CHAPTER 2

CRYSTALLOGRAPHIC ANALYSIS

2.1 INTRODUCTION

The only benzoic acid derivative complexes which yielded diffraction quality crystals suitable for single crystal studies were the 2-fluoro, 3-fluoro, 3-amino benzoate and unsubstituted benzoate complexes. Note that the crystal structure for the benzoate complex had already been solved by photographic methods [1], however, the results obtained from the diffractometer for the complex in this thesis were of a much higher quality.

All the remaining benzoic acid derivative complexes had a generic look when viewed under the microscope. The crystals were very thin, hair-like in nature. However, powder diffraction studies of these complexes showed that they were not all identical.

In an attempt to obtain more diffraction quality single crystals, complexes were synthesised that contained BF_4^- and PF_6^- as the anions. This proved fruitful and two further crystal structures were obtained. However, it must be noted that the PF_6^- complex was prepared from $TlNO_3$ and not Tl_2CO_3 and therefore there is a possibility of NO_3^- contamination in the complex.

Another diffraction quality single crystal was prepared using the 4-aminobenzoic acid as the anion, the precursor (without thiourea) isolated to prove that the synthesis route applied included the formation of this species. This was also in accordance with at least nine examples in the literature [2, 9].

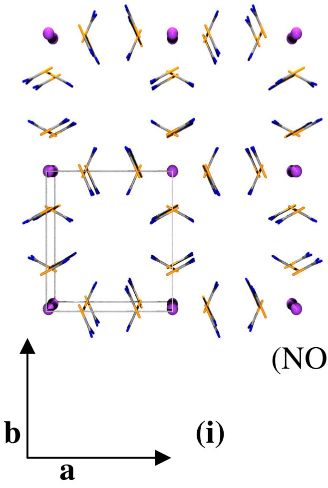
Another crystal structure that could be determined resulted from the synthesis, in the same manner as the other benzoic acid derivative complexes, in this case the 2-aminobenzoic acid as the anion. However, the structure obtained was most different to the other structures
And its space group was $P2_1/c$ (monoclinic). The other four benzoates all crystallised in Cmcm (orthorhombic). The structure's results are given in this chapter, however, it was suspected that the formation of this product resulted from some irreproducible change in reaction conditions. Unfortunately no spectroscopic data was obtained to help clarify the structure as there was insufficient material available.

The BF_4^- and PF_6^- complexes were not fully analysed with all the spectroscopic methods used for the analysis of the benzoate complexes as these two products were obtained using $TlNO_3$ as starting material. As there was some uncertainty about a possible NO_3^- contamination of these crystals, the PF_6-complex was subjected to analysis using a nitrate-specific electrode, showing that there was no NO_3^- present. At this stage the BF_4^-complex was not analysed by other spectroscopic methods, as the structure was solved and refined correctly without any disorder. The PF_6^-complex was refined in the space group P4cc and could not be solved and refined with success in P4/mcc (the space group suggested for the NO_3^- complex). The 4-aminobenzoate non-thiourea complex was analysed in both the IR/Raman and thermal analysis chapters in order to confirm the bands/peaks which related specifically to thiourea.

2.2 SINGLE CRYSTAL STUDY

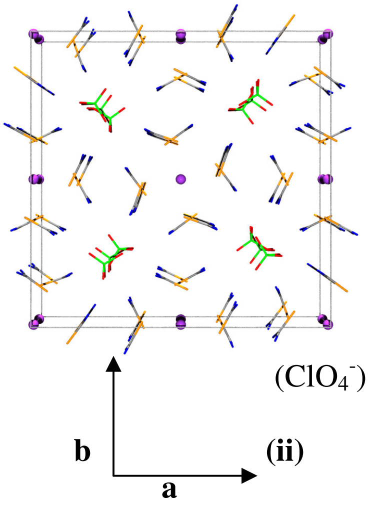
The resulting molecular structures produced from the single crystal analysis of the 2-fluoro, 3-fluoro, 3-amino and benzoate complexes are very similar to those reported for the benzoate [1]/ NO_3^-/ ClO_4^-/ ClO_3^-/ $P(OH)_2O^-$ complex [3]. Note that the non-thiourea 4-aminobenzoate complex has a different structure and will be discussed later.

Thallium - Thiourea Complexes - Crystal Structures with various anions



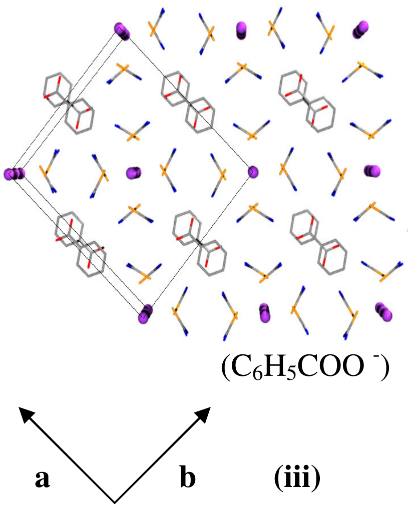
(NO_3^-)

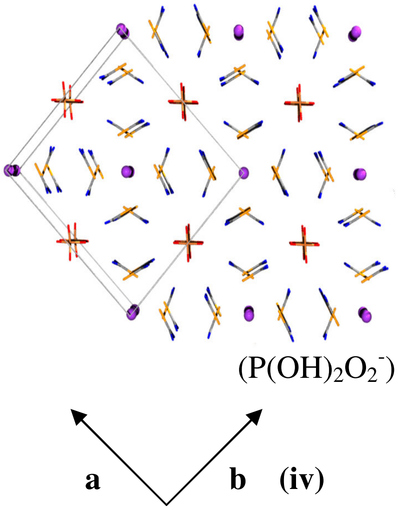
(i)

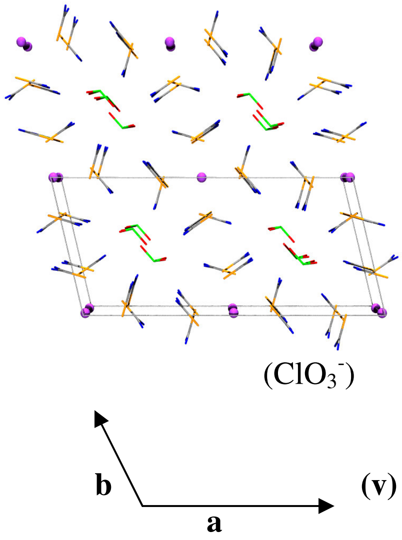


(ClO_4^-)

(ii)







(i)NO_3^- Tetragonal, P4/mcc
a = b = 10.34Å, c = 8.29Å
Viewed along the c axis

(ii)ClO_4^- Tetragonal, P4/mnc
a = b = 21.07Å, c = 8.28Å
Viewed along the c axis

(iii)$C_6H_5COO^-$ Orthorhombic, Cmcm
a = 15.64Å, b = 17.09Å, c = 8.15Å
Viewed along the c axis

(iv)$P(OH)_2O_2^-$ Orthorhombic, Cccm
a = 15.40Å, b = 14.64Å, c = 8.27Å
Viewed along the c axis

(v)ClO_3^- Monoclinic, B2/m
a = 22.037Å, b = 9.869Å, c = 8.201Å
$\gamma = 103.95^\circ$
Viewed along the c axis

Fig. 2.1 Projection of Thallium – Thiourea complexes generated from the Cambridge database (version 5.26, as well as the 2005 updates during February, May, August) (i) to (v) viewed along the c-axis.

The above structures were generated from the Cambridge Database (version 5.26, as well as the 2005 updates during February, May, August) [4] and clearly show that in all cases the thallium and thiourea molecules arrange themselves in such a way as to form an open channel in the centre of the complex. This cavity is filled by the various anionic moieties that are added to the thallium and thiourea in the synthesis, i.e. in terms of this thesis it is the benzoic acid derivatives, the BF_4^- and PF_6^- anions.

2.2.1 EXPERIMENTAL

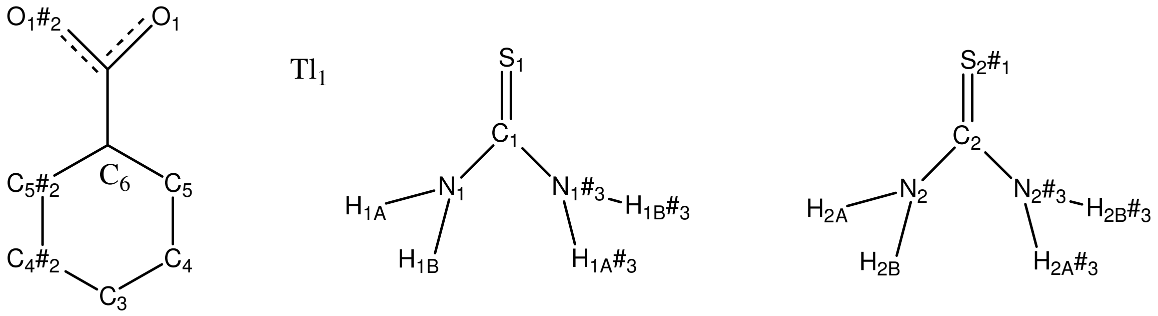
The crystal data and processing parameters are given in Tables 2.1 – 2.12, 2.19 – 2.30 and 2.33 – 2.56. Data collection, cell refinement and data reduction was executed using the SMART software [5].

Programs used to determine and refine the structures :
SHELXS 97 and SHELXL 97 [6]
Molecular graphics : Ortep – 3 [7]
POV-Ray. [8]

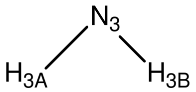
The structures were in general determined using Patterson methods and a series of difference maps yielded the remaining atom positions, after subsequent refinement. The hydrogen atoms were experimentally located and refined without any restrictions, apart from those hydrogen atoms in the PF_6^- and 4-aminobenzoate complexes which were placed in theoretical positions and included in the refinements. The improved structural data for the benzoate complex did not reveal any additional structural detail not already indicated by the original report [1].

2.2.2 CRYSTALLOGRAPHIC LABELLING SYSTEM

The labelling system used for the crystallographic tables that follow is seen below in Fig. 2.2, taking the symmetry operators of the space group Cmcm into consideration:



Various Substituents: F_1



The hydrogen atoms on the benzoate rings were labelled according to the parent carbon atom.

Note: Symmetry transformations used to generate equivalent atoms:

#1	x, y-1, z	only for Cmcm
#2	-x, y, -z + ½	
#3	x, y, -z + ½	

Fig. 2.2 **Crystallographic labelling system for the complexes**

2. 3 CRYSTALLOGRAPHIC RESULTS FOR THE FOUR BENZOATE COMPLEXES

2.3.1 RESULTS FOR THE 2-FLUORO COMPLEX CRYSTAL ANALYSIS

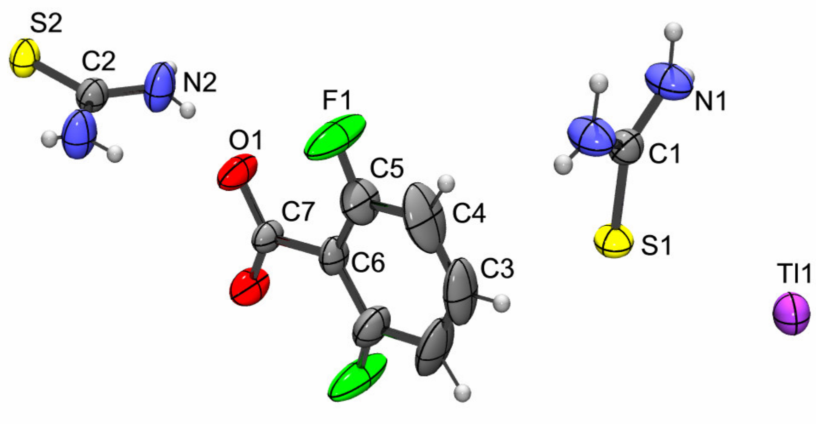


Fig. 2.3 **Molecular structure of the components involved in the 2-Fluoro complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.**

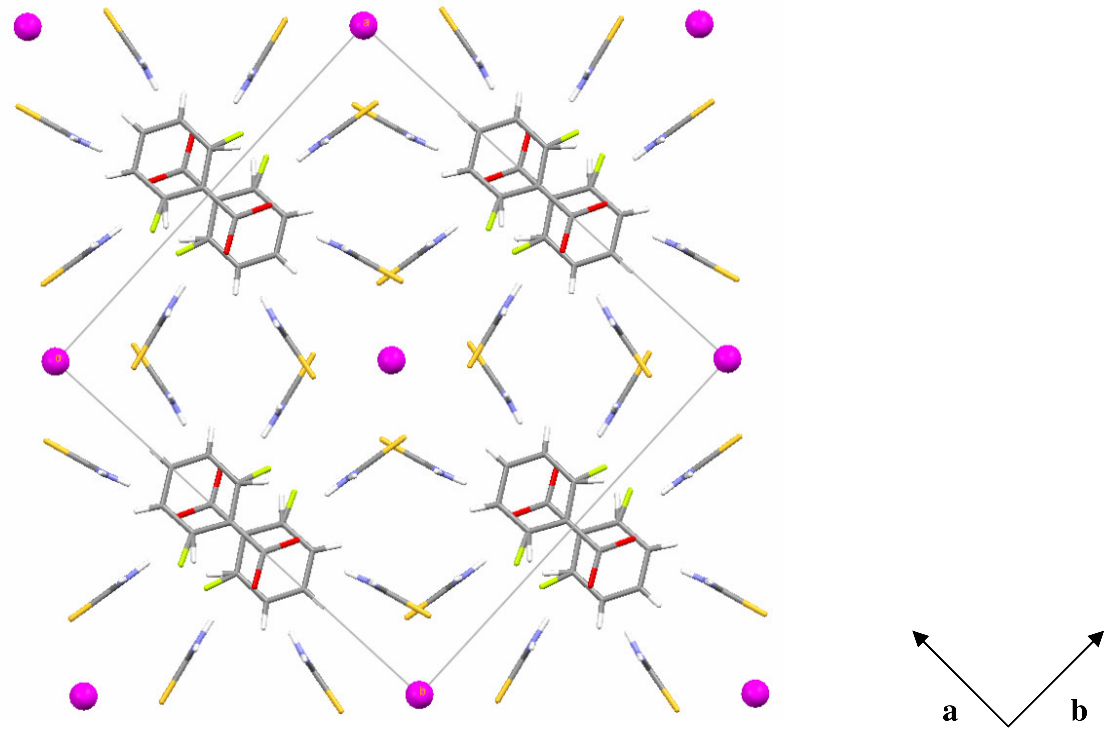


Fig. 2.4 **Molecular packing of the 2-Fluoro complex viewed along the direction of the c axis. The direction of the a and b axes are shown above.**

CRYSTAL STRUCTURE TABLES FOR 2-FLUORO COMPLEX

Identification code	nb11_abs	
Empirical formula	$C_{11} H_{20} F N_8 O_2 S_4 Tl$	
Formula weight	647.96	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c m	
Unit cell dimensions	a = 15.7317(10) Å	α= 90°.
	b = 17.0319(11) Å	β= 90°.
	c = 8.0881(5) Å	γ = 90°.
Volume	2167.1(2) $Å^3$	
Z	4	
Density (calculated)	1.986 Mg/m^3	
Absorption coefficient	7.870 mm^{-1}	
F(000)	1248	
Crystal size	0.30 x 0.25 x 0.20 mm^3	
Theta range for data collection	2.59 to 26.45°.	
Index ranges	-18<=h<=16, -20<=k<=21, -10<=l<=3	
Reflections collected	5739	
Independent reflections	1177 [R(int) = 0.0309]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.207 and 0.125	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1177 / 0 / 105	
Goodness-of-fit on F^2	1.230	
Final R indices [I>2σ(I)]	R1 = 0.0373, wR2 = 0.0745	
R indices (all data)	R1 = 0.0384, wR2 = 0.0757	

Extinction coefficient	0.0068(4)
Largest diff. peak and hole	1.313 and -3.027 e.Å^{-3}

* $w = 1/ [\sigma^2 (F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/ 3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.1 Crystal data and structure refinement for Tl^{+1} 4(TU) 2-Fluorobenzoate.

