CRYSTALLOGRAPHIC STUDY OF

IONIC THIOUREA COMPLEXES

by

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Die kristalstrukture van die $T\ell(C_6H_5COO)\cdot 4(SC(NH_2)_2$ en $T\ell H_2PO_4\cdot 4(SC(NH_2)_2)$ komplekse is deur middel van drie-demensionale X-straal diffraksiemetodes bepaal. Dit is gevind dat die strukture $(T\ell^+\cdot 4TU)_n$ koordinasiekolomme bevat (TU=tioureum) met mm en 2 simmetrie respektiewelik en dat daar 'n merkwaardige ooreenkoms is met die $^4/_m$ simmetrie van die tioureumkomplekse van die ander talliumsoute. In die geval van die fosfaat komplekse lê die swaelatome van die tioureum wat die talliumione omring, op die hoeke van 'n vervormde Archimediese antiprisma met die talliumatome die middelpunt daarvan. Die anione $H_2PO_4^-$ en $C_6H_5COO^-$ van die komplekse kom ook in lineêre koordinasiekolomme voor en word omring deur die amiengedeeltes van die tioureummolekules.

In die bensoaatkompleks is die wisselwerking van die amiengedeeltes van die tioureum op die anioon in die lineêre kolomme nie almal dieselfde nie. Die wat teenoor die karboksielgroep lê, in dieselfde vlak is sterk deur middel van 'n waterstofband gebind, sodat die dipoolmoment van die tioureummolekule daardeur beïnvloed word. Die verandering van dipoolmoment het 'n sterker interaksie tussen die talliumioon en ook tussen 'n soortgelyke geaktiveerde naburige swaelatoom tot gevolg. Die laasgenoemde interaksie sluit moontlik 'n swak π-bandvorming in en lei tot vervorming van die viervoudige simmetrie van die koordinasiekolom.

Dit is gevind dat die fosfaatione in die fosfaatkompleks posisies inneem in die anioonkolom wat verskil van die van die komplekse van $T\ell ClO_4$, $T\ell NO_3$, CsCl, CsF, RbI en $T\ell C_6H_5COO$. Die anione van laasgenoemdes kom voor in posisies wat maksimum verpakking bevoordeel maar die posisies wat die fosfaatione inneem, is meer bevorderlik vir waterstofbandvorming.

SUMMARY

The crystal structures of the complexes $Tl(C_6H_5COO)\cdot 4(SC(NH_2)_2)$ and $TlH_2PO_4\cdot 4(SC(NH_2)_2)$ have been determined by three-dimensional X-ray diffraction methods. These structures are characterised by $(Tl^+\cdot 4TU)_n$ co-ordination columns (TU=thiourea) with mm and 2 symmetry respectively and both are remarkably similar to those with $^4/_m$ symmetry observed before in the thiourea complexes of other thallous salts. In the case of the phosphate complex the sulphur atoms of the thiourea, which surround the thallous ions, lie at the corners of distorted Archimedean antiprisms centering at the positions of the thallous ions. The anions $H_2PO_4^-$ and $C_6H_5COO^-$ also occur in linear co-ordination columns and are surrounded by the amino ends of the thiourea molecules.

The amino ends of the thiourea molecule do not all interact with the benzoate anions in the linear stacks in an equivalent fashion. Those facing the carboxyl group directly are strongly hydrogen bonded to it and the dipole moment of the thiourea molecule is enchanced because of this. This enhancement leads to stronger interaction of the sulphur, not only with the thallous ion, but also with a similarly activated neighbouring sulphur atom. This latter interaction probably involves weak Π- bonding and it leads to a distortion of the co-ordination column away from the familiar four-fold symmetry.

The phosphate ions of the phosphate complex were found to occupy positions different from those of the other series of this family, viz. $TlClO_4$, $TlNO_3$, CsCl, CsF, RbI and TlC_6H_5COO thiourea complexes. Whereas the latter anions occupy positions of optimum packing the phosphate ions are in positions more favourable for hydrogen bonding.

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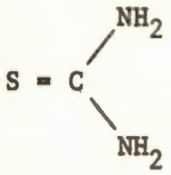
CHAPTER I

INTRODUCTION

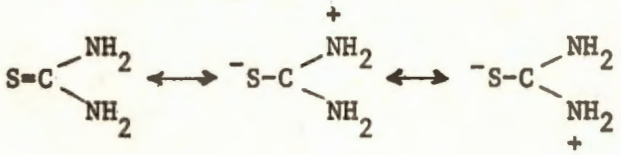
I. 1. THE THIOUREA MOLECULE

Thiourea is the sulphur analogue of urea and has the chemical formula $SC(NH_2)_2$ whereas the structural formula is usually written as:



The bond between S and C as determined by X-ray diffraction[1] has a length of 1.71Å and is, hence, somewhat longer than the double bond in carbon disulphide[2] which measures 1.56Å.

The bond in thiourea therefore shows some single bond character. This effect is explained by assuming that the true structure is a compromise between the three extreme resonance structures shown below, with structures (2) and (3) predominating in complexing reactions:[1, 3]



(1) (2) (3)

From the electronic structure of thiourea with electron configuration $(3s)^2(3p)^4$ for sulphur and $(2s)^2(2p)^3$ for nitrogen it follows that the reactivity, in general terms, can depend either on the pair of free electrons on the sulphur or on the lone pairs of electrons of the amide groups. From the many metal salts which form thiourea compounds with different degrees of stability, it was possible to establish that thiourea becomes co-ordinated through the lone pair of the sulphur electrons and not through

those of the nitrogen.[4]

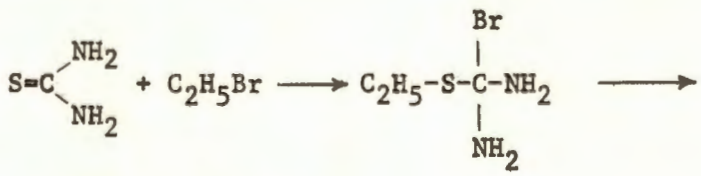
The fact that thiourea compounds of elements such as silver. gold, copper, cadmium, thallium, and palladium (especially in weakly alkaline solutions) are converted to the sulphides of these metals, as in the following reaction,

$$MeCl_2 + SC(NH_2)_2 + 2KOH \longrightarrow MeS + CNNH_2 + 2KCl + 2H_2O$$

further indicates co-ordination through the lone pair of electrons on the sulphur atom. Such a conversion was observed during the heating of aqueous solutions of thiourea compounds, and sometimes simply on standing. It apparently occur more readily if the thiourea compound already possessed an ionic Me:S bond, which become a more covalent bond on the formation of the metal sulphide.[4]

Proof that the bonding of a metal's central atom with thiourea occurs through sulphur will be found in the papers which showed that not only thiourea but also other sulphur-containing ligands (thioether,[5] thiosulphates,[6] sulphites,[7, 8] etc.) display a high trans-effect.

Thiourea compound formation through the sulphur atom can also be observed in such compounds as thiourea-halogen alkyls, first obtained by Claus[9, 10, 11] e.g.



$$C_2H_5SH + HBr + N{\equiv}C\text{-}NH_2$$

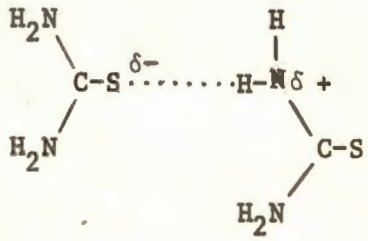
I. 2. THIOUREA AS A COMPLEXING AGENT

The "mono-acidic" base properties of thiourea make it one of the most versatile and powerful complexing agents known. It's versatility is the consequence of its zwitterion structure as shown by its behaviour in chemical reactions.

I. 2. a. INCLUSION COMPLEXES

The electronic structure of thiourea enables it to form inclusion complexes with branched-chain hydrocarbons [1]. The formation of these complexes is all the more remarkeble because of the fact that even saturated hydrocarbons, which as a rule are relatively unreactive, are complexed with thiourea with comparative ease.

The reason for this is that thiourea molecules can combine by forming hydrogen bonds such as



In this manner a three-dimensional framework is built up. Since such a structure contains a large amount of free space in the form of long open channels it cannot exist independently. When thiourea crystallizes in the presence of long chain hydrocarbons, however, these channels become occupied by the hydrocarbon molecules which have exactly the correct dimensions to fill them. The structural details of these so-called adducts were determined by x-ray diffraction methods [12].

I. 2. b. COMPLEXES WITH ORGANIC SUBSTANCES

The resonance structure of thiourea further enables it to form complexes by a distinctly different mechanism, namely by forming covalent bond complexes with various other organic substances such as, for example, with hydrazine hydroiodide $\{(SC(NH_2)_2)_4 \cdot (NH_2)_2 \cdot HI\}$ or pyridine hydroiodide

$\{(SC(NH_2)_2)_4 \cdot C_5H_5N \cdot HI\}$ [13].

I. 2. c. CO-ORDINATION COMPLEXES WITH TRANSITION METAL IONS

Thiourea also forms co-ordination complexes with transition metal ions. Numerous complexes of this type are known and some of their structures have been determined by X-ray diffraction [14]. One typical example is the tris (thiourea) copper (I) chloride complex investigated by Pepinsky and his co-workers [15]. In this complex each cuprous ion is tetrahedrally surrounded by four sulphur atoms one of which is shared between two cuprous ions. The average separation of 2.35 Å between copper and sulphur atoms shows that the thiourea molecules are co-ordinated to the copper through sulphur.

I. 2. d. IONIC COMPLEXES

Thiourea has also been reported to form stable complexes with salts of elements which do not form covalent bonds to co-ordination ligands. Another explanation must be sought then for the occurrence of these complexes.

The work done by Boeyens and Herbstein [17, 18] on complexes of thiourea with thallium nitrate and thallium perchlorate indicates that the average thallium-sulphur distance is 3.44Å, which is considerably longer than the separation between sulphur atoms of co-ordinated ligands and metal atoms. Indeed, the sum of the atomic radii of thallium and sulphur is about 2.7Å whereas the sum of their ionic radii is about 3.3Å. This strongly suggest that these are ionic complexes and that the major cohesion in the crystal is due to ion-dipole interactions.

The prototype of these ionic thiourea complexes is $NH_4Br \cdot 4TU$ (TU=thiourea) first described by Reynolds [16]. The isostructural series includes the complexes formed with

some halides of potassium, rubidium and caesium, with many ammonium and thallium (I) salts and with some lead (II) salts. These are all stoichiometric complexes and, depending on the oxidation number of both the cation (M) and anion (X), they have the general formulae:

$$MX \cdot 4TU$$

$$M_2X \cdot 8TU$$

$$MX_2 \cdot 6TU$$

The properties of this family of compounds were investigated by combined chemical and crystallographic methods (17, 18, 19, 20, 21, 22) Preparations reported in the earlier literature were repeated and checked by these authors and some new complexes were also prepared. All the complexes were examined by single-crystal or powder X-ray diffraction techniques and the unit-cell dimensions, space group and density (of the single crystals only) determined. On this basis some thirty odd related complexes were further subdivided into groups of isomorphous or nearly isomorphous structures. Representative complexes from each group were then chosen for structural analysis, thus enabling the relationship between the groups to be established.

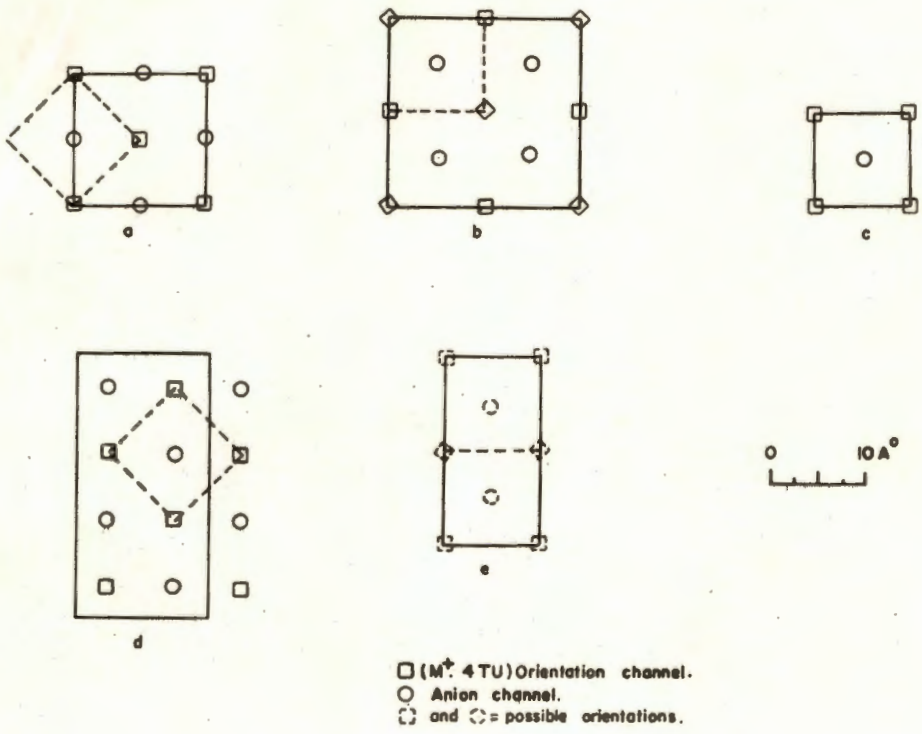
I. 2. d. (i) CLASSIFICATION ACCORDING TO CELL DIMENSIONS AND SPACE GROUPS

The unit cell dimensions and space groups showed that the complexes fall into a number of well-defined groups.

The largest group comprises the tetragonal 1:4 complexes and includes those formed by most alkali bromides and iodides, thallous bromide, and thallous

iodide. These complexes all have a≈21Å, c≈8.2Å and space group P4/mnc and have ordered structures (see fig. 1. 1(b)).

FIGURE 1.1



$TlClO_4$.4TU and RbI.4TU are typical representatives of this group of complexes and their structures were determined by Boeyens and Herbstein [17] and by Kruger and Boeyens [22] respectively.

A second, smaller, group closely related to the first, includes the thallium (I) nitrate, and sulphate (1:8) complexes, which have a≈10Å, c≈8.2Å and space group P4/mcc (see fig. 1. 1(c))

An interesting fact about this group is that a Weissenberg photograph of the $Tl NO_3 \cdot 4TU$ complex at $-160^{\circ}C$ showed that at this temperature the complex has a $\simeq 20\text{A}$, c $\simeq 8 \cdot 3\text{A}$ and space group P4/mnc. It appears that the smaller unit cell is a partially disordered version of the larger ordered cell, with the cell edges remaining in the same directions for both structures. The structure of $Tl NO_3 \cdot 4TU$ was established in detail [17] as a representative of this group.

A third group include the complexes of the alkali and thallium (I) chlorides, with cell dimensions a $\simeq 32\text{A}$, b $\simeq 13\text{A}$, c $\simeq 8 \cdot 5\text{A}$ and space group Bbam. Two complexes from this group namely $CsF \cdot 4TU \cdot 2H_2O$ with cell dimensions a$\simeq 17 \cdot 0\text{A}$, b$\simeq 12 \cdot 5\text{A}$, c$\simeq 8 \cdot 45\text{A}$ and space group Ibam [19] and $CsCl \cdot 4TU \cdot H_2O$ with cell dimensions a$=32 \cdot 1\text{A}$, b$=13 \cdot 22\text{A}$, c$=8 \cdot 51\text{A}$, space group Bbam and eight molecules per unit cell [20] were investigated structurally. Because of the close relationship of the caesium fluoride structure to that of the chloride complexes it was placed in this group. The anhydrous forms of the complexes in this group (except caesium fluoride, from which no anhydrous form could be obtained) were all fibrous and therefore unsuitable for structure analysis. Fig. 1. 1(d) shows the relationship of this group to the other complexes.

Another group is represented by the two complexes $Tl ClO_3 \cdot 4TU$ and $Tl CNS \cdot 4TU$, which both have a$\simeq$ 2b$\simeq$ 21A and c$\simeq$ 8$\cdot$2A. In these complexes it seems reasonable to suppose that the ordering has taken place in one direction only and that a resultant distortion had led to a lowering of the unit cell symmetry. A structure analysis

of a representative of this group has not yet been carried out (see fig. 1. 1(e)).

The last group, represented by fig. 1. 1(a) and characterised by cell dimensions $a \simeq b \simeq 14\text{Å}$, $c \simeq 8{\cdot}3\text{Å}$ and the space group Cccm, includes the complexes of Tl_2CO_3, $TlNO_2$ with thiourea. In the nitrite and carbonate structures a different type of distortion leads to lowering of symmetry; in these complexes the cell diagonals of the disordered unit cell become the edges of the ordered orthorhombic unit cell and this leads to fairly complicated domain structures in the ordered crystals. The positions occupied by the anions will most probably be of the same type as the position occupied by the disordered NO_3^- in the $TlNO_3$ complex. $TlH_2PO_4 \cdot 4TU$ of which single crystals were obtained and which was shown also to belong to this class was chosen for a structure analysis in the present work. Another reason for selecting this complex comes from the work of Pfrepper [23] who claims the preparation of $aTl_3PO_4 \cdot 6TU$ complex. From experience, the existance of the thiourea complexes seems to be related to the formation of co-ordination columns with a Tl:S ratio of 1:4 [17, 18, 21] which is at variance with the Pfrepper formulation. It was therefore of interest to investigate this complex, but unfortunately no single crystal could be obtained.

I. 2. d. (ii) EFFECT OF ANION SIZE ON THE CO-ORDINATION COLUMN

An interesting observation made during the study of the thiourea ionic complexes was that all the struc-

tures seem to contain close-packed tetragonal $(M^{+}\cdot 4TU)_n$ co-ordination columns.[17, 18, 21] The very existence of such a column is however refuted by the proposed (Pfrepper) stoichiometry of the complex $Tl_3PO_4\cdot 6TU$. Complete disruption of the expected column seems to be caused here by the relatively small number of available anions. Excessively large voids would exist if the normal type of packing prevailed. Another instance where the geometry of the column is affected by the anion is found in the structure of $TlClO_4\cdot 4TU$[18] and also $RbI\cdot 4TU$[22]. In this case two types of column are found in the same structure. One of these is slightly distorted to allow for anionic protrusion.

Since these structures usually involve heavy cations, the interatomic distances are not generally sufficiently accurate to detect small distortions in the co-ordination columns, particularly when these distortions have the same symmetry as the column. It is thus desirable to investigate the effect of an anion which is large enough possibly to perturb the column, but not sufficiently symmetrical to have the same effect on all sides of the column. A likely candidate appeared to be the benzoate ion whose thallous salt forms a well-defined complex with thiourea. These effects were investigated further and the results are described in this thesis.

Complete single crystal X-ray structure analysis of $Tl_2H_2PO_4\cdot 4TU$ and $Tl(C_6H_5COO)\cdot 4TU$ have been done. Cell dimensions, space group, and density measurements have been carried out for the oxalate and formate complexes.

A powder diffractometer pattern of $Tl_3PO_4 \cdot 6TU$ has been obtained and indexed for hexagonal unit cell dimensions.

