_2\)trz (where NH\(_2\)trz = 4-Amino-1,2,4-Triazole).

Information is stored on magnetic storage media in binary format, i.e. 1’s and 0’s. A spin-transition material with its hysteresis loop around room temperature (\(T_c^{\downarrow} < T_{\text{Room}} < T_c^{\uparrow}\)) can be used in a similar way, with the low-spin state symbolising 0 and the high-spin state symbolising 1. If the material is heated to above \(T_c^{\uparrow}\), the compound changes to the high-spin state and a 1 is stored. When the compound is cooled to below \(T_c^{\downarrow}\), the compound changes to the low-spin state and a 0 is stored. As long as \(T_{\text{Room}}\) stays between \(T_c^{\downarrow}\) and \(T_c^{\uparrow}\), the spin state (observed optically or magnetically) gives an indication of the last operation performed on the material and thus a memory effect is obtained. Figure 8 is a diagrammatic representation of this memory effect in spin-transition materials.
Incorporation of a spin-transition compound into a display device makes it necessary to implement it in a homogeneous layer. This has been performed with screen printing technology. Resistive heating and Peltier element cooling is used for switching the display elements (pixels) between the two states.\cite{7}

Kahn & Martinez\cite{3} have proposed possible application of spin-transition compounds as in situ temperature indicators in magnetic resonance imaging (MRI). Garcia et al.\cite{76} proposed the application of a specific spin-transition compound, which exhibits non-classical spin-transition behaviour, in the simple, accurate detection of a specific temperature.

Zarembowitch & Kahn\cite{73} investigated the possibilities of spin-transition compounds in signal processing, but a lot of work still needs to be done.
Chapter 2 – Spin-transition uncovered

2.6 [Fe(Htrz)₃](ClO₄)₂ and [Fe(NH₂trz)₃](ClO₄)₂ as subjects for further investigation

As stated in Chapter 1, it is imperative that researchers start focussing on new materials that have the potential to become essential parts of tomorrow’s high-technologies. By taking into consideration the information discussed above, the two spin-transition polymers [Fe(Htrz)₃](ClO₄)₂ and [Fe(NH₂trz)₃](ClO₄)₂ (with Htrz = 1H-1,2,4-Triazole and NH₂trz = 4-NH₂-1,2,4-Triazole) were identified for further investigation on the grounds that:

- they exhibit the spin-transition phenomenon (i.e., no fatigability)
- they are Fe(II) spin-transition compounds (i.e., no obscuring intraligand or charge-transfer bands, and thus a colour change from purple to white during the LS→HS transition)
- they are polymeric (i.e., abrupt transitions and hysteresis), and
- they have been used in molecular alloying to obtain Tₖ near room temperature.

For these reasons, the two compounds hold great promise for application in molecular electronics.

2.6.1 Available information on [Fe(Htrz)₃](ClO₄)₂ and [Fe(NH₂trz)₃](ClO₄)₂

The first compound is [Fe(Htrz)₃](ClO₄)₂ with Htrz = 1H-1,2,4-Triazole (see Figure 9 of 1H-1,2,4-Triazole)

![Figure 9 1H-1,2,4-Triazole](image)

Htrz is known to bridge metal ions through the 1,2 or, more exceptionally the 2,4-nitrogen positions⁷⁷ leading to polymeric structures, as shown in the Figure 10.
The polymeric structures favour cooperativity. When perfectly dry, the compound shows a smooth spin-transition around 265K with a small thermal hysteresis of ± 5K. With the addition of a small amount of water (1 drop in 50mg [Fe(Htrz)3](ClO4)2) the transition becomes very abrupt in both the warming and cooling phase with $T_c^\uparrow = 313K$ and $T_c^\downarrow = 296K$. The addition of water probably causes an increase in the number of hydrogen bonds leading to an increase in the cooperativity (see section 4 above). The transition is accompanied by a purple↔white colour change as discussed in Section 2.1.

The second compound is [Fe(NH2trz)3](ClO4)2 with NH2trz = 4-NH2-1,2,4-Triazole. According to Kroher et al, the pure material shows a smooth transition around $T_\gamma = 130K$. Note - This value of $T_\gamma$ differs from the $T_\gamma$ observed by Lavrenova et al and the $T_\gamma$ observed in the Raman study presented in Chapter 5 but it is assumed that the difference is caused by differences in sample preparation.

From literature it was also found that [Fe(Htrz)3](ClO4)2 and other similar compounds, are generally found to be poorly crystalline powders and that different batches of the same compound tended to behave very differently as a result of small differences in preparation. It can be assumed that these are the reasons why no Powder Diffraction File (PDF) for [Fe(Htrz)3](ClO4)2 could be found in the literature.
No suitable single crystals of these compounds have been obtained. Single crystal X-ray diffraction can therefore not be used to determine the structural changes associated with the spin-transition in these compounds. Other workers have, however, succeeded in characterising similar linear tri-nuclear Fe$^{2+}$ species with 4-substituted-1,2,4-triazole ligands triply bridging the metal ions [14]. According to Kahn and Martinez [3] the structure of Iron(II)-(4-substituted triazole) spin-transition compounds in the low-spin state consists of linear chains in which the neighbouring Fe atoms are triply bridged by the 4-substituted triazole ligands through the N-atoms occupying the 1- and 2-positions (see Figure 10 above).

The FeN$_6$ core is close to a regular octahedron. An Fe-Fe-Fe linear path is confirmed by EXAFS and LAXS spectra [66, 67]. In the high-spin state, the chain structure is retained but the FeN$_6$ core is distorted and the peaks characteristic of a three-Fe-atom linear path disappear.

Various infrared studies have shown the effect of spin-transition on the metal-ligand stretching vibrations [53-56, 60-62] and these can be related to the Fe-N bond lengths. Lavrenova et al. [78] specifically studied $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ (Htrz = 1H-1,2,4-triazole) and the NH$_2$trz-analogue (NH$_2$trz = 4-amino-1,2,4-triazole) using magnetic susceptibility, X-ray powder diffraction, Mössbauer-, diffuse reflectance- and IR-spectrometry but the focus of the study was different from the research presented here.

2.6.2 Conclusions from review of the literature on $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ and $[\text{Fe(NH}_2\text{trz)}_3](\text{ClO}_4)_2$

- More information is required on the structures of $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ and $[\text{Fe(NH}_2\text{trz)}_3](\text{ClO}_4)_2$ and on the structural changes that occur during spin-transition.
- Information is required on the factors that influence the crystallinity of the materials.
2.6.3 Methods selected for investigation

Vibrational spectroscopy (Infrared and Raman) was selected for investigating the structural changes that occur in [Fe(Htrz)₃](ClO₄)₂ and [Fe(NH₂trz)₃](ClO₄)₂ during spin-transition. These techniques are generally viewed as complimentary, and sometimes alternative, methods to single-crystal X-ray diffraction for obtaining structural information on materials.

Since X-ray powder patterns are critical for phase characterisation and identification, an X-ray powder diffraction study was undertaken. The aim of the study was to overcome the problems of poor crystallinity and batch-to-batch variation mentioned in section 6.1.
Chapter 3 – Experimental and Other Special Considerations

As stated in Chapter 2, the methods selected for the study were Infrared and Raman spectroscopy and X-ray powder diffraction. In this chapter, the experimental details and special considerations of three studies are reported.