Tl(1)-S(1)	3.3792(7)		
Tl(1)-S(2)#1	3.4235(8)	S(1)-Tl(1)-S(2)#1	67.539(16)
S(1)-C(1)	1.708(4)	C(1)-S(1)-Tl(1)	111.28(8)
C(1)-N(1)	1.319(3)	N(1)#3-C(1)-N(1)	117.6(3)
N(1)-H(1A)	0.89(4)	N(1)-C(1)-S(1)	121.18(17)
N(1)-H(1B)	0.70(5)	C(1)-N(1)-H(1A)	118.4(15)
S(2)-C(2)	1.710(3)	C(1)-N(1)-H(1B)	129(4)
C(2)-N(2)	1.313(3)	H(1A)-N(1)-H(1B)	112(4)
N(2)-H(2A)	0.78(4)	N(2)-C(2)-N(2)#3	117.0(4)
N(2)-H(2B)	0.62(5)	N(2)-C(2)-S(2)	121.48(19)
O(1)-C(7)	1.234(4)	C(2)-N(2)-H(2A)	114(2)
C(3)-C(4)#2	1.361(8)	C(2)-N(2)-H(2B)	126(5)
C(3)-C(4)	1.361(8)	H(2A)-N(2)-H(2B)	120(5)
C(3)-H(3)	0.89(10)	C(4)#2-C(3)-C(4)	121.0(6)
C(4)-C(5)	1.412(6)	C(4)#2-C(3)-H(3)	119.5(3)
C(4)-H(4)	0.92(6)	C(4)-C(3)-H(3)	119.5(3)
C(5)-F(1)	1.159(7)	C(3)-C(4)-C(5)	118.9(6)
C(5)-C(6)	1.372(5)	C(3)-C(4)-H(4)	114(4)
C(6)-C(5)#2	1.372(5)	C(5)-C(4)-H(4)	127(4)
C(6)-C(7)	1.537(7)	F(1)-C(5)-C(6)	126.9(5)
C(7)-O(1)#2	1.234(4)	F(1)-C(5)-C(4)	110.9(5)

C(6)-C(5)-C(4)	122.2(5)	C(5)#2-C(6)-C(7)	121.5(3)
C(5)-C(6)-C(5)#2	116.9(6)	O(1)#2-C(7)-O(1)	124.8(5)
C(5)-C(6)-C(7)	121.5(3)	O(1)#2-C(7)-C(6)	117.6(2)
O(1)-C(7)-C(6)	117.6(2)		

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z   #2 -x,y,-z+1/2   #3 x,y,-z+1/2

Table 2.2 **Bond lengths [Å] and angles [º] for Tl^{+1} 4(TU) 2-Fluorobenzoate**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)#4	0.89(4)	2.19(4)	2.974(4)	147(2)
N(2)-H(2A)...O(1)	0.78(4)	2.30(4)	3.044(4)	160(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z   #2 -x,y,-z+1/2   #3 x,y,-z+1/2   #4 -x+1/2,y-1/2,-z+1/2

Table 2.3 **Hydrogen bonds for Tl^{+1} 4(TU) 2-Fluorobenzoate [Å and º].**

2.3.2 RESULTS FOR THE 3-FLUORO COMPLEX CRYSTAL ANALYSIS

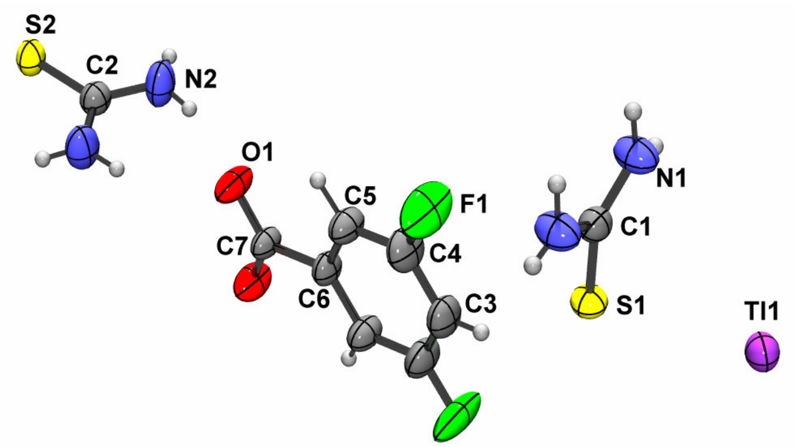


Fig. 2.5 Molecular structure of the components involved in the 3-Fluoro complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.

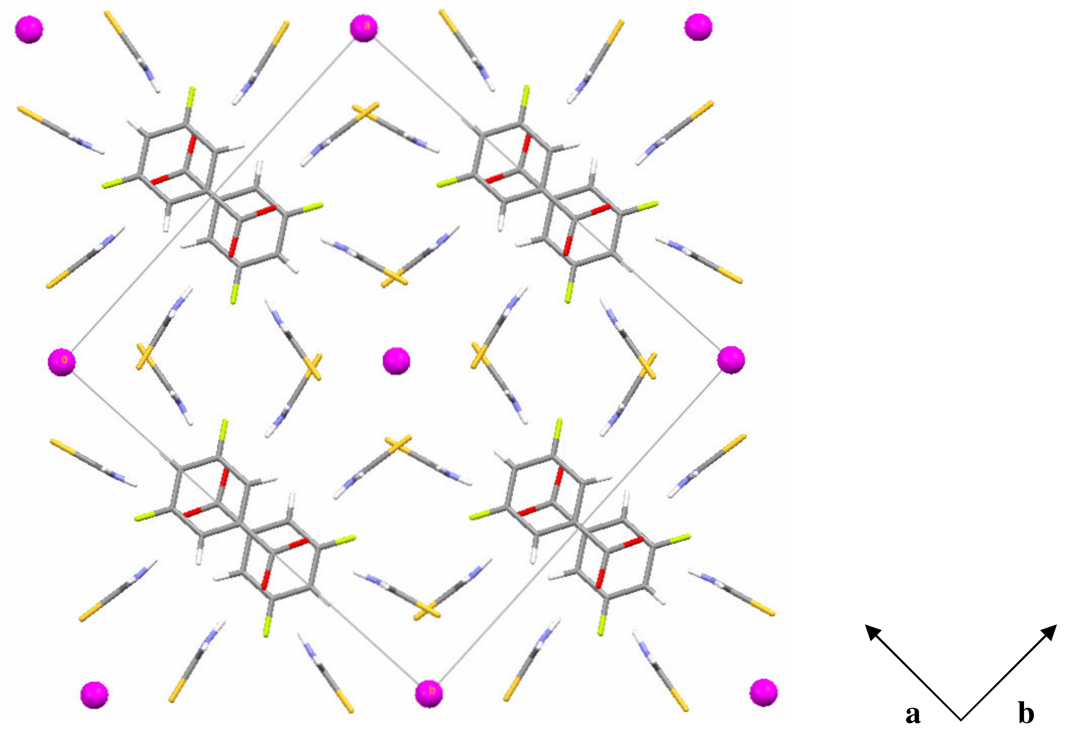


Fig. 2.6 Molecular packing of the 3-Fluoro complex viewed along the direction of the c axis. The direction of the a and b axes are shown above

CRYSTAL STRUCTURE TABLES FOR 3-FLUORO COMPLEX

Identification code	nb18_abs	
Empirical formula	$C_{11} H_{20} F N_8 O_2 S_4 Tl$	
Formula weight	647.96	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c m	
Unit cell dimensions	a = 15.6079(8) Å	α= 90°.
	b = 17.1485(9) Å	β= 90°.
	c = 8.0752(4) Å	γ = 90°.
Volume	2161.34(19) Å^3	
Z	4	
Density (calculated)	1.991 Mg/m^3	
Absorption coefficient	7.891 mm^{-1}	
F(000)	1248	
Crystal size	0.31 x 0.25 x 0.24 mm^3	
Theta range for data collection	2.38 to 26.57°.	
Index ranges	-17<=h<=19, -21<=k<=19, -3<=l<=10	
Reflections collected	5754	
Independent reflections	1183 [R(int) = 0.0249]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.150 and 0.118	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1183 / 0 / 105	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2σ(I)]	R1 = 0.0226, wR2 = 0.0594	
R indices (all data)	R1 = 0.0237, wR2 = 0.0605	

Extinction coefficient	0.00075(14)
Largest diff. peak and hole	0.561 and -0.563 e.Å^{-3}

* $w = 1/ [\sigma^2 (F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/ 3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.4 Crystal data and structure refinement for Tl^{+1} 4(TU) 3-Fluorobenzoate.

Tl(1)-S(1)	3.3537(7)		
Tl(1)-S(2)#1	3.4142(8)	S(1)-Tl(1)-S(2)#1	67.231(16)
S(1)-C(1)	1.707(3)	C(1)-S(1)-Tl(1)	111.74(8)
C(1)-N(1)	1.319(3)	N(1)#3-C(1)-N(1)	117.4(3)
N(1)-H(1A)	0.89(3)	N(1)-C(1)-S(1)	121.32(17)
N(1)-H(1B)	0.70(4)	C(1)-N(1)-H(1A)	118.2(17)
S(2)-C(2)	1.711(3)	C(1)-N(1)-H(1B)	125(4)
C(2)-N(2)	1.315(3)	H(1A)-N(1)-H(1B)	116(4)
N(2)-H(2A)	0.83(4)	N(2)#3-C(2)-N(2)	117.5(4)
N(2)-H(2B)	0.80(4)	N(2)-C(2)-S(2)	121.27(18)
C(3)-C(4)#2	1.382(5)	C(2)-N(2)-H(2A)	116(2)
C(3)-C(4)	1.382(5)	C(2)-N(2)-H(2B)	120(3)
C(3)-H(6)	0.85(7)	H(2A)-N(2)-H(2B)	123(4)
C(4)-F(1)	1.258(6)	C(4)#2-C(3)-C(4)	118.9(5)
C(4)-C(5)	1.392(5)	C(4)#2-C(3)-H(6)	120.5(2)
C(5)-C(6)	1.382(4)	C(4)-C(3)-H(6)	120.5(2)
C(5)-H(4)	0.95(5)	F(1)-C(4)-C(3)	118.1(4)
C(6)-C(5)#2	1.382(4)	F(1)-C(4)-C(5)	121.3(5)
C(6)-C(7)	1.522(6)	C(3)-C(4)-C(5)	120.6(4)
C(7)-O(1)#2	1.242(3)	C(6)-C(5)-C(4)	120.4(4)
C(7)-O(1)	1.242(3)	C(6)-C(5)-H(4)	116(3)

C(4)-C(5)-H(4)	124(3)	O(1)#2-C(7)-O(1)	124.5(5)
C(5)#2-C(6)-C(5)	119.2(5)	O(1)#2-C(7)-C(6)	117.8(2)
C(5)#2-C(6)-C(7)	120.4(2)	O(1)-C(7)-C(6)	117.8(2)
C(5)-C(6)-C(7)	120.4(2)		

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y,-z+1/2 #3 x,y,-z+1/2

Table 2.5 Bond lengths [Å] and angles [°] for Tl^{+1} 4(TU) 3-Fluorobenzoate.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)#4	0.89(3)	2.12(3)	2.922(4)	150(2)
N(1)-H(1B)...S(2)#5	0.70(4)	2.74(4)	3.413(3)	165(5)
N(2)-H(2A)...O(1)#2	0.83(4)	2.28(4)	3.057(4)	156(3)
N(2)-H(2B)...S(1)#6	0.80(4)	2.66(4)	3.449(3)	171(5)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y,-z+1/2 #3 x,y,-z+1/2 #4 x+1/2,y-1/2,z

#5 x,-y+1,z+1/2 #6 x,-y+1,z-1/2

Table 2.6 Hydrogen bonds for Tl^{+1} 4(TU) 3-Fluorobenzoate [Å and °].

2.3.3 RESULTS FOR THE 3-AMINO COMPLEX CRYSTAL ANALYSIS

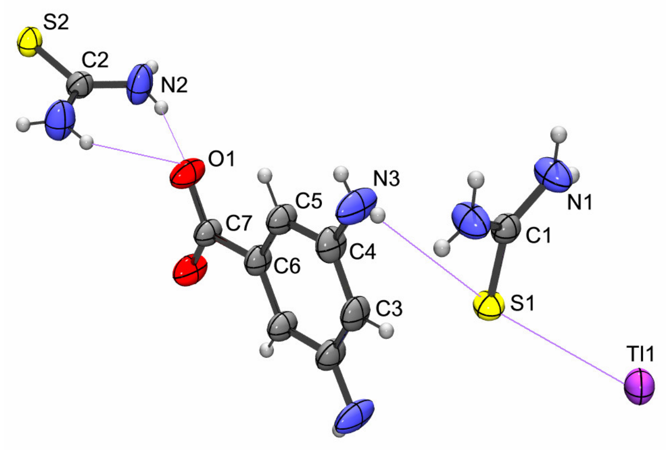


Fig. 2.7 Molecular structure of the components involved in the 3-Amino complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown. Close contacts are also indicated

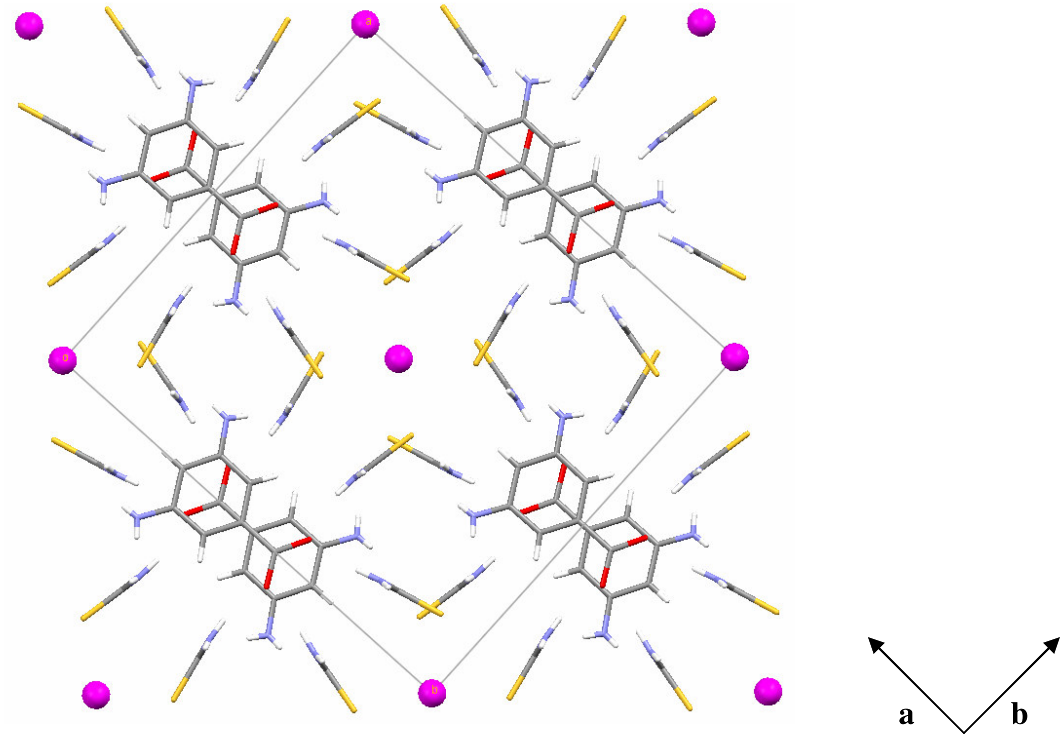


Fig. 2.8 Molecular packing of the 3-Amino complex viewed along the direction of the c axis. The direction of the a and b axes are shown above.

CRYSTAL STRUCTURE TABLES FOR 3-AMINO COMPLEX

Identification code	nb09_abs	
Empirical formula	C_{11} H_{22} N_9 O_2 S_4 Tl	
Formula weight	645.05	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c m	
Unit cell dimensions	a = 15.5683(11) Å	α= 90°.
	b = 17.1150(12) Å	β= 90°.
	c = 8.1352(5) Å	γ = 90°.
Volume	2167.6(3) Å^3	
Z	4	
Density (calculated)	1.977 Mg/m^3	
Absorption coefficient	7.848 mm^{-1}	
F(000)	1136	
Crystal size	0.34 x 0.26 x 0.26 mm^3	
Theta range for data collection	2.62 to 26.54°.	
Index ranges	-18<=h<=19, -21<=k<=20, -3<=l<=10	
Reflections collected	5782	
Independent reflections	1172 [R(int) = 0.0248]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.130 and 0.102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1172 / 0 / 111	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2σ(I)]	R1 = 0.0247, wR2 = 0.0627	
R indices (all data)	R1 = 0.0255, wR2 = 0.0637	

Extinction coefficient	0.0128(5)
Largest diff. peak and hole	1.171 and -0.985 e.$Å^{-3}$

* $w = 1/[\sigma^2(F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/3$

$\Delta\rho$ max = 1.2 e.$Å^{-3}$ (0.5Å from C1)

$\Delta\rho$ min = -1.69e.$Å^{-3}$

Table 2.7 Crystal data and structure refinement for Tl^{+1} 4(TU) 3-Aminobenzoate.

