

Pd-C (*trans* to Cl) = 2.12      C-C = 1.36  
 Pd-C (*trans* to Cl) = 2.12      C-C = 1.40.

Although the lengthening of the C-C bonds is hardly significant ( $\Delta/\sigma = 3.8$ ) such lengthening is consistent with a 'trans influence' of the arsine ligands.

The dihedral angle between the plane of the allyl ligand and the As(1)-Rh-As(2) plane is 126.6°, in good agreement with the angle of 125° predicted on the basis of a trigonal model (Vrieze, McLean, Cossee & Hilbers, 1966). The methyl group is displaced from the allyl plane 0.2 Å towards the Rh<sup>III</sup> ion. Such distortions, which are common to methylallyl compounds (Churchill & Mason, 1967) were originally thought to be a consequence of asymmetric metal-allyl bonding (Canadine, 1967). This explanation, considered unlikely by us, is now seen to be incorrect.

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## Crystal Chemistry of the Ionic Thiourea Complexes

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Thiourea forms a series of stoichiometric complexes with the salts of alkali metals and related cations. For monovalent cations to which the discussion is restricted a cation: thiourea ratio of 1:4 is favoured and eightfold coordination occurs invariably. The cations occur in linear stacks at characteristic separations and each cation is surrounded by eight sulphur atoms at the corners of a cubically distorted antiprism. The thiourea molecules lie at right angles to the axis through the cationic chains which represent the spines of coordination columns with -NH<sub>2</sub> groups at the surface. These columns pack together in such a way as to create channels of appropriate dimensions for the associated anions to fit snugly into them. The complexes are stabilized by attractions between free ions and dipoles and the limited number of structure types corresponding to the nature of the anions all have very similar Madelung constants. The influence on the structures of factors such as ionic size and shape and hydrogen bonding is examined critically.

### Introduction

The series of thiourea complexes of ionic salts of monovalent cations is characterized by a small number of related structure types. The complexes usually crystallize in the form of delicate needles elongated along an axis (for convenience always called *c*) measuring about 8.2 Å. In structures containing heavy cations, oscillation X-ray photographs taken about this axis always show odd layer lines of relatively low intensity.

This suggests that the cations occur in linear stacks parallel to [001] and with a pitch of approximately *c*/2. It is thus not surprising to find that complexes with a common cation have virtually identical *c* axes, irrespective of the space group. On the other hand, complexes with a common anion usually have a common space group.

In (001) projection, the crystallographic unit cells are always simply related to a tetragonal cell of edge approximately 10 Å. This means that the chains of

cations always occur at a separation of about 10 Å and that their mutual arrangement is determined by the nature of the anion, which therefore determines the details of the structure.

The structures of complexes representative of each of the known structure types and the calculations of their lattice energies have now been published and the variations in structure type can be assessed quantitatively. All the complexes examined structurally to date have eightfold coordination of sulphur atoms around a central cation. As pointed out by Verhoef & Boeyens (1968), there is, however, reason to believe that an entirely different type of coordination will be found in the complex  $Tl_3PO_4 \cdot 6\text{thiourea}$ , where the cation:ligand ratio is different from 1:4. This special case will not be discussed here and attention will be focused on the structures with eightfold coordination.

### The coordination polyhedron

Dunitz & Orgel (1960) have shown that on the basis of maximum repulsion the eight ligand ions around a central ion should ideally lie at the corners of an Archimedean antiprism, Fig. 1. Assuming the dimensions of the antiprism to be determined only by S-S interactions, all the edges shown in Fig. 1 should be identical and equal to the S-S van der Waals separation,  $d$  say. The cation-sulphur distance then becomes  $d/2(2+1/\sqrt{2})^{1/2} = 0.823d$ . Successive cations lie on the common 8-axes of contiguous sulphur polyhedra and their separation is therefore equal to the height of the antiprism, viz.  $2^{-1/4}d$ . A typical van der Waals radius for sulphur is 1.85 Å (Evans, 1964). For this value a regular antiprism yields  $d(M^{+} \cdots S) = 3.045$  Å and  $d(M^{+} \cdots M^{+}) = 3.11$  Å. The sum of  $M^{+}$  and S van der Waals radii as well as the interionic distances in alkali metal crystals, which range from 3.716 Å for Na to 5.309 for Cs (*Tables of Interatomic Distances and Configurations in Molecules and Ions*, 1958), suggest that both of these calculated distances are too short. For a cubic arrangement based on  $r(S) = 1.85$  Å the cation-