I. 3. PREPARATION OF THE COMPLEXES

Pfrepper[23] obtained buff-coloured crystals by slow cooling of an aqueous solution containing Tl_3PO_4 and thiourea. An attempt to repeat the preparation led to the precipitation of Tl_2S together with a white complex of micro-crystalline quality. This is reminiscent of the reaction between $Pb(ClO_4)_2$ and thiourea which in aqueous solution leads to the precipitation of PbS and the formation of a 1:6 complex not of the present type,[18] whilst in perchloric acid medium[24] no precipitation occurs and the 1:6 complex which is formed belongs to the present family. Acidification with orthophosphoric acid introduces the anion $H_2PO_4^-$ in excess. Thus, although the precipitation of Tl_2S is suppressed by addition of H_3PO_4, the complex of TlH_2PO_4 and not that of Tl_3PO_4 is obtained.

Slow cooling of the acidified solution of Tl_3PO_4 and thiourea in water, yielded twinned needlesof $TlH_2PO_4 \cdot 4TU$. Good single crystals were obtained, however, by mechanically splitting these along their needle axes.

The benzoate, formate and oxalate complexes were also prepared by dissolving the constituents in the ratios $(C_6H_5COO)Tl$: 4TU, $(HCOO)Tl$:4TU and $(COO)_2Tl_2$:8TU in boiling water. In all cases needles crystallized on cooling. The crystals of the formate complex were however too small for single crystal investigation.

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CHAPTER II

STRUCTURE ANALYSIS

II. 1. CRYSTAL CHOICE

The choice of a suitable crystal depends mainly on its external form and composition. Single crystals with well-developed faces, without any cracks or secondary crystals, were selected by microscopic examination. To diminish the effects of absorption, cylindrical crystals of average diameter 0·08 mm. and length 0·3 mm. were selected.

II. 2. CRYSTAL DATA

To determine the cell dimensions and space groups of the crystals, 20° oscillation photographs and the corresponding zero and first layer Weissenberg photographs over a range of 210° were taken according to standard techniques (25, 26, 27, 28, 29)

The length of the needle axes was obtained directly from the oscillation photographs by using the relationship

$$c=\lambda\frac{n}{\rho_n} \qquad (2.1)$$

where λ=wavelength of the X-rays. Cuk$_\alpha$ Ni filtered-radiation was used in the present work.

The lengths of the two other axes of the unit cell were determined from the zero layer line Wiesenberg photograph.

The density of the crystals was determined experimentally by using the flotation method with bromoform and p-cimeen as suspension liquids (30). The measured density was used to determined the number of formula units (Z) per unit cell;

$$\rho_{calc}/Z=M/VN_0 \qquad (2.2)$$

where V= volume of the unit cell, N_o= avogadro number, and

M= formula weight.

Space groups were determined by inspection of the zero and first layer line photographs for systematic absences.

II. 3. INTENSITY MEASUREMENTS AND CORRECTIONS

The multiple film technique [26] was used for intensity measurements. Seven films were placed one behind the other in a Weissenberg camera and exposed to the diffracted X-rays. The absorption of each film reduces the diffracted X-ray intensity by a constant factor so that a series of spots of decreasing intensity is obtained for each reflection.

The same exposure time was used for all layer lines. The intensity of each recorded spot was estimated visually by comparison with a standard intensity strip. Before processing of the measured reflection intensities, a value of one third of the minimum measurable value was assigned to all reflections which were too weak to measure. This is in keeping with theoretical considerations for centrosymmetric crystals [31]. The intensities measured on the succesive films were converted to the same arbitrary scale by multiplication by suitable inter-film factors (see appendix A).

Standard corrections for equi-inclination Weissenberg photographs must be applied to the measured intensity (I_{meas}) of a reflection, to yield the corrected intensity ($I_{corr.}$) and hence the observed structure factor amplitude (F_o). The relationship between $I_{meas.}$ and $I_{corr.}$ can be formulated as

$$I_{corr.} = I_{meas.} \cdot S.C.A^*.S^*.(Lp)^{-1} \qquad (2.3)$$

where S= scale factor applied to the intensities of each layer line to get F_o on an absolute scale, C= splitting factor, as a result of splitting of spots due to the α_1, α_2 doublet of Kα radiation, A*= absorption correction, S*= spot shape factor for higher layer lines, and Lp= combined Lorentz and polarization

factor.

Corrections on the measured intensities were done by using a computer program described in appendix B. The size of the crystal did not justify the application of absorption corrections (see §II.1).

II. 4. THE FOURIER SYNTHESIS

By definition and theory of the structure factor it is possible to derive the intensity of the scattered reflections from given atomic coordinates in a crystal, but for practical structure analysis with X-rays it is necessary to deduce the atom coordinates from the measured reflection intensities.

Let $\rho(x, y, z)$ represent the electron density of scattering matter at any point x, y, z in the unit cell of a crystal. The quantity of scattering material in the volume element dxdydz is then equal to $\rho(xyz)\frac{V}{a.b.c}$ dxdydz where the crystal axes, a, b, c are inclined at any angles and where V represents the volume of the unit cell. The number of electrons in the unit cell is thus proportional to the scattering material in the unit cell. The scattering matter in each volume element of this continuous distribution will make a contribution to the resultant amplitude for the whole unit cell, and for the general plane (hkℓ) the phase change from the origin to the point x, y, z is $2\pi\left(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c}\right)$

The structure factor or amplitude equation for j atoms in the unit cell

$$F(hk\ell)=\sum_{j}^{N} f_j e^{2\pi i\left(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c}\right)} \qquad (2.4)$$

could be written in the integral form

$$F(hk\ell)=\frac{V}{abc}\int_0\int_0\int_0 \rho(xyz)e^{2\pi i\left(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c}\right)}\,dxdydz \qquad (2.5)$$

It can be shown that any one-dimensional periodical function can be expressed as a Fourier series [32, 33];

$$F(x)=A_o+ A_1\cos 2\Pi(\frac{x}{a} +\alpha_1) + A_2\cos 2\Pi(\frac{2x}{a} + \alpha_2)+ \ldots\ldots$$
$$=\sum_{n=o}^{\infty} A_n \cos 2\Pi(\frac{nx}{a} + \alpha n) \qquad (2.6)$$

where A is the amplitude of the cosine wave, a the identity period and α the phase angle. For all centrosymmetric functions, with the origin as centre, the phase angle α could only be 0^o or 180^o and the equation reduces to

$$F(x)=\sum_{n=o}^{\infty} A_n \cos 2\Pi n \frac{x}{a} \qquad (2.7)$$

Every coefficient of this eguation must possess the correct sign, viz. positive if the phase angle is 0^o and negative when the phase angle is 180^o. The equation implies that any one dimensional centrosymmetric pattern with identity period could be represented as a sum of an infinite number of cosine waves with various amplitudes and wavelengths.

The electron density function $\rho(x, y, z)$ of a crystal is also a periodic function but in three dimensions with periodicities a, b, c, and could be expressed as a Fouries series, viz.

$$\rho(xyz)=\sum_{h'=-\infty}^{+\infty}\sum_{k'=-\infty}^{+\infty}\sum_{\ell'=-\infty}^{+\infty} C(h'k'\ell')\exp 2\Pi i(\frac{hx}{a} + \frac{ky}{b} + \frac{\ell z}{c}) \qquad (2.8)$$

with $h'k'\ell'$ integers with values from $+\infty$ to $-\infty$, and $C(h'k'\ell')$ the coefficients of the Fourier series that must be determined.

Calculation of the Fourier coefficients followed by substitution of the value of $\rho(xyz)$ from equation 2.8 gives

$$F(hk\ell)=\frac{V}{abc}\int_o^a\int_o^b\int_o^c \sum_{h',k',\ell'=-\infty}^{+\infty}\sum\sum C(h'k'\ell')\exp 2\Pi i(\frac{h'x}{a} + \frac{k'y}{b} + \frac{\ell'z}{c}).$$
$$\exp 2\Pi i(\frac{hx}{a} + \frac{ky}{b} + \frac{\ell z}{c}).\ dxdydz \qquad (2.9)$$

The quantity $\int_o^a e^{2\Pi i\Theta/a}$ vanishes for all the terms in the equation

except those for which $h'=\bar{h}$, $k'=\bar{k}$, $\ell'=\bar{\ell}$ and the quantity $e^{2\pi i(o)}=1$. The result of all these summations and integrations is

$$F(hk\ell)=V.C(\bar{h}\bar{k}\bar{\ell})$$

or

$$C(\bar{h}\bar{k}\bar{\ell})=F(hk\ell)/V \qquad (2.10)$$

From this it follows that $h',k',\ell'\equiv \bar{h},\bar{k},\bar{\ell}$ and the Fourier coefficients $C(h'k'\ell')$ can be replaced by the structure factor $F(hk\ell)$ divided by the unit cell volume. The electron density equation to use in a Fourier synthesis is as follows:-

$$\rho(xyz)=\frac{1}{V}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{\ell=-\infty}^{+\infty} \pm |F(hk\ell)| \exp\{-2\pi i(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c})\}$$

or

$$\rho(xyz)=\frac{1}{V}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{\ell=-\infty}^{+\infty} \pm |F(hk\ell)| \cos 2\pi(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c}) \qquad (2.11)$$

for a centrosymmetric crystal structure. With this formula it is theoretically possible to determine the structure of a crystal if the structure factors and the cell dimensions are known. These Fourier summations will give the atomic positions as maxima in the electron density function $\rho(xyz)$ with peak heights proportional to the number of electrons per atom.

The square roots of the measured intensities, after the necessary corrections have been applied, give the Fourier coefficients $F(hk\ell)$ on a relative scale. As shown above the phases of $F(hk\ell)$ are necessary for summation of the Fourier synthesis which will give the electron density for any point x,y,z in the unit cell. The phases are the only thing that could not be determined in practice. This gives rise to the so-called phase problem.

II. 5. THE PHASE PROBLEM

For centrosymmetric crystals with the origin of co-ordinates chosen at the centre, the structure factor equation 2.4 reduces to

$$F(hk\ell)_A = 2 \sum_{j}^{N/2} f_j \cos 2\pi\left(\frac{hx_j}{a^j} + \frac{ky_j}{b^j} + \frac{\ell z_j}{c^j}\right) \qquad (2.12)$$

This equation is directly related to the measured intensity I obtained from X-ray diffraction by

$$I(hk\ell) = /F(hk\ell)/^2 \qquad (2.13)$$
$$= A^2 + B^2$$

where

$$F(hk\ell) = A + iB$$

and

$$A = 2 \sum_{j}^{N/2} f_j \cos 2\pi\left(\frac{hx_j}{a^j} + \frac{ky_j}{b^j} + \frac{\ell z_j}{c^j}\right)$$

$$B = 2 \sum_{j}^{N/2} f_j \sin 2\pi\left(\frac{hx_j}{a^j} + \frac{ky_j}{b^j} + \frac{\ell z_j}{c^j}\right)$$

In this relationship the sign of $F(hk\ell)$ is undefined. For a centrosymmetric structure, however, the sign of $F(hk\ell)$—a real, positive or negative number—could be $F \gtrless o$ for phase angle 0^o and $F < o$ for phase angle 180^o. The measured intensity I for this kind of structure is thus the resultant vector of the sum of all the positive and negative structure factors.

A direct complicated statistical method exists for the determination of the phases if the structure contains no heavy atom. For a crystal structure that contains a heavy atom the position thereof could be determined and approximate amplitudes and phase angles could be calculated. The validity of such

calculated amplitudes and phase angles could be verified by comparing the calculated structure amplitudes ($F_{calc.}$) with the observed structure factors ($F_{obs.}$). Various methods exist for the determination of the position of the heavy atom from which a structure can be derived. Only two of the methods used in the present study will be described briefly.

II. 6. THE PATTERSON SYNTHESIS

Instead of the structure factors, Patterson [32, 33] used the squares of the moduli as Fourier coefficients; these quantities are directly related to the observed intensities and so they can always be measured. Patterson showed that the resulting synthesis was related in a simple way to the crystal structure, and could give direct evidence about atomic positions with no preliminary assumptions. It can however rarely be used to work out complete structures, but in some cases it may play a major role in producing the final solution.

From the electron density function

$$\rho(xyz)=\frac{1}{V}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{\ell=-\infty}^{+\infty}\pm|F(hk\ell)|\cos 2\pi\left(\frac{hx}{a}+\frac{ky}{b}+\frac{\ell z}{c}\right)$$

the Patterson function was defined as

$$P(uvw)=\int_0^1\int_0^1\int_0^1\rho(xyz).\,\rho(x+u,y+v,z+w)V\,dx\,dy\,dz \qquad (2.14)$$

In this expression, (x+u,y+v,z+w) gives the distribution about (x,y,z) as a function of the parameters u, v, w and it represents a distribution similar to $\rho(x,y,z)$ but displaced from the point (x,y,z) through a distance whose components are (u,v,w). This Patterson function reduces to

$$P(uvw)=\frac{1}{V}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{\ell=-\infty}^{+\infty}|F(hk\ell)|^2\cos 2\pi\left(\frac{hu}{a}+\frac{kv}{b}+\frac{\ell w}{c}\right) \qquad (2.15)$$

by expanding the two density functions as Fourier series and integrating.

For every pair of atoms in the crystal unit cell with coordinates x_j, y_j, z_j and x_k, y_k, z_k there will be a maximum in the Patterson function at $u=x_j-x_k$, $v=y_j-y_k$, $w=z_j-z_k$ and on the end point of a vector from atom k to atom j. The peak height will depend on the product $z_j.z_k$ of the atomic numbers z_j and z_k of the atoms concerned. This product is also directly proportional to the number of electrons of atoms j and k. This property makes it a very useful method because in the vector map the vectors between heavy atoms can usually easily be distinguished.

With N atoms in the unit cell, the electron density will have N peaks, but in the Patterson unit cell or vector map there will be a total of N^2 peaks of which N(N-1)/2 peaks will in general be resolved, in addition to the N-fold origin peak. Since both functions are determined by the same number of Fourier coefficients, the resolution of peaks in the Patterson synthesis will be poorer than in the synthesis of the electron density. The Fourier coefficients of the Patterson synthesis are all real, and it will always possess a centre of symmetry. This means that the symmetry of the Patterson function is equal to or higher than that of the electron density function.

Some important modifications of the Patterson method were made by Harker by the use of three dimensional series, simplified by the symmetry properties of the crystal and applied to the detection of certain special vectors. For example, if the crystal has a c-glide plane perpendicular to a, an atom at (x, y,z) is accompanied by one at the equivalent point $(\bar{x},y,\frac{1}{2}+z)$ and the vector between these atoms has the components $(2x,o,\frac{1}{2})$.

The function P(u,v,w), therefore, has a maximum at $(2u,o,\frac{1}{2})$ corresponding to this interatomic distance.

To find maxima of this kind it is only necessary to evaluate P(u,v,w) in the plane v=o and $w=\frac{1}{2}$. The equation may therefore be written as

$$P(u,o,\tfrac{1}{2})=\sum_{h=-\infty}^{+\infty}\sum_{k=}\sum_{\ell=} F^2(hk\ell)\cos 2\pi\left(\frac{hu}{a}+\tfrac{1}{2}\right) \qquad (2.16)$$

by neglecting absolute values. This is effectively a one-dimensional summation, and the numerical work is not formidable. There is an excellent chance of resolving the required vector peaks, because all the measured values of F(hkl) are used, and because interatomic vectors not parallel to the plane v=o and $w=\frac{1}{2}$ are eliminated. This set of maxima between symmetry related atoms was called Harker peaks and could be found on the corresponding Harker section v=o and $w=\frac{1}{2}$. Enough information to localise some atoms, especially the heavy atoms in the molecule, may be derived from these Harker peaks.

For the interpretation of the Patterson function, information such as known interatomic distances and the closest approach between atoms of neighbouring molecules, the so-called van der Waals distances, could be used. A trial structure could be derived in such a way and this structure may be used for calculation of the phases for the Fourier synthesis or refinement of the trial structure with aid of a computer program (see appendix C).

II. 7. THE HEAVY ATOM METHOD

The presence of a heavy atom in a crystal facilitates the structure determination considerably. The general effect of an atom of high scattering power on the X-ray structural problem is to convert the unknown and unmeasurable phase relationship

into certain intensity relationships which are susceptible to direct measurement.

There are at least two methods to locate the position of the heavy atom in the unit cell without any previous knowledge about the crystal structure. The first is based on symmetry relationships and is applicable when the number of heavy atoms in the unit cell is small and when they can only occur in one or more sets of equivalent positions in the unit cell. The second method for localising the heavy atom is by aid of the Patterson synthesis.

The phase angles or signs caused by the heavy atom only, can be determined. It is accepted that the heavy atom with its dominating scattering power dominates the phases of some or all of the intensities. When an electron density map then is obtained, the most prominent peaks on it will be those of the heavy atom, but other atomic positions will also appear as a result of the dominating effect. Additional atomic positions may be found in this way and by repetition more and more reflections with correct phases can be included, until the correct structure is obtained.

For the successful use of this method the square of the sum of the atomic numbers of the light atoms must be equal or nearly equal to that of the heavy atoms. If the scattering power of the heavy atom is much more than the sum of the scattering powers of the lighter atoms only, the position of the heavy atom will be sharply defined in the Fourier synthesis.

II. 8. REFINEMENT AND MOLECULAR PARAMETERS

The standard theory of least squares, the method which was used in this work, is well known and is described in various texts [34, 27]. Basically the idea is to change the atomic

coordinates of the trial structure in such a way as to improve the agreement between the observed structure factors ($F_{obs.}$) and the calculated structure factors ($F_{calc.}$).

If the error of the visually measured $F_{obs.}$ quantities followed a normal Gaussian distribution law, the "best" atomic parameters would then be obtained by minimization of

$$R=\sum_{\omega}\omega(hk\ell)(|F_{obs.}(hk\ell)|-k|F_{calc.}(hk\ell)|)^2 \qquad (2.17)$$

where ω is the weight of a particular term and is inversely proportional to the square of the standard error in $F_{obs.}$ The quantity R, which is called the residual or reliability factor, is usually expressed as a percentage and depends not only upon the positional atomic parameters but also upon the scale factors, overall temperature factor and anisotropic or individual isotropic temperature factors, as required.

The overall agreement between the observed and calculated structure factors is expressed in terms of the mean discrepancy.

$$R=\frac{\Sigma(|F_{obs.}|-|F_{calc.}|)}{\Sigma|F_{obs.}|} \qquad (2.18)$$

Refinement of the structures of the $TR_2PO_4\cdot 4TU$ and $TR(C_6H_5COO)\cdot 4TU$ complexes was done on atomic coordinates, temperature factors and scale factors without differential weighting.

Refinement of the trial structures as well as the determination of the interatomic distances and angles between atoms were carried out with a computer program described in appendix D.

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CHAPTER III

STRUCTURE OF THE THALLOUS DIHYDROGEN PHOSPHATE THIOUREA COMPLEX

III. 1. CELL DIMENSIONS AND DENSITY

The cell constants of the $Tl H_2PO_4 .4TU$ complex were measured from an {001} oscillation photograph and (hk0) and (hkl) equi-inclination Weissenberg photographs with Cukα radiation as described in paragraph II.2. The cell dimensions are

$$a = 15.40 \pm 0.05 \text{ Å}$$

$$b = 14.64 \pm 0.05 \text{ Å}$$

$$c = 8.27 \pm 0.05 \text{ Å}$$

with the volume of the unit cell

$$V = 1864.169 \text{ Å}^3$$

The density of 2.153g. $cm.^{-3}$ calculated for four formula units per unit cell compares well with the density of 2.151 g. $cm.^{-3}$ as measured by flotation.