Tl(1)-S(1)	3.3588(6)	N(3)-H(3A)	0.56(7)
Tl(1)-S(2)#1	3.4209(7)	N(3)-H(3B)	0.66(8)
S(1)-C(1)	1.715(3)		
S(2)-C(2)	1.713(3)	S(1)-Tl(1)-S(2)#1	66.867(15)
O(1)-C(7)	1.248(3)	C(1)-S(1)-Tl(1)	111.56(8)
C(1)-N(1)	1.316(3)	N(1)-C(1)-N(1)#3	118.2(3)
C(3)-C(4)	1.386(5)	N(1)-C(1)-S(1)	120.91(16)
C(3)-C(4)#2	1.386(5)	C(4)-C(3)-C(4)#2	121.3(4)
C(3)-H(3)	0.85(6)	C(4)-C(3)-H(3)	119.3(2)
N(1)-H(1A)	0.82(3)	C(4)#2-C(3)-H(3)	119.3(2)
N(1)-H(1B)	0.72(4)	C(1)-N(1)-H(1A)	121.0(16)
C(5)-C(6)	1.380(4)	C(1)-N(1)-H(1B)	124(3)
C(5)-C(4)	1.402(5)	H(1A)-N(1)-H(1B)	114(4)
C(5)-H(5)	0.89(5)	C(6)-C(5)-C(4)	121.4(4)
C(7)-O(1)#2	1.248(3)	C(6)-C(5)-H(5)	117(3)
C(7)-C(6)	1.514(6)	C(4)-C(5)-H(5)	122(3)
C(6)-C(5)#2	1.380(4)	O(1)#2-C(7)-O(1)	123.3(4)
N(2)-C(2)	1.317(3)	O(1)#2-C(7)-C(6)	118.3(2)
N(2)-H(2A)	0.81(3)	O(1)-C(7)-C(6)	118.3(2)
N(2)-H(2B)	0.79(4)	C(5)#2-C(6)-C(5)	118.8(5)
C(4)-N(3)	1.285(8)	C(5)#2-C(6)-C(7)	120.6(2)

C(5)-C(6)-C(7)	120.6(2)	C(3)-C(4)-C(5)	118.5(4)
C(2)-N(2)-H(2A)	116(2)	N(2)#3-C(2)-N(2)	117.4(3)
C(2)-N(2)-H(2B)	120(3)	N(2)-C(2)-S(2)	121.28(17)
H(2A)-N(2)-H(2B)	123(4)	C(4)-N(3)-H(3A)	125(8)
N(3)-C(4)-C(3)	118.4(5)	C(4)-N(3)-H(3B)	108(6)
N(3)-C(4)-C(5)	123.1(5)	H(3A)-N(3)-H(3B)	127(10)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y,-z+1/2 #3 x,y,-z+1/2

Table 2.8 Bond lengths [Å] and angles [º] for Tl^{+1} 4(TU) 3-Aminobenzoate.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)#4	0.82(3)	2.20(3)	2.908(4)	145(2)
N(2)-H(2A)...O(1)	0.81(3)	2.27(3)	3.022(4)	156(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y,-z+1/2 #3 x,y,-z+1/2 #4 -x+1/2,y-1/2,-z+1/2

Table 2.9 Hydrogen bonds for Tl^{+1} 4(TU) 3-Aminobenzoate [Å and º].

2.3.4 RESULTS FOR THE BENZOATE COMPLEX CRYSTAL ANALYSIS

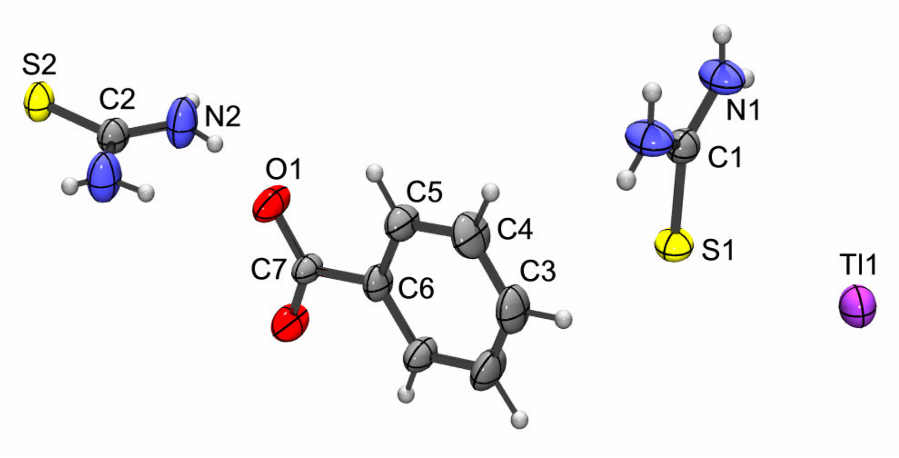


Fig. 2.9 **Molecular structure of the components involved in the Benzoate complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.**

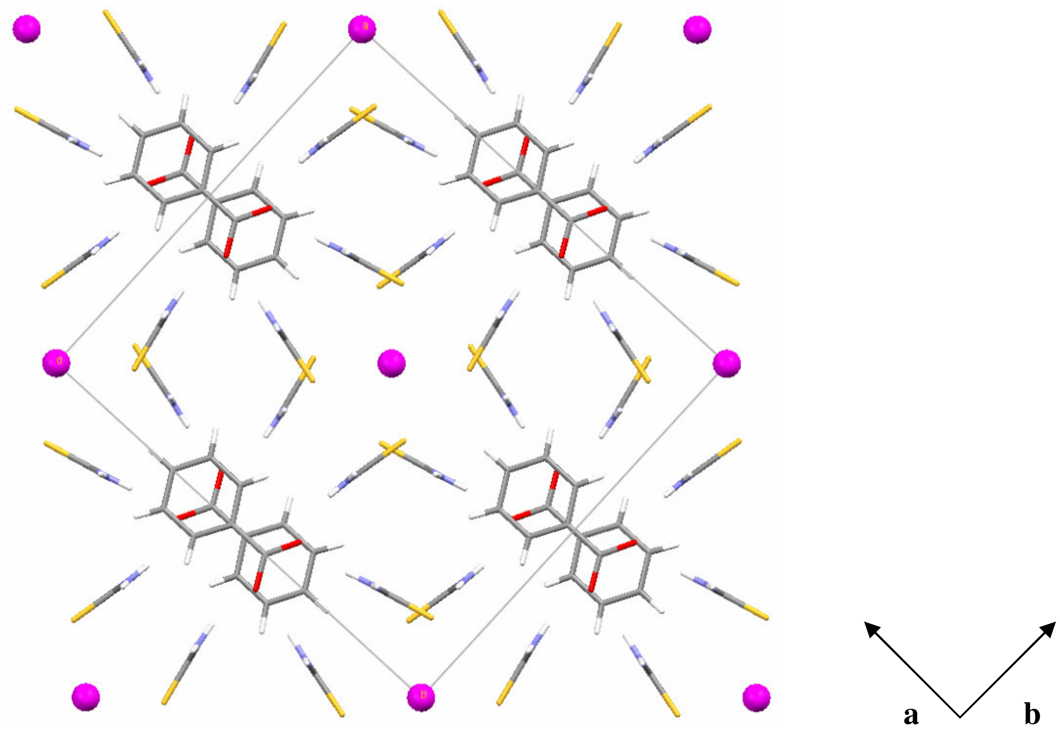


Fig. 2.10 **Molecular packing of the Benzoate complex viewed along the direction of the c axis. The direction of the a and b axes are shown above.**

CRYSTAL STRUCTURE TABLES FOR BENZOATE COMPLEX

Identification code	nb10_abs	
Empirical formula	$C_{11} H_{21} N_8 O_2 S_4 Tl$	
Formula weight	629.97	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c m	
Unit cell dimensions	a = 15.5482(11) Å	α= 90º.
	b = 17.0021(12) Å	β= 90º.
	c = 8.0954(6) Å	γ = 90º.
Volume	2140.0(3) $Å^3$	
Z	4	
Density (calculated)	1.955 Mg/m^3	
Absorption coefficient	7.961 mm^{-1}	
F(000)	1216	
Crystal size	0.40 x 0.18 x 0.16 mm^3	
Theta range for data collection	2.62 to 26.43º.	
Index ranges	-18<=h<=19, -7<=k<=21, -10<=l<=9	
Reflections collected	5719	
Independent reflections	1157 [R(int) = 0.0285]	
Completeness to theta = 25.00º	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.280 and 0.146	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1157 / 0 / 102	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.0789	
R indices (all data)	R1 = 0.0340, wR2 = 0.0808	

Extinction coefficient	0.0046(4)
Largest diff. peak and hole	1.574 and -1.865 e.Å^{-3}

* $w = 1/ [\sigma^2 (F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/ 3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.10 Crystal data and structure refinement for Tl^{+1} 4(TU) Benzoate.

Tl(1)-S(1)	3.3642(7)		
Tl(1)-S(2)#1	3.4345(9)	S(1)-Tl(1)-S(2)#1	67.103(15)
S(1)-C(1)	1.718(4)	C(1)-S(1)-Tl(1)	111.10(8)
C(1)-N(1)	1.316(3)	N(1)#3-C(1)-N(1)	119.0(4)
N(1)-H(1A)	0.73(3)	N(1)-C(1)-S(1)	120.52(19)
N(1)-H(1B)	0.81(4)	C(1)-N(1)-H(1A)	117.1(18)
S(2)-C(2)	1.710(3)	C(1)-N(1)-H(1B)	125(4)
C(2)-N(2)	1.315(3)	H(1A)-N(1)-H(1B)	118(4)
N(2)-H(2A)	0.86(4)	N(2)#3-C(2)-N(2)	117.5(4)
N(2)-H(2B)	0.68(4)	N(2)-C(2)-S(2)	121.27(18)
O(1)-C(7)	1.243(4)	C(2)-N(2)-H(2A)	113(2)
C(3)-C(4)#2	1.373(5)	C(2)-N(2)-H(2B)	126(4)
C(3)-C(4)	1.373(5)	H(2A)-N(2)-H(2B)	121(4)
C(3)-H(3)	1.01(8)	C(4)#2-C(3)-C(4)	121.3(5)
C(4)-C(5)	1.407(5)	C(4)#2-C(3)-H(3)	119.4(2)
C(4)-H(4)	0.98(5)	C(4)-C(3)-H(3)	119.4(2)
C(5)-C(6)	1.381(5)	C(3)-C(4)-C(5)	119.1(4)
C(5)-H(5)	0.92(5)	C(3)-C(4)-H(4)	118(3)
C(6)-C(5)#2	1.381(5)	C(5)-C(4)-H(4)	122(3)
C(6)-C(7)	1.523(6)	C(6)-C(5)-C(4)	120.7(4)
C(7)-O(1)#2	1.243(4)	C(6)-C(5)-H(5)	122(3)

C(4)-C(5)-H(5)	117(3)	O(1)-C(7)-O(1)#2	124.6(5)
C(5)#2-C(6)-C(5)	119.0(6)	O(1)-C(7)-C(6)	117.7(2)
C(5)#2-C(6)-C(7)	120.5(3)	O(1)#2-C(7)-C(6)	117.7(2)
C(5)-C(6)-C(7)	120.5(3)		

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y,-z+1/2 #3 x,y,-z+1/2

Table 2.11 Bond lengths [Å] and angles [º] for Tl^{+1} 4(TU) Benzoate.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)#4	0.73(3)	2.25(3)	2.900(4)	150(2)
N(2)-H(2A)...O(1)	0.86(4)	2.22(4)	3.038(4)	161(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y,-z+1/2 #3 x,y,-z+1/2 #4 -x+1/2,y-1/2,-z+1/2

Table 2.12 Hydrogen bonds for Tl^{+1} 4(TU) Benzoate [Å and º].

2.4 STRUCTURAL ANALYSIS OF THE FOUR BENZOIC ACID DERIVATIVE COMPLEXES

2.4.1 CELL DIMENSIONS AND VOLUMES

What is most evident in the four benzoic acid derivative structures obtained in this study, is that they are all isostructural, space group Cmcm. In fact their unit cell dimensions and volumes are almost identical which would indicate that the channel/cavity is of a fixed size and that varying the substituents on the aromatic ring makes little to no difference to the channel size.

COMPLEX	UNIT CELL DIMENSIONS (Å) AND VOLUMES (Å^3)			
	a	b	c	VOLUME
2-Fluoro	15.7317(10)	17.0319(11)	8.0881(5)	2167.1(2)
3-Fluoro	15.6079(8)	17.1485(9)	8.0752(4)	2161.34(19)
3-Amino	15.5683(11)	17.1150(12)	8.1352(5)	2167.6(3)
Benzoate	15.5482(11)	17.0021(12)	8.0954(6)	2140.0(3)

Table 2.13 **Table showing how similar the unit cell dimensions and volumes are for the four benzoic acid derivative complexes.**

This is most clearly illustrated by an overlay of the molecular packing of all four structures, Shown in Fig 2.11.

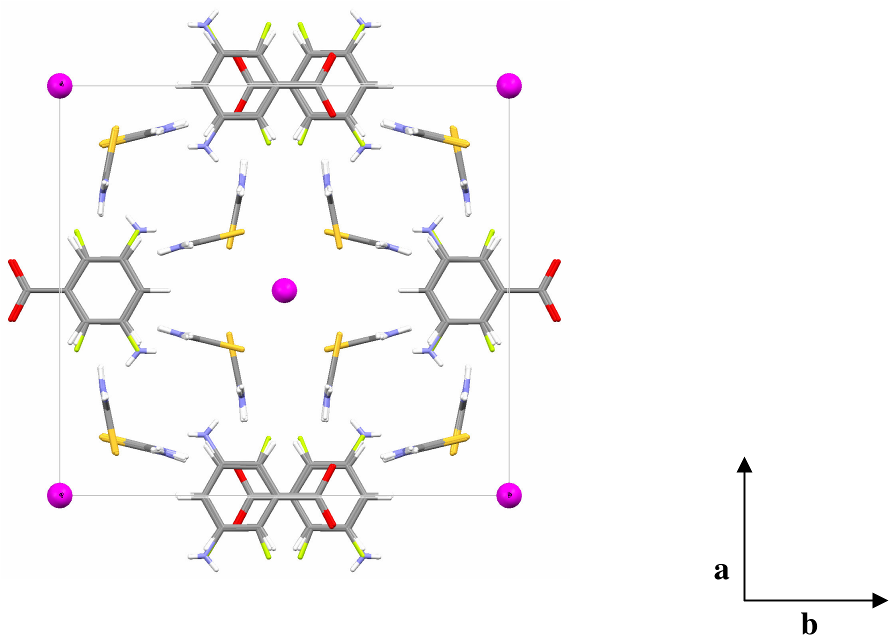


Fig.2.11 **An overlay of the molecular packing of all four benzoic acid derivative complexes viewed along the direction of the c axis. The direction of the a and b axes are shown above.**

2.4.2 CHANNEL SIZES

The channel sizes of the four complexes were in fact measured and the results confirmed that they are of very similar sizes. The two channels of each complex that were measured were the thallium cation channel and the benzoate derivative anion channel.

As was reported for the original benzoate complex [1], the thallium channel size was found by measuring the distances between the following:

- The sulphur atoms of the thiourea molecules involved in the Tl-S close approaches – referred to in Table 2.14 as S1 distances.
- The sulphur atoms of the thiourea molecules involved in van der Waal contacts – referred to Table 2.14 as S2 distances.
- The sulphur atoms belonging to thiourea molecules of unlike type – referred to in Table 2.14 as S3 distances.

Table 2.14 gives the values found for the four complexes prepared in this study as well as those reported for the original benzoate structure. Note how similar all the distances are to each other. The largest differences with in the S1, S2 and S3 values of the four complexes are 0.032 Å, 0.078 Å and 0.045 Å respectively. This suggests that the size of the substituents do not have any significant effect on the packing in the solid state. From Fig. 2.11 it is also clear that there is sufficient space between the 2 different amino groups of the thiourea molecules to accommodate the different substituents on the benzoate moiety. Thus, it seems that the lattice described by Tl^+ and the four thiourea molecules do not require much adjusting to accommodate a variety of substituent groups (with in reason). The meta substituents show similar distances from the two closest $(TU)NH_2$ groups. This suggests that other meta substituted benzoates may also crystallise in this space group (see Table 2.15).

COMPLEX	**S1 DISTANCES (Å)**	**S2 DISTANCES (Å)**	**S3 DISTANCES (Å)**
2-Fluoro	3.366	4.476	3.781
3-Fluoro	3.334	4.470	3.747
3-Amino	3.345	4.462	3.736
Benzoate	3.352	4.517	3.758
Benzoate #	3.360	4.540	3.770

Note: Benzoate # [1]

Table 2.14 Table showing the similar sulphur distances used to indicate the size of the cation channels in the four complexes.

ATOMS ANALYSED	INTERATOMIC DISTANCES (Å)	
$(TU)NH_2$……2F	3.173	
$(TU)NH_2$……2H	3.273	
$(TU)NH_2$……3F	3.210	3.332
$(TU)NH_2$……3H	3.201	3.434
$(TU)NH_2$……3N(H_2)	3.236	3.355

Note: $(TU)NH_2$ refers to the hydrogens associated with the thiourea molecule
2F refers to the fluorine atom in the 2-fluoro complex
2H refers to the ortho hydrogen atom in the benzoate complex
3H refers to the meta hydrogen atom in the benzoate complex
3F refers to the fluorine atom in the 3-fluoro complex
3N refers to the nitrogen atom at the meta position in the 3-amino complex

Table 2.15 **Interatomic distances between the hydrogens of the thiourea molecule and the ortho-fluorine atom, ortho-hydrogen of benzoate, meta-fluorine atom, meta-hydrogen atom and meta-nitrogen of amino the substituent.**

The anionic channel containing the benzoate derivatives was not measured for the original benzoate structure [1]. For the four complexes, three different measurements as an approximation of the size of each channel were taken. Firstly the width of the channel was measured by the distance between two H1 hydrogens from similar thiourea molecules on either side of the width of the cavity (referred to as distance 1 in Table 2.16). The second measurement was the length of the channel which was measured by the distance between two H2 hydrogens from similar thiourea molecules on either side of the length of the cavity (referred to as distance 2 in Table 2.16). The final measurement was taken from the para hydrogen on a benzoate anion to the para hydrogen of the second benzoate anion with in the same cavity (referred to as distance 3 in Table 2.16).