sulphur distance is 3.204 Å and the cation-cation distance is 3.70 Å. It follows that more realistic interatomic distances will be obtained by a tetragonal elongation of the antiprism and/or distortion towards a cube. Both types of distortion are encountered experimentally although the cubic distortion is always more pronounced.

Even more general than the tetragonal elongation is an increase in the van der Waals separation of the sulphur atoms. Whereas elongation retains short S-S distances in the squares and leads to longer S-S approaches between the squares, in practice there seems to be a tendency for equal S-S distances which are considerably larger than the expected van der Waals distances. This is more apparent in the case of large cations where elongation which increases the interionic distance is inevitable, but where its effect is masked by a parallel increase in the size of the sulphur squares

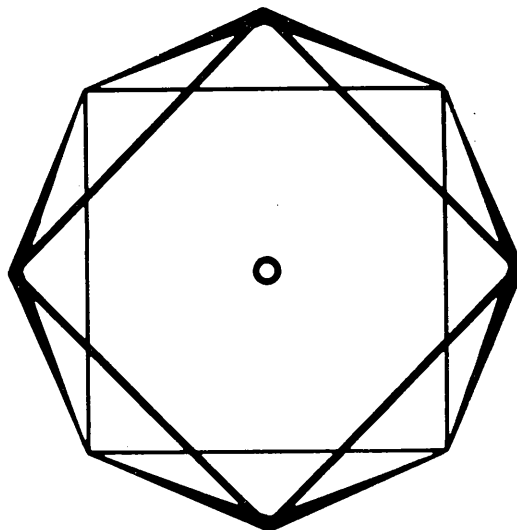


Fig. 1. The square antiprism. All the corners are at the same distance from the centre and each corner is equidistant from four neighbouring corners.

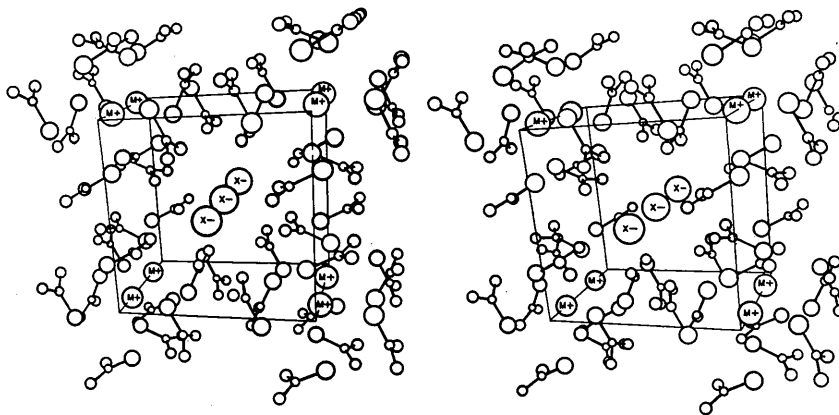


Fig. 2. Stereoscopic drawing of the model structure of an  $MX \cdot 4\text{thiourea}$  complex, based on the structure of  $TiNO_3 \cdot 4\text{thiourea}$ .