3.1 Materials

3.1.1 Syntheses

The two compounds under study were synthesised using the method of Kröber et al.\[6\]. [Fe(Htrz)\(_3\)](ClO\(_4\))\(_2\) was prepared by dissolving 2.9g of Fe(ClO\(_4\))\(_2\).6H\(_2\)O (Aldrich, USA) in 100ml of a methanol solution containing 0.040g ascorbic acid; 1.656g of 1H-1,2,4-Triazole (Aldrich, USA) was dissolved in 100ml of methanol, and this solution was added to the iron(II) perchlorate / ascorbic acid solution. The mixture was stirred and then quickly roto-evaporated until almost dry. The complex was allowed to air-dry. The other compounds were prepared similarly but with FeCl\(_2\) (FlukaChemie) or FeSO\(_4\).7H\(_2\)O (Saarchem-Holpro Analitic RSA) instead of the Fe(ClO\(_4\))\(_2\).6H\(_2\)O for [Fe(Htrz)\(_3\)]Cl\(_2\) and [Fe(Htrz)\(_3\)]SO\(_4\), respectively, and with 4NH\(_2\)-1,2,4-Triazole (Aldrich, USA) instead of the 1H-1,2,4-Triazole for [Fe(NH\(_2\)trz)\(_3\)](ClO\(_4\))\(_2\).

3.1.2 Special Considerations

In the syntheses of the two complexes with FeCl\(_2\) and FeSO\(_4\).7H\(_2\)O, the choice of the Fe(II) salts were made according to availability in the laboratory, without any reference to the literature. According to Haasnoot\[83\], the use of higher ligand to metal ratios with 4-alkyl substituted triazoles may give low-spin complexes with a Fe\(_3\)A\(_2\) composition. Haasnoot expected that such complexes were also chains of triply bridged iron(II) ions. The same assumptions were made for the compounds [Fe(Htrz)\(_3\)]Cl\(_2\) and [Fe(Htrz)\(_3\)]SO\(_4\), in this study, but the ligands were Htrz.
3.2 Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were performed using a Gouy-balance with [Ni(en)₃]S₂O₃ (en = ethylenediamine) for calibration. A discussion of the process followed for calculating the spin states of all the studied compounds at room temperature, together with the diamagnetic corrections used for the calculation of the unpaired electrons in each complex are given in Annex 1.

3.3 Elemental Analysis of [Fe(Htrz)₃](ClO₄)₂

Elemental analysis was performed on the four different samples of [Fe(Htrz)₃](ClO₄)₂ that were used in the powder diffraction study. These analyses were performed using a Carlo Erba NA 1500 C/N/S Analyser (with a modification to determine H) for the C, N, and H. The Fe content was determined with ICP-OE. The results from these analyses are given in Annex 2 together with the theoretical mass percentages of two possible forms of the compound.

3.4 Infrared Spectra

3.4.1 Sample Preparation

The mid-infrared spectra (4000 - 400 cm⁻¹) and far-infrared spectra (650 - 50 cm⁻¹) were recorded using a Bruker IFS 113v FT-IR spectrometer. Samples were recorded as KBr pellets in the mid-infrared and polyethylene pellets in the far-infrared. To avoid the influence of an externally applied pressure, the far-infrared spectra of the low-pressure phase transition in [Fe(Htrz)₃](ClO₄)₂ were obtained by preparing an ordinary polyethylene pellet and dripping the complex, suspended in methanol, onto the pellet. The sample was allowed to dry in air, leaving only the [Fe(Htrz)₃](ClO₄)₂ complex on the surface. Therefore, the [Fe(Htrz)₃](ClO₄)₂ complex was not mixed with the polyethylene and subjected to pressure when the pellet was prepared. Low pressures were obtained in the evacuated sample chamber of the infrared instrument. The high-temperature far-infrared spectra of [Fe(Htrz)₃](ClO₄)₂ were obtained by heating the sample pellet and metal pellet holder to 353K in a furnace and recording.
the spectrum before the sample could cool to below 323K. The low-temperature far-infrared spectra of \([\text{Fe(NH}_2\text{trz)}_3]\)(\text{ClO}_4)_2 were recorded using a liquid nitrogen cryostat to maintain the temperature of the sample.

### 3.5 Raman Spectra

#### 3.5.1 General Considerations

Given the structural complexity of the studied systems, (i.e. the presence of multiple organic ligands, triply bridging between two metal centres at a time, forming chains of unknown length) complete assignment of their solid state Raman spectra would seem very difficult. The interest in this Raman study was mainly focused on the structural changes that occur in the Fe-N\(_6\) coordination sphere during spin-transition, and therefore no special interest was paid to the internal modes of the NH\(_2\)trz and Htrz rings. Literature data on 1H-1,2,4-Triazole\(^{[84,85]}\), and the ClO\(_4\) and SO\(_4^{2-}\) anions\(^{[86]}\) were, however, useful in recognition of the X-Triazole (X = H, NH\(_2\)) and the anion modes, which were not expected to suffer major changes upon complexation. Since \(XH\) (X = C, N) stretching bands (expected to dominate above 1800 cm\(^{-1}\)), ring stretching and deformations (expected in the 1800-1100 cm\(^{-1}\) region) and CH deformations (found below 1100 cm\(^{-1}\)) were not of interest, the spectra discussed here were recorded in the low-wavenumber region (650-50 cm\(^{-1}\)), where lattice modes and metal-ligand stretchings could be expected.

#### 3.5.2 Sample Preparation and Instrumental Parameters

The Raman spectra of the powdered samples were recorded using the 10X objective of the Dilor XY Raman microprobe with a spectral resolution of 2 cm\(^{-1}\). The samples were excited using the 514nm line of an argon-ion laser (Coherent Model Innova 300) with a laser output power of 100mW and an integration time of 60s. The low-temperature spectra were recorded with the aid of a Linkum TMS93 liquid nitrogen cryostat, fitted with an HFS91 stage and LNP cooling pump.
3.6 X-ray Powder Diffraction

3.6.1 General Considerations

For the purpose of the powder diffraction study presented here, four different sample batches of \([\text{Fe}(\text{Htrz})_3](\text{ClO}_4)_2\) were prepared using the method described above. The ages of the different samples at the time of the investigation, are given in Table 1.

Table 1 Ages of the four different \([\text{Fe}(\text{Htrz})_3](\text{ClO}_4)_2\) samples at the time of investigation.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sample Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1 day</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1 week</td>
</tr>
<tr>
<td>Sample 3</td>
<td>15 months</td>
</tr>
<tr>
<td>Sample 4</td>
<td>2 hours</td>
</tr>
</tbody>
</table>

At the end of the syntheses, the complex, a white paste on the walls of the flask, was scraped onto a watch glass to air-dry. It turned purple upon cooling to room temperature. The soft paste quickly dried to form a very hard solid. It is assumed that this quick drying/setting behaviour probably retards further evaporation of the solvent from the product. The older samples (2 and 3) were stored in closed bottles, from directly after synthesis, in the form of the hard solid mentioned above. Any further evaporation of the solvent from the samples was considered negligible.

The elemental analyses of the samples (Annex 2) showed that the proper formula for the compound is \([\text{Fe}(\text{Htrz})_3](\text{ClO}_4)_2\cdot1.85\text{H}_2\text{O}\). This formula is only used in the discussion of the X-ray powder diffraction study, since the degree of hydration of the compound was not of particular importance in the infrared and Raman studies.

3.6.2 Sample Preparation and Instrumental Parameters

All samples were ground by hand in an agate mortar and specimens were left in open air to dry at room temperature when required.
The XRD analyses were performed on a Siemens D-501 automated diffractometer. Instrumental conditions are summarised in Annex 3. The various ranges of 2θ, step sizes, measuring times and internal d-spacing standards (where applicable) are given together with the relevant patterns.
In this chapter the results of the infrared study of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) and \([\text{Fe(NH}_2\text{trz})_3](\text{ClO}_4)_2\) are reported and discussed.

4.1 Mid-infrared

4.1.1 Assignment of the bands

The room temperature mid-infrared spectra of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\), \([\text{Fe(NH}_2\text{trz})_3](\text{ClO}_4)_2\), \([\text{Fe(Htrz)}_3]\text{SO}_4\) and \([\text{Fe(Htrz)}_3]\text{Cl}_2\) are shown in Figure 11.