It should be noted that distances 1 and 3 are measured from atoms which are not in the same plane as each other, however, the same atoms were measured in all four complexes, therefore, these distances used to indicate the relative sizes of the anionic channels for all four complexes.

As with the thallium cation channel, the Table 2.16 indicates the similarity of the sizes of the channels in all four complexes. The largest differences with in the distance 1, 2 and 3 values are 0.289 Å, 0.204 Å and 0.370 Å respectively. These distances may appear significantly larger than for the cation channel differences, but these values are for channels containing bulky ligands as compared to those around a single Tl^+ atom.

COMPLEX	DISTANCE 1 (Å)	DISTANCE 2 (Å)	DISTANCE 3 (Å)
2-Fluoro	5.947	8.666	8.967
3-Fluoro	5.806	8.709	8.770
3-Amino	5.916	8.710	8.740
Benzoate	6.095	8.506	9.110

Table 2. 16 Table showing the similar distances used to indicate the size of the anion channels in the four complexes.

2.4.3 ATOMIC INTERACTIONS

As was reported for the original benzoic acid complex [1], the four complexes also show two distinct Tl – S interactions within each of the complexes.

COMPLEX	Tl(1) – S(1) Ǻ	Tl(1) – S(2)#1 Ǻ
2-Fluoro	3.3792(7)	3.4235(8)
3-Fluoro	3.3537(7)	3.4142(8)
3-Amino	3.3588(6)	3.4209(7)
Benzoate	3.3642(7)	3.4345(9)

Table 2.17 Table showing the two different Tl – S interatomic distances

In terms of hydrogen bond interactions the four benzoic acid derivative complexes once again correspond to the results of the initial benzoate complex where by each benzoate ion is hydrogen bonded to the surrounding amino groups of the thiourea molecules and that there are two different NH…O approaches. Those ranging between 2.90 – 2.97 Ǻ which indicate powerful hydrogen bonds and those ranging from 3.02 – 3.06 Å which are within the range of O-H-N hydrogen bonds given by Pimentel and Mc Clellan [1]. The exact values are given in the respective tables for each complex. There is also a certain amount of hydrogen bonding within the other complexes of this chapter and as with the benzoic acid derivative complexes, the hydrogen bond values are given in the relevant tables.

COMPLEX	**N(1)……O(1) (Å)**	**N(2)……O(1) (Å)**
2-Fluoro	2.974(4)	3.044(4)
3-Fluoro	2.922(4)	3.057(4)
3-Amino	2.908(4)	3.022(4)
Benzoate	2.900(4)	3.038(4)

Table 2.18 Common N…O distances between the four complexes and the two thiourea molecules involved in hydrogen bonding.

Table 2.18 indicates that the two distances associated with the 3-fluoro and 3-amino benzoate complexes differ for both complexes. Also in terms of the 3-substituted complexes (3-benzoate, 3-fluoro and 3-amino benzoates) the 3-amino benzoate has the shorter N……O distance, and the 3-fluoro benzoate has the longer N……O distance. This is in accordance with the electron donating character of the 3-amino group, that results in a higher concentration of electron density on the oxygen atoms. The more electronegative fluorine substituent causes the opposite effect, as could be expected. The N……O distances for the benzoate complex and the 2-fluoro benzoate complex are such that the hydrogen bonding for the benzoic acid complex is stronger than that for the 2-fluoro complex, again as a result of the electronegativity of the fluorine atom.

2.5 CRYSTALLOGRAPHIC RESULTS FOR THE REMAINING COMPLEXES

2.5.1 RESULTS FOR THE PF_6^- COMPLEX CRYSTAL ANALYSIS

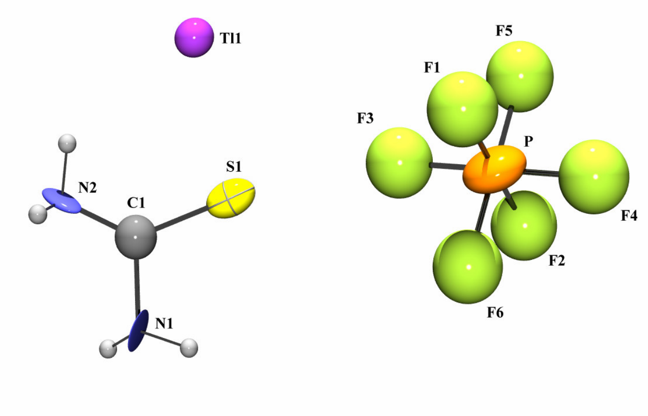


Fig. 2.12 Molecular structure of the components involved in the PF_6^- complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.

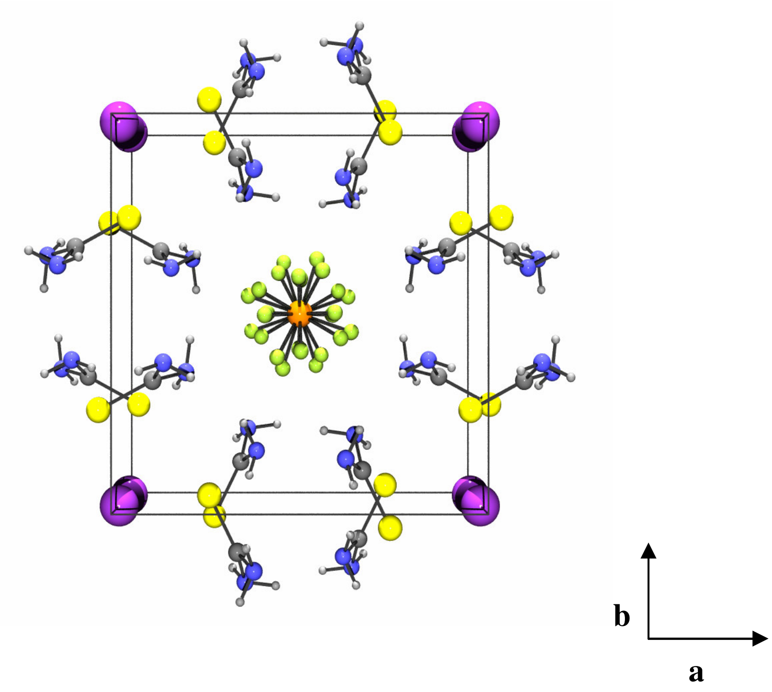


Fig. 2.13 Molecular packing of the PF_6^- complex viewed along the direction of the c axis. The direction of the a and b axes are shown above.

CRYSTAL STRUCTURE TABLES FOR PF_6^- COMPLEX

Identification code	nb01	
Empirical formula	$C_4 H_{16} F_6 N_8 P S_4 Tl$	
Formula weight	653.83	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4cc	
Unit cell dimensions	a = 10.4608(3) Å	α= 90º.
	b = 10.4608(3) Å	β= 90º.
	c = 8.2304(5) Å	γ = 90º.
Volume	900.64(7) $Å^3$	
Z	2	
Density (calculated)	2.411 Mg/m^3	
Absorption coefficient	9.584 mm^{-1}	
F(000)	620	
Crystal size, colour	0.32 x 0.17 x 0.15 mm, (cream needles)	
Theta range for data collection	2.75 to 26.54º.	
Index ranges	-13<=h<=12, -12<=k<=13, -3<=l<=10	
Reflections collected	4318	
Independent reflections	555 [R(int) = 0.0309]	
Completeness to theta = 25.00θ	99.5 %	
Absorption correction	Multi scan (SADABS, Buker 2001)	
Max. and min. transmission	1.0 and 0.813205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	555 / 1 / 49	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0671, wR2 = 0.1848 *	
R indices (all data)	R1 = 0.0683, wR2 = 0.1856	

Absolute structure parameter	0.10(7)
Largest diff. peak and hole	1.203 and -1.689 e.Å^{-3}

* $w = 1/[\sigma^2(F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.19 Crystal data and structure refinement for Tl^{+1} 4(TU) PF$_6^-$

S(1)-C(1)	1.71(2)				
C(1)-N(2)	1.34(4)				
C(1)-N(1)	1.45(5)				
P-F(1)	1.56	P-F(2)	1.57		
P-F(4)	1.56	P-F(3)	1.57		
P-F(6)	1.57	P-F(5)	1.57		
N(2)-C(1)-N(1)	116(2)				
N(2)-C(1)-S(1)	134(3)				
N(1)-C(1)-S(1)	109(3)				
F(1)-P-F(4)	90.5	F(1)-P-F(2)	1.79.6	F(3)-P-F(4)	179.4
F(1)-P-F(6)	90.4	F(1)-P-F(3)	89.8	F(5)-P-F(6)	179.3
F(4)-P-F(6)	90.2	F(1)-P-F(5)	90.3		

Symmetry transformations used to generate equivalent atoms:

Table 2.20 Bond lengths [Å] and angles [°] for Tl^{+1} 4(TU) PF$_6^-$.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...F(6)#1	0.86	1.94	2.70(7)	147.1
N(1)-H(1A)...F(4)#2	0.86	1.96	2.8(2)	153.6
N(1)-H(1A)...F(5)#3	0.86	1.97	2.78(19)	156.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,z   #2 x,y-1,z   #3 y,-x,z

Table 2.21 Hydrogen bonds for Tl^{+1} 4(TU) PF_6^{-1} [Å and °].

2.5.2 RESULTS FOR THE BF_4^- COMPLEX CRYSTAL ANALYSIS

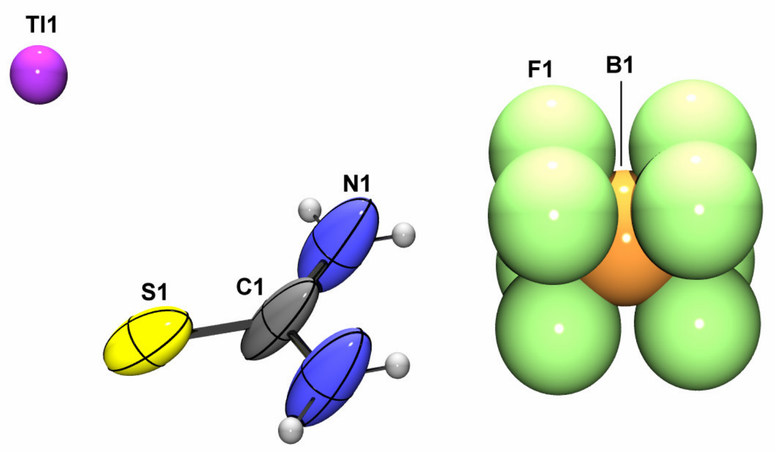


Fig. 2.14 **Molecular structure of the components involved in the BF_4^- complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.**

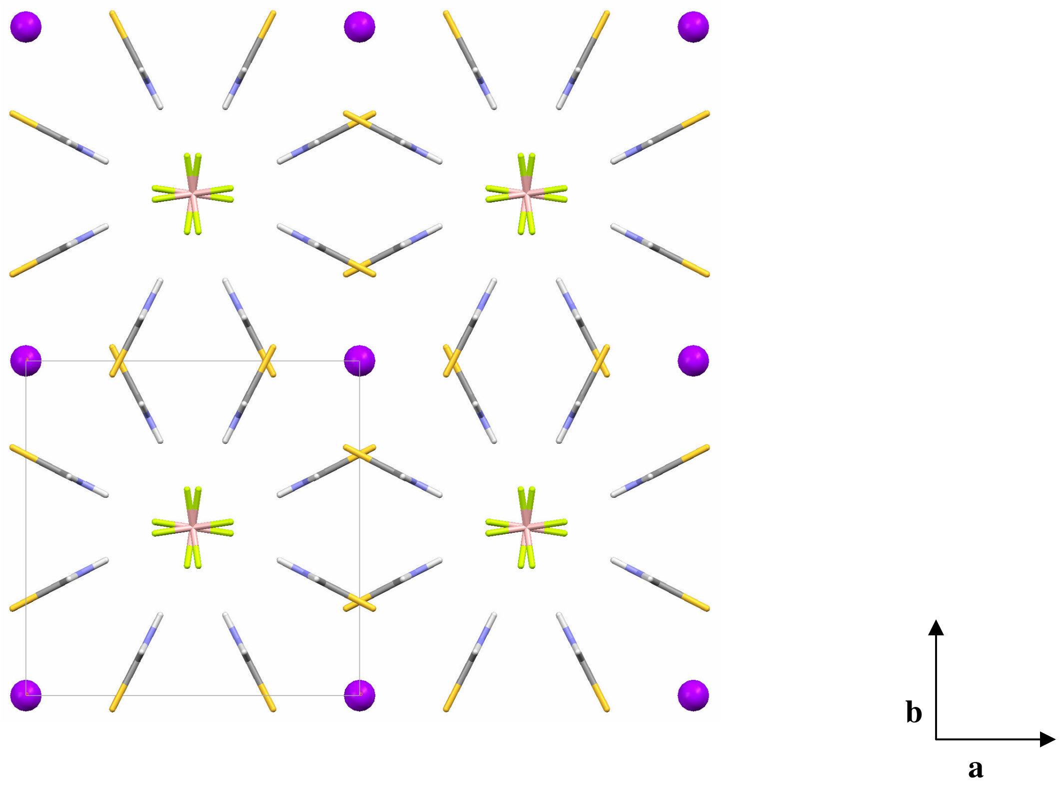


Fig. 2.15 **Molecular packing of BF_4^- complex viewed along the direction of the c axis. The direction of the a and b axes are shown above.**

CRYSTAL SRUCTURE TABLES FOR BF_4^- COMPLEX

Identification code	nb05_abs	
Empirical formula	$C_4 H_{16} B F_4 N_8 S_4 Tl$	
Formula weight	595.67	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P 4/m c c	
Unit cell dimensions	a = 10.3640(4) Å	α = 90º.
	b = 10.3640(4) Å	β = 90º.
	c = 8.2340(7) Å	γ = 90º.
Volume	884.43(9) $Å^3$	
Z	2	
Density (calculated)	2.237 Mg/m^3	
Absorption coefficient	9.645 mm^{-1}	
F(000)	564	
Crystal size	0.24 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.78 to 26.50º.	
Index ranges	-7<=h<=12, -12<=k<=12, -10<=l<=6	
Reflections collected	4272	
Independent reflections	475 [R(int) = 0.0244]	
Completeness to theta = 25.00º	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.381 and 0.240	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	475 / 2 / 29	
Goodness-of-fit on F^2	1.410	
Final R indices [I>2σ(I)]	R1 = 0.0269, wR2 = 0.0713	
R indices (all data)	R1 = 0.0318, wR2 = 0.0761	

Extinction coefficient	0
Largest diff. peak and hole	1.232 and -0.488 e.Å^{-3}

* $w = 1/ [\sigma^2 (F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/ 3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.22 Crystal data and structure refinement for Tl^{+1} 4(TU) BF_4^-.

Tl(1)-S(1)	3.4103(19)
S(1)-C(1)	1.709(12)
C(1)-N(1)#1	1.330(8)
C(1)-N(1)	1.330(8)
N(1)-H(1)	0.8600
N(1)-H(2)	0.8600
B(1)-F(1)	1.307(13)
C(1)-S(1)-Tl(1)	104.6(3)
N(1)#1-C(1)-N(1)	117.8(10)
N(1)#1-C(1)-S(1)	121.1(5)
N(1)-C(1)-S(1)	121.1(5)
C(1)-N(1)-H(1)	120.0
C(1)-N(1)-H(2)	120.0
H(1)-N(1)-H(2)	120.0
F(1)-B(1)-F(1)#2	99.9(7)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z #2 y,-x+1,-z

Table 2.23 Bond lengths [Å] and angles [°] for Tl^{+1} 4(TU) BF_4^-.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...F(1)#3	0.86	2.02	2.84(2)	161.1

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z   #2 y,-x+1,-z   #3 -y+1,x,-z

Table 2.24 Hydrogen bonds for Tl^{+1} 4(TU) BF_4^- [Å and º].

2.5.3 RESULTS FOR THE THALLIUM – 4-AMINOBENZOATE CRYSTAL ANALYSIS

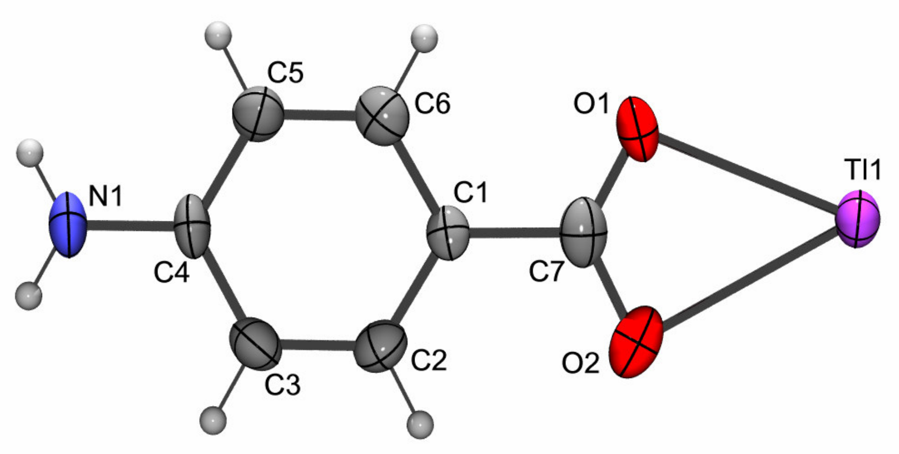


Fig. 2.16 Molecular structure of the components involved in the thallium – 4-aminobenzoate, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.