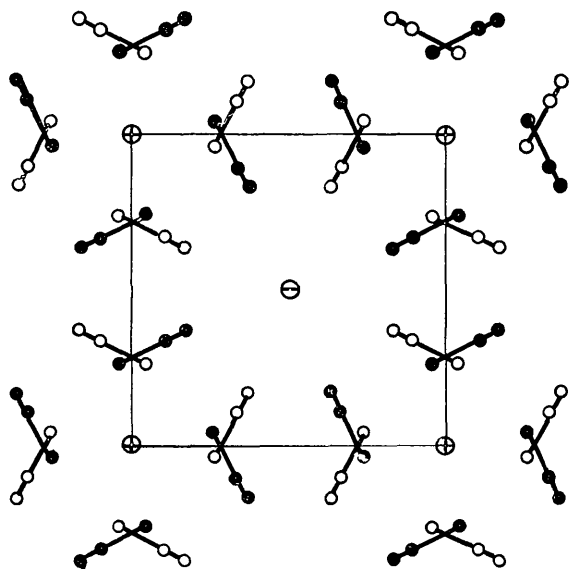


Fig. 3. Projection along [001] of the model structure shown in Fig. 2. Atoms represented by open and solid circles are associated with molecules lying across the mirror planes at  $z = \frac{1}{2}$  and 0. The cations lie at  $z = \frac{1}{4}, \frac{3}{4}$ . In this and all subsequent projections, the origin is at the right-hand top. The  $a$  and  $b$  axes run respectively horizontally and vertically across the page.

which is necessary to accommodate the large cation. This effect is found in the structures of the Cs salt complexes (Boeyens, 1968*a, b*) where the average  $d(\text{S} \cdots \text{S}) = 4.25 \text{ \AA}$ . In all thallium salt complexes, however (*e.g.* Boeyens & Herbstein, 1967), the average  $d(\text{S} \cdots \text{S}) \simeq 3.9 \text{ \AA}$ , and in the RbI complex (Kruger & Boeyens, 1968)  $d(\text{S} \cdots \text{S})_{\text{av}} \simeq 4.0 \text{ \AA}$ .

The intercationic distance in a structure is found directly from the  $c$  cell-parameter and has average values of 4.14, 4.16 and 4.24  $\text{\AA}$  for  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  respectively. These values are all about 0.85 of the separations in crystals of the metals, but are considerably higher than twice the van der Waals (ionic) radii.

In analysing the  $\text{M}^+ \cdots \text{S}$  interactions, the ionic radii for eightfold coordination of the cations are more appropriate than the metallic radii. In Table 1 are summarized some of the  $d(\text{M}^+ \cdots \text{S})$  values obtained crystallographically in studies of these complexes [ $\text{Cs}^+$ , Boeyens (1968*a, b*);  $\text{Rb}^+$ , Kruger & Boeyens (1968);  $\text{Tl}^+$ , Boeyens & Herbstein (1967), Verhoef & Boeyens (1968, 1969);  $\text{Pb}^{2+}$ , Boeyens & Herbstein (1967)]. Subtraction of the van der Waals radii,  $r(\text{M})$ , where  $r(\text{M})$  is 1.036 times the six coordination values given by Wells (1962), gives the effective radius of sulphur in these complexes as 1.97  $\text{\AA}$ , allowing for some covalency in the  $\text{Pb} \cdots \text{S}$  bonds alone.

