properties of the various fractions resolved by this technique.

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IONIC COMPLEXES OF THIOUREA

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THIOUREA is one of the most versatile complexing agents yet discovered. It forms the well-known inclusion complexes with branched-chain hydrocarbons[1] and also has the ability to complex with various other organic substances[2] and with some salts of virtually every metal.

This latter property is largely a result of the formation of covalent sulphur-to-metal bonds[3]. However, thiourea has also been reported to form stable complexes with salts of elements which do not form covalent bonds to co-ordinated ligands. Another explanation must be sought for the existence of these complexes.

The prototype of these thiourea complexes is NH_4Br.4TU (TU, thiourea), first described by Reynolds in 1888 [4]. 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 cation and anion, they have the general formulae:

MX.4 TU
M_2X.8 TU
MX_2.6 TU

The nature of this family of complexes has now been established by a correlated chemical and crystallographic investigation. The preparations reported in the literature have been repeated and checked and some new complexes have been prepared. All the complexes have been examined by single-crystal or powder X-ray diffraction techniques and the unit-cell dimensions, space group and density (of single crystals only) determined. This has enabled some thirty-odd related complexes to be 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. Some measure of disorder appears to be a feature of many of the structures at room temperature. While this has prevented determination of all the details of the structures, their main outlines have been settled. A broad survey and general description of the results obtained will be given in this article, to be followed by a series of more detailed papers now in preparation.

Classification of the Complexes

Morphologically the solid complexes are usually fibrous masses and only in some cases could single crystals suitable for crystallographic work be obtained. Well-defined X-ray powder patterns have, however, always been obtained.

The unit-cell dimensions and space groups show that the complexes fall into a number of well-defined groups. The largest of these includes the 1 : 4 complexes of alkali bromides and iodides, thallium (I) bromide, iodide and perchlorate. These crystals are all tetragonal with $a \sim 20$ Å, $c \sim 8{\cdot}3$ Å and space group $P4/mnc$. Closely related to these is a smaller group of complexes, including the thallium (I) nitrate, and sulphate (1 : 8) complexes, which have $a \sim 10$ Å, $c \sim 8{\cdot}3$ Å, space group $P4/mcc$. A Weissenberg photograph of the $TlNO_3$.4 TU complex at −160° C showed that at this temperature this complex had $a \sim 20$ Å, $c \sim 8{\cdot}3$ Å and space group $P4/mnc$. Thus the smaller unit cell appears to be a partially disordered version of the larger ordered cell; this was established in detail by determining the structures of $TlClO_4$.4 TU and $TlNO_3$.4 TU at room temperature (the super-lattice reflexions of the latter are too weak even at −160° C to allow reliable determination of the differences between the partially disordered and the ordered version of this structure). Two other ordered structures have been obtained. In one of these $a \sim b \sim 14$ Å, $c \sim 8{\cdot}3$ Å, while in the other $a \sim 2b \sim 21$ Å, $c \sim 8{\cdot}2$ Å. These structures, which have not been determined, would be expected to differ in detail only from that of $TlClO_4$.4 TU.

Another group is formed by the complexes of the alkali and thallium (I) chlorides, which have $a \sim 32$ Å, $b \sim 13$ Å, $c \sim 8{\cdot}5$ Å and space group $Bbam$ (this is the orientation most convenient for comparison with the other complexes). These complexes have only been obtained in polycrystalline (fibrous) form but one fluoride complex, CsF.4 TU. 2 H_2O has cell dimensions ($a \sim 17{\cdot}0$ Å, $b \sim 12{\cdot}5$ Å, $c \sim 8{\cdot}45$ Å, space group $Ibam$, four formula units per unit cell) which are closely related to those of the chloride complexes. Single crystals of this fluoride complex have only been obtained recently and its structure has not yet been determined.

All the complexes discussed until now have been of thiourea with salts of monovalent metals, but two related complexes of divalent lead salts have also been reported: these are $Pb(NO_3)_2$.6 TU[5] and $Pb(ClO_4)_2$.6 TU[6]. Crystallographic investigations have shown that these two complexes also belong to this general family despite the difference in the ratio of cations to thiourea molecules. Both complexes have partially disordered structures (of different types) at room temperature, but X-ray structure analysis has revealed the general outlines of their structures and in particular has shown how a cation : thiourea ratio of 1 : 6 is possible.