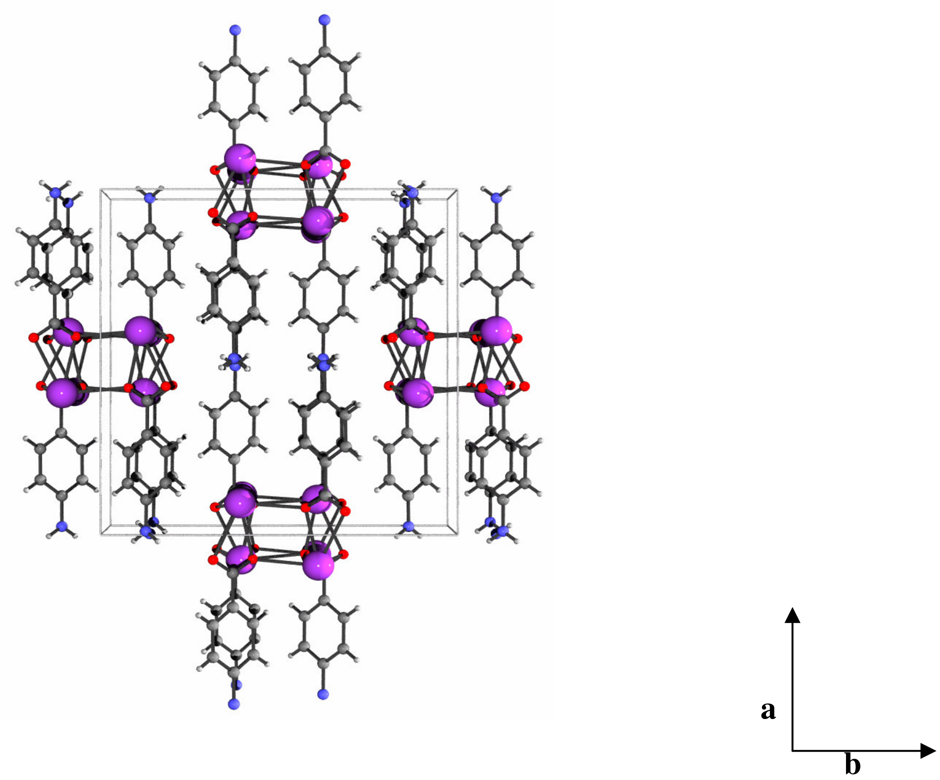


Fig. 2.17 Molecular packing of the thallium – 4-aminobenzoate viewed along the direction of the c axis. The direction of the a and b axes are shown above.

CRYSTAL STRUCTURE TABLES FOR THALLIUM – 4-AMINOBENZOATE

Identification code	nb13a_abs1	
Empirical formula	$C_7 H_6 N O_2 Tl$	
Formula weight	340.50	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	I b a 2	
Unit cell dimensions	a = 14.6579(14) Å	α= 90°.
	b = 15.1020(14) Å	β= 90°.
	c = 6.9606(6) Å	γ = 90°.
Volume	1540.8(2) $Å^3$	
Z	8	
Density (calculated)	2.936 Mg/m^3	
Absorption coefficient	20.908 mm^{-1}	
F(000)	1216	
Crystal size	0.12 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.70 to 26.35°.	
Index ranges	-18<=h<=18, -18<=k<=16, -8<=l<=3	
Reflections collected	3916	
Independent reflections	980 [R(int) = 0.0414]	
Completeness to theta = 25.00°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.188 and 0.086	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	980 / 1 / 101	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	R1 = 0.0269, wR2 = 0.0664	
R indices (all data)	R1 = 0.0273, wR2 = 0.0668	

Absolute structure parameter	0.04(2)
Extinction coefficient	0.0058(3)
Largest diff. peak and hole	1.343 and -1.594 e.Å^{-3}

* $w = 1/ [\sigma^2 (F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/ 3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.25 Crystal data and structure refinement for thallium – 4-aminobenzoate.

Tl(1)-O(1)	2.628(6)	N(1)-H(1B)	0.8600
Tl(1)-O(1)#1	2.785(7)		
Tl(1)-O(2)	2.796(7)	O(1)-Tl(1)-O(1)#1	70.9(2)
O(1)-C(7)	1.235(15)	O(1)-Tl(1)-O(2)	48.08(18)
O(1)-Tl(1)#2	2.898(7)	O(1)#1-Tl(1)-O(2)	112.21(16)
O(2)-C(7)	1.278(16)	C(7)-O(1)-Tl(1)	98.7(6)
O(2)-Tl(1)#3	2.837(7)	C(7)-O(1)-Tl(1)#1	117.7(8)
C(1)-C(2)	1.395(10)	Tl(1)-O(1)-Tl(1)#1	102.5(2)
C(1)-C(6)	1.417(11)	C(7)-O(1)-Tl(1)#2	115.7(9)
C(1)-C(7)	1.495(11)	Tl(1)-O(1)-Tl(1)#2	106.2(2)
C(2)-C(3)	1.383(10)	Tl(1)#1-O(1)-Tl(1)#2	113.1(2)
C(2)-H(2)	0.9300	C(7)-O(2)-Tl(1)	89.7(6)
C(3)-C(4)	1.411(13)	C(7)-O(2)-Tl(1)#3	105.3(8)
C(3)-H(3)	0.9300	Tl(1)-O(2)-Tl(1)#3	103.4(2)
C(4)-C(5)	1.380(13)	C(2)-C(1)-C(6)	116.6(6)
C(4)-N(1)	1.380(9)	C(2)-C(1)-C(7)	122.8(8)
C(5)-C(6)	1.372(9)	C(6)-C(1)-C(7)	120.6(8)
C(5)-H(5)	0.9300	C(3)-C(2)-C(1)	121.6(7)
C(6)-H(6)	0.9300	C(3)-C(2)-H(2)	119.2
N(1)-H(1A)	0.8600	C(1)-C(2)-H(2)	119.2

C(2)-C(3)-C(4)	120.6(7)	C(5)-C(6)-C(1)	121.8(7)
C(2)-C(3)-H(3)	119.7	C(5)-C(6)-H(6)	119.1
C(4)-C(3)-H(3)	119.7	C(1)-C(6)-H(6)	119.1
C(5)-C(4)-N(1)	121.4(9)	O(1)-C(7)-O(2)	123.5(9)
C(5)-C(4)-C(3)	118.2(7)	O(1)-C(7)-C(1)	119.5(10)
N(1)-C(4)-C(3)	120.4(8)	O(2)-C(7)-C(1)	116.7(10)
C(6)-C(5)-C(4)	121.1(8)	C(4)-N(1)-H(1A)	120.0
C(6)-C(5)-H(5)	119.4	C(4)-N(1)-H(1B)	120.0
C(4)-C(5)-H(5)	119.4	H(1A)-N(1)-H(1B)	120.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,z #2 x+0,-y+1,z-1/2 #3 x+0,-y+1,z+1/2

Table 2.26 Bond lengths [Å] and angles [º] for thallium – 4-aminobenzoate.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1B)...O(2)#4	0.86	2.40	3.063(9)	133.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,z #2 x+0,-y+1,z-1/2 #3 x+0,-y+1,z+1/2

#4 -x+3/2,y-1/2,z

Table 2.27 Hydrogen bonds for thallium – 4-aminobenzoate [Å and º].

2.5.4 RESULTS FOR THE 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) COMPLEX CRYSTAL ANALYSIS

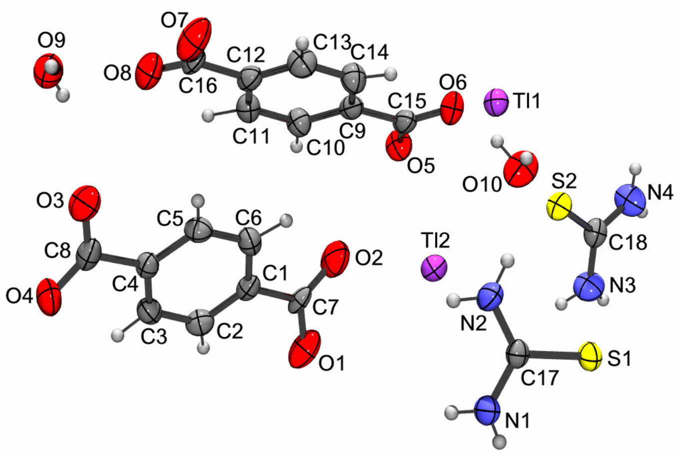


Fig. 2.18 **Molecular structure of the components involved in the 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) complex, with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown.**

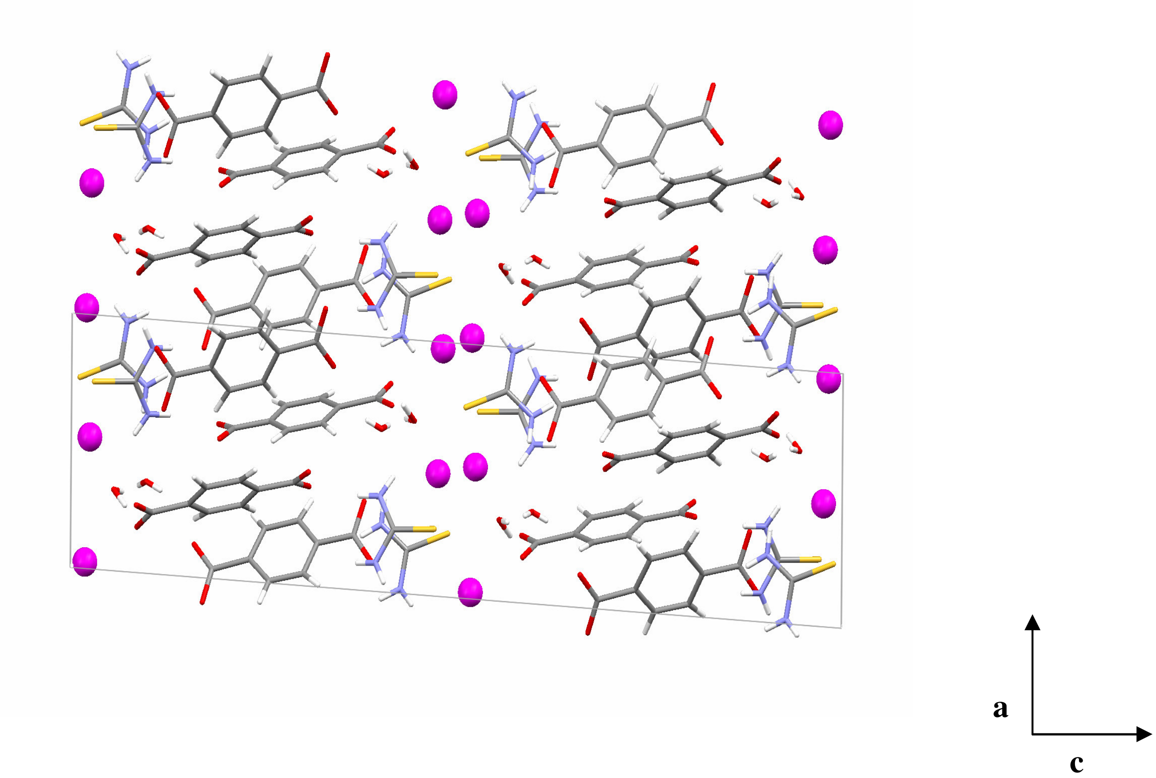


Fig. 2.19 **Molecular packing of 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) complex viewed along the direction of the b axis. The direction of the a and c axes are shown above.**

CRYSTAL STRUCTURE TABLES FOR 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) COMPLEX

Identification code	nb12a_abs	
Empirical formula	$C_{18} H_{20} N_4 O_{10} S_2 Tl_2$	
Formula weight	925.24	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.4682(4) Å	α= 90°.
	b = 9.6750(5) Å	β= 93.2990(10)°.
	c = 30.4239(16) Å	γ = 90°.
Volume	2488.5(2) $Å^3$	
Z	4	
Density (calculated)	2.470 Mg/m^3	
Absorption coefficient	13.162 mm^{-1}	
F(000)	1720	
Crystal size	0.26 x 0.22 x 0.18 mm^3	
Theta range for data collection	2.50 to 26.57°.	
Index ranges	-3<=h<=10, -12<=k<=11, -38<=l<=36	
Reflections collected	13135	
Independent reflections	4748 [R(int) = 0.0298]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.094 and 0.061	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4748 / 0 / 406	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2σ(I)]	R1 = 0.0295, wR2 = 0.0767	

R indices (all data)	R1 = 0.0323, wR2 = 0.0785
Extinction coefficient	0.00370(13)
Largest diff. peak and hole	1.534 and -0.834 e.Å^{-3}

* $w = 1/ [\sigma^2 (F_0^2) + (0.0707P)^2 + 0.0977P]$ where $P = (F_0^2 + 2Fc^2)/ 3$

$\Delta\rho$ max = 1.2 e.Å^{-3} (0.5Å from C1)

$\Delta\rho$ min = -1.69e.Å^{-3}

Table 2.28 **Crystal data and structure refinement for 2Tl(I), 2(TU) 2(Tph) 2H_2O (Tph = terephthalate benzene-1,4-dicarboxylate).**

Tl(1)-O(5)	2.792(4)	N(1)-H(1A)	0.84(6)
Tl(1)-S(2)	3.1303(13)	N(1)-H(1B)	0.67(6)
Tl(1)-S(1)#1	3.6870(12)	N(2)-C(17)	1.310(6)
Tl(2)-S(1)	3.2962(13)	N(2)-H(2A)	0.84(6)
Tl(2)-S(2)	3.3623(13)	N(2)-H(2B)	0.83(6)
S(1)-C(17)	1.717(4)	N(3)-C(18)	1.315(7)
S(2)-C(18)	1.714(5)	N(3)-H(3A)	0.91(6)
O(1)-C(7)	1.204(7)	N(3)-H(3B)	0.84(9)
O(2)-C(7)	1.225(6)	N(4)-C(18)	1.314(7)
O(3)-C(8)	1.244(7)	N(4)-H(4A)	0.79(6)
O(4)-C(8)	1.250(7)	N(4)-H(4B)	0.78(5)
O(5)-C(15)	1.255(6)	C(1)-C(6)	1.373(7)
O(6)-C(15)	1.252(6)	C(1)-C(2)	1.380(8)
O(7)-C(16)	1.211(7)	C(1)-C(7)	1.465(6)
O(8)-C(16)	1.216(7)	C(2)-C(3)	1.379(8)
O(9)-H(9A)	0.97(11)	C(2)-H(2)	0.94(6)
O(9)-H(9B)	0.64(7)	C(3)-C(4)	1.376(7)
O(10)-H(10A)	0.68(7)	C(3)-H(3)	0.91(7)
O(10)-H(10B)	1.01(13)	C(4)-C(5)	1.389(7)
N(1)-C(17)	1.325(6)	C(4)-C(8)	1.532(6)

C(5)-C(6)	1.373(7)
C(5)-H(5)	0.82(6)
C(6)-H(6)	0.94(5)
C(9)-C(14)	1.367(7)
C(9)-C(10)	1.398(7)
C(9)-C(15)	1.519(6)
C(10)-C(11)	1.385(8)
C(10)-H(10)	0.91(5)
C(11)-C(12)	1.361(7)
C(11)-H(11)	1.03(6)
C(12)-C(13)	1.376(8)
C(12)-C(16)	1.457(6)
C(13)-C(14)	1.389(7)
C(13)-H(13)	0.86(6)
C(14)-H(14)	0.96(6)

O(5)-Tl(1)-S(2)	87.66(9)
O(5)-Tl(1)-S(1)#1	111.31(9)
S(2)-Tl(1)-S(1)#1	147.46(3)
S(1)-Tl(2)-S(2)	143.85(3)
C(17)-S(1)-Tl(2)	101.37(16)
C(18)-S(2)-Tl(1)	101.75(17)
C(18)-S(2)-Tl(2)	103.00(18)
Tl(1)-S(2)-Tl(2)	80.05(3)
C(15)-O(5)-Tl(1)	95.4(3)
H(9A)-O(9)-H(9B)	119(9)
H(10A)-O(10)-H(10B)	109(9)
C(17)-N(1)-H(1A)	125(4)
C(17)-N(1)-H(1B)	127(5)
H(1A)-N(1)-H(1B)	108(6)
C(17)-N(2)-H(2A)	115(4)
C(17)-N(2)-H(2B)	122(4)
H(2A)-N(2)-H(2B)	124(6)
C(18)-N(3)-H(3A)	124(3)
C(18)-N(3)-H(3B)	116(7)
H(3A)-N(3)-H(3B)	116(8)
C(18)-N(4)-H(4A)	119(4)
C(18)-N(4)-H(4B)	117(4)
H(4A)-N(4)-H(4B)	123(6)
C(6)-C(1)-C(2)	123.2(5)
C(6)-C(1)-C(7)	119.4(5)
C(2)-C(1)-C(7)	117.3(5)
C(3)-C(2)-C(1)	117.3(5)
C(3)-C(2)-H(2)	126(4)
C(1)-C(2)-H(2)	116(4)
C(4)-C(3)-C(2)	121.3(5)
C(4)-C(3)-H(3)	122(4)
C(2)-C(3)-H(3)	117(4)
C(3)-C(4)-C(5)	119.6(5)
C(3)-C(4)-C(8)	120.1(5)
C(5)-C(4)-C(8)	120.3(5)
C(6)-C(5)-C(4)	120.5(5)
C(6)-C(5)-H(5)	120(4)
C(4)-C(5)-H(5)	120(4)
C(5)-C(6)-C(1)	118.1(5)
C(5)-C(6)-H(6)	128(3)
C(1)-C(6)-H(6)	114(3)
O(1)-C(7)-O(2)	123.7(5)
O(1)-C(7)-C(1)	118.5(5)
O(2)-C(7)-C(1)	117.8(4)
O(3)-C(8)-O(4)	126.7(5)
O(3)-C(8)-C(4)	117.4(5)