III. 2. SPACE GROUP AND SYMMETRY OPERATORS

Conditions for possible reflections from (hk0) and (hkl) equi-inclination Weissenberg photographs were

hkℓ for h+k=2n

hko for h+k=2n

okℓ for k=2n and ℓ=2n

hoℓ for h=2n and ℓ=2n

which define the space group Cccm (No 66 in the International Tables 1952) [42] or its non-centrosymmetric counterpart which was ruled out by the successful structure analysis using Cccm.

The conditions h+k=2n for all hkℓ reflections indicates a C-centered Bravais lattice.The conditions for hko, okℓ and hoℓ reflections originate from $\frac{a+b}{2}$, $\frac{b}{2}$ and $\frac{c}{2}$ glide planes with glide components of respectively and include an $\frac{a}{2}$ component.

The combination of all these symmetry elements give rise to further symmetry elements to define the space group Cccm. The space group symbol specifies only the major symmetry elements viz. a c-glide plane perpendicular to the a axis or parallel to the (100) plane, a c-glide plane perpendicular to the b axis or parallel to the (010) plane and a mirror plane in the a,b plane perpendicular to the c axis.

Symmetry related positions occur at

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})+$$

$$x,y,z;\ \bar{x},\bar{y},z;\ \bar{x},y,\tfrac{1}{2}-z;\ x,\bar{y},\tfrac{1}{2}-z$$

$$\bar{x},\bar{y},\bar{z};\ x,y,\bar{z};\ x,\bar{y},\tfrac{1}{2}+z;\ \bar{x},y,\tfrac{1}{2}+z$$

III. 3. PATTERSON SYNTHESIS

For the space group Cccm

$$F(hk\ell) = A$$

$$= 16\cos^2 2\pi\frac{h+k}{4}\cos 2\pi(hx-\frac{\ell}{4})\cos 2\pi(ky+\frac{\ell}{4})\cos 2\pi\ell z \quad (3.1)$$

If $h+k=2n$ and $\ell=2n$ the equation reduces to;

$$F(hk\ell)_A = 16\cos 2\pi hx\cos 2\pi ky\cos 2\pi\ell z \quad (3.2)$$

where

$$F(hk\ell) = F(\bar{h}\bar{k}\ell) = F(\bar{h}k\ell) = F(h\bar{k}\ell) = F(hk\bar{\ell})$$

When $h+k=2n$ and $\ell=2n+1$ equation 3.1 reduces to;

$$F(hk\ell)_A = -16\sin 2\pi hx\sin 2\pi ky\cos 2\pi\ell z \quad (3.3)$$

When $h=o$ or $k=o$, $A=B=o$ and

$$F(hk\ell)=F(\bar{h}\bar{k}\ell)=-F(\bar{h}k\ell)=-F(h\bar{k}\ell)=F(hk\bar{\ell})$$

If $h+k=2n+1$, $A=B=0$

The squares of the structure factors given by equation 3.1 were used as coefficients in the Patterson synthesis, using the computer program described in appendix C.

A three dimensional Patterson synthesis was obtained from the 661 hkℓ data (including 54 unobserved). Eleven equally spaced sections along z, each consisting of a grid of 50x50 points, between z=o and z=½ were obtained. The following peaks were located in this three dimensional map with the peak maxima in pa-

renthesis (see fig. 3.1, and 3.2)

Table 3.1

z	x	y	z	x	y	z	x	y
0	0	0(2724)	25	11	14(316)	½	0	0(2230)
	½	½(2724)		15	11(364)		½	½(2230)
	0	½(749)		35	39(364)		½	0(851)
	½	0(749)		39	36(316)		0	½(851)

Comparison with similar structures determined before [17,18,19,20,21,22] indicated that all the peaks with relatvie heights of more than 2000 were caused by the Tℓ-Tℓ vectors, the peaks of about 750 by Tℓ-P and the peaks of about 350 by the Tℓ-S vectors.

The relatively weak intensities of the uneven layer lines (special conditions limiting possible reflections for hkℓ is ℓ=2n) compared with the even layer lines further indicated that the heavy atoms (Tℓ) could only occupy one of the following sets of special positions,

		(0,0,0; ½,½,0)+
d	2/m	0,½,0; 0,½,½
c	2/m	0,0,0; 0,0,½
b	222	0,½,¼; 0,½,¾
a	222	0,0,¼; 0,0,¾

since there are only four molecules per unit cell. The thallium atoms may occupy any position with Wyckoff notation a,b,c or d; the correct set was however derived from the Tℓ-S peaks on the Patterson map. But to show how the correct interpetation of the Patterson map was obtained it is necassary to described the procedure in full.

The peak maxima found on the Patterson map (Table 3.1 and fig 3.1) are in agreement with the Harker section, viz.

0,0,0; 0,0,½

½,½,0; ½,½,½

FIGURE 3.1

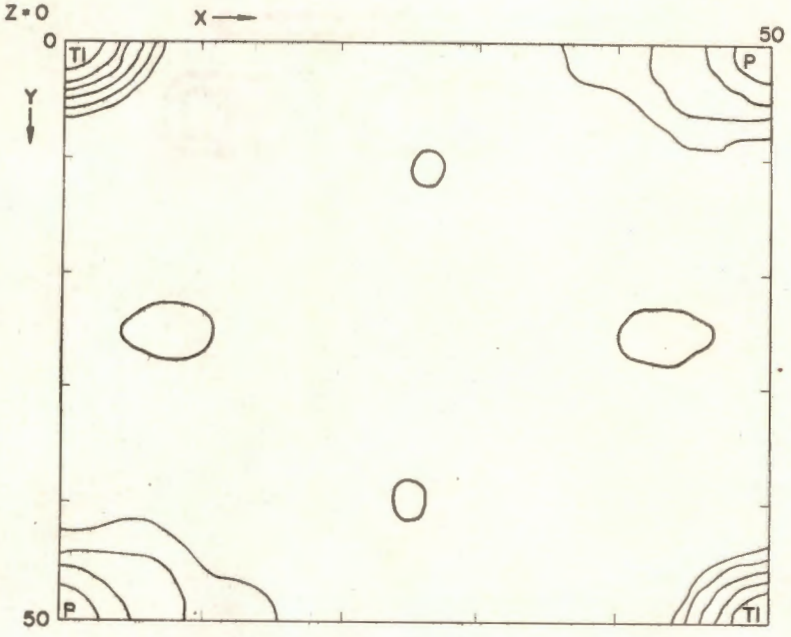
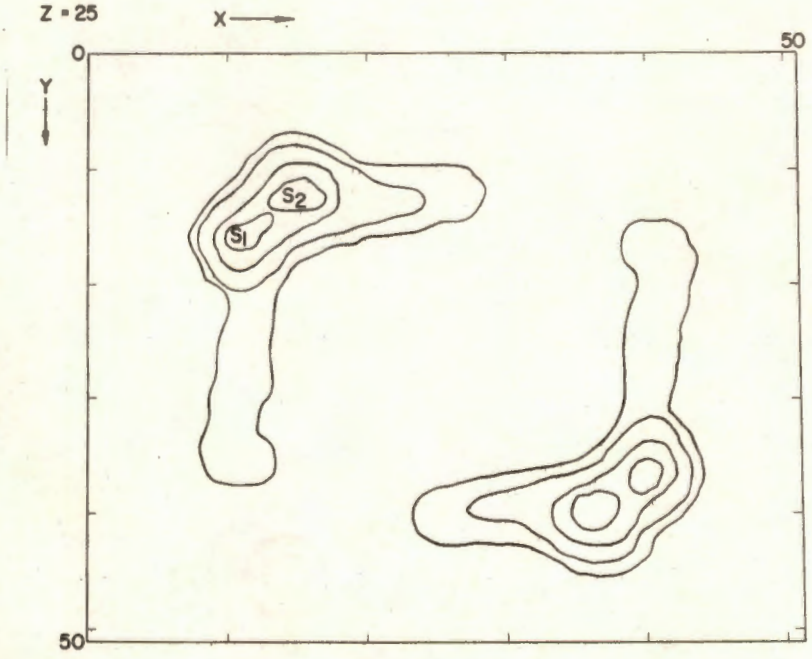


FIGURE 3.2



for the Tℓ....Tℓ vectors of the space group Cccm and symmetry 2/m (notation c).

Further examination of the Patterson map, however, indicated that two unrelated thiourea molecules exist (see fig. 3.2) in the unit cell. The peaks of the sulphur and the expected carbon atoms of both molecules indicated that both sulphur and the carbon atoms must occupy the special positions x,y,z with $z=\frac{1}{4},\frac{3}{4}$ and with eight atoms per unit cell. Inspection of the co-ordinates of equivalent positions of the space group gives only one set of positions for the sulphur atoms in the x,y plane, viz.

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)+$$

8 ℓ m x,y,o; $\bar{x},\bar{y},o$; $\bar{x},y,\frac{1}{2}$; $x,\bar{y},\frac{1}{2}$

with symmetry m, which agrees with previous investigations.

The Tℓ....S vectors derived from the co-ordinates of equivalent positions with Wyckoff notations c and ℓ indicated that both the Tℓ....Tℓ and Tℓ....S vectors must appear on the same section that is on $z=o,\frac{1}{2}$ of the Patterson map. This result is, however, in contradiction with peak maxima that were found on the Patterson map.

This problem could be solved by transferring the origin of the axis of the unit cell through a quarter of the unit cell in the z-direction. The Tℓ....Tℓ vectors then appear on $z=\frac{1}{4},\frac{3}{4}$ and the Tℓ....S vectors on the $z=o,\frac{1}{2}$ sections. Co-ordinates of equivalent positions of the Tℓ atoms then must be.

4 a 222 $0,0,\frac{1}{4}$; $0,0,\frac{3}{4}$; $\frac{1}{2},\frac{1}{2},\frac{1}{4}$; $\frac{1}{2},\frac{1}{2},\frac{3}{4}$

and with Harker section the same as before namely

$$0,0,0;\ 0,0,\tfrac{1}{2}$$

$$\tfrac{1}{2},\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$$

As mentioned before the sulphur atoms must occupy the positions given by Wyckoff notation ℓ. The Tℓ....S vectors obtained from the difference between co-ordinates of equivalent

positions with notation a and ℓ now give the Harker section which indicates that the Tℓ....S peaks must appear on the $z=\frac{1}{4}$ and $\frac{3}{4}$ sections with x and y to be determined. This result is in agreement with that found on the Patterson map.

On the Patterson map (see fig. 3.2 and also table 3.1) four Tℓ....S peaks appear; two of them with peaks 364 are symmetry related and so are the other two with maxima 316. The maximum 316 with co-ordination 11,14,0 (before translation the co-ordination was 11,14,25) was deduced to be S_1. With interatomic distances and the space group Cccm as criterion and the mmm symmetry of the Patterson map in mind, S_2 was located to be at 15,11,50 (before translation : 15,11,25).

With the positions of the thallous and the sulphur ions fixed the position of the phosphorous was also derived and established to be at the special positions.

4 b 222 $0,\frac{1}{2},\frac{1}{4}$; $0,\frac{1}{2},\frac{3}{4}$; $\frac{1}{2},0,\frac{1}{4}$; $\frac{1}{2},0,\frac{3}{4}$

The co-ordinates of these atoms in the asymmetric unit as found from the Patterson map are as follows.

Table 3.2

Atom	x	y	z
Tℓ	0	0	0.25
S_1	0.11	0.145	0
S_2	0.145	0.11	0.50
P	0.50	0	0.25

III. 4. ELECTRON DENSITY PROJECTION

The atomic co-ordinates derived from the Patterson function were used to phase a three-dimensional Fourier synthesis.

The electron density function $\rho(x,y,z)$ for the space group Cccm is given by

$$\rho(xyz)=\frac{8}{v_c}\{\Sigma\sum_{0}^{\infty}\Sigma F(hk\ell)\cos 2\pi hx\cos 2\pi ky\cos 2\pi \ell z-\Sigma\sum_{0}^{\infty}\Sigma^{\ell=2n} F(hk\ell)\sin 2\pi hx\sin 2\pi ky\cos 2\pi \ell z\} \qquad (3.4)$$

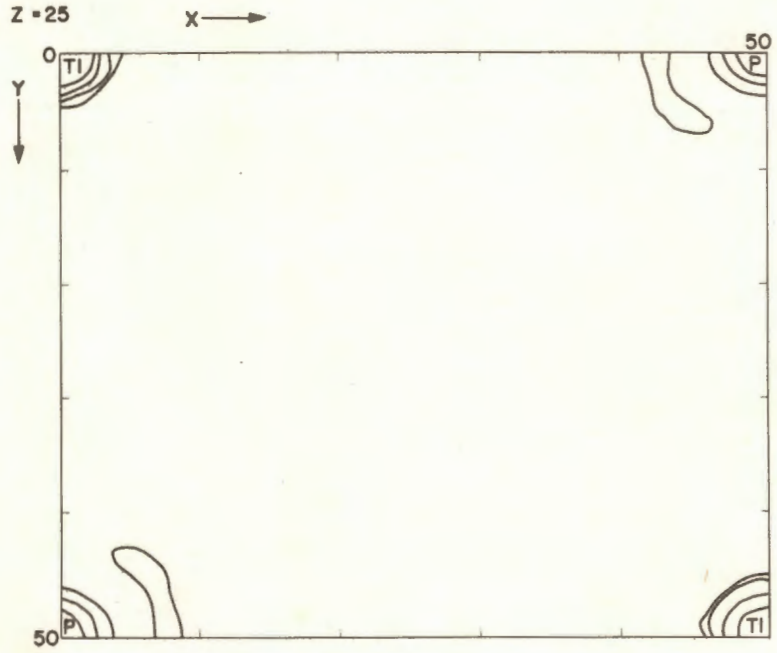
This function was evaluated by using the scattering factor tables [35,36] for thallium (+1), sulphur, and phosphorous and the co-ordinates of thallium, sulphur and phosphorous derived from the Patterson synthesis.

The first Fourier synthesis gave an R value of 24.9% and the positions of all the other atoms in the unit cell, were obtained, namely;

atom	x	y	z
N_1	0.25	0.11	0.15
N_2	0.10	0.26	0.35
C_1	0.22	0.12	0.0
C_2	0.11	0.22	0.50
O	0.44	0.06	0.20

All the electron density peaks were sharp and spherical except those associated with the oxygen atoms. These were more diffuse and considerably elongated, indicating disorder in the oxygen positions (see fig. 3.3).

Figure 3.3.



III. 5. LEAST SQUARE REFINEMENT, INTER ATOMIC DISTANCES AND ANGLE DETERMINATION.

A full-matrix least square refinement was carried out on the observed and calculated structure factors without any differential weighting factors. The parameters which were refined included preliminary co-ordinates (not special positions), an isotropic temperature factor equal to 3.0 for every atom and a scale factor for each layer line. The R-factor decreased as follows through the refinement

cycle	R
1	19.0%
2	10.5%
3	9.3%
4	9.3%

The parameter shifts in the last cycle were less than 0.1 of their estimated standard deviations.

The final atomic parameters and estimated standard deviations are reproduced in table 3.3, while the observed and calculated structure factors on absolute scale, F_{ooo}=1088 are compared in table 3.4

Table 3.3

Fractional co-ordinates and temperature factors of the atoms in the asymmetric unit, with estimated standard deviations (below each value).

Atom	x	y	z	B(A^2)
Tl	0	0	¼	3.85
				0.06
S_1	0.1039	0.1496	0	3.55
	0.0006	0.0006		0.21
S_2	0.1470	0.1075	½	3.14
	0.0006	0.0006		0.20
C_1	0.2115	0.1188	0	3.78
	0.0024	0.0025		0.75
C_2	0.1100	0.2215	½	3.40

	0.0022	0.0023		0.69
N_1	0.2541	0.1049	0.1353	5.09
	0.0016	0.0016	0.0035	0.53
N_2	0.0940	0.2608	0.3614	4.80
	0.0015	0.0016	0.0034	0.52
P	½	0	¼	2.85
				0.23
0	0.4395	0.0585	0.1518	9.63
	0.0018	0.0019	0.0042	0.82

Tabel 3.4

Observed and calculated structure factors on absolute scale.

H=0, L=0

K	Fo	Fc
2	314	324
4	159	157
6	143	131
8	332	313
10	207	159
12	143	125
14	76	78
16	57	51
18	52	63

H=1, L=0

K	Fo	Fc
1	264	271
3	97	81
5	182	169
7	282	268
9	189	188
11	99	107
13	66	79
15	47	48
17	24	26

H=2, L=0

K	Fo	Fc
0	306	332
2	287	319
4	418	445
6	279	284
8	174	160
10	115	96
12	170	139
14	114	118
16	57	65
18	26	38

H=3, L=0

K	Fo	Fc
1	78	79
3	312	298
5	292	281
7	182	153
9	95	97
11	99	102
13	95	89
15	53	66
17	28	33

H=4, L=0

K	Fo	Fc
0	178	166
2	367	427
4	248	266
6	219	231
8	144	152
10	192	191
12	123	110
14	92	80
16	73	78
18	20	39

H=5, L=0

K	Fo	Fc
1	193	190
3	272	277
5	202	170
7	130	92
9	153	144
11	99	102
13	44	45
15	45	47
17	52	53

H=6, L=0

K	Fo	Fc
0	96	97
2	310	318
4	200	224
6	208	226
8	150	159
10	191	191
12	93	92
14	63	59
16	52	64

H=7, L=0

K	Fo	Fc
1	264	264
3	180	169
5	129	103
7	114	89
9	135	135
11	91	89
13	37	46
15	19	25
17	37	38

H=8, L=0

K	Fo	Fc
0	304	294
2	188	185
4	136	138
6	158	172
8	172	187
10	145	136
12	98	92
14	60	64
16	25	37

H=9, L=0

K	Fo	Fc
1	187	187
3	111	106
5	150	140
7	130	128
9	51	52
11	52	39
13	78	73
15	48	45

H=10, L=0

K	Fo	Fc
0	198	181
2	105	96
4	213	207
6	205	193
8	147	128
10	38	36
12	93	88
14	76	89
16	20	37

H=11, L=0

K	Fo	Fc
1	123	112
3	97	104
5	122	116
7	112	101
9	22	32
11	42	40
13	56	57
15	37	39

H=12, L=0

K	Fo	Fc
0	177	161
2	140	130
4	142	126
6	114	98
8	132	105
10	83	80
12	63	68
14	31	40