The structural results will now be described in more detail. Some of the structures have been analysed by three-dimensional methods and some by two-dimensional methods; intensities were measured visually from Weissenberg photographs taken with copper $K\alpha$ radiation. The structures were generally solved by Patterson methods and refined by Fourier and least-square techniques. The R-factors are all below 12 per cent and there are no

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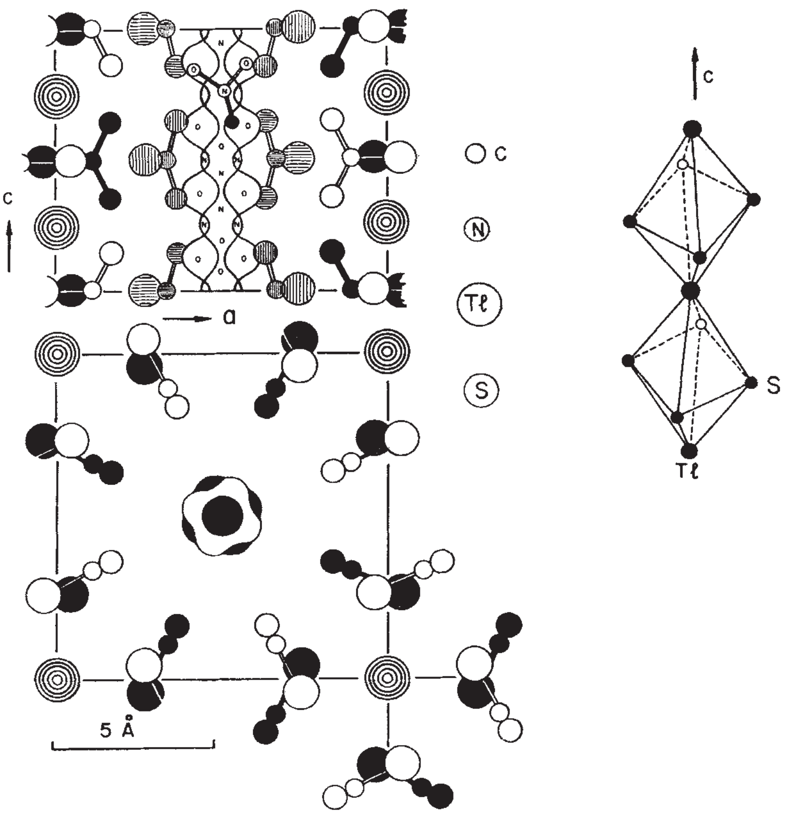

Fig. 1. The crystal structure of the $TlNO_3$.4 TU complex shown in projection down [001] and [010]. On the right the arrangement of sulphur atoms and thallium ions in one of the chains along [001] is shown. In the projection down [001] the atoms represented by full circles lie in the plane of the paper while those represented by open circles are in the mirror plane lying $c/2$ above or below the plane of the paper. In the [010] projection the full-circle molecules lie about $a/4$ below the plane of the paper while those with open circles lie the same distance above it. The horizontally shaded molecules are about $a/2$ below the plane of the paper and the vertically shaded molecules the same distance above it

outstanding discrepancies between observed and calculated structure factors.

Structure of $TlNO_3$.4 TU

These crystals have $a = 10{\cdot}34$ Å, $c = 8{\cdot}29$ Å, space group $P4/mcc$, two formula units per unit cell. The results of the crystal-structure analysis are summarized in Fig. 1. The essential feature of this structure type, and the family as a whole, is the existence of separated cations and anions bridged by polar thiourea molecules. Each cation is surrounded by eight sulphur atoms at the corners of a distorted cube centring on the cation site (Fig. 1, right). The average thallium–sulphur distance is 3·43 Å, 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 2·7 Å whereas the sum of their ionic radii is about 3·3 Å. Thus it is clear that these are ionic complexes and that the major cohesive interactions in the crystals are ion-dipole interactions. The arrangement shown in Fig. 1 can be described as a linear chain of metal ions surrounded by neutral but polar thiourea molecules with the sulphur atoms of a set of thiourea molecules bridging successive cations. The separation between neighbouring cations in a chain is 0·5 c, or approximately 4·1 Å.

The thiourea molecules point away from the arrays of cations situated along the four [001] edges of the unit cell and in this way they enclose a cylindrical channel with its axis along [$\frac{1}{2}\frac{1}{2}z$]. The anions are in these channels and in an idealized structure would lie along the cylinder axis which is also a crystallographic four-fold axis. In the crystals that have been investigated the anions have lower symmetry and hence are disordered positionally. This type of structure is not directly comparable with the channel structures of the thiourea–hydrocarbon complexes since the thiourea molecules are not connected through S...H—N hydrogen bonds.