O(4)-C(8)-C(4)	115.9(5)	C(9)-C(14)-C(13)	121.1(5)
C(14)-C(9)-C(10)	119.3(5)	C(9)-C(14)-H(14)	119(3)
C(14)-C(9)-C(15)	121.4(5)	C(13)-C(14)-H(14)	119(3)
C(10)-C(9)-C(15)	119.2(5)	O(6)-C(15)-O(5)	123.9(4)
C(11)-C(10)-C(9)	120.0(5)	O(6)-C(15)-C(9)	117.9(5)
C(11)-C(10)-H(10)	117(3)	O(5)-C(15)-C(9)	118.2(5)
C(9)-C(10)-H(10)	122(3)	O(7)-C(16)-O(8)	123.0(5)
C(12)-C(11)-C(10)	119.1(5)	O(7)-C(16)-C(12)	118.7(5)
C(12)-C(11)-H(11)	116(3)	O(8)-C(16)-C(12)	118.4(5)
C(10)-C(11)-H(11)	125(3)	N(2)-C(17)-N(1)	118.3(5)
C(11)-C(12)-C(13)	122.3(5)	N(2)-C(17)-S(1)	121.5(4)
C(11)-C(12)-C(16)	118.8(5)	N(1)-C(17)-S(1)	120.2(4)
C(13)-C(12)-C(16)	118.9(5)	N(4)-C(18)-N(3)	118.0(5)
C(12)-C(13)-C(14)	118.2(5)	N(4)-C(18)-S(2)	121.3(4)
C(12)-C(13)-H(13)	120(4)	N(3)-C(18)-S(2)	120.7(4)
C(14)-C(13)-H(13)	121(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

Table 2.29 **Bond lengths [Å] and angles [°] for 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(3)#2	0.84(6)	2.08(7)	2.915(6)	177(6)
N(1)-H(1B)...S(1)#3	0.67(6)	2.88(6)	3.552(5)	172(6)
N(2)-H(2A)...O(4)#2	0.84(6)	2.24(7)	3.001(6)	152(6)
N(2)-H(2B)...O(9)#4	0.83(6)	2.36(6)	3.184(7)	168(5)
N(3)-H(3A)...O(8)#5	0.91(6)	2.30(6)	3.171(7)	160(5)
N(3)-H(3B)...O(10)#6	0.84(9)	2.10(9)	2.915(8)	164(9)
N(4)-H(4A)...O(4)#7	0.79(6)	2.07(7)	2.829(7)	161(6)
N(4)-H(4B)...O(6)#8	0.78(5)	2.13(5)	2.891(7)	163(5)
O(9)-H(9A)...O(5)#9	0.97(11)	1.94(11)	2.872(6)	160(8)
O(9)-H(9B)...O(3)	0.64(7)	2.27(7)	2.854(6)	153(9)
O(10)-H(10A)...O(9)#9	0.68(7)	2.21(7)	2.873(7)	164(7)
O(10)-H(10B)...O(6)	1.01(13)	1.80(13)	2.763(7)	159(10)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x,y-1/2,-z+3/2 #3 -x,-y,-z+2

#4 -x+1,y-1/2,-z+3/2 #5 x,-y+1/2,z+1/2 #6 -x+1,-y+1,-z+2

#7 x+1,-y+1/2,z+1/2 #8 -x+2,-y+1,-z+2 #9 -x+1,y+1/2,-z+3/2

Table 2.30 **Hydrogen bonds for 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) [Å and °].**

2.6 STRUCTURAL ANALYSIS FOR THE REMAINING COMPLEXES

2.6.1 PF_6^- COMPLEX

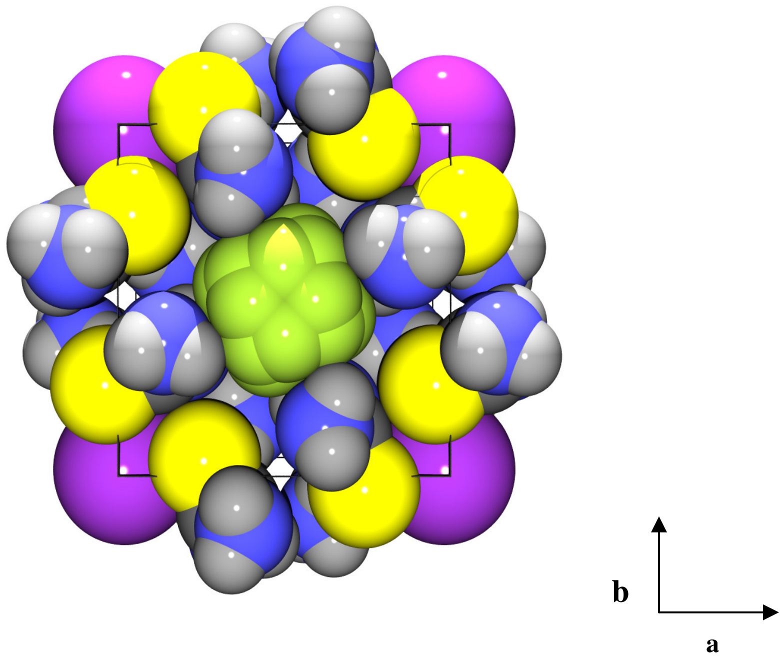


Fig. 2.20 **Space filling drawing showing the efficient packing of the PF_6^- complex viewed along the direction of the c axis. The direction of the a and b axes are shown above.**

As can be seen from Fig. 2.20, 24 phosphorus-fluorine bonds are seen to be generated rather than the expected 6 bonds of the PF_6^- molecule. The reason behind this is disorder that the 4-fold axis of symmetry does not run directly through the F-P-F bonds. Instead the entire PF_6^-molecule is tilted and the 4-fold axis runs through the P-atom and the molecule as shown below.

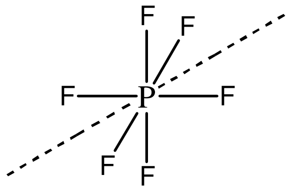


Fig2.21 **Position of 4-fold axis**

Due to this occurrence 24 F atoms are generated with fractional site occupancies. The fact that the PF_6^- is tilted is an interesting phenomenon as it is further proof that the channel with in the complex remains approximately the same size relative to the substituents added based on the isostructural nature of the complexes.

The PF_6^- anion had to be refined as a rigid body and C(1) could not be refined satisfactorily with anisotropic thermal parameters.

Some evidence for H-bonding was observed from the close contacts between the (N)H…..F atoms. Table 2.31 lists these short contacts, and this is supportive of the observations in the Raman and IR studies (see chapter 3).

H-bonding :
N1…..F2 = 3.070Å (HN1B…..F2 = 2.597Å)
N1…..F6 = 3.149Å (HN1B…..F6 = 2.465Å)
N2…..F3 = 2.868Å (HN2B…..F3 = 2.292Å)
N2…..F1 = 2.770Å (HN2B…..F1 = 2.293Å)
N2…..F5 = 3.061Å (HN2B…..F5 = 2.443Å)

Table 2.31 Close contacts between N(H)…..F atoms

2.6.2 BF_4^- COMPLEX

It is of interest to note that the PF6 and BF4 complexes crystallise in different tetragonal space groups but with almost identical unit cell parameters. The unit cell volumes differ by less than 16 Å.

2.6.3 THALLIUM - 4-AMINOBENZOATE

The unequal Tl – O distances observed are also reflected in all the related structures in the Cambridge Database Version 5.26, also included 2005 updates during Feb., May, Aug.[4]. The shorter distance of 2.628(6) Å compares favourably with 2.597 Å calculated as the average of the 12 shorter contacts. The larger distance of 2.796(7) Å also compares well with the average of the

12 larger contacts (2.810 Å). For the 4-aminobenzoate complex this difference can be explained in terms of the fact that the oxygen with the larger Tl – O distance is also hydrogen bonded to the one thiourea NH_2 group.

2.6.4 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) COMPLEX

The asymmetric unit containing 2Tl(I), 2(TU) 2(Tph) and $2H_2O$ molecules are included as waters of crystallization. The two H_2O molecules are hydrogen bonded to each other (Table 2.31) as well as to two of the four carboxylate groups, and to both of the two amino groups of thiourea. The carboxylate group containing O1 and O2 are not hydrogen bonded to any other donor/receptor, but all three other carboxylate groups are hydrogen bonded to thiourea. All four thiourea NH_2 groups are involved in hydrogen bonding.

There is a short contact of 2.792(4) Å between Tl 1 and O5. This distance is comparable with the values of 2.628(6) Å and 2.796(7) Å observed for the 4-aminobenzoate complex without thiourea.

All hydrogen atoms were located from experimental data, and included in the refinement without any restrictions. Even the four hydrogen atoms for the $2H_2O$ molecules were located and refined under similar conditions. The refinement proceeded smoothly and no significant residual peaks that could be ascribed to additional hydrogen atoms were observed. The areas around the carboxylate groups were especially studied. If the two thallium atoms are both Tl^+ the remaining 2 hydrogen atoms will have to be placed in theoretical positions at two carboxylate oxygen atoms. When comparing the different C-O distances in the carboxylate functional groups, the following distances are observed:

C7 – O1:	1.204(7) Å	C7 - O2:	1.225(6) Å
C8 – O3:	1.244(7) Å	C8 - O4:	1.250(7) Å
C15 – O5:	1.255(6) Å	C15 - O6:	1.252(6) Å

C16 – O7 1.211(7) Å C16 - O8 : 1.216(7) Å

These distances are relatively similar and do not clearly indicate possible oxygen atoms for the addition of the two hydrogen atoms not observer experimentally.

Both thallium1 and thallium 2 are in close contact with sulphur, oxygen and the carbonyl carbon atom (see Table 2.32).

ATOM 1	ATOM 2	SYMM. OP. 1	SYMM. OP. 2	LENGTH (Å)
Tl1	S1	x,y,z	1+x, -1+y, z	3.687
Tl1	S1	x,y,z	1-x, 1-y, 2-z	3.376
Tl1	S2	x,y,z	x,y,z	3.13
Tl1	S2	x,y,z	2-x, 1-y, 2-z	3.434
Tl1	O1	x,y,z	1+x, y, z	3.103
Tl1	O5	x,y,z	x,y,z	2.792
Tl1	O6	x,y,z	x,y,z	2.918
Tl1	C15	x,y,z	x,y,z	3.168
Tl2	S1	x,y,z	x, -1+y, z	3.296
Tl2	S1	x,y,z	1-x, 1-y, 2-z	3.401
Tl2	S2	x,y,z	x,y,z	3.362
Tl2	S2	x,y,z	1-x, 1-y, 2-z	3.23
Tl2	O2	x,y,z	x,y,z	3.113
Tl2	O5	x,y,z	x,y,z	2.926
Tl2	C15	x,y,z	x,y,z	3.625
Tl2	O10	x,y,z	1-x, 1-y, 2-z	2.893

Table 2.32 **Symmetry operations and close contacts of the two thallium atoms with S, O and C (carbonyl) atoms.**

2.7 POWDER DIFFRACTION STUDY

All benzoic acid derivative complexes were analysed using x-ray powder diffraction. The instrument used for this analysis was a Siemens D-501 Automated diffractometer using a Cu target (λ = 1.5406 Å) operated at 40 KV and 40 mA. The instrument was equipped with a diffracted beam graphite monochromator, divergence slot of 1º, receiving slit of 0.05º and a scintillation counter. A sample spinner was used. The samples were step scanned at 2θ from 5˚ to 70˚ with steps of 0.01˚ at Ψ with a fixed counting time of 1.15 sec at a mean temperature of 25˚C.

The diffraction patterns of all the complexes including the four diffraction quality single crystals are shown in Fig 2.22 – 2.29. They can be split into eight different groupings. These are (1) the four complexes for which the single crystal structures were obtained, (2) eight complexes with only 2- and 4-substituted benzoates, (3) three groups of pairs of similar complexes, and (4) three complexes with no similarity to the others.

The reason for the remaining complexes falling into different powder patter groupings may be due to the fact that they crystallise as different crystal structures giving rise to different diffraction patterns. No further analysis of the powder data was done, but these results clearly suggest that a project to investigate the structure of the eight compounds with very similar powder patterns could prove of importance. A powder pattern of the 4-amino complex with no thiourea was also run to ensure none of the synthesised complexes had formed without thiourea. The results showed that the non thiourea 4-amino complex gave a completely different powder pattern to any of the other complexes.

2.7.1 EXPERIMENTAL POWDER X-RAY DIFFRACTION PATTERNS

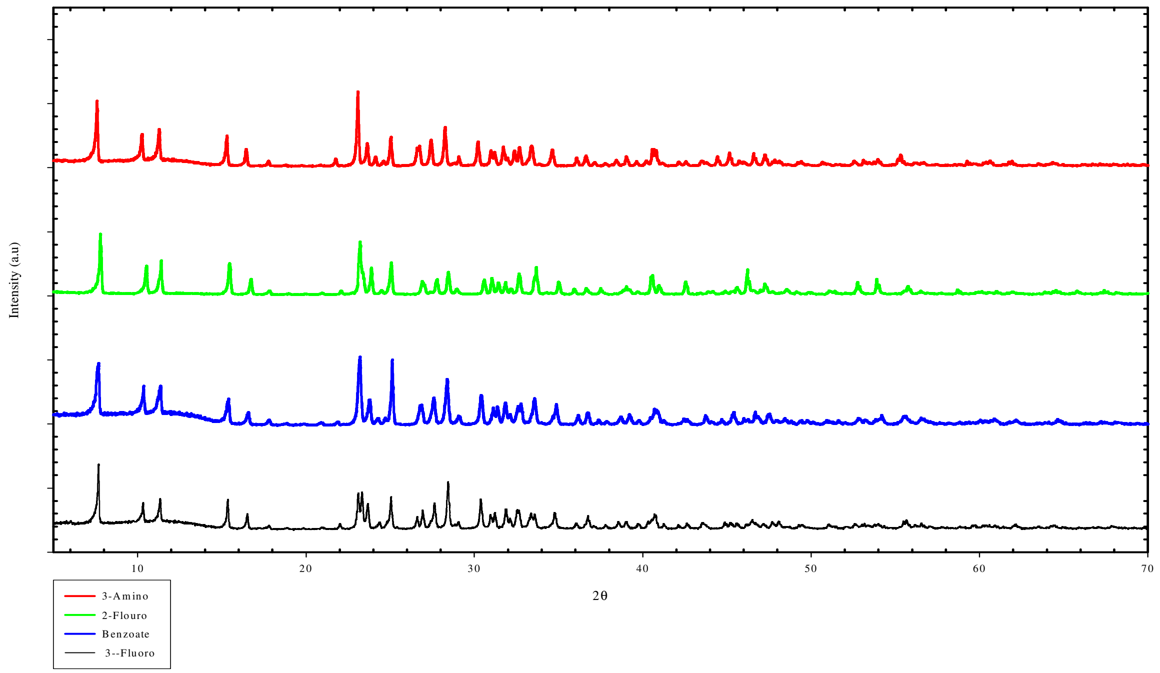


Fig. 2.22 **Experimental powder x-ray diffraction patterns of the 3-amino, 2-fluoro, 3-fluoro, benzoate complexes showing identical position and intensity of reflections**

The theoretical powder diffraction patterns were compared with the experimental powder diffraction patterns and the excellent agreement is shown in Fig 2.23 – 2.26.