H=13, L=0

K	Fo	Fc
1	89	90
3	96	92
5	44	48
7	54	58
9	83	70
11	63	58
13	14	13

H=14, L=0

K	Fo	Fc
0	93	92
2	154	129
4	120	88
6	68	64
8	81	76
10	81	88
12	28	39

H=15, L=0

K	Fo	Fc
1	53	56
3	87	74
5	42	44
7	28	32
9	61	57
11	42	40

H=16, L=0

K	Fo	Fc
0	62	51
2	108	88
4	86	82
6	56	65
8	38	40
10	39	50

H=17, L=0

K	Fo	Fc
1	27	26
3	54	48
5	68	64
7	30	30
9	15	17

H=18, L=0

K	Fo	Fc
0	56	56
2	40	47
4	46	55
6	51	59

H=19, L=0

K	Fo	Fc
1	45	45

H=1, L=1

K	Fo	Fc
3	105	-95
5	80	76
7	46	-41
9	24	-22
11	33	27
13	19	17

H=2, L=1

K	Fo	Fc
2	20	20
4	108	110
6	11	19
8	90	-94
10	16	12
12	61	58
14	19	-15
16	23	-26

H=3, L=1

K	Fo	Fc
1	82	89
3	42	-43
5	68	68
7	111	-118
9	25	-26
11	51	55
13	19	24
15	25	-27

H=4, L=1

K	Fo	Fc
2	50	-41
4	50	44
6	59	52
8	8	0
10	16	-10

H=5, L=0

K	Fo	Fc
1	92	-95
3	123	-142
5	7	-6
7	77	73
9	22	21
11	44	-45
13	11	-17
15	17	18

H=6, L=1

K	Fo	Fc
2	10	-6
4	16	-19
6	26	22
8	61	64
10	30	-26
12	48	-39
14	10	11
16	20	19

H=7, L=1

K	Fo	Fc
1	32	28
3	74	86
5	98	-97
7	15	3
9	29	17
11	11	-8

H=8, L=1

K	Fo	Fc
2	112	113
4	8	-4
6	74	-66
8	10	4
10	18	20

H=9, L=1

K	Fo	Fc
1	19	22
3	41	56
5	37	-40
7	10	-12
9	11	3
11	19	15

H=10, L=1

K	Fo	Fc
2	9	-7
4	9	-2
6	10	7
8	26	-20

H=11, L=1

K	Fo	Fc
1	32	-25
3	39	-35
5	60	50
7	11	10
9	19	-17

H=12, L=1

K	Fo	Fc
2	69	-74
4	10	-9
6	44	43
8	19	-6

H=13, L=1

K	Fo	Fc
1	26	-17
3	32	-33
5	46	36

H=14, L=1

K	Fo	Fc
2	11	3
4	11	11
6	10	-10
8	10	-9
10	9	1
12	11	13

H=15, L=1

K	Fo	Fc
1	26	21
3	32	27

H=16, L=1

K	Fo	Fc
2	30	26

H=17, L=1

K	Fo	Fc
1	9	8
3	9	9
5	25	-20

H=18, L=1

K	Fo	Fc
2	14	3

H=0, L=2

K	Fo	Fc
2	360	-365
4	443	-441
6	248	-223
8	145	-126
10	151	-148
12	141	-131
14	92	-90
16	71	-82
18	11	-32

H=1, L=2

K	Fo	Fc
3	103	-314
5	242	-227
7	134	-135
9	111	-111
11	117	-117
13	71	-61
15	57	-62
17	32	-40

H=2, L=2

K	Fo	Fc
0	353	-360
2	346	-334
4	275	-258
6	233	-202
8	220	-202
10	158	-170
12	118	-107
14	69	-72
16	67	-69
18	35	-48

H=3, L=2

K	Fo	Fc
1	313	-311
3	138	-115
5	129	-113
7	198	-172
9	170	-169
11	93	-93
13	47	-56
15	31	-34
17	39	-38

H=4, L=2

K	Fo	Fc
0	432	-447
2	263	-257
4	165	-162
6	246	-222
8	201	-213
10	150	-143
12	103	-109
14	79	-83
16	37	-39
18	28	-49

H=5, L=2

K	Fo	Fc
1	235	-236
3	126	-114
5	194	-184
7	169	-160
9	97	-92
11	68	-59
13	89	-95
15	35	-41
17	12	-18

H=6, L=2

K	Fo	Fc
0	242	-235
2	227	-203
4	234	-228
6	257	-252
8	142	-150
10	83	-83
12	120	-106
14	114	-104
16	35	-45

H=7, L=2

K	Fo	Fc
1	149	-146
3	173	-166
5	186	-173
7	126	-124
9	63	-61
11	61	-56
13	73	-71
15	56	-53
17	13	-23

H=8, L=2

K	Fo	Fc
0	147	-140
2	216	-208
4	221	-209
6	202	-162
8	131	-127
10	118	-116
12	84	-86
14	58	-61
16	48	-55

H=9, L=2

K	Fo	Fc
1	111	-120
3	176	-175
5	92	-92
7	70	-68
9	101	-92
11	83	-87
13	18	-23
15	27	-30

H=10, L=2

K	Fo	Fc
0	141	-145
2	193	-184
4	159	-151
6	96	-89
8	121	-119
10	139	-134
12	64	-67
14	14	-25

H=11, L=2

K	Fo	Fc
1	118	-119
3	121	-109
5	69	-58
7	61	-63
9	88	-90
11	71	-65

H=12, L=2

K	Fo	Fc
0	144	-141
2	125	-121
4	119	-117
6	109	-101
8	92	-95
10	77	-74
12	53	-54
14	30	-44

H=13, L=2

K	Fo	Fc
1	76	-69
3	60	-67
5	104	-96
7	67	-67
9	26	-30
11	27	-24
13	38	-47

H=14, L=2

K	Fo	Fc
0	109	-98
2	89	-78
4	103	-102
6	114	-109
8	60	-59
10	22	-27
12	39	-52

H=15, L=2

K	Fo	Fc
1	67	-64
3	27	-38
5	64	-60
7	60	-56
9	15	-26

H=16, L=2

K	Fo	Fc
0	113	-99
2	78	-73
4	39	-43
6	62	-60
8	58	-61
10	28	-44

H=17, L=2

K	Fo	Fc
1	56	-55
3	37	-33
5	14	-17
7	27	-34

H=18, L=2

K	Fo	Fc
0	34	-46
2	57	-59
4	43	46
6	22	34

H=19, L=2

K	Fo	Fc
1	9	16
3	34	42

H=1, L=3

K	Fo	Fc
1	17	11
3	107	98
5	29	34
7	51	-51
9	50	-50
11	50	49
13	10	18
15	9	-16
17	16	-15

H=2, L=3

K	Fo	Fc
2	22	-24
4	9	7
6	7	7
8	99	-102
10	38	35
12	41	43
14	10	0
16	27	-29

H=3, L=3

K	Fo	Fc
1	85	-66
3	40	42
5	53	57
7	22	16
9	45	-43
11	40	36

H=4, L=3

K	Fo	Fc
2	67	-73
4	42	-41
6	21	16
8	25	-23
10	16	13

H=5, L=3

K	Fo	Fc
1	10	-16
3	25	17
5	28	22
7	40	45
9	9	0
11	35	-28
13	17	-12

H=6, L=3

K	Fo	Fc
2	49	-46
4	53	-51
6	8	-6
8	65	62
10	24	-24
12	18	-27
14	9	8
16	11	20

H=7, L=3

K	Fo	Fc
1	49	47
3	7	-0
5	24	-24
7	9	14
9	34	38
11	40	-34

H=8, L=3

K	Fo	Fc
2	78	93
4	8	8
6	66	-76
8	24	12
10	18	7

H=9, L=3

K	Fo	Fc
1	72	73
3	50	42
5	22	-19
7	58	-54

H=10, L=3

K	Fo	Fc
2	9	-6
4	9	10
6	24	14

H=11, L=3

K	Fo	Fc
1	50	-49
3	51	-59
5	34	31
7	18	24
9	17	-12

H=12, L=3

K	Fo	Fc
2	50	-47
4	10	5
6	44	45

H=13, L=3

K	Fo	Fc
1	25	-27
3	10	-4
5	10	8
7	10	0
9	9	-14
13	13	13

H=16, L=3

K	Fo	Fc
2	26	27
4	8	1
6	19	-20

H=17, L=3

K	Fo	Fc
1	23	16
3	13	10
5	16	-14

H=0, L=4

K	Fo	Fc
2	212	-217
4	114	102
6	261	243
8	201	189
10	139	129
12	69	82
14	63	79
16	31	36

H=1, L=4

K	Fo	Fc
1	292	272
3	106	93
5	133	120
7	118	127
9	116	114
11	58	54
13	76	70
15	16	29
17	20	27

H=2, L=4

K	Fo	Fc
0	209	221
2	227	222
4	194	179
6	220	199
8	151	151
10	112	125
12	90	99
14	70	77
16	32	43

H=3, L=4

K	Fo	Fc
1	107	101
3	237	216
5	186	184
7	93	99
9	43	52
11	77	73
13	66	64
15	54	53

H=4, L=4

K	Fo	Fc
0	84	93
2	194	193
4	308	299
6	189	166
8	129	115
10	83	97
12	86	93
14	60	68
16	53	67

H=5, L=4

K	Fo	Fc
1	116	112
3	184	189
5	79	99
7	91	93
9	86	95
11	92	94
13	11	19
15	41	42

H=6, L=4

K	Fo	Fc
0	254	253
2	212	200
4	166	164
6	88	75
8	146	149
10	132	140
12	68	78
14	23	28
16	37	50

H=7, L=4

K	Fo	Fc
1	124	131
3	104	110
5	74	80
7	82	92
9	99	99
11	77	75
13	24	29
15	18	23

H=8, L=4

K	Fo	Fc
0	207	196
2	147	150
4	134	140
6	139	136
8	102	110
10	70	76
12	64	69
14	46	59

H=9, L=4

K	Fo	Fc
1	116	114
3	44	56
5	100	106
7	99	98
9	61	58
11	26	28
13	52	58
15	12	28

H=10, L=4

K	Fo	Fc
0	166	150
2	127	127
4	82	98
6	125	142
8	73	82
10	45	48
12	50	58
14	49	66

H=11, L=4

K	Fo	Fc
1	72	68
3	68	69
5	108	102
7	79	70
9	26	31
11	9	24
13	40	51

H=12, L=4

K	Fo	Fc
0	79	79
2	106	110
4	92	97
6	90	97
8	53	61
10	45	57
12	37	48

H=13, L=4

K	Fo	Fc
1	70	74
3	77	65
5	33	30
7	44	40
9	49	57
11	30	44

H=14, L=4

K	Fo	Fc
0	83	88
2	87	92
4	55	60
6	17	36
8	65	68
10	62	72

H=15, L=4

K	Fo	Fc
1	38	40
3	67	61
5	28	33
7	8	27
9	27	35

H=16, L=4

K	Fo	Fc
0	22	37
2	47	50
4	77	80
6	40	48
8	21	35

H=17, L=4

K	Fo	Fc
1	23	23
3	28	37
5	31	43

H=18, L=4

K	Fo	Fc
0	42	51
2	20	34

H=1, L=5

K	Fo	Fc
3	33	26
5	27	23
7	40	-37
9	31	-29
11	33	33

H=2, L=5

K	Fo	Fc
4	28	34
6	7	10
8	62	-67
10	23	18
12	33	33
14	8	-4
16	16	-21

H=3, L=5

K	Fo	Fc
1	28	-26
3	6	-4
5	32	30
7	20	-18
9	27	-25
11	33	31

H=4, L=5

K	Fo	Fc
2	32	-32
4	7	1
6	27	26

H=5, L=5

K	Fo	Fc
1	26	-26
3	24	-27
5	8	1
7	35	32
9	9	5
11	28	-22

H=6, L=5

K	Fo	Fc
2	21	-15
4	27	-22
6	8	6
8	47	45
10	17	-18
12	26	-24

H=7, L=5

K	Fo	Fc
1	31	26
3	14	12
5	34	-35
7	9	8
9	17	23
11	16	-19

H=8, L=5

K	Fo	Fc
2	62	68
4	9	4
6	49	-50

H=9, L=5

K	Fo	Fc
1	44	41
3	36	35
5	9	-17
7	29	-30
9	9	5
11	14	12

H=11, L=5

K	Fo	Fc
1	33	-29
3	33	-35
5	33	29

H=12, L=5

K	Fo	Fc
2	37	-41
4	9	-0
6	27	31

H=16, L=5

K	Fo	Fc
2	16	20

All unobserved reflections have $F_o \leq 27$ in table 3.4

Interatomic distances up to 4.0A and the angles between the various atoms in the unit cell were calculated with the "ORFFE" programme described in appendix D. These data are given in table 3.5 together with experimental errors.

Table 3.5

Interatomic distances (in Angstrom)

Tℓ-S_1*	3.4098	±	0.0083
Tℓ-S_2*	3.4463	±	0.0082
S_1-S_2*	3.8222	±	0.0138
S_1-S_2*	3.9133	±	0.0142
S_1-C_1	1.7184	±	0.0375
S_1-N_1	2.6522	±	0.0270
C_1-N_1	1.3125	±	0.0314
S_2-C_2	1.7640	±	0.0345
S_2-N_2	2.6493	±	0.0255
C_2-N_2	1.3057	±	0.0297
P-O	1.5033	±	0.0304
N_1-H...O	2.9387	±	0.0375
N_2-H---O	3.2045	±	0.0397

Bond angles (in degrees)

S_1-$\hat{S}_2$-S_1*	89.0423	±	0.2715
S_2-$\hat{S}_1$-S_2*	90.9577	±	0.2706
S_1-$\hat{C}_1$-N_1	121.5301	±	1.8127
N_1-$\hat{C}_1$-N_1	94.1039	±	1.9570
O-$\hat{P}$-O**	114.6072	±	2.5057
O-$\hat{P}$-O**	103.4126	±	2.2551

*See fig. 3.4

** PO_4^{3-} is not a symmetrical tetrahedron

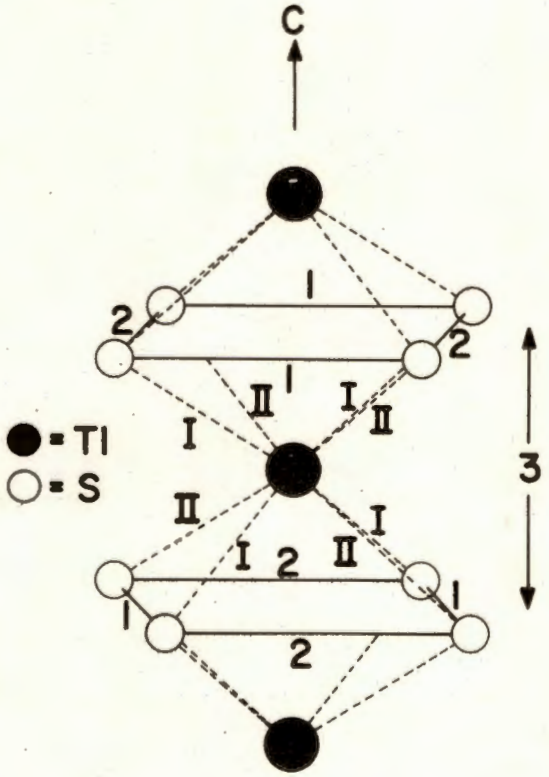
Figure 3.4

Schematic representation of the arrangement of sulphur atoms arround a chain of thallous ions. The interatomic distances are:

1=3.913±0.014Å, 2=3.822±0.014Å

1=3.446±0.008Å, II=3.410±0.008Å

3=4.233±0.014Å. *The bond angles are top left front = top right back=below left back=below right front*=89.0±0.3° *with the remaining four angles*=91.0±0.3°



III. 6. DESCRIPTION OF THE STRUCTURE

The X-ray investigation on the $Tl H_2PO_4.4TU$ complex shows the existance of co-ordination columns containing linear arrangements of cations and anions.

The eight thiourea groups in the unit cell were found to occupy positions at the corners of a square- antiprism, distorted towards a cube [37] (see fig. 3.4 and 3.5) and centered on the thallium atoms, 4.13Å apart in the columns. Each of the eight ligands is considered as a donor of unpaired electrons to the metal ions to bring about an ionic bridge bonding between two thallium ions. Although the cationic columns only have symmetry 2 they are remarkably similar to the tetragonal $(Tl^{+}S_4)_n$ columns

found in the complexes of $TlClO_4$ and $TlNO_3$[18]. The important dimensions and composition of the co-ordination polyhedron are shown in fig. 3.4. The angle of distortion of the antiprism is 26°.

Further details of the packing are illustrated in fig. 3.5 which shows the (001) projection of the structure. Although

Figure 3.5.

Projection of the stracture along {001}. *Shaded circles represent atoms lying at* $C = \frac{1}{2}$. *Open and full circles refer to atoms lying above and below this plane respectively. All the symmetry axes parallel to the paper are at* $c = \frac{1}{4}$. *Hydrogen bondings between amino groups and oxygen are represented by dottet lines.*

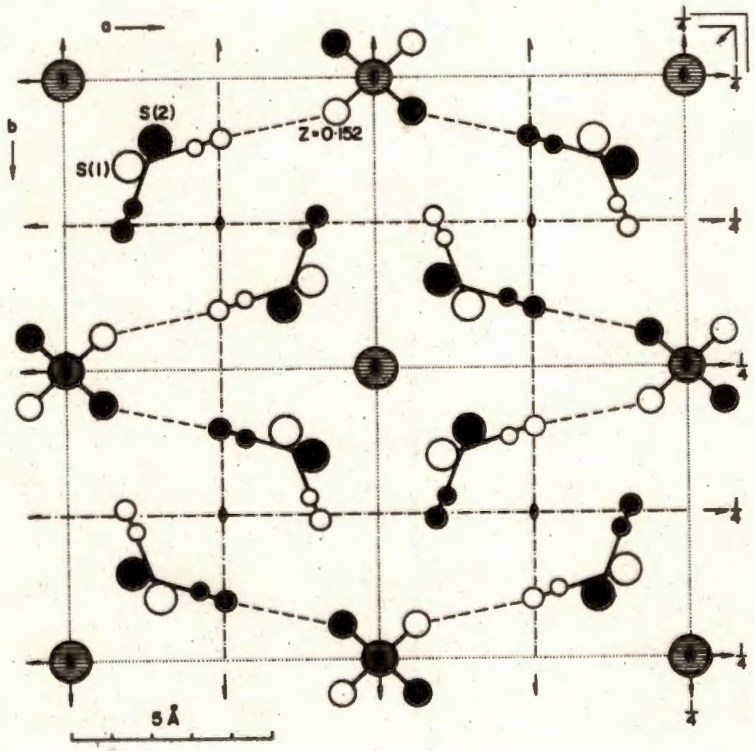
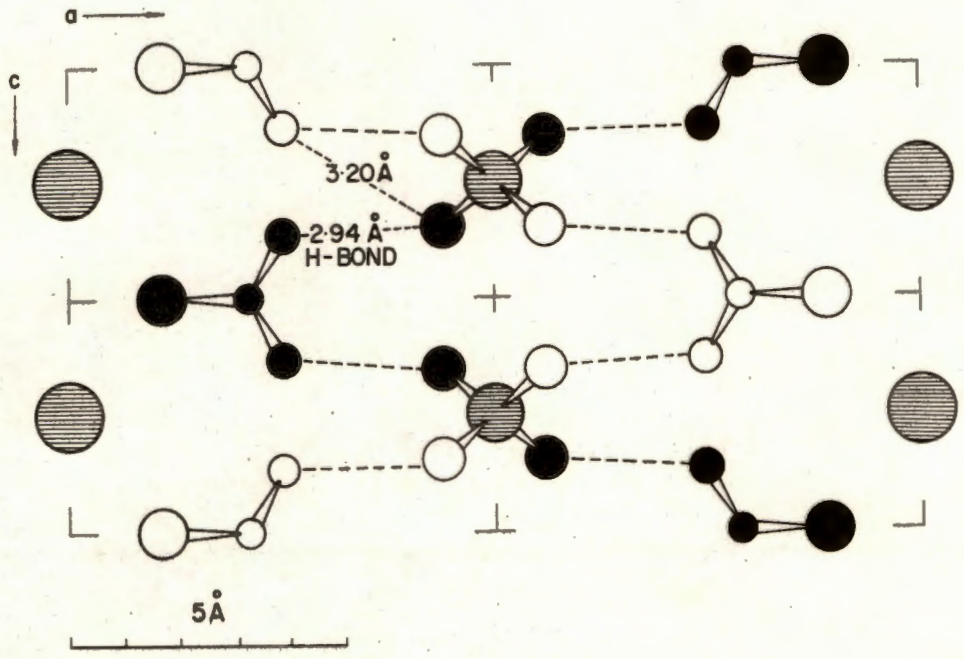


Figure 3.6

(010) *projection of the surroundings of the phosphate ion. Only molecules in non-overlap positions are shown to illustrate the system of hydrogen bonds.*



the thiourea molecules appear to be slightly distorted, they possess mm symmetry to within the limits of the experimental error. The molecular dimensions of the thiourea molecule do not differ significantly from the dimensions of free thiourea,[38] but are nevertheless reproduced in table 3.5.