![Mid-infrared spectra of compounds](image)

Figure 11 Mid-infrared spectra of (from top to bottom): A. \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\), B. \([\text{Fe(NH}_2\text{trz})_3](\text{ClO}_4)_2\), C. \([\text{Fe(Htrz)}_3]\text{Cl}_2\), and D. \([\text{Fe(Htrz)}_3]\text{SO}_4\).

Annex 4 Table 1 compares the mid-infrared spectra of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\), \([\text{Fe(Htrz)}_3]\text{Cl}_2\) and the free ligand 1,2,4-Triazole. This shows that the bands observed for the complexes are mainly due to vibrations of the ligand, slightly perturbed by coordination. This observation has been made before for similar compounds such as \([\text{Fe(bipy)}_3]^{2+}\), \([\text{Ni(phen)}_3]^{2+}\) and \([\text{Zn(phen)}_3]^{2+}\) (where bipy = 2,2'-bipyridine and...
Chapter 4 – Infrared Study: Results and Discussion

phen = 1,10-phenanthroline\[^{[87]}\]. The infrared vapour-phase fundamentals for the free 1,2,4-Triazole have been assigned by Bougeard et al.\[^{[84]}\], who stated that the fundamental frequencies show no great differences for the gas and solid phases. The ClO$_4^-$-anion has characteristic vibrational frequencies at 935 cm$^{-1}$ (medium), 460 cm$^{-1}$ (very weak), 1050-1170 cm$^{-1}$ (broad strong) and 630 cm$^{-1}$ (strong). These peaks obscure the Htrz-peaks in the mid-infrared spectrum of the complex, hence the spectrum of the [Fe(Htrz)$_3$]Cl$_2$ complex was used to eliminate the interfering ClO$_4^-$-peaks.

4.1.2 1,2-Bicoodination of the ligands

According to Haasnoot et al.\[^{[88]}\] the absence or strongly reduced intensity of the first ring torsion (R$_8$ in Annex 4 Table 1) of Htrz, indicates C$_{2v}$ symmetry and 1,2-cooordination of the ligand. A band around 1215 cm$^{-1}$ is always found in 1,2-bi-coordinating triazole and, in all bidentate triazole spectra, the CH-bending vibration is found around 1305 cm$^{-1}$. Careful inspection of the recorded mid-infrared spectra shows the absence or strong reduction of the R$_8$ ring torsion in all four compounds. The other vibrations that are indicative of 1,2-bicooordination can also be seen in the spectra of compounds [Fe(Htrz)$_3$](ClO$_4$)$_2$, [Fe(Htrz)$_3$]Cl$_2$ and [Fe(Htrz)$_3$]SO$_4$. This leads to the conclusion that [Fe(Htrz)$_3$]Cl$_2$ and [Fe(Htrz)$_3$]SO$_4$ indeed contain the bidentate ligand in a bridging coordination and could therefore have the same chain structure as [Fe(Htrz)$_3$](ClO$_4$)$_2$. The R$_9$ ring torsion vibrations of [Fe(Htrz)$_3$]Cl$_2$ and [Fe(Htrz)$_3$]SO$_4$ split into more than one overlapping band. This would indicate an inequivalence of the coordinated bridging ligand molecules, as has been observed for similar compounds\[^{[89]}\].

It is important to note that the mid-infrared spectra of [Fe(Htrz)$_3$](ClO$_4$)$_2$ and [Fe(NH$_2$trz)$_3$](ClO$_4$)$_2$ also contain strong peaks near 635 cm$^{-1}$. These are assigned to a combination of the out-of-plane vibration of the ligands and a strong ClO$_4^-$-band that occurs at 630 cm$^{-1}$ (see Figure 11).
4.1.3 Hydration-dehydration during spin-transition

A broad band at 3500 cm\(^{-1}\) in the low temperature (low-spin) mid-infrared spectrum of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) disappears upon heating the sample to above \(T_c\) (323 K). This peak reappears with the same intensity upon cooling to room temperature. It is possible that this band represents OH stretching vibrations of adsorbed water and could then indicate that dehydration occurs during the low-spin to high-spin transition and that re-hydration occurs during the high-spin to low-spin transition. The possibility of dehydration / re-hydration during the low-spin to high-spin transition would not be surprising as it has been observed in other spin transition compounds \[79\]. The influence of water of crystallisation on the spin transition of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) was also studied by Lavrenova et al \[78\]. According to the authors the compound \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\_\text{H}_2\text{O}\), which is low-spin at room temperature, is converted to a high-spin compound upon the loss of water. The possibility of hydration-dehydration was not investigated here in detail.

4.1.4 Mid-infrared of \([\text{Fe(NH}_2\text{trz)}_3](\text{ClO}_4)_2\)

The mid-infrared spectrum of \([\text{Fe(NH}_2\text{trz)}_3](\text{ClO}_4)_2\) contains, as was the case for \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) and \([\text{Fe(Htrz)}_3]Cl_2\), mainly the vibrations of the ligand, slightly perturbed by coordination. Strong peaks of the ClO\(_4\)-counter anion again obscure the same regions.

4.2 Far-infrared

4.2.1 Pressure dependence of the spin state of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\)

The changes in the far-infrared spectrum of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) at pressures between 200mbar and 110mbar are shown in Figure 12. Various studies have been performed on spin-transition compounds where the high-spin to low-spin transition is brought about under high pressures\[18,37,58,90,91,92\]. In these studies, various problems related to high-pressure experiments e.g. shear stress and gasket related difficulties, were usually experienced.
Here the far-infrared spectra show that, in the opposite direction, the low-spin to high-spin transition in \([\text{Fe}(\text{Htrz})_3](\text{ClO}_4)_2\) is also brought about by lowering the pressure on the sample to 110mbar. In iron(II) spin-transition compounds the Fe-ligand stretching vibration frequency shifts towards lower wavenumbers from around 400 cm\(^{-1}\) in the low-spin state to around 250 cm\(^{-1}\) in the high-spin state. This is also observed here for \([\text{Fe}(\text{Htrz})_3](\text{ClO}_4)_2\) with the Fe-N stretching frequency at 299 cm\(^{-1}\) in the low-spin state and at 263 cm\(^{-1}\) in the high-spin state. This decrease in frequency results from the double occupation of the anti-bonding \(e_g\) orbitals of the \(d^6\) Fe(II) in the high-spin state, leading to the weakening (and lengthening) of the Fe-N bonds.

Faniran and Bertie\(^{[85]}\) predicted and assigned all 15 infrared-active lattice modes for the free Htrz-ligand. All 15 frequencies are at wavenumbers below 200 cm\(^{-1}\), thus the
two peaks at 299 cm\(^{-1}\) and 221 cm\(^{-1}\) in the far-infrared spectrum of the low-spin state of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) can be assigned to the Fe-N stretching and N-Fe-N bending modes, respectively. Similar assignments have been made for \([\text{Fe(bipy)}_2](\text{ClO}_4)_2\) (bipy = 2,2'-bipyridine) by Hutchinson et al.\(^{[82]}\).

In the high-spin state the Fe-N stretching vibrations move towards lower wavenumbers, viz. 263 cm\(^{-1}\) for the stretching mode, with a overlapping band appearing at 280 cm\(^{-1}\), and 214 - 204 cm\(^{-1}\) for the N-Fe-N bending vibration. The latter band consists of at least three overlapping bands in the high-spin state.