The structures of a number of crystals are known in which similar, approximately cubic arrangements of sulphur atoms about potassium and ammonium ions are found (for review see Wells[7]), while another close comparison can be made with the arrangement in thalloso-thallic sulphide, $Tl_2^{III}S_3.Tl_2^{I}S$ (refs. 8, 9, also ref. 7, pp. 900–901). The thallium (III) atoms in this structure are linked by sulphur atoms ($d(S\text{-}Tl^{III}) \sim 2{\cdot}6$ Å) to form chains of tetrahedra sharing opposite edges, while the thallium (I) atoms lie between the chains with eight sulphurs around them ($d(S\text{-}Tl^{I}) \sim 3{\cdot}3$ Å). The interactions between the sulphur and thallium (I) atoms appear to be ionic interactions somewhat similar to those found in the present family of complexes (however, ion-dipole forces are unlikely to be important in TlS).

Ordered Structure as found in $TlClO_4$.4 TU

These crystals have $a = 21{\cdot}07$ Å, $c = 8{\cdot}28$ Å, space group $P4/mnc$, eight formula units per unit cell. Their structure, which is characteristic of the majority of these complexes, differs from the $TlNO_3$.4 TU structure in that two neighbouring cation–thiourea chains are not crystallographically equivalent but are rotated to a small extent relative to one another and have slightly different ($\sim 0{\cdot}05$ Å) thallium positions; the doubling of the a axis is a consequence of these differences. The space group no longer requires the anions to lie on the axis of the cylindrical channel.

The structural details of the $TlClO_4$ and $TlNO_3$ complexes provide the key to most of the general crystallographic properties of the ionic thiourea complexes. In particular an explanation is provided for the fact that most of the complexes crystallize with a unit cell having $a \sim 20$ Å while the strongest reflexions define a sub-cell with $a \sim 10$ Å. If only the sub-cell is considered, both the cations and anions will be arranged in a linear chain with periodicity $c/2$. This is possible only if the distances between neighbouring cations and neighbouring anions are fortuitously the same. In the general case, therefore, the anionic arrangement is non-linear. This causes slight distortion of the cylindrical anionic channel of the sub-cell and the appearance of the superstructure. In the nitrate complex the deviation of the anionic chain from linearity is either masked by rotational disorder or else is so slight that it is beyond the limits of detection, but in the $TlClO_4$.4 TU structure the perchlorate tetrahedra are in an ordered array and displaced off the cylinder axis.

Complexes of Divalent Metal Salts

The complexes of this family formed by the salts of divalent metals (lead is the only known example) are essentially isostructural with the complexes of monovalent metal salts. The 1 : 6 ratio encountered in these complexes can arise in one of two ways, exemplified by the structures of the $Pb(NO_3)_2$ and $Pb(ClO_4)_2$ complexes.

Structure of the $Pb(NO_3)_2$.6 TU Complex

This complex caused some controversy in the past. It was described first by Rosenheim and Meyer[5], who assigned to it the formula $2Pb(NO_3)_2$.11 TU. The analytical work of Mahr and Ohle[6] supported the 2 : 11 ratio, but Brú *et al.*[10] concluded from crystallographic considerations that the most probable formula was 6 $Pb(NO_3)_2$.32 TU. However, the experimental crystal density of 2·03 g/cm^3 is in good agreement with the 1 : 6 ratio deduced by Haworth and Mann[11] from their analytical results, but not with the densities calculated on the basis of the other proposed compositions. We have therefore used the 1 : 6 formulation. It should be emphasized that the crystal structure at room temperature is such that the $Pb(NO_3)_2$: thiourea ratio is not determined by space group considerations (in contrast, for example, to the 1 : 4 ratio in the $TlNO_3$ complex) and is not necessarily rational. The value used is an experimental value derived from chemical analyses and density measurements.

The complex has the space group *P*4/*mcc* characteristic of the $TlNO_3$.4 TU structure type. It has also $a = 10·3$ Å, but $c = 24·6$ Å, which is three times the *c*-axis of the other structures. There are four formula units per unit cell. Oscillation photographs about [001] show additional diffuse layer lines which indicate that there is considerable disorder in the structure. This has not been explained in detail. The electron-density projection down [001] is very similar to that obtained for $TlNO_3$.4 TU and this shows that the atomic arrangement must be essentially the same in both complexes. The suggestion of Brú[12] that this structure consists of an ordered framework of thiourea molecules which has tubular cavities in which lead nitrate molecules are contained is not correct.