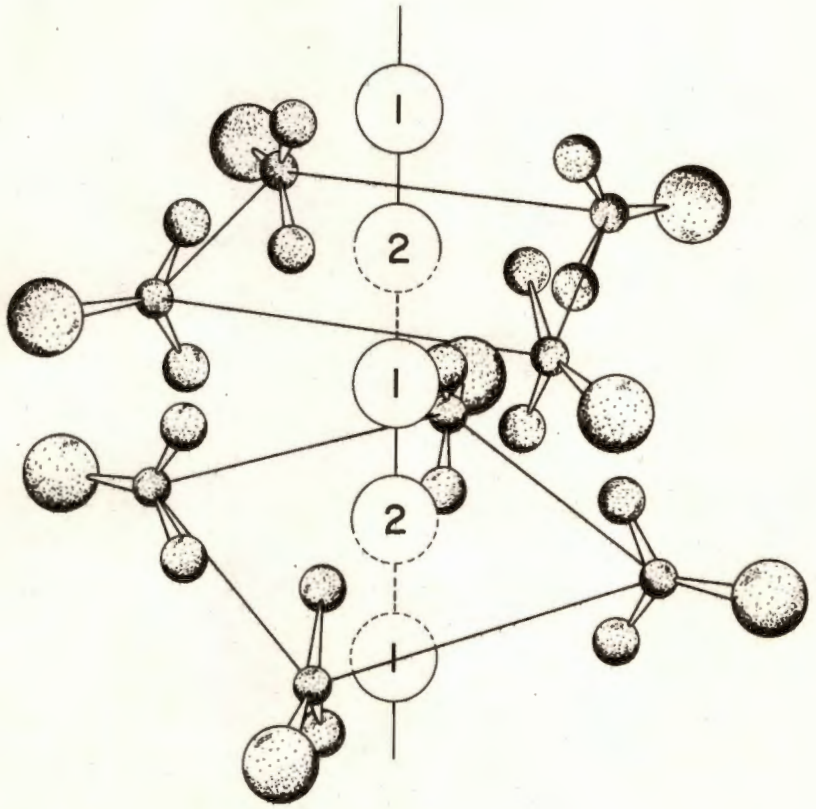
The positive end of the polarized thiourea molecule viz. the amino groups, forms another column with the anions. The unsymmetrical anions ($H_2PO_4^-$) occupy positions of symmetry 222 with the phosphorous atoms at $z=\frac{1}{4},\frac{3}{4}$. Fig. 3.6, the (010) projection shows in more detail the environment of the phosphate ion. The oxygen and hydroxyl groups of the ($H_2PO_4^-$) anions are statistically superimposed to mimic a tetrahedral arrangement. The P-O bond length is 1.5 ± 0.03Å and the two O-P-O angles are $103^{o}\pm2^{o}$ and $114^{o}\pm2^{o}$. There is thus considerable disorder which is also reflected in the high Debye-Waller factor observed for oxygen. The closest approach between the average position of such a disordered oxygen atom and a nitrogen atom associated with a thiourea molecule is 2.94 ± 0.04Å. This is well within the range of N-H....O hydrogen bonds given by Pimentel and McClellan [39].

III. 7. DISCUSSION OF THE STRUCTURE.

The most significant feature of this structure is the position occupied by the anion. In contradistinction to anions such as perchlorate, nitrate, bromide, iodide, sulphate [18] hydrated fluoride [19], and chloride [20], which all lie in the same mirror planes as the thiourea molecules when their salts form this type of complex, the phosphate occupies a position halfway between these mirror planes, as shown schematically in fig. 3.7. For the position (1) the conditions for hydrogen bonding with the amino groups is much more favourable than for the in plane type of position (2). Since the complexes of thallous dihydrogen phosphate, carbonate and nitrite constitute

an isomorphous series [18] it is fairly certain that hydrogen bonds play a similar rôle in all these complexes.

Figure 3.7



The dihydrogen phosphate, carbonate and the nitrite anions differ from those mentioned above in that they all derive from relatively weak acids. There would thus seem to be an inverse parallel between pK_α values of acids and the tendency of their anions to form hydrogen bonds. Although this tendency does not seem to have been described before, the direct corellation between pk_α values and hydrogen bonding of carboxylic acids has been described in detail in the literature [40]. It is suggested that these two phenomena are different aspects of the same effect. Highly ionizable hydrogens (in strong acids) have a higher tendency than weaker acids to form hydrogen bonds, whereas the anions of the weak acids are more dirmly attached to

their hydrogens in the acid, so that after ionization they should have a higher affinity for hydrogens and hydrogen bonding than the anions of the strong acids. It was considered of interest to see in how far these ideas would be substantiated by the structures of the thiourea complexes of thallous formate and oxalate.

III. 8. THE THALLOUS OXALATE AND FORMATE THIOUREA COMPLEXES.

The complexes of $T\ell HCOO.4TU$ and $T\ell_2(COO)_2.8TU$ were prepared by dissolving the constituents in 1:4 and 1:8 ratio respectively in boiling water. In both cases needles crystallized on cooling. The crystals of the formate complex were however too small for single crystal investigations. Single crystals of the oxalate complex were obtained and compared with the phosphate complex. The structure of the oxalate is not isomorphous but could be related to the Cccm group.

The cell constants for the oxalate complex are

$a = 15.91 \text{ Å}$ $\quad \rho_{calc.} = 2.078 \text{ g.cm}^{-3}$

$b = 13.24 \text{ Å}$ $\quad \rho_{obs.} = 2.21 \text{ g.cm}^{-3}$

$c = 8.39 \text{ Å}$ $\quad Z = 2$

Space group : Pnnm

These results suggest that a structural method could be developed which would allow differentiation between strong and weak hydrogen bonding anions.

III. 9. THE THALLOUS ORTOPHOSPHATE THIOUREA COMPLEX.

As discussed in chapter I the complex formulated as $T\ell_3PO_4.6TU$ by Pfrepper [10] was examined crystallographically, to establish whether the complex is a single phase and to analyse the structure.

Attempts to repeat the preparation described by Pfrepper to obtain suitable crystals of the complex were unsuccesful,

even with variation in conditions. From the powder pattern, however, we infer that it is a single phase and is in many respects similar to the present series of complexes. As shown in table 3.6,

Table 3.6

d(A)*	Intensity	$Sin^2\theta$(obs)	$Sin^2\theta$(calc.)	Index
11.472	10	0.0045	0.0045	110
9.883	38	0.0061	0.0061	200
7.4806	41	0.0106	0.0106	210
6.1712	2	0.0156	0.0156	201
5.7339	100	0.0181	0.0182	220
4.9511	11	0.0242	0.0242	400
4.5207	13	0.0291	0.0288	320
3.9551	1	0.0379	0.0379	500
3.8209	3	0.0406	0.0409	330
3.7261	6	0.0427	0.0424	420
3.6715	6	0.0440	0.0441	202
3.5643	22	0.0467	0.0470	510
3.2063	10	0.0577	0.0577	312
3.1530	26	0.0596	0.0591	520
3.0193	6	0.0651	0.0651	610
2.9134	7	0.0699	0.0698	412
2.8642	21	0.0723	0.0727	440
2.7944	7	0.0760	0.0759	502
2.7509	26	0.0784	0.0788	620

*Powder diffractometer pattern of Tl_3PO_4.6TU, indexed for a hexagonal unit cell. The intensities are non-integrated and estimated from peak heights. The d-values were obtained from NBS tables [41].

the powder pattern of the complex can be indexed in terms of a hexagonal unit cell with a=22.88Å, c=7.91Å. For Z=4 the density was calculated to be 2.16 g. cm^{-3}. No attempt was made to determine the density of the powder experimentally, but compared to the 2.15g. $cm.^{-3}$ for $T\ell H_2PO_4.4TU$ it appears to be of the correct magnitude.

III. 10. CONCLUSION

It has been shown that in the $T\ell H_2PO_4.4TU$ complex, the arrangement of the thallous ion corresponds to that found previously for $T\ell C\ell O_4$ and $T\ell NO_3$ complexes with thiourea, but that the $H_2PO_4^-$ occupies a position structurally different from that occupied by $C\ell O_4^-$ and NO_3^-. This difference is ascribed to different hydrogen bonding characteristics.

—oOo—

CHAPTER IV

STRUCTURE OF THE THALLOUS BENZOATE THIOUREA COMPLEX

IV. 1. CELL CONSTANTS.

By mechanically splitting a bunch of needle-shaped, hard, white crystals a single crystal was obtained.

Cell dimensions of the thallous benzoate thiourea crystal were determined by (001) oscillation, hko and hkl Weissenberg photographs;

$a = 15.64 \pm 0.05 \text{Å}$

$b = 17.09 \pm 0.05 \text{Å}$

$c = 8.15 \pm 0.05 \text{Å}$

and

$V = 2180.23 \text{Å}^3$

A density of 1.95gm.cm^{-3} was measured and the density calculated for four formula units per unit cell is 1.92g.cm^{-3}.

IV. 2. SPACE GROUP AND SYMMETRY OPERATORS.

From equi-inclination Weissenberg photographs the conditions for possible reflections were derived as:

hkl for h+k=2n	hko for h+k=2n
okl for k=2n	hol for l=2n, k=2n

These are consistent with the space groups $Cmc2_1$ was ruled out by the successful structure analysis using Cmcm (No 63 in the International tables).

Also, in this case, the condition h+k=2n for all hkl reflections gives rise to a C-centred Bravais lattice, and the conditions hko for h+k=2n, okl for k=2n, hol for l=2n and h=2n for possible reflections originate from glide planes with components $\frac{a+b}{2}$, $\frac{b}{2}$, $\frac{c}{2}$ and $\frac{a}{2}$ respectively.

The fundamental symmetry elements which define the space group Cmcm are a mirror plane perpendicular to the a and the c axis and a c-glide plane perpendicular to the b axis. These symmetry operations give rise to the following co-ordinations of general equivalent positions;

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)+$$

$x,y,z;$	$x,\bar{y},\bar{z};$	$x,y,\tfrac{1}{2}-z;$	$x,\bar{y},\tfrac{1}{2}+z$
$\bar{x},\bar{y},\bar{z};$	$\bar{x},y,z;$	$\bar{x},\bar{y},\tfrac{1}{2}+z;$	$\bar{x},y,\tfrac{1}{2}-z$

IV. 3. PATTERSON SYNTHESIS

For a centrosymmetric structure with space group Cmcm the structure factor equation 2.4 reduces to

$$F(hk\ell)^2_A = A = 16\cos^2 2\pi \frac{h+k}{4} \cos 2\pi hx \cos 2\pi\left(ky+\frac{\ell}{4}\right)\cos 2\pi\left(\ell z-\frac{\ell}{4}\right) \qquad (4.1)$$

with B=0. If h+k=2n and ℓ=2n for possible hkℓ reflections the equation 4.1 reduces to

$$A = 16\cos 2\pi hx \cos 2\pi ky \cos 2\pi \ell z \qquad (4.2)$$

with

$$F(hk\ell)=F(\bar{h}\bar{k}\bar{\ell})=F(\bar{h}k\ell)=F(h\bar{k}\ell)=F(hk\bar{\ell}).$$

Squares of the structure factors from equation 4.1 were used as coefficients in the Patterson synthesis which was calculated with a computer programme described in appendix C.

A three-dimensional Patterson synthesis based on 980 hkℓ data and with eleven equally spaced sections along z, each consisting of a grid of 50x50 points, between z=o and z=½ were obtained. From this three-dimensional map the following peaks were located with the peak maxima in parenthesis. (See also figures 4.1, 4.2 and 4.3).

z	x	y	z	x	y	z	x	y
0	0	0(2897)Tℓ	25	14	10(347)S_2	40	26	9(123)N_1
	½	½(2897)Tℓ		11	12(380)S_1		24	41(123)N_1
				39	38(380)S_1		11	23(109)N_2
10	26	10(115)N_1		36	40(347)S_2		39	27(109)N_2
	24	40(115)N_1		22	10(82)C_1			
	11	23(110)N_2		12	20(67)C_2	50	0	0(2414)Tℓ
	39	27(110)N_2		28	40(82)C_1		50	50(2414)Tℓ
				38	30(67)C_2			
				7	39(152)			
				43	11(152)			
				0	32(47)			
				50	18(47)			
				0	50(138)			
				50	50(138)			

In comparison with similar structures determined before [17,18,19,20,21,22] and from the relative peak heights it is clear that the Tℓ-Tℓ vectors appear at positions 0,0,0; 0,50,50; 50,0,0; and 50,50,50 on the Patterson. Similarly the peaks with maxima of 347 and 380 were in consequence of the Tℓ-S vectors. Maxima from 109 to 123 and 67 to 82 occurred as a result of the Tℓ-N and Tℓ-C vectors. From the Patterson it was further obvious that the anion must occupy positions at z=¼,¾ in the unit cell but the whole molecule was not resolved for reasons to be discussed later (see fig. 4.3) However, from the Patterson synthesis it was possible to find the positions of thallium atoms and thiourea molecules in the structure.

The relatively weak intensities of the uneven layer lines in comparison with the even layer lines indicated that the thallium atoms could only occupy one of the following sets of special positions

FIGURE 4.1

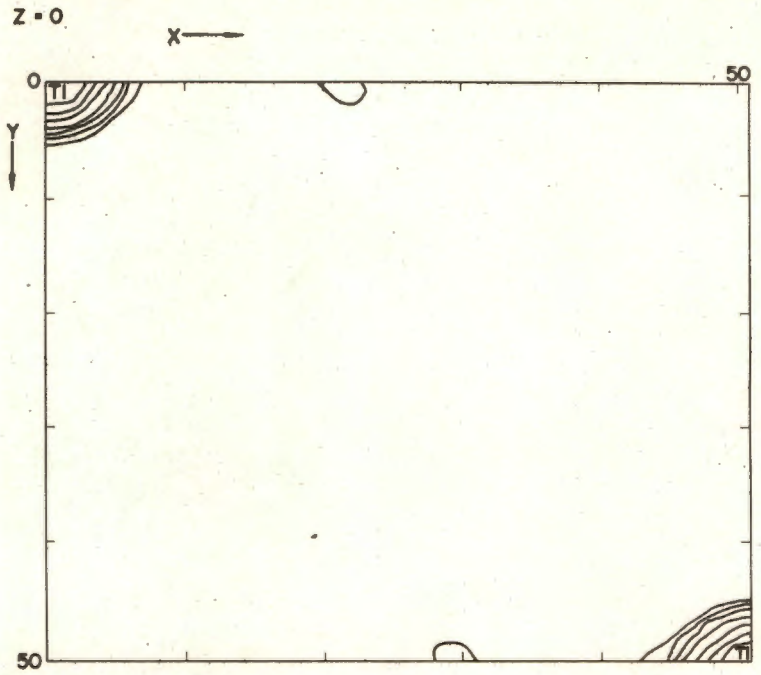
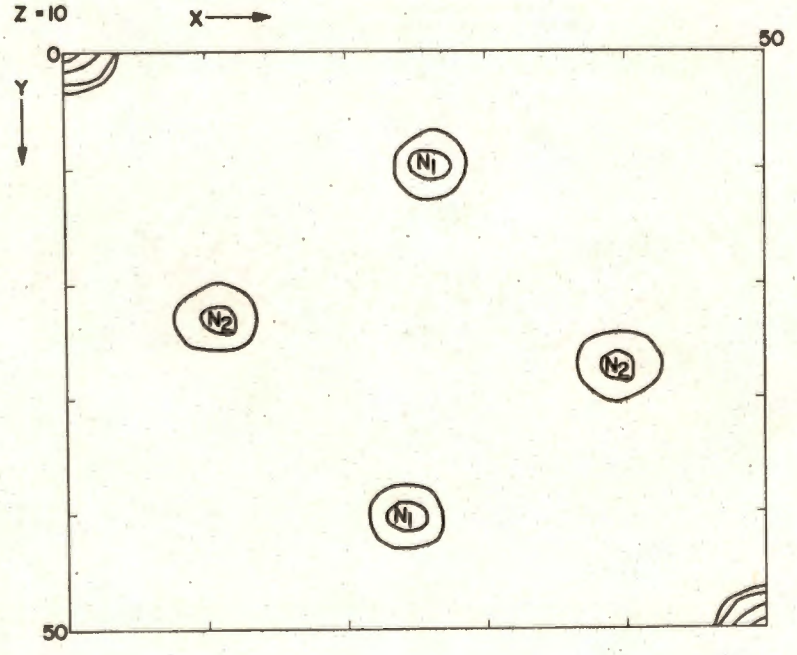


FIGURE 4.2



(0,0,0; ½,½,0)+

b $\frac{2}{m}$ 0,½,0; 0,½,½

a $\frac{2}{m}$ 0,0,0; 0,0,½

Peak maxima on the Patterson indicated that positions with Wyckoff notation a was correct.

With the positions of the thallium atoms determined it was further obvious, that peaks with maxima at x,y,z=¼, must be related to atoms occupying the following special positions;

(0,0,0; ½,½,0)+

8 g m x,y,¼; $\bar{x}$,y,¼; x,$\bar{y}$,¾; $\bar{x}$,$\bar{y}$,¾

As a result of the mmm symmetry of the Patterson map the sulphur and carbon atoms of both thiourea molecules appear on the z=¼ section. The fact that no symmetry relationship between these molecules exists in the space group Cmcm, maximum (380), labelled as sulphur one, was chosen to be at z=¼ and sulphur two (347) to be at z=¾.

The following atoms with co-ordinates

Tl;	0,0,0	S_2;	14,10,75
S_1;	11,12,25	C_2;	12,20,75
C_1;	22,10,25	N_2;	11,23,60
N_1;	26,10,10		

were used for the Fourier synthesis.

IV. 4. FOURIER SYNTHESIS

A three-dimensional Fourier synthesis was obtained from the atomic co-ordinates derived from the Patterson map.

The electron density function, equation 2.11, reduces to

$$\rho(xyz)=\frac{8}{V_c}\{\sum\sum\sum_{\substack{\ell=2n\\ \ell=2n}}^{\infty}(hk\ell)\cos 2\pi hx\cos 2\pi ky\cos 2\pi \ell z-\sum\sum\sum_{0}^{\infty}F(hk\ell)\cos 2\pi hx\sin 2\pi ky\sin 2\pi \ell z\} \qquad (4.3)$$

for the space group Cmcm. As for the Patterson the computer

programme described in appendix C was used for this synthesis. Scattering factor tables [35,36] for thallium (+1), sulphur, carbon and nitrogen were used.