The low-pressure spin-transition was observed here for the first time in the evacuated sample chamber of the FT-IR instrument. At 200mbar and 298 K the spectrum of the low-spin, purple state is obtained. At 110mbar and 298 K the spectrum of the high-spin white coloured state is obtained. The transition was confirmed by comparing the infrared spectrum of the low-pressure state with that of the high-spin state of the same compound obtained at high temperatures. The infrared spectrum of the high-temperature \((T > 323K)\), white coloured state (i.e. confirmed high-spin state) of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) was recorded at 200mbar and 330 K. The spectrum corresponds to the one recorded of the low-pressure \((110mbar)\), room temperature \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\). The low-pressure transition can also be observed visually by placing a sample of the low-spin, purple \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\) in a glass bottle and evacuating the bottle to 110mbar. As can be expected for a low-spin to high-spin transition, the sample changes colour from purple to white. Since the pressure change is very small compared to other pressure induced spin transitions, it is possible that the transition mechanism also includes some degree of hydration / de-hydration. This supposition is supported by the apparent de-hydration / hydration observed in the mid-infrared spectra (see above).
4.2.2 Far-infrared of \([\text{Fe(NH}_2\text{trz)}_3]\)(\text{ClO}_4)_2

The far-infrared spectra of \([\text{Fe(NH}_2\text{trz)}_3]\)(\text{ClO}_4)_2 in the temperature range 82 - 298 K are shown in Figure 13. The strong band at 250 cm\(^{-1}\) in the room temperature high-spin state is the Fe-N stretching vibration. It seems to consist of two overlapping bands at 254 cm\(^{-1}\) and 247 cm\(^{-1}\). The intensity of these bands decreases steadily with decreasing temperature.

4.2.3 Far-infrared of \([\text{Fe(Htrz)}_3]\)\text{Cl}_2 and \([\text{Fe(Htrz)}_3]\)\text{SO}_4

The far-infrared spectra of \([\text{Fe(Htrz)}_3]\)\text{Cl}_2 and \([\text{Fe(Htrz)}_3]\)\text{SO}_4 are compared in Figure 14. \([\text{Fe(Htrz)}_3]\)\text{SO}_4 has a strong, broad band at 249 cm\(^{-1}\), which represents the Fe-N stretching vibration of a high-spin \([\text{Fe(Htrz)}_3]\)^{2+} complex. This band in \([\text{Fe(Htrz)}_3]\)\text{SO}_4 is composed of two overlapping bands at 270 cm\(^{-1}\) and 249 cm\(^{-1}\).

![Figure 13 Temperature dependent far-infrared spectra of \([\text{Fe(NH}_2\text{trz)}_3]\)(\text{ClO}_4)_2.](image-url)
4.2.4 Changes in Fe-N bond lengths during spin-transition

The information obtained from the far-infrared spectra can be summarised as follows:

In the low-spin state spectra of [Fe(Htrz)_3](ClO_4)_2 and [Fe(Htrz)_3]Cl_2 a single band is observed for the Fe-N stretching vibration around 300 cm\(^{-1}\). A single band is observed for the N-Fe-N bending vibration in [Fe(Htrz)_3](ClO_4)_2 around 220 cm\(^{-1}\). This corresponds to the view of a regular octahedral coordination sphere with six equivalent Fe-N bonds.

For the high-spin state of [Fe(Htrz)_3](ClO_4)_2, [Fe(NH_2trz)_3](ClO_4)_2 and [Fe(Htrz)_3]SO_4 the Fe-N stretching frequency decreases to around 250 cm\(^{-1}\) and consists of at least two overlapping bands (280, 263 cm\(^{-1}\) for [Fe(Htrz)_3](ClO_4)_2 and 279, 247 cm\(^{-1}\) for [Fe(Htrz)_3]SO_4. This suggests that there are two different types of Fe-N bonds in the high-spin state.

![Figure 14 Comparison between the far-infrared spectra of low-spin [Fe(Htrz)_3]Cl_2 and high-spin [Fe(Htrz)_3]SO_4.](image-url)
Chapter 4 – Infrared Study: Results and Discussion

The results would indicate that, in going from the LS to the HS state, all six Fe-N bonds in the coordination sphere are weakened, but two of the bonds (e.g. along the z-axis) are weakened to a lesser degree than the other four. This would explain the doubly degenerate Fe-N bands in the high-spin infrared spectra and the distortion of the octahedral arrangement as discussed by Kahn and Martinez. The symmetry of the coordination sphere would thus change from $O_h$ to $D_{4h}$. It can also be expected that two types of Fe-N bonds in the coordination sphere will result in three types of N-Fe-N bending vibrations (strong-strong, strong-weak, and weak-weak). This would therefore explain the splitting of the N-Fe-N bending vibration of $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ into multiple bands.
Chapter 5 – Raman Study: Results and Discussion

In this Chapter the results of the Raman study of \([\text{Fe(NH}_2\text{trz)}_3]\text{(ClO}_4\text{)}_2\) and \([\text{Fe(Htrz)}_3]\text{(ClO}_4\text{)}_2\) are reported and discussed.

5.1 Composition of the Raman spectrum of \([\text{Fe(NH}_2\text{trz)}_3]\text{(ClO}_4\text{)}_2\)

\([\text{Fe(NH}_2\text{trz)}_3]\text{(ClO}_4\text{)}_2\) occurs in the high-spin state at room temperature\(^6\). Figure 15 shows the Raman spectrum of the high-spin state of \([\text{Fe(NH}_2\text{trz)}_3]\text{(ClO}_4\text{)}_2\) at room temperature. In this spectrum, the various bands can be assigned as follows: all bands below 200 cm\(^{-1}\) are NH\(_2\text{trz}\) lattice modes and the bands at 458 cm\(^{-1}\) and 625 cm\(^{-1}\) are respectively assigned to the \(v_2\text{(E)}\) and \(v_4\text{(F)}\) modes of the non-coordinated ClO\(_4\)-anion\(^6\). These assignments compare very well with the spectra of the pure constituent compounds, 4NH\(_2\)-1,2,4-Triazole and Fe(ClO\(_4\))\(_2\), and support the assumption that the lattice and anion modes do not suffer major changes during complexation. The tentative assignment of the NH\(_2\text{trz}\) and Htrz bands, together with those of the relevant anions in the studied complexes, are presented in Table I and Table II of Annex 5, respectively.

![Figure 15 Comparison of the Raman spectra of \([\text{Fe(NH}_2\text{trz)}_3]\text{(ClO}_4\text{)}_2\) with its pure starting materials, 4-NH\(_2\)-1,2,4-Triazole and Fe(ClO\(_4\))\(_2\)-6H\(_2\)O. (Note - The recorded spectrum of \([\text{Fe(NH}_2\text{trz)}_3]\text{(ClO}_4\text{)}_2\) was of very low intensity and has been amplified for comparison).](image-url)
5.2 Temperature dependence of the \([\text{Fe(NH}_2\text{trz}_3\text{)](ClO}_4\text{)_2}\) Raman spectrum

Upon lowering the temperature of the \([\text{Fe(NH}_2\text{trz}_3\text{)](ClO}_4\text{)_2}\) sample (Figure 16), the bands associated with the lattice modes grow increasingly resolved, as can be expected, however, a new band appears at 244 cm\(^{-1}\).

![Figure 16 Temperature dependent Raman spectra of \([\text{Fe(NH}_2\text{trz}_3\text{)](ClO}_4\text{)_2}\) ](image)

5.3 Comparison of the Raman spectra of \([\text{Fe(NH}_2\text{trz}_3\text{)](ClO}_4\text{)_2}\) with those of \([\text{Fe(Htrz}_3\text{)](ClO}_4\text{)_2}\), \([\text{Fe(Htrz}_3\text{)]Cl}_2\) and \([\text{Fe(Htrz}_3\text{)]SO}_4\)

Comparison of the spectra of all four investigated compounds in their various spin-states (Figure 16 and Figure 17), reveals an interesting trend: Figure 17 shows the spectra of the high-spin compound \([\text{Fe(Htrz}_3\text{)]SO}_4\) (Figure 17 – bottom) and the low-spin compound \([\text{Fe(Htrz}_3\text{)]Cl}_2\) (Figure 17 – top). Note that the high-spin \([\text{Fe(Htrz}_3\text{)]SO}_4\) spectrum only contains the lattice modes below 200 cm\(^{-1}\) and the E and F\(_2\) modes of the \(\text{SO}_4^{2-}\) anion\([86]^{86}\), whilst the low-spin \([\text{Fe(Htrz}_3\text{)]Cl}_2\) spectrum has another band at 281 cm\(^{-1}\) in addition to the lattice modes. Furthermore, if the
high-spin spectrum of $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ (Figure 17 - 2nd from bottom) is compared to its low-spin spectrum* (Figure 17 - 2nd from top), and it can be seen that the low-spin spectrum contains an extra band at 283 cm$^{-1}$. (*Note: Although $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ normally occurs in the low-spin state at room temperature, the sample had to be cooled to 123K for recording of the low-spin state Raman spectrum. This was done in order to prevent local heating, by the excitation laser, from thermally inducing the low-spin to high-spin transition, which is why the high-spin state Raman spectrum can be obtained at 298K).