Structure of the $Pb(ClO_4)_2$.6 TU Complexes

The $Pb(ClO_4)_2$.6 TU crystals have $a = 18·6$ Å, $c = 7·92$ Å, space group *P*4/*mcc*, four formula units per unit cell. The structure is based on that of the $TlClO_4$.4 TU complex, there being similar cation–thiourea chains along the cell edges and the central axis of the cell. The anion arrangements are also very similar. However, the cation sites along $[0\frac{1}{2}z]$ and $[\frac{1}{2}0z]$ are entirely vacant and these regions of the crystal contain half as many thiourea molecules as are in a cation–thiourea chain.

Water molecules can diffuse into these relatively open channels to give the hydrated complex $Pb(ClO_4)_2$.6 TU. 2 H_2O. The cell dimensions remain essentially unchanged when water is taken up in the structure, but the space group changes from *P*4/*mcc* to 14/*mcm*. A Fourier projection down [001] shows that the water and thiourea molecules in the regions about the empty channels are unresolved and it seems probable that what order there was in the positions of these thiourea molecules in the anhydrous crystals has become disrupted by the intruding water molecules.

Comparison of Structures of 1 : 4 and 1 : 6 Complexes

In the $TlNO_3$.4 TU complex there are two nitrate ions in each channel for each repeat distance of 8·2 Å along [001]; these ions do not completely fill the available space. In the $Pb(NO_3)_2$.6 TU complex there are eight nitrate ions in each channel for each repeat distance of 24·6 Å, or $2\frac{2}{3}$ per 8·2 Å. The available space in the channel is now completely filled. The requirements of stoichiometry result in there being four Pb^{++} ions to be distributed among the six cation sites of the one independent cation-molecule chain in each unit cell. Vacant cation sites result, the occurrence of diffuse scattering suggesting that these are not randomly arranged. The alternative of filling all cation sites in one set of chains and one-third of the cation sites in a second, non-equivalent, set is not used in this complex, presumably for both energetic and entropy reasons.

In the $Pb(ClO_4)_2$.6 TU complex quite a different means of compensating for the bivalent nature of the cations is used. The density of packing of perchlorate ions is much the same in the $TlClO_4$ and $Pb(ClO_4)_2$ complexes. In the $TlClO_4$.4 TU structure there are four Tl^+ ions for the two pairs of cation sites in the two crystallographically independent cation–molecule chains in the unit cell, but in a hypothetical $Pb(ClO_4)_2$ complex of the same structure there would be only two Pb^{++} ions for the four cation sites. Instead of half-filling all the sites in both chains, all the sites in one chain are filled and the other chain disappears. In its place one finds two thiourea molecules per unit cell (for the anhydrous complex) or two thiourea molecules and two water molecules (for the hydrated complex). These molecules do not appear to have any structural role in the crystals other than to fill space in the channels that exist in the loosely-bound framework formed by the cation–molecule chains and perchlorate ions. The differences in the two structures therefore stem from the different sizes of the nitrate and perchlorate ions.

Relationship of Other Complexes

The structures of a number of other complexes are known where a polar molecule forms a bridge between separated cations and anions. The greatest resemblance to the ionic thiourea complexes is shown by the ionic complexes $NaI.3(CH_3)_2NCHO$[12], $NaI.3(CH_3)_2CO$[13] and $NaI.3CH_3OH$[14]. These complexes all crystallize in hexagonal crystals and have similar structures. In the acetone complex, for example, there are chains of composition $(Na^+.3CH_3)_2CO$ running up the [00.1] axis. The iodide ions are in ordered positions in the channels between the hexagonally-arranged chains. Within a chain each Na^+ ion is surrounded by an octahedral arrangement of oxygen atoms of the carbonyl group while the methyl groups form the walls of the anion channel.

The approximately cubic and octahedral arrangements of sulphur and oxygen atoms about the cations of their respective complexes are in agreement with previous crystal-chemical results and can be explained in terms of the ratio of the radii of the ions involved (Pauling's[16] first rule). If comparable thiourea complexes of sodium salts can be prepared, then they will be expected to have an octahedral arrangement of sulphurs about sodium and thus will not belong to the present family of thiourea complexes. Similarly, complexes of oxygen-containing molecules with cations other than lithium and sodium will be expected to favour a cubic and not an octahedral arrangement of oxygen about the cations and thus differ from the complexes investigated by Piret *et al.*[15]. The fact that the crystals of the oxygen-containing molecules with sodium iodide favour hexagonal symmetry and those of the present thiourea complexes tetragonal symmetry follows from the respective octahedral and cubic arrangements in their cation–molecule chains.

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