With an R value of 21.3% the other atomic positions were obtained from the Fourier synthesis viz.;

Figure 4.3

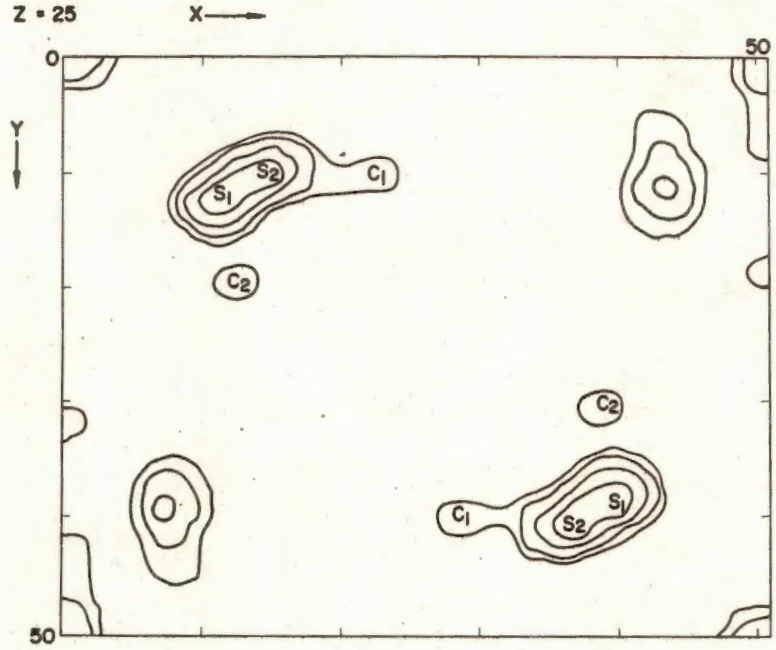
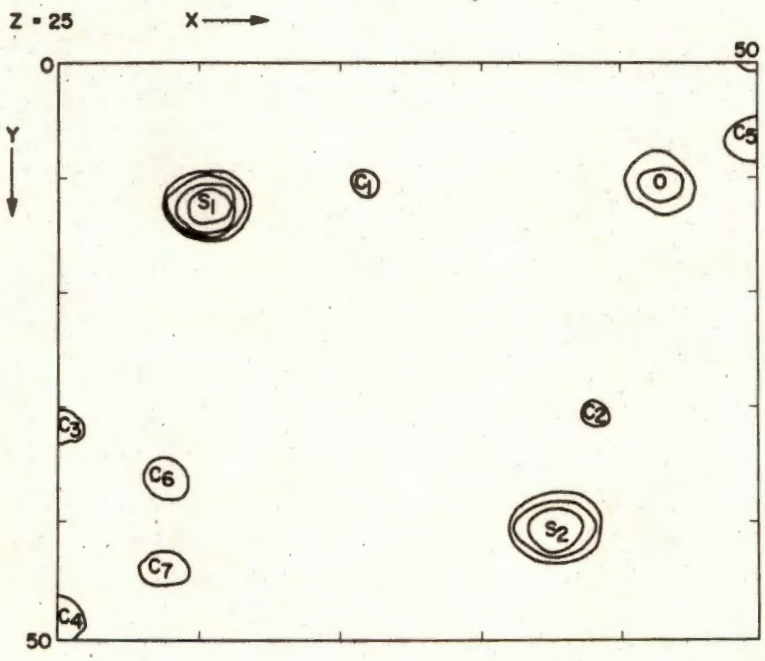


Figure 4.4



C_3; 0,32,25

C_4; 0,48,25

C_5; 50,7,25

C_6; 8,36,25

C_7; 8,44,25

O; 43,11,25

see figure 4.4 for the x,y,z=¼ projection.

The details of packing in the crystal are shown in figures 4.5 and 4.6.

IV. 5. DESCRIPTION OF THE STRUCTURE.

The space group for the complex $Tl C_6H_5COO.4TU$ differs from all the others encountered before for this family of thiourea complexes in that it has no mirror plares at z=o,½ but instead has mirror planes z=¼,¾. For the complex to have a related type of structure this requires the Tl^+ to occupy either positions a or b, symmetry $\frac{2}{m}$, of the space group.

In agreement with previous investigations on structures of this kind the benzoate complex also contains co-ordination columns of anions and cations, with the thiourea molecules as bridges in between. Like all the other structures of this family this structure is also stabilized by ion-dipole attractions.

The thallous ions each of which is surrounded by eight sulphur atoms arrange themselves into infinite linear chains. Also in contrast with previous investigations each of the four sulphur atoms at z=¼ and z=¾ respectively do not appear at the corners of a square but on the corners of a trapezium, which alternate with the long and the short base along the (001) axis (see fig. 4.5).

The benzoate ions with mm crystallographic symmetry are likewise stacked along (001) with their long axis alternately in the (010) and $(0\bar{1}0)$ directions. All the atoms of the benzoate

Figure 4.5

Projection of the structure alon (00l) to show the details of the packing and some important structural parameters. Dashed lines indicate hydrogen bonds.

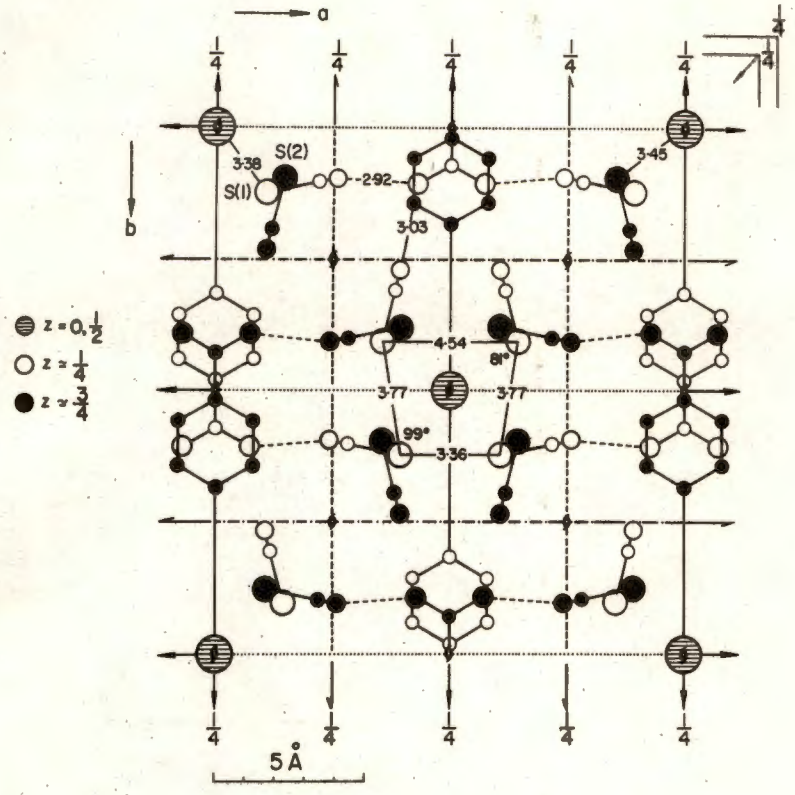
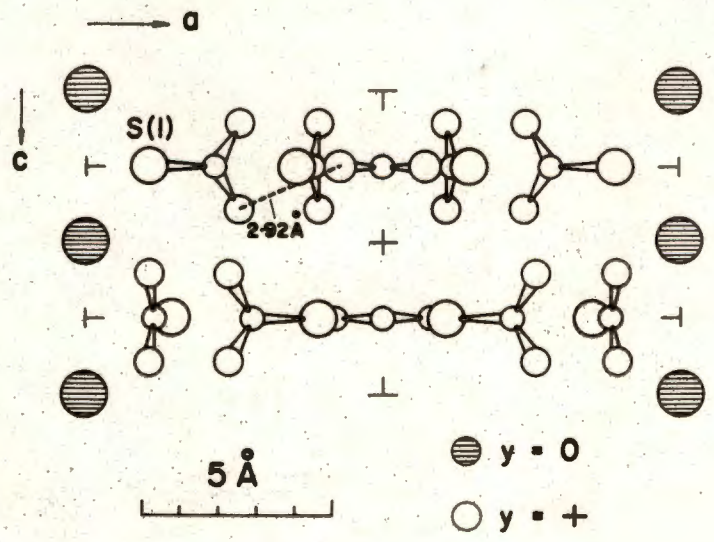


Figure 4.6

(010) projection of the surroundings of a benzoate ion. The benzoate in the upper half of the diagram is viewed from its polar end and the benzoate in the lower half from its apolar end.



ions lie in the same mirror planes at $z=\frac{1}{4},\frac{3}{4}$ which also contain the sulphur and carbon atoms of the thiourea molecules. Each benzoate has a polar and an apolar end, the former referring to the carboxyl group. Only the polar ends seem to interact with neighbouring thiourea molecules in the same mirror plane. This is shown distinctly in the (001) projection of the structure depicted in fig. 4.6. It is seen that the $-C(NH_2)_2$ groups are mirrored in the plane of the benzoate, whereas the apolar end is surrounded at van der Waals distances by the four sulphur atoms which are co-ordinated to thallous ions.

IV. 6. LEAST SQUARE REFINEMENT.

A full-matrix least square refinement was carried out on the observed and calculated structure factors without any differential weighting factors. Co-ordinates of atoms in general positions (not special positions), scale factor for each layer line and an isotropic temperature factor equal to 3.0 for every atom and an overall temperature factor were refined in various runs as parameters. Cycles in which overall temperature factors (without individual isotropic temperature factors), scale factor and atomic co-ordinates were parameters were run to give a minimum residual or reliability factor of 10.0%. Then refinement of isotropic individual temperature factors (without overall B) scale factors and atomic co-ordinates as parameters was done and considered complete when all parameter shifts were less than 0.1 of their estimated standard deviations. The value of R in this case remained on 9.1%.

The final atomic parameters, isotropic individual temperature factors and their estimated standard deviations are given in table 4.1, while the observed and calculated structure factors on an absolute scale (F_{ooo}=1128) are given in table 4.2, with all unobserved reflections $F_{obs.} \leq 20$.

Table 4.1

Fractional co-ordinates and temperature factors of the atoms in an asymetric unit, with estimated standard deviations below each value.

Atom	x	y	z	B($\AA^2$)
T1	0	0	0	3.09
				0.04
S(1)	.1073	.1236	¼	2.55
	.0004	.0003		0.12
S(2)	.1452	.0942	¾	3.00
	.0004	.0004		0.13
N(1)	.2591	.0944	.1060	3.78
	.0009	.0008	.0022	0.31
N(2)	.1065	.2332	.6106	4.69
	.0011	.0009	.0025	0.37
C(1)	.2174	.1025	¼	3.07
	.0016	.0014		0.47
C(2)	.1184	.1946	¾	2.91
	.0015	.0013		0.45
C(3)	0	.3159	¼	3.98
		.0023		0.81
C(4)	0	.4818	¼	1.95
		.0016		0.53
C(5)	½	.0715	¼	2.08
		.0017		0.53
C(6)	.0775	.3584	¼	4.14
	.0019	.0016		0.59
C(7)	.0786	.4416	¼	3.48
	.0016	.0014		0.47
O	.4294	.1056	¼	3.42
	.0011	.0010		0.34

Table 4.2

Observed and calculated structure factors on an absolute scale.

H	F_o	F_c
K=0, L=0		
4	106	108
6	87	86
8	365	356
10	231	205
12	181	167
14	126	119
16	103	88
18	84	80
K=1, L=0		
3	108	96
5	209	198
7	336	325
9	257	218
11	129	112
13	71	78
15	67	77
17	51	53
19	88	79
K=2, L=0		
2	245	239
4	317	182
6	284	268
8	215	188
10	137	121
12	181	169
14	149	146
16	86	83
18	48	51
K=3, L=0		
1	216	205
3	332	368
5	313	323
7	185	169
9	117	111
11	150	146
13	168	154
13	110	109
17	58	63
19	20	33
K=4, L=0		
0	42	28
2	319	347
4	286	286
6	315	305
8	195	168
10	197	193
12	128	118
14	112	95
16	90	92
18	42	62
K=5, L=0		
1	263	249
3	335	330
5	226	201
7	108	102
9	159	157
11	157	156
13	124	112
15	93	89
17	89	94
K=6, L=0		
0	44	20
2	331	329
4	287	274
6	279	257
8	144	128
10	193	193
12	101	110
14	77	79
16	73	85
18	67	68
K=7, L=0		
1	240	216
3	295	269
5	236	216
7	156	146
9	187	180
11	158	152
13	87	91
15	54	63
17	82	79
K=8, L=0		
0	336	323
2	258	220
4	157	128
6	135	115
8	172	178
10	165	170
12	95	99
14	44	56
16	48	57
18	65	70

H	F_o	F_c
K=9, L=0		
1	309	293
3	139	121
5	130	115
7	201	193
9	181	189
11	118	120
13	69	77
15	55	61
17	42	49
K=10, L=0		
0	319	302
2	134	123
4	193	179
6	172	167
8	176	184
10	68	69
12	96	94
14	91	99
16	53	62
K=11, L=0		
1	181	154
3	142	129
5	184	174
7	163	165
9	57	62
11	57	64
13	104	110
15	87	90
K=12, L=0		
0	172	158
2	125	119
4	194	186
6	185	171
8	121	122
10	37	48
12	91	98
14	95	100
16	52	54
K=13, L=0		
1	143	126
3	157	145
5	132	138
7	107	112
9	62	66
11	64	77
13	75	82
15	61	64
K=14, L=0		
0	86	83
2	159	145
4	129	124
6	103	114
8	72	84
10	90	97
12	68	74
14	44	51
K=15, L=0		
1	94	102
3	127	127
5	82	88
7	61	70
9	84	95
11	69	78
13	25	35
K=16, L=0		
0	80	95
2	128	139
4	80	73
6	55	65
8	66	79
10	112	119
12	45	49
K=17, L=0		
1	87	98
3	79	90
5	43	60
7	40	55
9	90	97
11	63	71
K=18, L=0		
0	75	77
2	75	81
4	65	76
6	38	55
8	34	48
10	54	60
K=19, L=0		
1	49	56
3	60	75
5	90	97
7	61	71
9	34	44

H	F_o	F_c
K=20, L=0		
0	67	68
2	27	41
4	47	65
6	49	57
K=21, L=0		
1	54	58
3	21	44
5	39	61
K=1, L=1		
3	62	-68
5	19	-20
7	43	32
9	37	-29
11	41	-42
13	28	20
15	26	19
17	10	-6
19	21	-12
K=2, L=1		
0	56	-51
2	55	47
4	85	-95
6	117	129
8	17	-12
10	68	-69
12	10	5
14	63	58
16	11	-7
18	37	-37
K=3, L=1		
1	47	-40
3	9	9
5	100	105
7	67	71
9	88	-94
11	48	-54
13	68	71
15	37	36
17	10	-21
19	24	-17
K=4, L=1		
0	84	-75
2	5	-3
4	70	-69
6	57	60
8	25	-26
10	38	-41
12	11	1
14	26	23
16	11	-19
18	16	-20
K=5, L=1		
1	96	92
3	54	-48
5	64	-62
7	24	19
9	60	57
11	19	11
13	25	-19
15	11	-18
17	10	8
19	18	17
K=6, L=1		
0	169	183
2	38	30
4	52	-52
6	97	-101
8	42	43
10	63	70
12	11	-9
14	40	-39
16	10	7
18	31	30
K=7, L=1		
1	73	-64
3	7	-2
5	14	-13
7	30	-30
9	59	53
11	24	17
13	63	-62
15	32	-29
K=8, L=1		
0	31	16
2	16	6
4	117	116
6	71	-75
8	30	-31
10	27	30
12	30	26
14	11	-6
16	18	15

H	F_o	F_c
K=9, L=1		
1	99	-92
3	63	54
5	55	47
7	34	-39
9	23	-21
K=10, L=1		
0	57	-60
2	8	-5
4	70	70
6	25	23
8	10	-13
10	11	-12
12	21	14
14	19	14
K=11, L=1		
1	9	-9
3	9	-2
5	10	-8
7	11	-17
9	55	-53
11	21	-19
13	28	22
15	20	16
K=12, L=1		
0	25	-24
2	10	6
4	10	-13
6	89	85
8	46	37
K=13, L=1		
1	69	60
3	53	-53
5	59	-61
7	11	6
9	12	-6
11	20	-11
K=14, L=1		
0	60	56
2	20	24
4	63	-68
6	26	15
8	40	32
K=15, L=1		
1	33	26
3	26	-28
5	21	-18
7	21	15
9	20	20
K=16, L=1		
0	21	20
2	12	1
4	12	1
6	21	-13
K=17, L=1		
1	33	-31
3	21	13
5	28	23
K=18, L=1		
0	20	-28
2	11	-5
4	42	48
K=19, L=1		
1	25	-30
3	28	29
5	20	21
7	23	-20
K=20, L=1		
0	27	-23
2	8	-2
4	23	20
K=0, L=2		
2	145	171
4	315	413
6	248	254
8	159	138
10	135	127
12	145	130
14	74	66
16	86	85
18	33	47
K=1, L=2		
1	258	283
3	301	437
5	260	270
7	154	140
9	148	135
11	215	200
13	175	143
15	140	118
17	83	82
19	20	37

H	F_o	F_c
K=2, L=2		
0	219	201
2	235	246
4	256	262
6	215	209
8	208	190
10	172	161
12	124	113
14	81	77
16	90	85
18	59	63
K=3, L=2		
1	320	323
3	195	187
5	199	190
7	256	237
9	246	228
11	156	136
13	88	89
15	73	74
17	91	78
19	69	68
K=4, L=2		
0	405	488
2	287	274
4	91	91
6	159	152
8	199	198
10	188	166
12	120	113
14	108	101
16	62	58
18	78	67
K=5, L=2		
1	310	299
3	148	138
5	234	224
7	268	257
9	215	205
11	116	105
13	113	114
15	66	68
17	34	51
19	57	79
K=6, L=2		
0	333	309
2	253	212
4	187	160
6	220	214
8	162	158
10	113	102
12	124	112
14	137	128
16	55	55
18	43	43
K=7, L=2		
1	236	204
3	216	181
5	238	220
7	198	191
9	110	110
11	89	85
13	129	123
15	100	95
17	38	46
K=8, L=2		
0	176	151
2	227	199
4	245	229
6	221	211
8	149	142
10	97	101
12	113	110
14	118	103
16	78	75
18	17	35
K=9, L=2		
1	156	132
3	254	235
5	197	189
7	126	124
9	89	88
11	114	113
13	94	87
15	91	81
17	55	59
K=10, L=2		
0	107	91
2	207	179
4	218	207
6	122	113
8	101	100
10	126	128
12	109	106
14	47	48
16	66	62