![Figure 17 Raman spectra of low-spin $[\text{Fe(Htrz)}_3]\text{Cl}_2$, low-spin $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$, high-spin $[\text{Fe(Htrz)}_3](\text{ClO}_4)_2$ and high-spin $[\text{Fe(Htrz)}_3]\text{SO}_4$.](image)

In summary, the spectra of all the investigated compounds in the low-spin state show a band in the region 200-300 cm$^{-1}$, which does not appear in the high-spin state.
The infrared study of these compounds (Chapter 4) showed that the Fe-N stretching vibration in the infrared spectra can be found at 299 cm\(^{-1}\) for [Fe(Htrz)\(_3\)](ClO\(_4\))\(_2\) in the low-spin state, at 300 cm\(^{-1}\) for [Fe(Htrz)\(_3\)]Cl\(_2\) in the low-spin state, and at 250 cm\(^{-1}\) for [Fe(NH\(_2\)trz)\(_3\)](ClO\(_4\))\(_2\) in the low-spin state. It is therefore reasonable to expect the Fe-N stretching vibration in the 200-300 cm\(^{-1}\) region of the Raman spectrum, possibly with the Fe-N stretching frequency of [Fe(NH\(_2\)trz)\(_3\)](ClO\(_4\))\(_2\) lower than that of [Fe(Htrz)\(_3\)](ClO\(_4\))\(_2\) and [Fe(Htrz)\(_3\)]Cl\(_2\).

### 5.4 Assignment of the Fe-N band

From the discussion above, it is proposed that the band that appears in the 200-300 cm\(^{-1}\) region of the Raman spectra of the low-spin compounds presented here, is the Fe-N stretching mode. This assignment is furthermore supported by a similar assignment of a 220-224 cm\(^{-1}\) iron-histidine Resonance Raman stretching vibration in deoxyhemoglobins from insect larvae\(^{[93]}\).

### 5.5 Obtaining the spin-transition function curve

Yet another supporting argument for the assignment of the new band to the Fe-N stretching vibration is as follows: The low-temperature induced spin-transition of [Fe(NH\(_2\)trz)\(_3\)](ClO\(_4\))\(_2\) was observed by Lavrenova et al.\(^{[78]}\) using magnetic susceptibility measurements. These authors constructed a transition curve by plotting \(\mu_{\text{eff}}\) against temperature. The spin-state of the compound changes gradually from high-spin to low-spin upon cooling to below 210K. By normalising the spectral intensities of the [Fe(NH\(_2\)trz)\(_3\)](ClO\(_4\))\(_2\) Raman spectra investigated here, with respect to the ClO\(_4\)-band at 464 cm\(^{-1}\), and then plotting the integrated areas under the 244 cm\(^{-1}\) peaks vs. temperature, a curve is obtained (Figure 18). This curve closely resembles the \(\mu_{\text{eff}}\) vs. temperature transition curve of Lavrenova et al.\(^{[78]}\). Since it is known that the Fe-N bond lengths change during spin-transition\(^{[3,6]}\), a change in the Fe-N stretching band can be expected and therefore the similarity to the \(\mu_{\text{eff}}\) vs. temperature curve is probably not a coincidence.
The absence of a comparable Fe-N stretching band in the high-spin spectra of the investigated compounds remains unexplained. It could be suggested that changes in the Fe site symmetry, that occur during the transition from the high-spin state to the low-spin state, lead to the band becoming inactive.

![Diagram](image)

**Figure 18** Transition curve obtained by plotting the intensity of the 244 cm$^{-1}$ peak (from Figure 16) as a function of temperature.
Chapter 6 – X-ray powder diffraction study: Results and Discussion

In this chapter the effects of proper drying and grinding of \( \text{[Fe(Htrz)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} \cdot 1.85H\textsubscript{2}O} \) specimens on the quality of X-ray powder patterns are reported and discussed.

6.1 Improvement of Crystallinity and Powder Patterns

Figure 19 shows that proper drying after the initial grinding increases the sample crystallinity and thereby the quality of the powder pattern. Pattern 1a is that of sample 4 directly after synthesis (note the amorphous region between 10° and 18° 2θ). 1b is the pattern of the same specimen after an additional 24 hours of drying (note the appearance of the peaks at ±11°, 12°, 16° and 18° 2θ). 1c shows the pattern of the specimen after 48 hours of drying and an additional 5 minutes of grinding.

![Figure 19 X-ray powder patterns of sample 4 showing that additional drying of the specimen increases crystallinity. (1a) No additional drying, (1b) 24h additional drying, (1c) 48h drying and 5 minutes grinding. [Pattern recording data: Range of 2θ: 3°-85° 2θ, step time: 3s]
6.2 Infrared Comparison of samples

Figure 20a and b show the mid- and far-infrared spectra of all four samples. In the mid-infrared spectra the absence of the Triazole ligand's $R_3$ ring torsion vibration (near 684 cm$^{-1}$) and the presence of the 1215 cm$^{-1}$ and 1305 cm$^{-1}$ bands show that all four samples are the same compound with 1,2-bicoordinating Htrz-ligands$^{[88]}$. In the far-infrared spectra, the position of the Fe-N stretching vibration at 300 cm$^{-1}$ shows that all four compounds are in the low spin state at room temperature. The spectrum of sample 1 in the high spin state is given for comparison. The broadening of the Fe-N bands in the spectra of sample 2, 3 and 4, compared to that of sample 1, is most probably caused by the difference in sample pellet preparation mentioned in the experimental section.

Figure 20 (a and b) Mid-infrared (Fig.20a) and Far-infrared (Fig.20b) spectra showing that all four samples are the same compound and in the low spin state at room temperature. The far-infrared spectrum of sample 1 in the high spin state is included for comparison.
6.3 Effects of preferential orientation on the powder patterns

In Figure 21 the X-ray powder diffraction patterns of sample 2 (21a), sample 3 (21b and 21c) and sample 1 (21d) are shown. As the infrared spectra in Figure 20 prove that all the samples are, in fact, the same compound, it is assumed that the differences between the powder patterns of the three compounds in Figure 21 can be attributed to preferential orientation effects. This assumption is supported by comparison of patterns 21a and 21b with patterns 21c and 21d. Note the high intensities of the peaks at 23.33° 2θ and 24.52° 2θ in 21a and 21b, as well as the presence of a small peak at 12.74° 2θ. Pattern 21c is of the same specimen as 21b, but with an additional 5 minutes of grinding. Here extra care was taken to avoid preferential orientation. After this additional treatment, the intensities of the two peaks at 23.33° 2θ and 24.52° 2θ are notably reduced and the peak at 12.74° 2θ has disappeared completely. Pattern 21c is thought to represent the true powder pattern of [Fe(Htrz)3](ClO4)2·1.85H2O, as further grinding, drying and specimen surface correction, in addition to the treatment mentioned above, did not appear to lead to further improvement in the quality of the pattern.