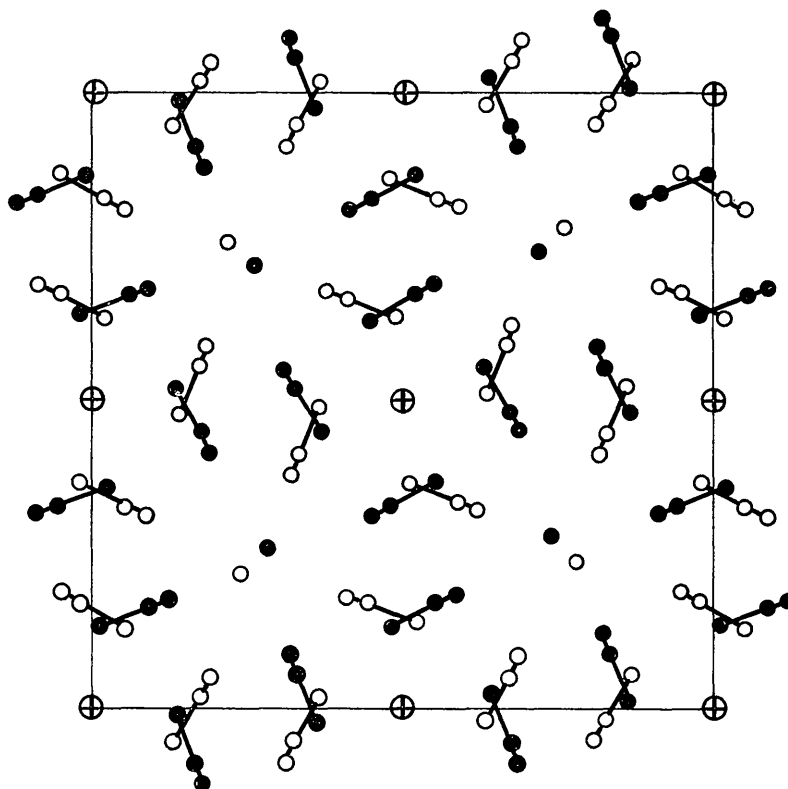


Fig. 4. Structure of the RbI-4thiourea complex in projection along [001] using the same convention as in Fig. 3.

Table 1. Derivation of an appropriate van der Waals radius,  $r(S)$ , for sulphur in ionic thiourea complexes

	$d(M^{+} \cdots S)$	$r(M)$	$r(S) = (d - r)$
Cs <sup>+</sup>	3.69	1.75	1.94
Rb <sup>+</sup>	3.53	1.53	2.00
Tl <sup>+</sup>	3.45	1.49	1.96
Pb <sup>2+</sup>	3.11	1.25	1.86

This value correlates well with the S-S distances in the thallium and rubidium salt complexes where the effect of cationic size is not severe. The fact that this radius is somewhat larger than the expected 1.85 Å has its origin in the sizeable negative charge on each sulphur atom in the dipolar thiourea molecule. A similar repulsion of like charges is responsible for the intercationic distances which are also observed to be larger than the expected van der Waals separations.

### The idealized structure

In terms of the arguments advanced above, an idealized structure determined mainly by electrostatic forces and which is not severely distorted by ionic sizes, can now be formulated. The cations in this structure would be regularly spaced in linear chains where they are each surrounded by eight sulphur atoms at the corners of a cubically distorted and slightly elongated antiprism, centred on the cation. The elongation occurs because cation-cation separations are on the average larger than the distance between interstitial positions between antiprismatically close-packed sulphur atoms, and the cubic distortion is necessary to simultaneously optimize the cation-sulphur and sulphur-sulphur distances. Each sulphur atom is equidistant from two neighbouring cations, and the top square of any antiprism thus forms the base square of the next.

The symmetry of this arrangement is  $4/m$  and in the ideal case this can be expected to appear as crystallographic symmetry. Since the mirror planes contain the sulphur squares, this condition requires the thiourea molecules to lie entirely within the mirror planes or to have their  $-NH_2$  groups symmetry-related across the mirror planes. It is immediately obvious that the latter arrangement will allow denser packing of the  $(M^+, 4\text{-thiourea})_n$  coordination columns in the tetragonal arrangement demanded by the crystallographic symmetry. To further facilitate the packing of the coordination columns, the thiourea molecules of neighbouring columns should point parallel to the  $[110]$  diagonals rather than directly at one another.

This packing leaves an open channel along  $\frac{1}{2}, \frac{1}{2}, z$  with fourfold symmetry and with  $-NH_2$  groups on the walls. This channel can only be occupied by the anions, which should lie on the fourfold axis to maintain the symmetry. Such a structure is depicted in the stereoscopic drawing shown in Fig. 2 and in (001) projection in Fig. 3. Evidently there are two possible types of position for the anions. At  $\frac{1}{2}, \frac{1}{2}, 0$  and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  they are cubically surrounded by  $-NH_2$  groups while at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$  and

$\frac{1}{2}, \frac{1}{2}, \frac{3}{4}$  they are antiprismatically surrounded by these. Calculation of the lattice energies for the two types of arrangement (Boeyens & Gafner, 1968) showed them to be energetically equivalent. Since the former type is preferred in most of the actual structures, it has been adopted in the drawing of Fig. 2.