H	F_o	F_c
K=11, L=2		
1	159	147
3	226	202
5	144	134
7	107	107
9	135	135
11	129	129
13	40	47
15	39	48
K=12, L=2		
0	178	173
2	173	155
4	118	106
6	64	65
8	115	119
10	141	135
12	69	69
14	12	24
16	41	51
K=13, L=2		
1	174	162
3	109	107
5	92	86
7	106	108
9	128	134
11	91	88
13	38	44
15	29	40
K=14, L=2		
0	167	145
2	111	108
4	91	97
6	113	106
8	93	93
10	69	68
12	55	56
14	55	61
K=15, L=2		
1	115	104
3	86	90
5	129	127
7	96	102
9	50	58
11	43	47
13	82	84
K=16, L=2		
0	88	82
2	69	74
4	86	95
6	128	117
8	56	60
10	12	22
12	45	54
K=17, L=2		
1	95	87
3	65	72
5	90	90
7	89	84
9	39	41
11	30	36
K=18, L=2		
0	75	78
2	74	75
4	54	64
6	72	80
8	71	71
10	40	48
K=19, L=2		
1	69	74
3	59	61
5	20	34
7	35	44
K=20, L=2		
0	38	57
2	61	69
4	61	58
6	36	43
K=21, L=2		
1	37	50
3	48	56
K=1, L=3		
1	78	60
3	9	-3
5	46	-50
7	49	-53
9	77	81
11	33	36
13	26	-26
15	36	-35
17	17	17

H	F_o	F_c
K=2, L=3		
0	56	-34
2	76	69
4	29	-28
6	42	-50
8	25	-28
10	98	97
12	32	-28
14	37	-41
16	11	-3
18	45	40
K=3, L=3		
1	44	-39
3	23	18
5	15	5
7	80	-82
9	60	62
11	20	17
13	30	-30
15	39	-35
17	24	24
K=4, L=3		
0	59	-50
2	64	56
4	33	28
6	14	7
8	16	-23
10	50	46
12	11	-13
14	12	-4
16	10	11
18	21	18
K=5, L=3		
0	91	-63
2	41	-46
4	43	38
6	45	43
8	10	-5
10	53	-59
12	26	13
14	26	21
16	10	-3
18	21	-25
K=7, L=3		
1	16	7
3	37	29
5	42	36
7	46	40
9	72	-83
11	12	-9
13	53	53
15	42	42
17	24	-26
K=8, L=3		
0	15	11
2	67	-72
4	9	-10
6	45	37
8	42	43
10	55	-67
K=9, L=3		
1	102	97
3	45	-51
5	61	-72
7	51	46
9	25	22
K=10, L=3		
0	109	103
2	9	-3
4	69	-77
6	38	-48
8	40	34
10	26	19
12	11	-12
14	22	-26
K=11, L=3		
1	10	-2
3	10	6
5	20	20
7	11	10
9	48	42
11	21	11
13	10	-12
15	14	-14
K=12, L=3		
0	36	-39
2	31	15
4	32	12
6	39	-39
8	48	-60
10	12	14
K=13, L=3		
1	40	-46
3	51	40
5	59	56
7	12	-15
9	21	18

H	F_o	F_c
K=14, L=3		
0	40	-51
2	21	15
4	26	21
6	12	-5
8	25	-34
K=15, L=3		
1	12	-23
3	27	23
5	21	19
K=16, L=3		
0	26	-30
2	12	-7
4	21	14
6	28	17
K=17, L=3		
1	28	25
K=18, L=3		
0	50	50
2	10	-7
4	34	-39
6	9	-8
8	30	30
K=19, L=3		
1	32	29
3	22	-25
5	17	-25
7	23	21
K=20, L=3		
0	26	20
K=0, L=4		
2	234	296
4	86	83
6	199	195
8	178	169
10	170	155
12	108	108
14	138	128
16	59	60
18	68	63
K=1, L=4		
1	219	218
3	78	86
5	165	168
7	196	208
9	187	177
11	74	67
13	79	79
15	42	49
17	56	52
K=2, L=4		
0	306	281
2	240	238
4	141	146
6	169	177
8	158	157
10	141	141
12	120	112
14	120	100
16	58	60
18	44	52
K=3, L=4		
1	186	171
3	238	236
5	202	201
7	127	134
9	88	93
11	118	119
13	115	109
15	92	85
17	40	48
K=4, L=4		
0	45	36
2	173	154
4	309	326
6	194	202
8	125	126
10	84	90
12	128	117
14	88	81
16	87	82
18	19	36
K=5, L=4		
1	153	134
3	263	262
5	173	170
7	103	102
9	73	79
11	128	133
13	83	79
15	106	89
17	49	61

H	F_o	F_c
K=6, L=4		
0	213	169
2	195	171
4	212	210
6	111	108
8	149	157
10	132	142
12	104	99
14	30	35
16	80	75
K=7, L=4		
1	208	194
3	196	179
5	116	113
7	110	120
9	139	151
11	128	133
13	47	53
15	47	49
17	51	61
K=8, L=4		
0	214	188
2	172	158
4	137	125
6	110	109
8	114	120
10	121	118
12	80	79
14	43	54
16	37	45
K=9, L=4		
1	199	183
3	113	105
5	132	127
7	128	136
9	121	132
11	70	77
13	76	78
15	36	48
K=10, L=4		
0	214	197
2	146	146
4	68	72
6	147	152
8	121	123
10	79	84
12	46	55
14	79	82
K=11, L=4		
1	162	147
3	70	77
5	116	115
7	120	117
9	73	80
11	35	44
13	90	88
15	48	56
K=12, L=4		
0	93	83
2	116	113
4	123	130
6	147	156
8	71	74
10	39	44
12	65	70
14	85	89
K=13, L=4		
1	69	73
3	127	123
5	129	131
7	78	85
9	30	36
11	43	54
13	69	74
K=14, L=4		
0	71	82
2	101	99
4	105	106
6	70	76
8	67	76
10	59	71
12	53	63
K=15, L=4		
1	92	95
3	100	93
5	40	45
7	52	62
9	75	81
11	66	73
K=16, L=4		
0	91	99
2	90	87
4	74	75
6	23	33
8	70	78
10	80	84

H	F_o	F_c
K=17, L=4		
1	51	65
3	78	79
5	51	56
7	32	48
9	50	63
K=18, L=4		
0	52	61
2	51	59
4	65	67
6	33	42
8	24	39
K=19, L=4		
1	48	52
3	40	55
5	54	70
K=20, L=4		
0	40	48
2	23	42
K=1, L=5		
1	23	-17
3	7	-10
5	22	22
7	36	34
9	41	-44
11	23	-29
13	23	19
15	24	22
K=2, L=5		
0	13	-6
2	19	-19
4	8	-7
6	52	56
8	11	4
10	61	-62
12	13	13
14	41	37
K=3, L=5		
1	18	9
3	8	-10
5	23	22
7	57	51
9	47	-50
11	23	-24
13	32	34
15	27	26
K=4, L=5		
0	26	9
2	14	-19
4	20	-29
6	18	14
8	11	3
10	27	-30
K=5, L=5		
1	34	25
3	9	-15
5	10	-17
7	20	12
9	27	22
K=6, L=5		
0	68	63
2	33	24
4	22	-28
6	37	-44
8	12	16
10	52	46
K=7, L=5		
1	10	-13
3	10	-10
5	20	-23
7	26	-27
9	35	32
11	13	11
13	36	-43
15	25	-28
K=8, L=5		
0	10	-3
2	42	29
4	45	35
6	26	-36
8	23	-24
10	44	39
K=9, L=5		
1	53	-65
3	51	37
5	48	43
7	23	-32
K=10, L=5		
0	56	-62
2	12	-1
4	59	56
6	32	29
8	23	-20
10	12	-13
12	11	11
14	21	17

H	F_o	F_c
K=11, L=5		
1	12	-5
3	12	-4
5	13	-9
7	13	-8
9	27	-35
11	11	-12
13	19	11
K=12, L=5		
0	28	14
2	12	-3
4	13	-11
6	46	40
8	42	37
K=13, L=5		
1	46	37
3	29	-34
5	33	-42
K=14, L=5		
0	45	40
2	13	-1
4	12	-30
6	12	7
8	27	24
K=15, L=5		
1	27	19
3	12	-19
5	11	-15
7	10	11
9	19	13
K=16, L=5		
0	25	20
K=17, L=5		
1	10	-20
3	10	8
5	20	16
K=18, L=5		
0	19	-32
2	8	1
4	34	33
K=19, L=5		
0	14	-0
K=0, L=6		
2	119	129
4	198	205
6	156	160
8	56	53
10	83	78
12	83	68
14	64	53
16	43	50
K=1, L=6		
1	150	133
3	182	210
5	156	159
7	85	79
9	85	85
11	125	111
13	108	92
15	73	70
K=2, L=6		
0	150	122
2	155	145
4	117	119
6	113	113
8	115	108
10	107	106
12	69	63
14	45	44
16	44	51
K=3, L=6		
1	200	175
3	114	106
5	94	99
7	125	133
9	134	134
11	91	85
13	56	52
15	42	47
K=4, L=6		
0	257	239
2	143	125
4	84	83
6	88	86
8	119	124
10	88	86
12	73	74
14	54	60

H	F_o	F_c
K=5, L=6		
1	189	159
3	99	86
5	120	117
7	146	149
9	108	109
11	73	68
13	66	67
15	46	48
K=6, L=6		
0	206	195
2	111	103
4	101	98
6	107	105
8	107	111
10	62	58
12	75	73
14	72	72
K=7, L=6		
1	139	119
3	107	102
5	111	118
7	107	115
9	65	66
11	51	55
13	72	71
15	45	60
K=8, L=6		
0	86	75
2	120	111
4	133	138
6	110	127
8	68	77
10	51	56
12	68	69
14	65	68
K=9, L=6		
1	65	69
3	134	138
5	116	123
7	64	72
9	51	51
11	64	65
13	59	59
K=10, L=6		
0	50	47
2	123	119
4	114	106
6	66	75
8	51	53
10	81	87
12	55	61
K=11, L=6		
1	89	95
3	111	113
5	71	73
7	53	60
9	84	92
11	77	78
K=12, L=6		
0	90	94
2	92	99
4	57	58
6	41	46
8	60	68
10	84	87
12	30	40
K=13, L=6		
1	90	95
3	63	68
5	54	57
7	55	66
9	71	81
11	43	54
K=14, L=6		
0	94	92
2	53	61
4	56	62
6	63	61
8	60	61
10	29	41
K=15, L=6		
1	68	67
3	44	55
5	65	74
7	59	66
K=16, L=6		
0	55	57
2	32	39
4	50	66
6	57	68
K=17, L=6		
1	41	50
3	36	47
5	36	58

The program "ORFLS" described in appendix D was used for the refinement.

IV. 7. BOND LENGTHS, INTERATOMIC DISTANCES AND ANGLES.

Interatomic distances up to 5.0Å and angles between various atoms in the unit cell were determined with the "ORFFE" programme also described in appendix D.

From the data obtained it is significant that the thiourea molecules do not interact identically with their neighbouring cations or among themselves (see fig. 4.7). Whereas one type is 3.45Å distant from the closest thallous ion, another type approaches a thallous ion at a distance of 3.38Å. Since d(Tℓ....S) ≃ 0.006Å, this difference is chemically significant. Compared to d(Tℓ....S) as observed in the structures of $T\ell NO_3$.4TU, $T\ell C\ell O_4$.4TU[18] and $T\ell H_2PO_4$.4TU the 3.45Å distance is seen to be the normal one. Furthermore, the sulphur atoms of the thiourea molecules involved in these close approaches are normally close to 3.36 ± 0.01Å, compared to the 4.54 ± 0.01Å between the sulphurs in van der Waals contact. There is an intermediate approach of 3.77 ± 0.01Å between sulphur atoms belonging to thiourea molecules of unlike type. The average distance between sulphurs in the three structures mentioned above is half-way between the intermediate and the long approaches observed here. Sulphur atoms with $\Delta z=\frac{1}{2}$ and in positions of near-overlap in (001) projection are 4.15 ± 0.01Å apart. This is in accordance with equivalent distances observed before, but the Tℓ....Tℓ distance in a stack ($\frac{c}{2}$ =4.075Å) is somewhat smaller than the interthallous distance of 4.145Å found in all other structures examined before.

As already mentioned there are two different types of thiourea molecule in the structure. The one type is involved in the close approaches described in paragraph IV.5 whereas the other type is not. The bond lengths of the two types will now be examined for possible effects of the close approaches. The molecular

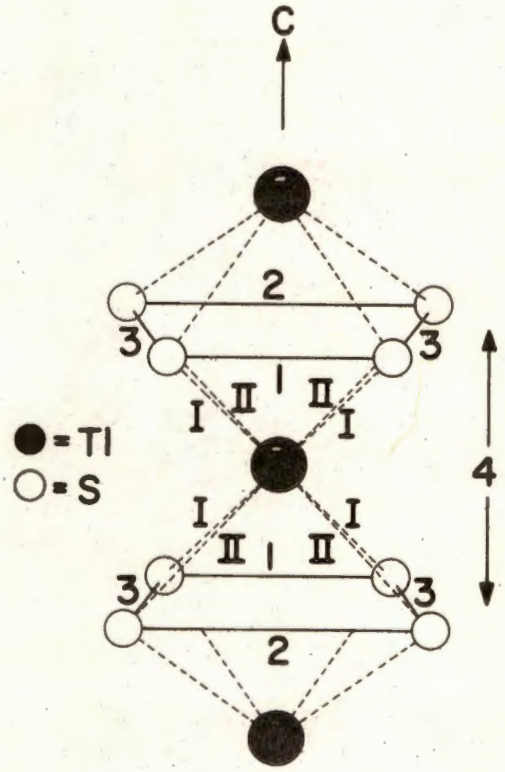
Figure 4.7

Schematic representation of the arrangement of sulphur atoms around a chain of thallous ions. The interatomic distances are:

1=3.36±0.01Å, 2=4.54±0.01Å, 3=3.77±0.01Å

4=4.15±0.01Å, I=3.38±0.006Å, II=3.45±0.006Å

The bond angles are: (2-3)=81°±0.1°, (1-3)=99°±0.1°



parameters for the two types are compared in table 5.3 with un-co-ordinated thiourea [38]. Except for the long S....C bonds which just fail to attain

Table 4.3

	type 1	type 2	σ	TU
S-C	1.76Å	1.77Å	0.02Å	1.720Å
C-N	1.35Å	1.33Å	0.02Å	1.34Å
S-N	2.69Å	2.70Å	0.02Å	2.66Å
N-N	2.35Å	2.27Å	0.03Å	2.31Å
NCN	121°	117°	2°	119°
SCN	120°	122°	1°	120.5°

significance level, the two types of molecule are very similar to free thiourea, and on this evidence are unaffected by any special interactions.

As mentioned before the benzoate ion has mm crystallographic symmetry. There are thus three crystallographic independent bonds in the benzene ring. These measure 1.41, 1.42 and 1.41 respectively (σ=0.03Å). The four independent CCC angles in the benzene ring are 118.5°, 121.5°, 118° and 121.5° (σ=3°). Although these data are not very accurate a normal benzene ring is indicated. The carboxyl C-C and C=O bonds are 1.53 ± 0.03Å and 1.25 ± 0.02Å. The angles CCO and OCO are $118^{\circ}\pm2^{\circ}$ and $124^{\circ}\pm3^{\circ}$. Because of the high standard deviations no meaningful departure from regularity can be claimed here either.

According to interatomic distances each benzoate ion is strongly hydrogen bonded to the surrounding amino groups belonging to the thiourea molecules. There are two different N-H....O approaches. That of 2.92 ± 0.02Å indicates a powerful hydrogen bond whereas the other of 3.03 ± 0.02Å is within the range of N-H-O hydrogen bonds given by Pimental and McClellan [39].

IV. 8. DISCUSSION OF THE STRUCTURE.

It is striking that the thiourea molecules involved in the shorter type of NH....O approach are the same molecules involved in the shorter Tl....S and S....S approaches. It thus appears as if only the 2.92Å NH....O approach describes a hydrogen bond, whereas the 3.03Å approach does not involve a hydrogen bond; this means that hydrogen bonding to the anion entails a considerable modification of the electronic structure of a thiourea molecule. A satisfactory description is that the dipole moment of the thiourea is enhanced by the hydrogen bonding. This leads automatically to a stronger electrostatic interaction with the thallous ion and when this induction operates into neighbouring

sulphur atoms the possibility of weak Π-bonding between the sulphur atoms results.

This effect was overlooked in the analysis of the $TlH_2PO_4.4TU$ structure because the sulphur atoms of the thiourea molecules involved in the hydrogen bonding in that structure are diametrically opposed in the (001) sulphur squares. The Π-bonding therefore does not occur and the sulphur squares appeared to be normal. Two different Tl....S distances were however observed, viz. 3.41 and 3.45Å, but the significance was not appreciated. The thiourea molecules with the short Tl....S distance are hydrogen bonded to the phosphate, viz. d(NH....O)= 2.94Å, and the others are not.

The reason why this effect is so obvious in the present structure is that, due to the asymmetry in the polarity of the benzoate ion, the $(Tl-S_4)_n$ co-ordination columns have geometries which are completely different from anything observed before. In the present case the symmetry of these colomns is mm (also $2_1/m$) compared with 4/m in all other-structures. The mm symmetry is necessary to avoid the direction of polar $-NH_2$ groups towards the apolar hydrocarbon part of the anion. With a 4/m column it is impossible to obtain an arrangement where <u>all</u> - NH_2 groups are directed towards one end of the anion.

The model which describes the ionic thiourea complexes in terms of the close-packing of anions and invariant co-ordination columns of symmetry 4/m except for small distortions, must therefore be revised. The problem is more general and best formulated in terms of the electrostatic interaction of the reacting species. Only when the anions can be approximated to point charges is the old model valid. In the case of more complicated anions however, their geometries also play a rôle and as demonstrated here the column is built up so as to interact

most effectively with the polar parts of such an anion.

The deviation in $Tl_3PO_4.6TU$ from the familiar Tl:S=1:4 ratio can now also be explained since the interaction of isolated anions with long $(Tl^+.4TU)_n$ columns depends on the number of effective contacts. For a cation : anion ratio of 3:1 these contacts would occur on the average every 12Å which is so inefficient that a column of a different geometry and composition and compatible with the 3:1 ratio is formed instead.

The fact that only very drastic conditions seem to cause the formation of co-ordination columns which are not of $^4/m$ type, indicates that this arrangement of sulphur atoms at the corners of a distorted Archimedean antiprism around the cation is energetically the most favourable. It even occurs when not favoured by stoichiometric relationships as in lead (II) salts complexes and complexes of the thallous salts of dibasic acids [18].

IV. 9. CONCLUSION.

The details of this structure have completely changed current ideas about the stability of the ionic thiourea complexes. It has been demonstrated that the very stable $(M^+.4TU)_n$ co-ordination column with symmetry $^4/m$ is not an essential structural unit. A better criterion is that these complexes will form whenever any three-dimensional arrangement of ions and dipoles in the same crystal gives a higher intrinsically negative lattice energy than the sum of the lattice energies of the separate crystals.

CHAPTER V

DISCUSSION OF THE IONIC THIOUREA COMPLEX STUCTURES

V. 1. THE IONIC COMPLEXES

The type of thiourea structure encountered in this thesis (17,18,19, and which has been investigated crystallographically 20,22) can conveniently be described as intermediate between the two known types of thiourea complexes, viz. the hydrocarbon adducts and the co-ordination complexes.

As in the case of the adducts the arrangement of the thiourea molecules in the structure can be described as constituting a framework. The important difference is that in the present case they are not interconnected by S..... H-N hydrogen bonds but arranged so as to enclose straight channels in the structure.