Figure 21 X-ray powder patterns of sample 2 (pattern 21a), sample 3 (21b and 21c) and sample 1 (21d) showing the effect of preferential orientation. Preferential orientation: 21a and 21b. No preferential orientation: 21c and 21d. [Pattern recording data: (21a, 21c and 21d) range of 2θ: 2.95°-64.96° 2θ, step time: 30s, Internal standard: Si(SRM640a). (21b) range of 2θ: 3°-85° 2θ, step time: 3s.]
6.4 Indexing of the powder pattern and comparison of structural data with \([\text{Cu(Hyetrz)}_3](\text{ClO}_4)_2\cdot3\text{H}_2\text{O}\)

Preliminary indexing of the X-ray powder diffraction pattern 21c was performed by means of the computer program DICVOL\textsuperscript{[84]}. 15 peak positions, with maximal absolute error of 0.04° 2θ, were used as input data (the peak at 10.798° 2θ was not used). The peak positions were obtained after Kα₂-stripping using the software package Diffrac plus, Eva version 3.0 from Bruker axs. The only possible solution proposed by the DICVOL program was that of a cell with monoclinic symmetry. The calculated and observed peak positions, intensities and Miller indexes, as well as the calculated cell parameters and figures-of-merit are shown in Table 9 in Annex 6.

The cell parameters are compared to those of the Cu compound \([\text{Cu(Hyetrz)}_3](\text{ClO}_4)_2\cdot3\text{H}_2\text{O}\) where Hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole\textsuperscript{[85]} in Table 2 below and it shows similar framework-building M(Ltrz₃) (M = Fe, Cu; L = H, C₂H₅O).

<table>
<thead>
<tr>
<th>Table 2 Comparison of cell parameters of ([\text{Fe(Htrz)}_3]\text{(ClO}_4)_2\cdot1.85\text{H}_2\text{O}) and ([\text{Cu(Hyetrz)}_3]\text{(ClO}_4)_2\cdot3\text{H}_2\text{O}).</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(Htrz)}_3]\text{(ClO}_4)_2\cdot1.85\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Cell parameters: in Å</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>β (°)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
</tr>
<tr>
<td>Space group</td>
</tr>
</tbody>
</table>

The parameter b = 23.023Å in the Cu compound decreases to 20.6125Å in the Fe compound because of the substitution of -CH₂CH₂OH in the Cu compound with -H in the Fe compound (see Figure 22). The parameters a and c in the Cu compound are close to the c and a, respectively, of the Fe compound.
Substitution of -CH₂CH₂OH in [Cu(Hyetrz)₃][ClO₄]²⁻·3H₂O, with -H in [Fe(Htrz)₃][ClO₄]₂ leads to shortened b-axis.

Figure 22 CRYSTAL MAKER™ Drawing of the compound Cu(Hyetrz)₃][ClO₄]²⁻·3H₂O where Hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole) (García et al. 1997). Inorganic Chemistry, 1997, 36, 6357-6365. Copyright 1997 American Chemical Society. Special thanks and acknowledgement to Y. Garcia for supplying the figure.
Chapter 7 – Conclusions and recommendations

As stated in Chapter 1, the aim of this research project was to study/ review the existing knowledge on spin-transition; to identify unknowns or inconclusive theories about spin-transition polymers; to investigate one or more of these unknowns in order to obtain a better understanding of spin-transition materials in general and polymeric spin-transition compounds in particular, and to add to the pool of knowledge on the subject.

From the literature study/review it was determined that more information was required on the structural changes that occur in polymeric spin-transition compounds during spin-transition.

The infrared study showed that the Fe-N₆ coordination sphere has six equal Fe-N bonds in the low-spin state. It also showed that these Fe-N bonds weaken/lengthen during the spin-transition, with two of the bonds lengthening to a lesser degree than the other four. The pressure-dependent low-spin⇌high-spin transition of [Fe(Htrz)₃](ClO₄)₂ was also discovered in the infrared study and a potential application of this is described in the box at the end of the chapter.

The Raman investigation showed that the Fe-N stretching mode that occurs in the region between 200 and 300 cm⁻¹ in the Raman spectra of these compounds only appears in the low-spin state. The increasing intensity of this peak as a function of temperature, was directly related to the spin-transition phenomenon by deriving a spin-transition function curve from the peak intensity data. It could be concluded with a reasonable amount of certainty, that the appearance/disappearance of the peak was indicative of a change in the symmetry within the coordination sphere.

The initial aim of the X-ray powder diffraction study was to obtain a good quality, repeatable powder pattern for the compound, [Fe(Htrz)₃](ClO₄)₂·1.85H₂O. This was
Chapter 7 – Conclusions and recommendations

achieved for the compound in the low-spin state. From the results obtained, a procedure is suggested to obtain specimens of \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2 \cdot 1.85\text{H}_2\text{O}\) that give reproducible, high-quality X-ray powder patterns:

1. After synthesis, the air-dried sample should be ground for ±5 minutes and then dried for an additional 24 to 48 hours. This is to eliminate any solvent that may be trapped within the powder. Improper drying of the sample leads to poor crystallinity and this in turn leads to a low-quality powder pattern with an amorphous region between 10° and 18° 2θ.

2. After proper drying, the sample should be ground for an additional 5 to 10 minutes after which other practical steps should be taken in order to avoid preferential orientation of the microcrystals (e.g., sieving and surface correction with a razor blade).

Although the X-ray powder study did not focus on the changes that occur during spin-transition, a lot of useful information was obtained from the indexing of the powder data. It was determined that the low-spin compound has monoclinic symmetry, with cell parameters: 
\[a = 13.0321 \text{ Å}, \ b = 20.6134 \text{ Å}, \ c = 15.8160 \text{ Å}, \ \beta = 103.83° \text{ and Volume} = 4125.633 \text{ Å}^3.\] These values were determined with figures of merit: \(M_{15} = 10.4\) and \(F_{15} = 22.0\) (0.0100, 68).

**Recommendation**

If additional studies were to be done on these compounds, it is suggested that attempts are made to obtain single crystals for the compound \([\text{Fe(Htrz)}_3]\text{SO}_4\). Although this compound does not undergo spin-transition, the infrared spectra show that it has a structure similar to \([\text{Fe(Htrz)}_3](\text{ClO}_4)_2\), and during this project a single crystal of \([\text{Fe(Htrz)}_3]\text{SO}_4\) was obtained. Unfortunately, the crystal was discarded at that time because it did not form part of the materials under study.
Potential application of spin-transition polymers in pressure sensors.

The figures below describe schematically how spin-transition compounds can be used in critical-pressure applications. In the first figure the pressure in the vacuum chamber is below the critical pressure, $P_c$, causing the spin-transition compound to turn white. The white surface reflects the laser light to the light detector, which can be connected to a computer or an alarm. In the second figure the pressure in the vacuum chamber is above the critical pressure, $P_c$, causing the spin-transition compound to turn purple. The purple surface will absorb the light or reflect it to a lesser degree, depending on the wavelength of the light used. The change in pressure can thus be observed at a critical point.
References

Note – Due to the fact that published studies on spin-transition often contain information obtained from more than one technique, some of the references have been grouped to simplify referencing in the main text. As a consequence of this, some duplicate inscriptions appear in the list below.


Grouped References (UV-vis spectroscopy)


Grouped References (magnetic susceptibility)


References


Grouped References (Mössbauer spectroscopy)


Grouped References (EPR spectroscopy)


Grouped references (Single crystal X-ray diffraction)


References

Grouped References (Powder X-ray diffraction)

Grouped References (Infrared Spectroscopy)

Grouped References (Raman Spectroscopy)


Annex 1 – Magnetochemical measurements

The values that are measured with the Gouy-balance are gram susceptibility, $\chi$. A more useful value in chemistry is the molar susceptibility, $\chi_m$, which is obtained by multiplying $\chi$ and the molar mass of the substance.

$$\chi_m = \chi \cdot M$$

Since the molar mass of the polymeric structures investigated here was not determined, the value of M was taken as the mass of the monomeric units that make up the polymer, i.e.

$$M = \text{mass of metal ion} + \text{mass of ligands} + \text{mass of counter anions}.$$ 

If $\chi_m$ is positive, the compound is paramagnetic, and if it is negative $\chi_m$ is negative. $\chi_m$ is described by the formula:

$$\chi_m^{(\text{complex})} = \chi_m^{(\text{metal ion})} + \chi_m^{(\text{ligands})} + \chi_m^{(\text{counter ions})}$$

It is necessary to correct for the diamagnetism of the other groups and therefore the main interest is in $\chi'_m$. The diamagnetic corrections that were used are given in Table 3.