A special feature of this ideal structure is the fact that the separation between anions is exactly the same as the separation between neighbouring cations. This structure type can thus only be expected in rare cases in which the cations and anions are very similar in size. It was noted before that the  $c$  cell parameter is strongly dependent on the nature of the cation. This shows that the strongest chemical interaction occurs in the coordination column and hence the pitch of a given cationic chain can be assumed to remain constant in all structures and in association with any anion. In cases of mismatch between anionic size and channel dimensions, only the ideal packing of the coordination columns can thus be expected to be disturbed and modified in such a way as to create optimum space for the anions between them. Two types of distortion can be anticipated for the case of mismatched spherically symmetrical anions which can be

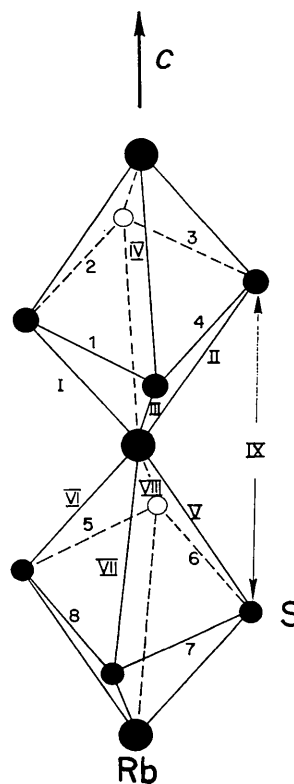


Fig. 5. The arrangement of sulphur atoms in a rubidium-thiourea coordination column. In the column along  $[00z]$ :  $1 = 2 = 3 = 4 = 3.93$  Å;  $5 = 6 = 7 = 8 = 4.09$  Å;  $I = II = III = IV = 3.52$  Å;  $V = VI = VII = VIII = 3.54$  Å;  $IX = 4.22$  Å. In the column along  $0, \frac{1}{2}, z$ :  $1 = 3 = 6 = 8 = 3.98$  Å;  $2 = 4 = 5 = 7 = 4.05$  Å;  $I = II = VII = VIII = 3.48$  Å;  $III = IV = V = VI = 3.58$  Å;  $IX = 4.29$  Å. The angles:  $1-4 = 92^\circ$ ,  $1-2 = 87^\circ$ .

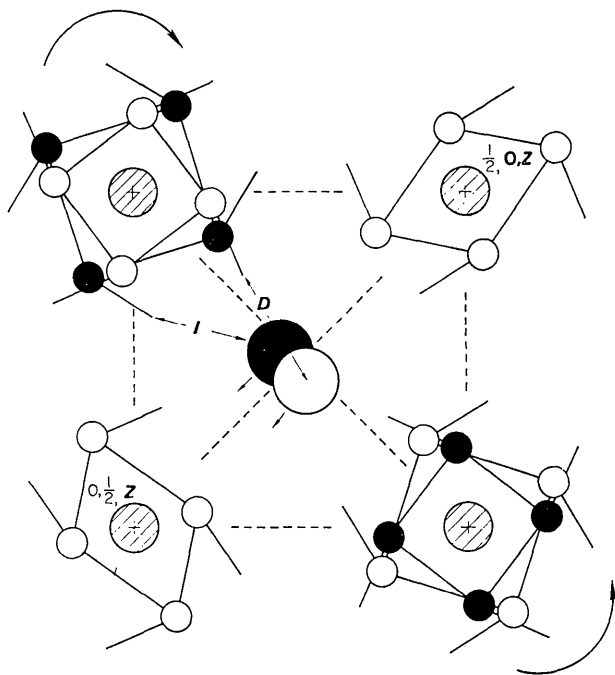


Fig. 6. Schematic illustration of the distortions in the Rb-thiourea columns caused by interference of the large iodide ions. Atoms shown as solid, shaded and open circles have  $z$  coordinates of  $0$ ,  $\frac{1}{4}$  and  $\frac{1}{2}$  respectively. The curved arrows indicate the rotations of the columns at  $0, 0, z$  and  $\frac{1}{2}, \frac{1}{2}, z$ . Small arrows indicate the displacement of the staggered iodide chain because of these rotations.  $I$  and  $D$  designate approaches which are respectively increased and decreased by the rotations.

either too large or too small for the available space in the normal channel. For irregularly shaped anions, various types of distortion are foreseen. Anions which can form strong hydrogen bonds with the  $-\text{NH}_2$  groups of thiourea can be expected to change the geometry of the coordination columns themselves.