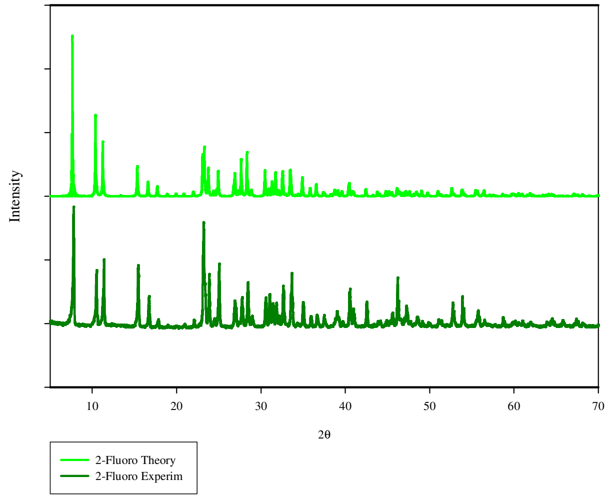


Fig. 2.23 **Comparison of experimental and theoretical powder patterns of the 2-fluoro complex**

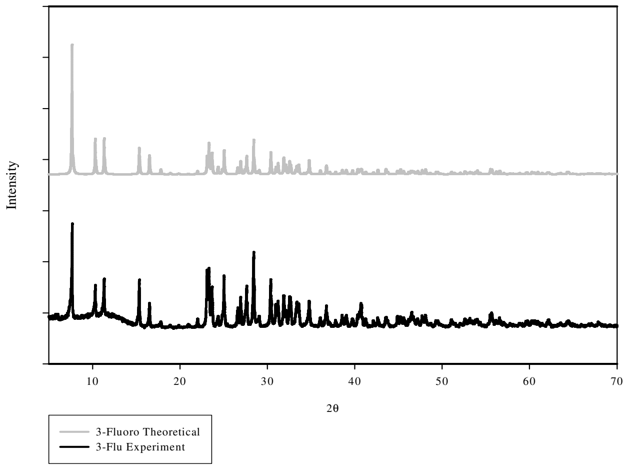


Fig. 2.24 Comparison of experimental and theoretical powder patterns of the 3-fluoro complex

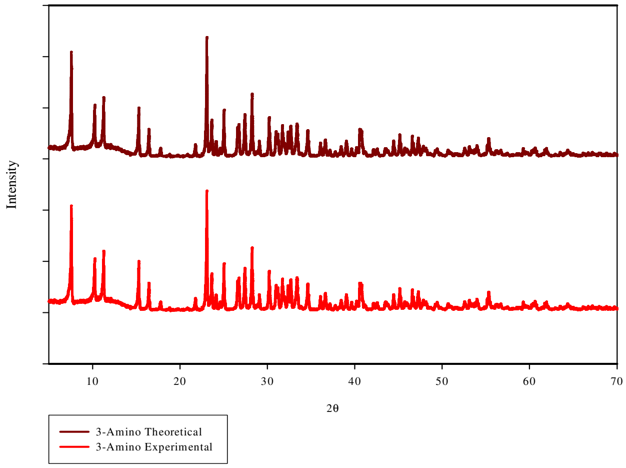


Fig. 2.25 Comparison of experimental and theoretical powder patterns of the 3-amino complex

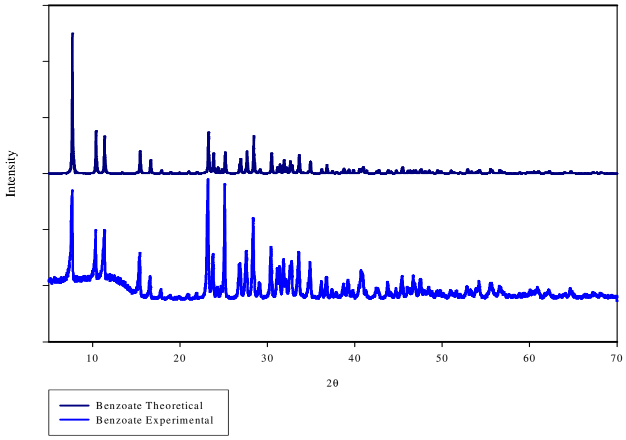


Fig. 2.26 Comparison of experimental and theoretical powder patterns of the benzoate complex

The group of eight compounds in Fig. 2.27 could also crystallise with the same crystal structure, based on the agreement between the various powder spectra.

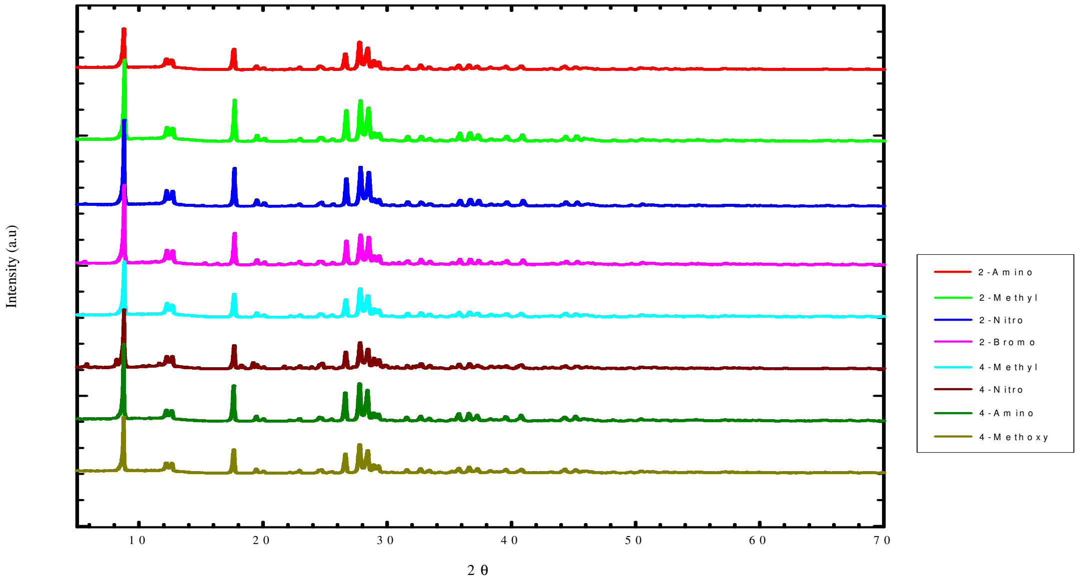


Fig. 2.27 **Experimental powder x-ray diffraction patterns of the eight complexes showing similarity in position and intensity of the reflections**

The same could be said for the next three groups of two compounds each, as depicted in Fig.2.28

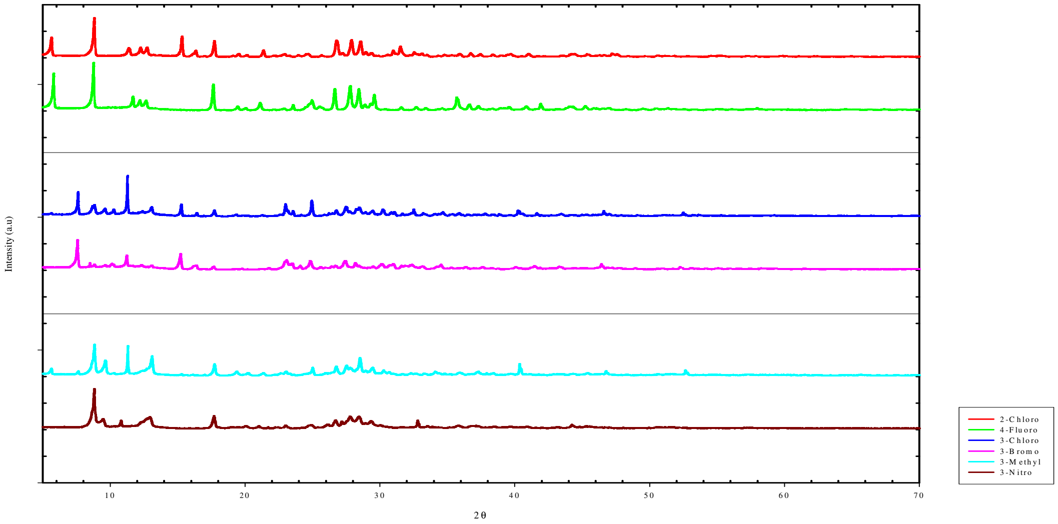


Fig. 2.28 **Experimental powder x-ray diffraction patterns of three groups of two complexes which show similarities in position and intensity of reflections**

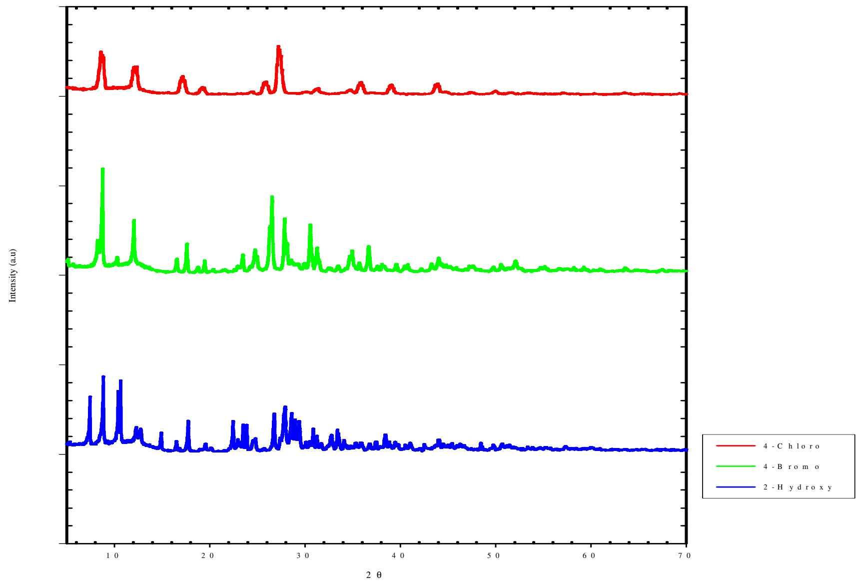


Fig. 2.29 Experimental powder x-ray diffraction patterns of three complexes which are not similar in position and intensity of the reflections to any other complexes

2.8 CONCLUSION

Both single crystal and powder diffraction data suggests that the 2-fluoro, 3-fluoro, 3-amino benzoate complexes, as well as the unsubstituted benzoate complex, are isostructural. The single crystal diffraction studies show that these four benzoate complexes all crystallise in the same space group and have almost identical crystal structures. The volumes of the four unit cells differ by less than 28 Å^3. This indicates that displacement of a hydrogen atom by a fluoro or amino group, as substituent on the benzoate, does not alter the packing requirements. The influence of the Tl…S interaction in packing in the solid state seems to be of importance as well.

The experimental and theoretical powder diffraction patterns for these four complexes are also almost identical in position and intensity, underlining the similarity in the crystal structures. None of the remaining complexes' powder diffraction patterns match those of the four benzoates listed above. However, of importance is the fact that some groups of compounds also have almost identical powder diffractograms – that is very similar 2θ° and intensity values. This may be a result of very similar crystal structures with in these groups. The main group of eight complexes is such a group. This group included electron withdrawing, electron donating and bulky groups, in both the ortho position as well as the para position. There are a further three groups with pairs of complexes that also both yield the same powder diffraction pattern. The powder diffraction patterns for 18 complexes were not all unique: one group of four, one group of eight, and three groups of two complexes had very closely related spectra. There were three complexes giving spectra that showed no clear correlation with any of the other spectra measured.

2.9 REFERENCES
CHAPTER 2

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2.10 APPENDIX – ADDITIONAL CRYSTALLOGRAPHIC DATA FOR THE COMPLEXES

2.10.1 Tl^{+1} 4(TU) 2-Fluorobenzoate complex

	x	y	z	U(eq)
Tl(1)	0	0	0	47(1)
S(1)	1070(1)	1245(1)	2500	39(1)
C(1)	2134(2)	1045(2)	2500	36(1)
N(1)	2559(2)	965(2)	1105(3)	49(1)
S(2)	1423(1)	9049(1)	2500	43(1)
C(2)	1173(2)	8072(2)	2500	41(1)
N(2)	1073(2)	7680(2)	1116(4)	61(1)
O(1)	695(2)	6055(2)	2500	55(1)
C(3)	0	3174(3)	2500	78(2)
C(4)	753(5)	3567(3)	2500	86(2)
C(5)	743(3)	4396(3)	2500	57(1)
C(6)	0	4818(4)	2500	38(1)
C(7)	0	5720(3)	2500	36(1)
F(1)	1429(3)	4646(3)	2500	106(3)

Table 2.33 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tl^{+1} 4(TU) 2-Fluorobenzoate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	49(1)	46(1)	46(1)	-6(1)	0	0
S(1)	27(1)	45(1)	44(1)	0	0	2(1)

C(1)	31(2)	31(1)	47(2)	0	0	1(1)
N(1)	32(1)	70(2)	45(1)	1(1)	2(1)	8(1)
S(2)	57(1)	31(1)	42(1)	0	0	-7(1)
C(2)	41(2)	35(2)	47(2)	0	0	-3(1)
N(2)	95(2)	39(1)	50(2)	-3(1)	-3(1)	-17(1)
O(1)	36(2)	30(1)	99(2)	0	0	-6(1)
C(3)	145(8)	25(3)	64(3)	0	0	0
C(4)	132(6)	38(3)	87(3)	0	0	42(3)
C(5)	57(3)	38(2)	76(2)	0	0	16(2)
C(6)	48(3)	22(2)	45(3)	0	0	0
C(7)	30(2)	22(2)	56(2)	0	0	0
F(1)	29(2)	35(3)	254(8)	0	0	2(2)

Table 2.34 **Anisotropic displacement parameters ($Å^2$x 10^3)for Tl^{+1} 4(TU) 2-Fluorobenzoate. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	x	y	z	U(eq)
H(1A)	3110(20)	873(15)	1160(30)	48(7)
H(1B)	2420(40)	1020(30)	290(50)	54(14)
H(2A)	910(20)	7250(30)	1250(40)	59(9)
H(2B)	1140(30)	7810(30)	410(60)	54(13)
H(3)	0	2650(60)	2500	90(20)
H(4)	1230(40)	3250(30)	2500	70(13)

Table 2.35 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Tl^{+1} 4(TU) 2-Fluorobenzoate.**

2.10.2 Tl^{+1} 4(TU) 3-Fluorobenzoate complex

	x	y	z	U(eq)
Tl(1)	0	0	0	45(1)
S(1)	1068(1)	1222(1)	2500	38(1)
C(1)	2142(2)	1034(2)	2500	36(1)
N(1)	2574(2)	961(2)	3895(3)	49(1)
S(2)	1432(1)	9062(1)	2500	44(1)
C(2)	1187(2)	8090(2)	2500	41(1)
N(2)	1089(2)	7702(2)	1108(3)	61(1)
C(3)	0	3228(3)	2500	51(1)
C(4)	763(3)	3637(2)	2500	55(1)
C(5)	764(2)	4449(2)	2500	46(1)
C(6)	0	4857(3)	2500	38(1)
C(7)	0	5745(3)	2500	37(1)
O(1)	-704(2)	6082(2)	2500	54(1)
F(1)	1451(3)	3255(3)	2500	90(2)

Table 2.36 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tl^{+1} 4(TU) 3-Fluorobenzoate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	46(1)	44(1)	43(1)	-6(1)	0	0
S(1)	29(1)	44(1)	42(1)	0	0	1(1)
C(1)	32(2)	32(2)	44(2)	0	0	0(1)
N(1)	34(1)	70(2)	43(1)	1(1)	-1(1)	5(1)

S(2)	59(1)	31(1)	40(1)	0	0	-5(1)
C(2)	42(2)	35(2)	46(2)	0	0	0(1)
N(2)	97(2)	38(1)	49(1)	-3(1)	-5(1)	-14(1)
C(3)	60(3)	28(2)	64(3)	0	0	0
C(4)	58(2)	33(2)	73(3)	0	0	10(2)
C(5)	36(2)	32(2)	69(2)	0	0	1(2)
C(6)	41(3)	24(2)	48(3)	0	0	0
C(7)	31(2)	23(2)	55(2)	0	0	0
O(1)	37(1)	34(1)	91(2)	0	0	6(1)
F(1)	55(3)	39(2)	175(6)	0	0	18(2)

Table 2.37 **Anisotropic displacement parameters (Å^{2}x 10^3)for Tl^{+1} 4(TU) 3-Fluorobenzoate. The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]**

	x	y	z	U(eq)
H(1A)	3140(20)	928(16)	3840(30)	51(8)
H(1B)	2400(30)	1010(30)	4680(40)	53(12)
H(2A)	920(20)	7250(20)	1200(40)	60(9)
H(2B)	1130(30)	7920(30)	240(40)	58(12)
H(4)	1270(30)	4760(30)	2500	42(10)
H(6)	0	2730(40)	2500	66(18)

Table 2.38 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) 3-Fluorobenzoate.**

2.10.3 Tl^{+1} 4(TU) 3-Aminobenzoate complex

	x	y	z	U(eq)
Tl(1)	0	0	0	42(1)
S(1)	1074(1)	1218(1)	2500	34(1)
S(2)	1433(1)	9060(1)	2500	37(1)
O(1)	705(2)	6094(2)	2500	49(1)
C(1)	2155(2)	1023(2)	2500	32(1)
C(3)	0	3237(3)	2500	42(1)
N(1)	2581(2)	946(1)	1113(3)	44(1)
C(5)	763(2)	4453(2)	2500	39(1)
C(7)	0	5748(2)	2500	34(1)
C(6)	0	4863(3)	2500	36(1)
N(2)	1080(2)	7697(2)	1116(3)	57(1)
C(4)	776(3)	3634(2)	2500	43(1)
C(2)	1177(2)	8087(2)	2500	36(1)
N(3)	1474(5)	3234(4)	2500	60(2)

Table 2.39 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) 3-Aminobenzoate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	45(1)	41(1)	41(1)	-6(1)	0	0
S(1)	27(1)	35(1)	39(1)	0	0	1(1)
S(2)	47(1)	27(1)	36(1)	0	0	-4(1)
O(1)	36(1)	28(1)	84(2)	0	0	-4(1)