<table>
<thead>
<tr>
<th>Species</th>
<th>Diamagnetic Correction $\times 10^8$ g$^{-1}$ atom$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-1,2,4-Triazole</td>
<td>35</td>
</tr>
<tr>
<td>4-NH$_2$-1,2,4-Triazole</td>
<td>43</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>23.4</td>
</tr>
<tr>
<td>ClO$_4$$^-$</td>
<td>32</td>
</tr>
<tr>
<td>SO$_4$$^{2-}$</td>
<td>40.1</td>
</tr>
</tbody>
</table>
The effective magnetic moment, $\mu_{\text{eff}}$, is obtained from the equation:

$$\mu_{\text{eff}} = 2.83 \sqrt{J_n T}$$

with $T$ = temperature in Kelvin and $\mu_{\text{eff}}$ in Bohr magnetons.

The number of unpaired electrons are then obtained from:

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$

The following mass measurements have to be made:

- mass of the empty tube, without the magnetic field, $W_1$
- mass of the empty tube in the magnetic field, $W_2$
- mass of the tube, filled to the mark with water, without the magnetic field, $W_3$
- mass of the tube, filled with the finely powdered complex, without the magnetic field, $W_4$
- mass of the tube, filled with the finely powdered complex, with the magnetic field on, $W_5$

The following relations can then be used:

$$\Delta_w = (W_5 - W_4) - (W_2 - W_1)$$

$$V = (W_3 - W_1)/\rho(H_2O) \quad (\rho(H_2O) = 0.998 \text{ g/cm}^3)$$

$$\gamma_0 = 0.36 \times 10^6 \quad \text{(Paramagnetic oxygen is displaced by the sample)}$$

$$m = W_4 - W_1$$

A standard with known magnetic moment is then used to calibrate the Gouy balance in order to use the relation:

$$\chi_s^' = (a\Delta_w + \gamma_0)V/m$$

A calibration constant, $a$, is obtained.

$$\chi_s^'([\text{Ni(en)}_3\text{S}_2\text{O}_3]) = 11.04 \times 10^{-6} \quad (20^\circ C)$$
[Ni(en)₃]S₂O₃ can be prepared with a high degree of purity. It is not hygroscopic, it is stable and gives good packing in the tube. The compound obeys the Curie-Weiss law with q = 43°.

Measurements of the susceptibilities, of all four the studied compounds at room temperature, gave the following results:

Purple [Fe(Htrz)₃](ClO₄)₂ (suspected low-spin):
0.39 ≈ 0 unpaired electrons (i.e. Low-spin)

White [Fe(NH₂trz)₃](ClO₄)₂ (suspected high-spin):
3.74 ≈ 4 unpaired electrons (i.e. High-spin)

Purplish-brown [Fe(Htrz)₃]Cl₂ (suspected low-spin):
0.995 ≈ 1 unpaired electron
(i.e. mixed state with majority of the Fe-centres Low-spin)
(Since the complex is supposed to be d⁶, this result is taken to imply that some of the Fe²⁺ has oxidised to Fe³⁺, indicated by the browning of the purple sample)

White [Fe(Htrz)₃]SO₄ (suspected high-spin):
4.066 ≈ 4 unpaired electrons (i.e. High-spin)
Annex 2 - Results from elemental analysis of the four samples used in the XRD study.

Table 4 Elemental analysis of sample 1 to 4 and theoretical mass percentages of two possible forms of the compound.

<table>
<thead>
<tr>
<th>Sample age at the start of the study</th>
<th>Fe(%)</th>
<th>C(%)</th>
<th>N(%)</th>
<th>H(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1 day</td>
<td>9.64</td>
<td>14.45</td>
<td>24.53</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1 week</td>
<td>9.85</td>
<td>15.11</td>
<td>25.45</td>
</tr>
<tr>
<td>Sample 3</td>
<td>15 months</td>
<td>9.51</td>
<td>15.14</td>
<td>25.62</td>
</tr>
<tr>
<td>Sample 4</td>
<td>2 hours</td>
<td>9.47</td>
<td>14.99</td>
<td>24.97</td>
</tr>
<tr>
<td>Theoretical calculation for <a href="ClO%E2%82%84">Fe(Htrz)₃</a>₂·1.85H₂O</td>
<td></td>
<td>11.28</td>
<td>14.55</td>
<td>25.45</td>
</tr>
<tr>
<td>Theoretical calculation for <a href="ClO%E2%82%84">Fe(Htrz)₃</a>₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The difference between the expected and found values of Fe is assumed to be due to insufficient sensitivity of the analysis technique. The stoichiometry of the four different samples indicate a partially hydrated compound with a proper formula: [Fe(Htrz)₃](ClO₄)₂·1.85H₂O.
Annex 3 – Instrument and Data collection parameters for Powder Diffraction Analysis

Table 5 Instrument and data collection parameters for X-ray powder diffraction analysis

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Siemens D-501</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Cu Kα (1.5418 Å)</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Specimen</td>
<td>flat-plate, rotating (30 RPM)</td>
</tr>
<tr>
<td>Power Setting</td>
<td>40 kV, 40 mA</td>
</tr>
<tr>
<td>Soller slits</td>
<td>2° (diffracted beam side)</td>
</tr>
<tr>
<td>Divergence slits</td>
<td>1°</td>
</tr>
<tr>
<td>Receiving slits</td>
<td>0.05°</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Secondary, graphite</td>
</tr>
<tr>
<td>Detector</td>
<td>scintillation counter</td>
</tr>
<tr>
<td>Step width</td>
<td>0.02° 2θ</td>
</tr>
</tbody>
</table>
Annex 4 – Mid-infrared frequencies of Htrz, [Fe(Htrz)₃](ClO₄)₂ and [Fe(Htrz)₃]Cl₂

Table 6 Comparison of the mid-infrared frequencies of the free Htrz ligand, [Fe(Htrz)₃](ClO₄)₂ and [Fe(Htrz)₃]Cl₂. *Centre of gravity of band **Several broad bands

<table>
<thead>
<tr>
<th>Frequencies / cm⁻¹</th>
<th>Published[184]</th>
<th>Observed</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Htrz</td>
<td><a href="ClO%E2%82%84">Fe(Htrz)₃</a>₂</td>
<td>[Fe(Htrz)₃]Cl₂</td>
<td></td>
</tr>
<tr>
<td>3124s, 3116s</td>
<td>3133s, 3121s, 3114s</td>
<td>3083s, 3095s</td>
<td>3090s, 3045s</td>
</tr>
<tr>
<td>2730 vs*</td>
<td>2853 s*</td>
<td>2985-2905**</td>
<td>2978-2970**</td>
</tr>
<tr>
<td>1830 m, 1547 m</td>
<td>1766 m, 1545 m</td>
<td>1809 m, 1536 m</td>
<td>-</td>
</tr>
<tr>
<td>1535 m</td>
<td>1532 m</td>
<td>1513 m</td>
<td>1513 s</td>
</tr>
<tr>
<td>1488 vs</td>
<td>1485 s</td>
<td>1419 m</td>
<td>1419 s</td>
</tr>
<tr>
<td>1383 m</td>
<td>1380 m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1300 m</td>
<td>1301 s</td>
</tr>
<tr>
<td>1364 vs, 1304 w</td>
<td>1362 w, 1302 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1272 vs</td>
<td>1273 s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1260 vs</td>
<td>1257 s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1184 m</td>
<td>1180 m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1050-1170 m</td>
<td>-</td>
</tr>
<tr>
<td>1146 s</td>
<td>1147 s</td>
<td>1146 s</td>
<td>1147 s</td>
</tr>
<tr>
<td>1058 m</td>
<td>1057 m</td>
<td>1046 s</td>
<td>1049 s</td>
</tr>
<tr>
<td>982 vs</td>
<td>980 s</td>
<td>996 m</td>
<td>996 m</td>
</tr>
<tr>
<td>908 m, 957 m, 950 m</td>
<td>956 m</td>
<td>914 w</td>
<td>-</td>
</tr>
<tr>
<td>943 m, 924 m</td>
<td>930 m</td>
<td>-</td>
<td>950 w</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>915 m</td>
<td>-</td>
</tr>
<tr>
<td>892 m, 885 m</td>
<td>884 s</td>
<td>824 m</td>
<td>858 m, 833 m</td>
</tr>
<tr>
<td>684 m, 680 m</td>
<td>683 s</td>
<td>-</td>
<td>677 vs</td>
</tr>
<tr>
<td>652 m</td>
<td>649 s</td>
<td>-</td>
<td>634 vs</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>630-460 vw</td>
<td>ClO₄⁻</td>
</tr>
</tbody>
</table>
Annex 5 – Low-frequency Raman bands of the complexes and their pure starting materials