The correspondence with the co-ordination complexes lies in the fact that the thiourea molecules are directed in such a manner that the cationic channel is enclosed exclusively by sulphur atoms, which, according to the Zwitter ion formulation carry residual negative charges. They differ from co-ordination complexes in that the average separation between the cations and the surrounding sulphur atoms is approximately 3·44Å which is too long to be considered a co-ordination bond. The most important way of assessing the nature of the bonding in these complexes are, in fact the distances between the thallium and sulphur atoms and the shape of the polyhedron of sulphurs about thallium.

V. 2. THE CO-ORDINATION POLYHEDRON

The covalent radii for thallium and sulphur can be taken as 1·5 and 1·0 Å respectively, whereas the corresponding ionic radii are 1·49 and 1·84 Å (44). Thus the Tl.....S distance found

in the complexes studied, all correspond to an ionic and not to a covalent interaction. The experimental value for d(Tℓ.....S) is about 0·10Å greater than the value obtained by summing the ionic radii. A similar lengthening of the Na.....O distances is found in some of the complexes of sodium iodide with oxygen-containing molecules [45,46,47]. (The appropriateness of the ionic radii of oxygen and sulphur used in these calculations is not established, however, and so the significance of the bond lengthening is not certain).

Various features of the structures of the two related families of complexes viz. thiourea and sodium iodide with oxygen containing molecules can be usefully discussed in terms of Pauling's rules [48]. It has already been shown, that in the family of thiourea complexes, the cation is surrounded by eight sulphur atoms in a distorted cubic arrangement (deviation was caused by hydrogen bonding in the benzoate complex) and that a similar arrangement of potassium and ammonium ions is found in $KFeS_2$ [49] and $NH_4Cu_7S_4$ [50] respectively. The complexes of NaI with oxygen-containing molecules on the other hand have a distorted octahedral arrangement of oxygen atoms about the cation. Sodium ions appear generally to have a octahedral environment of oxygen atoms and, in $NaCrS_2$ [51] there is also an octahedral environment of sulphur atoms about sodium. These observations are in agreement with Pauling's first rule, in terms of which the radius-ratio determines the co-ordination. The radius-ratios ($r^+/r-$) for various cations with oxygen, and sulphur are given in table 5.1 with the ionic radii in angstroms (co-ordination number 6) given in parenthesis.

Table 5.1

	O^{2-}(1·40)	S^{2-}(1·84)
Na^+(0.95)	0.68*	0.52*
K^+(1.33)	0.95	0.72**
Rb^+(1.48)	1.06	0.81**
Cs^+(1.69)	1.20	0.92**
Tl^+(1.44)	1.03	0.78**

*r^+/r^- values indicate where octahedral arrangements have been reported.

**Indicate a cubic arrangement of anions about cation. Complexes of the other type are not known.

In both families of complexes the co-ordination polyhedra about the cations are joined by shared faces. As would be expected, both co-ordination polyhedra are distorted so as to increase the distance between adjacent cations as a consequence of the repulsion of the like charges. Because the cations are singly charged, this effect is not sufficient to make the structure unstable (cf. Pauling's third rule). The shape and size of the co-ordination polyhedron of sulphur atoms about the thallium atom may also be compared with situations in other crystals (51,52,53,54).

V. 3. GEOMETRY OF THE THIOUREA MOLECULE

The dimensions of the thiourea molecules in the investigated complexes mentioned in paragraph V.1 do not differ significantly among thiourea molecules in the same complex, nor significantly from those of thiourea itself,(1) nor from those of thiourea in various covalently-bonded complexes(14). The presence of a relatively heavy metal atom in the structure makes it difficult to

validate small differences in environments.

V. 4. THE INFLUENCE OF THE ANION

In the anion channel the size and chemical properties of the anion play an important part in the formation of the structure and also determines the space group.

In the columns of the structures the ideal case is that the four-fold column axis should also be a crystallographic four-fold axis with one column per tetragonal {100} repeat distance. In this case the channel between the columns also has tetragonal or cylindrical symmetry. This situation can occur only if the dimension of the anion fits the geometry of the channel exactly. This has so far only been encountered in the room temperature structures of the 1:4TℓNO_3 and 1:8 $T\ell_2SO_4$- thiourea complexes [17]. The basic requirement for the occurrence of this structure type is that the equilibrium separations between cations and between anions in their linear chains must be the same whilst the anions extend sufficiently in the direction normal to the chain to make close-packed contacts with the walls of the retaining channel. In the $T\ell NO_3$.4TU room temperature structure both conditions are satisfied, the latter due to the disc-like nature of the rotationally disordered flat nitrate groups. In the $T\ell_2SO_4$.8TU structure there are only half as many sulphate as thallous ions in the parallel chains. The tetrahedral sulphate groups are not large enough to butress the walls of the channel, but few enough to fit linearly into the channel. With twice the number of sulphate groups steric interference in a chain, with its pitch fixed by the equilibruim separation of thallous ions, would have occured.

This situation is encountered in the structures of the bromide, iodide and perchlorate complexes. To match the pitch of the cation chain these anions must take up a staggered arrange-

ment whereby the tetragonal symmetry of the channel is destroyed. To accomodate such a staggered chain, adjacent co-ordination columns cannot maintain their identical orientations, but by only a small relative rotation, create a channel, distorted away from cylindrical symmetry, into which the anions can fit non-linearly. No relative displacement of the column is necessary to ensure contact between the included anions and the channel walls on all sides. The structures are still tetragonal, but now with two columns per (100) repeat distance.

For elongated anions a parallel elongation of the cross-section of the channel is required and column displacements occur. This leads to orthorombic symmetry and is exemplified by the $CsF \cdot 4TU \cdot 2H_2O$ [19], $CsCl \cdot 4TU$ [20] $TlC_6H_5COO \cdot 4TU$ structures. In the fluoride complex the included anion is the elongated $(F \cdot 2H_2O)^-$ hydrogen bonded unit. A somewhat similar situation is encountered in the CsCl structure. In this case, however, the chloride is not hydrogen bonded to the water in the channel ($d(Cl \cdots O) = 3.2$ Å) and the anhydrous complex can also exist with the same structure. In the benzoate structure the size and dimensions of the benzoate molecule also require elongation of the channel in a similar way as for the fluoride complex. A novel feature of these structures is that the amino ends of the thiourea molecules which define a specific channel do not occur alternately at different levels when considered cyclically. In all the other complexes with known structure, the anion pair within one asymmetric unit is surrounded by eight thioureas lying alternately in the mirror planes at $z = 0, \frac{1}{2}$. This ensures close-packed contacts on all four sides. The chloride ions, however, are too small to make simultaneous contacts with eight close-packed thiourea molecules. If in close-packed contact on three sides the available space on

the fourth side cannot accommodate two further thiourea molecules in the alternating cyclic sequence. The closest they can get is to pack out of phase and in contact only with thiourea molecules already in contact with the chloride ions. This results in an elongated channel resembling an elliptical cylinder. The chloride ions are situated near one of the focal axes whilst the vicinity of the second focal axes is void and with the sequence on this side disturbed. Water molecules can diffuse into the void to restore close-packing throughout the structure. It is interesting that the new environment of the chloride ions, established by the intrusion of the water, can once more be described as a cyclic alternation of nitrogen or oxygen atoms between the levels $z=o,\frac{1}{2}$. It becomes readily understood why recrystallization of the anhydrous material should occur in contact with moist air, but difficult to see why instead of hydrated crystals of the complex only the components crystallize from aqueous or aqueous alcohlic solutions.

A quite different phenomenon in the benzoate complex is responsible for the non-appearance of the eight thiourea molecules alternately at different levels when considered cyclic. The polar end of the benzoate molecule is surrounded by four thiourea molecules in the same mirror plane. Two of the four thiourea molecules are strongly hydrogen bonded (as described in Chapter IV) through the amino groups to the oxygens of the carboxyl group. The other two could also be involved in weak hydrogen bonding. The existence of the four thiourea molecules in the same mirror plane is a result of mm symmetry of the carboxyl group. The polar end of the benzoate molecule is not surrounded by any of the four other amino groups left in the same level, but these four amino groups surrounded also a carboxyl

group in a mirror plane $^{c}/_{2}$ away and in the same way as described.

As has been pointed out the thiourea molecules arrange themselves, within limits, in such a way as to define a close-packed anion channel. The way of packing of the anions in these channels explains why the nature of the cation and not that of the anion determines the c spacings of the series of complexes. The a and b spacings on the other hand depend on the size of the anion.

V. 5. THE MADELUNG ENERGY OF IONIC THIOUREA COMPLEXES

The non-existence of the Na^{+} and Li^{+} salt complexes, which is based on ionic radii alone, seems to be caused by unfavourable radius ratios. But the existence, as indicated in this thesis, of the complex $Tl_3PO_4 \cdot 6TU$, which is still very similar in crystal habit to the crystals of the regular complexes, despite the absence of the tetragonal co-ordination columns, indicates that the ionic radii ratios alone do not satisfactorily explain the phenomenon of the non-existence of the alkali salt complexes. Although radius ratios may thus demand a different geometry for the complexes of Na^{+} and Li^{+} salts, they do not rule out their formation. From the energetic point of view, however, it is clear that solid complexes can not be formed unless their lattice free energies are less than the sum of the lattice free energies of the components. The non-existence of the salt complexes marked negatively in table 5.2 should thus relate either to size or energy factors.

Table 5.2

	Li	Na	K	Rb	Cs
F	240	215	190	182	173
	-	-	-	-	+
Cl	195	180	165	160	150
	-	-	-	+	+
Br	185	172	158	154	146
	-	-	+	+	+
I	173	162	149	145	139
	-	-	+	+	+

Cohesive energies (kcal/mole) of the alkali halides according to Ketelaar[56].

The + sign indicates that the alkali halide thiourea complexes have been prepared successfully[18]. Complexes of the other alkali halides are not know.

It has been demonstrated that cohesion in the thiourea complexes of ionic salts is largely of electrostatic origin and that all the complexes have closely related structures, their Madelung constants likewise being very similar. Boeyens and Gafner[55] calculated the lattice energies of these thiourea complexes and found that all have lattice energies amounting to about 180 kcal/mole. With the contribution of the four thiourea molecules in the complex eliminated, one expects that only those ionic salts with lattice energies of less than about 160 kcal/mole can gain by forming 1:4 complexes with thiourea.

In table 5.2 CsF is an exception. CsF represents a special case, however, since its complex has been obtained from aqueous medium only and is doubly hydrated[19] to give a hydrogen bonded anion ($F \cdot 2H_2O^-$).

It appears that all the ionic thiourea complexes have lattice energies of very nearby the same magnitude which is equal to the lattice energy of four moles of thiourea plus 160 Kcal/mole.

V. 6. THE HYDROGEN BOND IN THE IONIC THIOUREA COMPLEX

The role of the hydrogen bond in both the phosphate and benzoate complexes, the only two from all the complexes which have been investigated yet, in which such hydrogen bonds between the anions and the amino ends of the thiourea was found, is a quite interesting phenomenon.

The phosphate ion, as described before, occupies a position more favourable for hydrogen bonding. Both amino ends of the thiourea molecule are involved in hydrogen bonding with the oxygens of two neighbouring phosphate ions. This hydrogen bonds which are parallel to the a axis but perpendicular to the b and c axis are responsible for an increase in the length of the a axis in comparison with the b axis. In the direction parallel to the b axis and perpendicular to the a and c axis a decrease of the length of the b axis was caused by amino groups and oxygen atoms at different levels which sliding slightly one over the other and which could therefore occupies closer-packing. No deviations from regularity have been observed in the cation co-ordination polyhedra due to hydrogen bonding.

In the case of the benzoate complex the anion and thus the carboxyl group appears in the same mirror plane as the thiourea molecules which means that either of the two or both of the amino ends of the same thiourea molecule are involved in hydrogen bonding with the oxygen atom.

As mentioned before in the cation co-ordination column, remarkable deviation from what has been observed before, was found. The only reasonable explanation for this deviation is

that it was caused by the hydrogen bonding which reduced the dipole moment of the thiourea molecules with an equivalent reduction in repulsion of the two sulphur atoms in related positions in the same mirror plane.

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APPENDIX.

A. INTER-FILM FACTOR PROGRAM

The intensity measurements from the different films of each layer line are placed on the same relative scale by applying factors to the measurements from each film. These inter-film factors are obtained by taking the mean of the inter-film factors that can be calculated from the measured intensities for all the reflections. The intensity for each reflection is then given by the average of the values over all relevant films, after the film factors have been applied. A computer program, "FILMFACT", was written by J. Admiraal for use on an IBM 360/40 computer, and used to carry out this computation for each layer line.

B. INTENSITY CORRECTIONS PROGRAM

All the intensities were corrected by making use of the computer program "CORRECT", written by E.G. Boonstra.

C. FOURIER AND PATTERSON SYNTHESIS

For the Patterson and Fourier synthesis all the measured intensities were used in the calculations by means of the "CENTROSY" centrosymmetric Fourier program written by Gantzel and Hope (U.C.L.A.) and modified for use on the IBM 360/40 by Miss. J. Hewitt.

D. REFINEMENT AND INTERATOMIC ANGLES AND DISTANCE DETERMINATIONS

Refinement of the trial structure was done using the full- matrix least squares program "ORFLS" of Busing, Martin and Levy and atomic scattering factors as supplied by Hanson et al.[35]

Interatomic distances and bond angles with their estimated standard deviations were calculated by means of the functions and error computer program "ORFFE" of Busing, Martin and Levy.

Alteration to "ORFLS" as well as "ORFFE" to allow their use on the IBM 360/40 computer of the C.S.I.R., were made by H. Messerschmidt of IBM(S.A.).

REFERENCES

1. N.R. Kuncher and M.R. Truter, J.Chem. Soc., 2551 (1958).
2. O. Hassel and H. Viervoll, Acta Chem. Scand., 1, 149 (1947).
3. K.W.F. Kohlrausch and J. Wagner, Z. phys. Chem., B45, 229 (1940).
4. V.A. Golovnia and I.V. Prokof'ieva, Izv. sekt. platiny An SSSR no.27, 62 (1952).
5. L.A. Chugaiev and V. Subbotin, Ber., 43, 1200 (1910).
6. D.I. Riabchikov and A.P. Isakova., DAN SSSR, 41, no.4, 169 (1943).
7. V.V. Lebiedinskii and E.V. Shenderetskaia, Izv. Sektora platiny IONKh AN SSSR no.21, 164 (1948).
8. Z.M. Novozheniuk, Kand. dissert Arch. bibl. OKhN AN SSSR, M. (1950).
9. Ad. Claus, Ber., 7, 235 (1874).
10. Ad. Claus, Ber., 8, 43 (1875).
11. Ad. Claus, Lieb. Ann., 179, 146 (1875-1876).
12. C. Hermann and H.U. Lenne, Naturwiss., 39, 234 (1952).
13. W.R.G. Atkins and E.A. Werner, J. Chem. Soc., 101, 1982 (1912).
14. M. Nardelli, G.F. Gasparri and P. Boldrini, Acta Cryst., 18, 618 (1965).
15. C.B. Knobler, Y. Okava and R. Pepinsky, Z. Krist., 111, 385 (1959).
16. J.E. Reynolds, J. Chem. Soc., 53, 857 (1888).
17. J.C.A. Boeyens and F.H. Herbstein, Nature, 211, 588 (1966).
18. J.C.A. Boeyens and F.H. Herbstein, Inorganic Chem., 6, 1408 (1967).
19. J.C.A. Boeyens, Acta Cryst., B24, 199 (1968).
20. J.C.A. Boeyens, Acta Cryst., B24, 1191 (1968).
21. J.C.A. Boeyens, Nucleon, 7, 14 (1965).
22. G.J. Kruger and J.C.A. Boeyens, J.S. Afr. chem. Inst., 21, 136 (1968).
23. G. Pfrepper, Z. anorg. allg. Chem., 347, 160 (1966).

24. C. Mahr and H. Ohle, Ann. Chem. Liebigs, 542, 44 (1939).

25. M.J. Buerger, X-ray Crystallography, Wiley London, (1962).

26. M.J. Buerger, Crystal Structure Analysis, Wiley London, (1960).

27. H. Lipson and W. Cochran, The Determination of Crystal Structures, Vol. III, Bell and Sons, London, (1953).

28. R.W. James, The Optical Principles of the Diffraction of X-rays, Vol. II, Bell and Sons, London, (1948).

29. W.L. Bragg and W.H. Bragg, The Crystalline State, Vol I, Bell and Sons, London, (1933).

30. International Tables of X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, (1952).

31. W.C. Hamilton, Acta Cryst., 8, 185 (1955).

32. A.L. Patterson, Phys. Rev., 46, 372 (1934).

33. A.L. Patterson, Z. Krist., 90, 517 (1935).

34. J.M. Robertson, Organic Crystals and Molecules, Cornell Univ. Press. Ithaca, N.Y., (1953).

35. H.P. Hanson, F. Herman, et al., Acta Cryst., 17, 1040 (1964).

36. D.T. Cromer, et al., Acta Cryst., 17, 1044 (1964).

37. E. Cartnell and G.W.A. Fowles, Valency and Molecular Structure, Butterworths, London, (1961), p. 237.

38. M.R. Truter, Acta Cryst., 22, 556 (1967).

39. G.C. Pimental and A.L. McClellan, The Hydrogen Bond, W.H. Freeman and Co., San Francisco, (1960), p. 289.

40. G. Allen and E.F. Caldin, Quart. Revs. (London), 7, 255 (1953).

41. Tables for conversion of X-ray diffraction angles to interplanar spacing (1950), NBS Applied Mathematics series 10, U.S. Government Printing Office, Washington.

42. International Tables for X-ray Crystallography, Vol. I, Kynoch Press, Birmingham, (1952), p. 155.

43. International Tables for X-ray Crystallography, Vol I, Kynoch Press, Birmingham, (1952) p. 152.

44. A.F. Wells, Structural Inorganic Chemistry, 3rd ed., Claredon Press, Oxford, (1962), p. 71.

45. Y. Gobillon, P. Piret and M. van Meerssche, Bull. Soc. Chim. France, 551 (1962).

46. P. Piret, Y. Gobillon and M van Meerssche, ibid., 205 (1963).

47. P. Piret and G. Mesureur, J. Chim. Phys., 62,287 (1965).

48. A.F. Wells, Structural Inorganic Chemistry, 3rd ed., Claredon Press, Oxford, (1962), pp. 83-86.

49. J.W. Boon and C.H. MacGillavry, Rec. Trav. Chim., 61, 910 (1942).

50. G. Gattow, Acta Cryst., 10, 549 (1947).

51. A.F. Wells, Structural Inorganic Chemistry 3rd ed., Claredon Press, Oxford, (1962), pp. 534-539.

52. H.Hahn and W. Klinger, Z. Anorg. Chem., 260, 110 (1949).

53. V. Scatturin and E. Frasson, Ric. Sci. Suppl., 26, 3382 (1956).

54. C.D. West, Z. Krist., 88, 97 (1934).

55. J.C.A. Boeyens and G. Gafner, J. Chem. Phys., 49, 2435 (1968).

56. J.A.A. Ketelaar, Chemical Constitution, Elsevier Publ. Co., Amsterdam, (1953), p. 40.

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