C(1)	30(2)	26(1)	40(1)	0	0	-1(1)
C(3)	50(3)	21(2)	55(2)	0	0	0
N(1)	33(1)	63(1)	36(1)	1(1)	1(1)	6(1)
C(5)	36(2)	23(2)	58(2)	0	0	0(1)
C(7)	30(2)	22(2)	51(2)	0	0	0
C(6)	40(3)	23(2)	45(3)	0	0	0
N(2)	90(2)	34(1)	46(1)	-4(1)	-2(1)	-13(1)
C(4)	46(2)	27(2)	55(2)	0	0	7(1)
C(2)	34(2)	32(2)	42(1)	0	0	-3(1)
N(3)	39(4)	21(3)	119(7)	0	0	3(3)

Table 2.40 **Anisotropic displacement parameters ($Å^2$x 10^3)for Tl^{+1} 4(TU) 3-Aminobenzoate. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	x	y	z	U(eq)
H(5)	1240(30)	4730(30)	2500	34(8)
H(1A)	3100(20)	901(15)	1110(30)	40(7)
H(3)	0	2740(40)	2500	52(15)
H(2A)	928(18)	7250(20)	1200(30)	47(8)
H(1B)	2390(30)	1000(20)	310(50)	44(10)
H(2B)	1090(30)	7920(30)	270(40)	54(12)
H(3A)	1490(50)	2900(40)	2500	21(19)
H(3B)	1800(50)	3480(40)	2500	28(19)

Table 2.41 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Tl^{+1} 4(TU) 3-Aminobenzoate.**

2.10.4 Tl^{+1} 4(TU) Benzoate complex

	x	y	z	U(eq)
Tl(1)	0	0	0	45(1)
S(1)	1078(1)	1235(1)	2500	36(1)
C(1)	2160(2)	1029(2)	2500	33(1)
N(1)	2580(2)	947(2)	3900(3)	44(1)
S(2)	1453(1)	9052(1)	2500	40(1)
C(2)	1188(2)	8075(2)	2500	38(1)
N(2)	1086(2)	7685(2)	1112(4)	57(1)
O(1)	708(2)	6061(2)	2500	49(1)
C(3)	0	3190(3)	2500	50(1)
C(4)	769(3)	3586(2)	2500	52(1)
C(5)	765(2)	4414(2)	2500	40(1)
C(6)	0	4826(4)	2500	35(1)
C(7)	0	5721(3)	2500	31(1)

Table 2.42 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) Benzoate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	46(1)	44(1)	45(1)	-6(1)	0	0
S(1)	26(1)	40(1)	42(1)	0	0	3(1)
C(1)	28(2)	29(1)	43(2)	0	0	1(1)
N(1)	26(1)	62(1)	43(1)	2(1)	0(1)	7(1)
S(2)	54(1)	28(1)	39(1)	0	0	-5(1)
C(2)	39(2)	30(2)	46(2)	0	0	-1(1)

N(2)	90(2)	36(1)	45(2)	-2(1)	-3(1)	-14(1)
O(1)	32(2)	28(1)	85(2)	0	0	-5(1)
C(3)	65(4)	24(2)	60(3)	0	0	0
C(4)	51(3)	30(2)	75(3)	0	0	13(2)
C(5)	31(2)	26(2)	63(2)	0	0	2(1)
C(6)	39(3)	22(2)	44(3)	0	0	0
C(7)	22(2)	23(2)	49(2)	0	0	0

Table 2.43 **Anisotropic displacement parameters (Å^{2}x 10^3)for Tl^{+1} 4(TU) Benzoate. The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]**

	x	y	z	U(eq)
H(1A)	3040(20)	886(15)	3850(30)	35(8)
H(1B)	2360(40)	960(30)	4810(40)	40(13)
H(2A)	940(20)	7200(20)	1260(40)	50(8)
H(2B)	1140(30)	7830(30)	330(50)	41(12)
H(3)	0	2600(50)	2500	90(20)
H(4)	1300(30)	3280(30)	2500	55(11)
H(5)	1290(30)	4670(30)	2500	45(10)

Table 2.44 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) Benzoate.**

2.10.5 Tl^{+1} 4(TU) PF_6^- complex

	x	y	z	U(eq)
Tl(1)	0	0	1280(4)	50(1)
S(1)	411(6)	2570(5)	3840(20)	55(1)
C(1)	-1040(20)	3320(20)	3720(60)	51(6)
N(1)	-1390(20)	3790(30)	5310(30)	68(9)
N(2)	-1888(19)	3500(20)	2520(30)	38(5)
P	5000	5000	4030(50)	81(7)
F(1)	5020(60)	5910(30)	2540(60)	111(11)
F(2)	4970(60)	4070(30)	5540(60)	111(11)
F(3)	3624(14)	4530(30)	3550(70)	111(11)
F(4)	6369(14)	5450(30)	4530(90)	111(11)
F(5)	5600(30)	3900(30)	2980(70)	111(11)
F(6)	4400(30)	6080(30)	5100(70)	111(11)

Table 2.45 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) PF_6^-. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	52(1)	52(1)	45(1)	0	0	0
S(1)	76(4)	52(3)	36(2)	-4(6)	-4(8)	-4(2)
N(1)	24(10)	130(20)	48(14)	-38(15)	-32(11)	14(13)
N(2)	42(11)	50(11)	22(8)	13(9)	26(9)	23(9)
P	104(7)	104(7)	40(20)	0	0	0

Table 2.46 **Anisotropic displacement parameters (Å^{2}x 10^3)for Tl^{+1} 4(TU) PF_6^-. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	x	y	z	U(eq)
H(1A)	3979	-2582	2561	57
H(1B)	3375	-1680	1390	57
H(2A)	4056	-2073	5231	117
H(2B)	3527	-863	5906	117

Table 2. 47 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) PF_6^{-1} .**

2.10.6 Tl^{+1} 4(TU) BF_4^- complex

	x	y	z	U(eq)
Tl(1)	0	0	2500	51(1)
S(1)	-403(4)	2592(2)	0	92(1)
C(1)	1063(13)	3347(7)	0	99(4)
N(1)	1654(8)	3648(5)	-1383(5)	125(3)
B(1)	5000	5000	0	250(50)
F(1)	5170(20)	6135(13)	660(30)	246(13)

Table 2.48 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Tl^{+1} 4(TU) BF_4^-. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

Tl(1)	54(1)	54(1)	45(1)	0	0	0
S(1)	184(2)	57(1)	36(1)	0	0	7(1)
C(1)	219(12)	37(3)	41(4)	0	0	-39(5)
N(1)	256(8)	77(3)	41(2)	2(2)	4(3)	-66(4)

Table 2.49 **Anisotropic displacement parameters (Å^{2}x 10^{3})for Tl^{+1} 4(TU) BF$_4^-$. The anisotropic displacement factor exponent takes the form: -2p^{2}[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}**

	x	y	z	U(eq)
H(1)	2393	4025	-1363	149
H(2)	1297	3466	-2298	149

Table 2.50 **Hydrogen coordinates (x 10^{4}) and isotropic displacement parameters (□^{2}x 10^{3}) for Tl^{+1} 4(TU) BF$_4^-$.**

2.10.7 thallium – 4-aminobenzoate

	x	y	z	U(eq)
Tl(1)	8900(1)	5903(1)	4311(2)	35(1)
O(1)	9257(5)	4250(4)	3394(10)	43(1)
O(2)	8157(4)	4300(4)	5574(10)	48(2)
C(1)	8701(5)	2894(4)	4613(9)	25(2)
C(2)	8148(5)	2435(5)	5907(10)	35(2)
C(3)	8159(5)	1521(5)	6014(11)	37(2)
C(4)	8724(7)	1020(5)	4785(15)	32(2)
C(5)	9273(5)	1468(5)	3501(12)	37(2)
C(6)	9262(5)	2375(5)	3396(12)	36(2)
C(7)	8700(6)	3881(6)	4460(30)	37(3)
N(1)	8732(5)	108(5)	4895(13)	47(2)

Table 2.51 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for thallium – 4-aminobenzoate.. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	47(1)	26(1)	33(1)	1(1)	1(1)	3(1)
O(1)	54(3)	24(2)	50(3)	8(2)	3(3)	-4(3)
O(2)	54(3)	36(3)	55(4)	-10(3)	-5(3)	10(3)
C(1)	32(3)	24(3)	19(5)	-1(3)	-9(3)	-3(3)
C(2)	38(4)	36(4)	32(4)	-7(3)	2(3)	2(3)
C(3)	39(4)	37(4)	36(3)	4(3)	5(3)	-7(3)
C(4)	42(4)	18(3)	36(6)	4(3)	-8(3)	-2(3)
C(5)	30(3)	35(4)	45(3)	-2(3)	2(3)	-1(3)

C(6)	34(4)	39(4)	35(4)	-1(3)	-5(3)	-5(3)
C(7)	36(3)	30(3)	45(8)	3(5)	-15(7)	1(3)
N(1)	53(4)	19(3)	68(6)	-1(3)	11(3)	-4(3)

Table 2.52 **Anisotropic displacement parameters (Å^{2}x 10^3)for thallium – 4-aminobenzoate. The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]**

	x	y	z	U(eq)
H(2)	7763	2752	6717	42
H(3)	7791	1233	6905	45
H(5)	9658	1150	2694	44
H(6)	9633	2658	2502	43
H(1A)	9084	-194	4153	56
H(1B)	8384	-159	5704	56

Table 2.53 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for thallium – 4-aminobenzoate.**

2.10.8 2Tl(I), 2(TU) 2(Tph) 2H_2O (Tph = terephthalate benzene-1,4-dicarboxylate) complex

	x	y	z	U(eq)
Tl(1)	9746(1)	2829(1)	9815(1)	40(1)
Tl(2)	4813(1)	2552(1)	9761(1)	42(1)
S(1)	2487(1)	-133(1)	9887(1)	35(1)
S(2)	7377(1)	4713(1)	10293(1)	38(1)
O(1)	1144(6)	2402(5)	8904(1)	63(1)
O(2)	3478(5)	3144(6)	8805(1)	67(1)
O(3)	1278(5)	4154(5)	6608(1)	63(1)
O(4)	-947(5)	3005(5)	6717(1)	57(1)
O(5)	7365(5)	2436(4)	9153(1)	46(1)
O(6)	8209(4)	4599(4)	9142(1)	47(1)
O(7)	6097(6)	4845(5)	6915(1)	69(1)
O(8)	5520(6)	2700(6)	6926(1)	68(1)
O(9)	3601(5)	4615(5)	5981(2)	50(1)
O(10)	6821(6)	6976(6)	9443(2)	59(1)
N(1)	178(5)	-522(5)	9277(2)	41(1)
N(2)	2642(6)	-463(5)	9027(1)	41(1)
N(3)	6263(6)	3563(6)	10999(2)	52(1)
N(4)	8872(6)	4039(6)	11051(2)	53(1)
C(1)	1710(6)	3008(5)	8201(2)	34(1)
C(2)	480(6)	2217(6)	8022(2)	38(1)
C(3)	87(6)	2377(5)	7578(2)	37(1)
C(4)	879(5)	3300(5)	7326(2)	32(1)
C(5)	2115(6)	4073(5)	7520(2)	36(1)
C(6)	2542(5)	3929(6)	7960(2)	38(1)
C(7)	2132(6)	2836(5)	8671(1)	31(1)
C(8)	365(6)	3507(6)	6840(2)	41(1)

C(9)	7139(5)	3643(5)	8469(2)	33(1)
C(10)	6453(6)	2494(6)	8255(2)	39(1)
C(11)	6069(6)	2542(6)	7806(2)	39(1)
C(12)	6368(5)	3718(6)	7580(2)	36(1)
C(13)	7021(6)	4872(6)	7783(2)	44(1)
C(14)	7407(6)	4812(6)	8232(2)	42(1)
C(15)	7602(5)	3554(6)	8958(2)	37(1)
C(16)	5977(5)	3758(6)	7108(1)	34(1)
C(17)	1724(5)	-385(5)	9358(1)	30(1)
C(18)	7518(6)	4055(5)	10817(2)	37(1)

Table 2.54 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 2Tl(I), 2(TU) 2(Tph) 2H$_2$O (Tph = terephthalate benzene-1,4-dicarboxylate). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	44(1)	41(1)	36(1)	4(1)	0(1)	1(1)
Tl(2)	43(1)	44(1)	40(1)	0(1)	5(1)	1(1)
S(1)	34(1)	41(1)	28(1)	-1(1)	-3(1)	-2(1)
S(2)	45(1)	36(1)	33(1)	5(1)	2(1)	2(1)
O(1)	95(3)	60(3)	34(2)	9(2)	13(2)	13(2)
O(2)	66(3)	100(4)	34(2)	-5(2)	-7(2)	16(3)
O(3)	67(2)	90(4)	31(2)	14(2)	4(2)	-8(2)
O(4)	54(2)	72(3)	42(2)	-10(2)	-14(2)	-1(2)
O(5)	55(2)	48(2)	35(2)	9(2)	-3(2)	-3(2)
O(6)	58(2)	49(2)	35(2)	-7(2)	-2(2)	0(2)
O(7)	94(3)	77(3)	35(2)	6(2)	5(2)	29(3)
O(8)	77(3)	91(4)	36(2)	-7(2)	3(2)	-10(3)

O(9)	54(2)	52(3)	44(3)	-6(2)	2(2)	2(2)
O(10)	82(3)	43(3)	55(3)	7(2)	15(2)	-1(2)
N(1)	36(2)	57(3)	28(2)	-2(2)	-1(2)	-2(2)
N(2)	39(2)	55(3)	29(2)	-5(2)	5(2)	2(2)
N(3)	58(3)	55(3)	45(3)	14(2)	8(2)	-5(2)
N(4)	53(3)	58(3)	46(3)	21(3)	-7(2)	0(2)
C(1)	38(2)	37(3)	26(2)	0(2)	2(2)	10(2)
C(2)	41(3)	36(3)	39(3)	7(2)	7(2)	2(2)
C(3)	35(2)	37(3)	41(3)	-3(2)	0(2)	-2(2)
C(4)	33(2)	33(3)	29(2)	-1(2)	-2(2)	6(2)
C(5)	35(2)	37(3)	37(3)	7(2)	6(2)	-3(2)
C(6)	36(2)	40(3)	37(3)	-3(2)	-4(2)	-2(2)
C(7)	45(3)	32(3)	17(2)	3(2)	5(2)	16(2)
C(8)	48(3)	44(3)	30(2)	-4(2)	-2(2)	14(2)
C(9)	30(2)	41(3)	29(2)	3(2)	1(2)	4(2)
C(10)	41(3)	38(3)	36(3)	5(2)	-3(2)	-1(2)
C(11)	41(3)	37(3)	37(3)	-2(2)	-3(2)	1(2)
C(12)	35(2)	45(3)	28(2)	2(2)	4(2)	5(2)
C(13)	49(3)	43(3)	40(3)	11(2)	3(2)	-4(2)
C(14)	49(3)	38(3)	38(3)	1(2)	-1(2)	-7(2)
C(15)	30(2)	50(3)	29(2)	0(2)	2(2)	2(2)
C(16)	38(2)	46(3)	17(2)	3(2)	6(2)	7(2)
C(17)	35(2)	25(2)	30(2)	-2(2)	0(2)	1(2)
C(18)	48(3)	27(2)	35(2)	2(2)	0(2)	3(2)

Table 2.55 Anisotropic displacement parameters (Å^{2}x 10^3) for 2Tl(I), 2(TU) 2(Tph) 2H$_2$O (Tph = terephthalate benzene-1,4-dicarboxylate). The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	x	y	z	U(eq)
H(2)	90(60)	1530(70)	8207(19)	54(17)
H(3)	-770(70)	1890(70)	7470(20)	62(19)
H(5)	2600(60)	4620(70)	7370(19)	57(18)
H(6)	3350(60)	4400(60)	8124(16)	37(13)
H(10)	6100(50)	1760(50)	8407(15)	26(12)
H(11)	5610(60)	1720(70)	7621(19)	52(16)
H(13)	7190(60)	5600(70)	7633(19)	50(16)
H(14)	7710(60)	5650(70)	8386(18)	47(15)
H(1A)	-260(70)	-640(70)	9030(20)	52(18)
H(1B)	-390(70)	-390(70)	9420(20)	50(20)
H(2A)	2160(70)	-600(70)	8780(20)	54(18)
H(2B)	3620(70)	-370(60)	9061(18)	47(16)
H(3A)	6300(60)	3120(60)	11260(20)	42(15)
H(3B)	5480(110)	3390(110)	10830(30)	120(40)
H(4A)	8940(60)	3620(70)	11280(20)	44(16)
H(4B)	9600(60)	4380(60)	10947(17)	33(15)
H(9A)	3420(110)	5550(120)	5870(30)	130(40)
H(9B)	3300(80)	4430(90)	6160(20)	60(30)
H(10A)	6900(70)	7600(70)	9340(20)	40(20)
H(10B)	7460(130)	6270(130)	9290(40)	160(40)

Table 2.56 **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 2Tl(I), 2(TU) 2(Tph) 2H_2O (Tph = terephthalate benzene-1,4-dicarboxylate).**