Table 7 Recorded low-frequency Raman bands (in cm\(^{-1}\)) of \([\text{Fe} (\text{NH}_2 \text{trz})_3] [\text{ClO}_4]_2\) and its pure starting materials.

<table>
<thead>
<tr>
<th>Pure NH(_2)trz</th>
<th>Pure Fe(\text{ClO}_4)(_2)</th>
<th>([\text{Fe} (\text{NH}_2 \text{trz})_3] [\text{ClO}_4]_2) Complex</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Tentative Assignment</td>
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</tr>
<tr>
<td></td>
<td>Low-spin state (158K)</td>
<td>High-spin state (249K)</td>
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</tr>
<tr>
<td>55</td>
<td>60</td>
<td>-60</td>
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</tr>
<tr>
<td>67</td>
<td>75</td>
<td>75</td>
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</tr>
<tr>
<td>102</td>
<td>115</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>136</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>153</td>
<td></td>
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<td>162</td>
<td></td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>173</td>
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<td>172</td>
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</tr>
<tr>
<td>198</td>
<td></td>
<td>180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>464</td>
<td>458</td>
<td></td>
</tr>
<tr>
<td></td>
<td>458</td>
<td>v(_2) (E) (ClO(<em>4))^(</em>{186})</td>
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</tr>
<tr>
<td></td>
<td>627</td>
<td>637</td>
<td></td>
</tr>
<tr>
<td></td>
<td>621+633</td>
<td>625</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>v(_4) (F(_2)) (ClO(<em>4))^(</em>{180})</td>
<td></td>
</tr>
</tbody>
</table>
Table 8 Low-frequency Raman bands (in cm$^{-1}$) of the three Htrz-containing complexes and their pure starting materials. (sh = shoulder, b = broad)

<table>
<thead>
<tr>
<th>Raman Frequency</th>
<th>Description</th>
<th>Pure Htrz from literature$^{[a,b]}$</th>
<th>Pure Htrz Observed</th>
<th>Pure Fe(ClO$_4$)$_2$ salt</th>
<th><a href="ClO$_4$">Fe(Htrz)$_3$</a>$_2$ complex</th>
<th>[Fe(Htrz)$_3$]Cl$_2$</th>
<th>FeSO$_4$ salt</th>
<th>[Fe(Htrz)$_3$]SO$_4$</th>
<th>high-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>low-spin (77K)</td>
<td>high-spin (298K)</td>
<td>low-spin</td>
<td>high-spin</td>
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<td></td>
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<tr>
<td>54</td>
<td>Interchain</td>
<td>54</td>
<td>41</td>
<td>50</td>
<td>50</td>
<td>50 sh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>Interchain</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>NH-N Bend</td>
<td>58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>NH-N Bend</td>
<td>61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>NH-N Bend</td>
<td>67-69</td>
<td>64</td>
<td>65</td>
<td>65 sh</td>
<td>70-75 vs</td>
<td></td>
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<tr>
<td>71</td>
<td>NH-N Bend</td>
<td>76</td>
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<td></td>
<td></td>
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</tr>
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<td>83</td>
<td>Chain torsion</td>
<td>86</td>
<td>89</td>
<td>89 sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>105</td>
<td>NH-N Bend</td>
<td>118</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>117</td>
<td>NH-N Bend</td>
<td>112</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>128</td>
<td>NH-N Bend</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>120 sh, b</td>
<td>114</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>131</td>
<td>NH-N Bend</td>
<td>130</td>
<td>134</td>
<td>142 sh, b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>155</td>
<td>NH-N Bend</td>
<td>157</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>162</td>
<td>Interchain</td>
<td>157</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>176</td>
<td>Interchain</td>
<td>199</td>
<td></td>
<td></td>
<td></td>
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<td>200</td>
<td>Combination</td>
<td>201</td>
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</tr>
<tr>
<td>199</td>
<td>NH-N stretch</td>
<td>199</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>NH-N stretch</td>
<td>201</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_2(E)$</td>
<td>(ClO$_4^-$/SO$_4^{2-}$ anion)</td>
<td>464</td>
<td>458</td>
<td>465</td>
<td>450</td>
<td>450</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_4(F_2)$</td>
<td>(ClO$_4^-$/SO$_4^{2-}$ anion)</td>
<td>627</td>
<td>624</td>
<td>623</td>
<td>620</td>
<td>606+623</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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Annex 6 – Powder Diffraction Data

Table 9 X-ray powder diffraction data and calculated cell parameters for sample 3 of the compound \[\text{Fe(Htrz)₃ClO}_₄\cdot2·1.85\text{H₂O}\]

<table>
<thead>
<tr>
<th>2θ_cal (°)</th>
<th>2θ_obs (°)</th>
<th>d_cal (Å)</th>
<th>d_obs (Å)</th>
<th>I/I₀ (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.920</td>
<td>7.941</td>
<td>11.163</td>
<td>11.125</td>
<td>61</td>
</tr>
<tr>
<td>8.200</td>
<td>8.188</td>
<td>10.784</td>
<td>10.789</td>
<td>56</td>
</tr>
<tr>
<td>10.940</td>
<td>(10.798)</td>
<td>8.085</td>
<td>(8.187)</td>
<td>27</td>
</tr>
<tr>
<td>11.970</td>
<td>11.948</td>
<td>7.395</td>
<td>7.401</td>
<td>22</td>
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<tr>
<td>14.670</td>
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<td>16.464</td>
<td>5.392</td>
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<td>17.197</td>
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<td>17.210</td>
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<td>5.153</td>
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<td>5.038</td>
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<td>17.620</td>
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<td>$\theta_{\text{calc}}$ (°)</td>
<td>$\theta_{\text{obs}}$ (°)</td>
<td>$d_{\text{calc}}$ (Å)</td>
<td>$d_{\text{obs}}$ (Å)</td>
<td>$I/I_0$ (hkl)</td>
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<td>4.229</td>
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<td>3.888</td>
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<td>22.950</td>
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<td>3.805</td>
<td>86 332</td>
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<td>23.500</td>
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<td>3.786</td>
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<td>242</td>
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<td>23.910</td>
<td>23.912</td>
<td>3.721</td>
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<td>3.632</td>
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<td>24.720</td>
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<td>251</td>
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<td>3.452</td>
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<td>061</td>
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Cell parameters: Monoclinic system with $a = 13.0321$ Å, $b = 20.6134$ Å, $c = 15.8160$ Å, $\beta = 103.83^\circ$ and Volume = 4125.633 Å³. 

$[M_{15} = 10.4] [F_{15} = 22.0 (0.0100, 68)]$