#### The effect of a large anion

The hypothetical structure discussed under the previous heading can most probably never occur in nature since a spherical anion small enough to follow the pitch of the column will be too small to make van der Waals contact with the walls of the channel. The only examples of this structure type (space group  $P4/mcc$ ) are  $\text{TlNO}_3 \cdot 4\text{thiourea}$  at room temperature,  $\text{Tl}_2\text{SO}_4 \cdot 8\text{thiourea}$  and the severely disordered  $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{thiourea}$ . Of the anions involved, only the tetrahedral sulphate ion has anything approaching the required fourfold symmetry. By taking up two possible orientations at random, it simulates this requirement. The sulphate ions are large enough to fill the channel between four coordination columns and, because of the double negative charge, are present in sufficiently small numbers in comparison with the number of thallos ions so as not to be crowded along  $[001]$ . A higher

degree of disorder is required of nitrate ions to satisfy the symmetry requirements. Rotational disorder around its threefold axis will, however, ensure close contact with the walls of the channel while a plane-to-plane approach between the flat ions eliminates steric interference at the required separation.

The perchlorate ion is about the same size as a sulphate ion, but since twice the number occur per unit length of channel in the  $\text{TlClO}_4 \cdot 4\text{thiourea}$  complex, steric interference can be expected. In the actual structure (Boeyens & Herbstein, 1967) the anions are found to increase their separation by adopting a staggered arrangement. This structure has the space group  $P4/mnc$  which predominates in the complexes formed by simple salts. This is expected since anions are usually larger than cations. This structure type is exemplified by the complex  $\text{RbI} \cdot 4\text{thiourea}$  (Kruger & Boeyens, 1968) shown in projection along  $[001]$  in Fig. 4. The coordination columns along  $0, 0, z$  and  $0, \frac{1}{2}, z$  are no longer identical and both differ significantly from the regular arrangement in the  $P4/mcc$  structures. The differences are summarized in the caption to Fig. 5 and all the irregularities can be shown to be direct consequences of the steric influences of the large anion.

A channel of elliptical cross section is required to accommodate the staggered chain of iodide ions. Starting with all columns in parallel alignment as in the ideal structure, this is achieved by rotation of the two columns along  $0, 0, z$  and  $\frac{1}{2}, \frac{1}{2}, z$  in clockwise and anti-clockwise directions and leaving the two along  $0, \frac{1}{2}, z$  and  $\frac{1}{2}, 0, z$  in their original orientations. An exaggeration of the effect of these rotations is illustrated schematically in Fig. 6. These rotations bring two thiourea molecules on one side of the plane through  $0, 0, z$  and  $\frac{1}{2}, \frac{1}{2}, z$  closer to it and move two others on the opposite side away from this plane. Instead of occurring in this plane, the staggered chain therefore moves towards  $0, \frac{1}{2}, z$ , thus maintaining its centring with respect to the surrounding  $-\text{NH}_2$  groups. The chain is now closer to the column at  $0, \frac{1}{2}, z$  than to the column at  $\frac{1}{2}, 0, z$  and as a consequence it is found that the column at  $0, \frac{1}{2}, z$  is elongated in a direction parallel to the plane containing the iodide chain, while the column at  $\frac{1}{2}, 0, z$  is elongated towards this plane. Two diagonally opposed sulphur atoms in each of the resulting rectangles are now closer to iodide ions than are the other two and, because of this steric hindrance, the rectangles compress into parallelograms. Another effect of the relative rotation of the columns is best illustrated by considering only the column along  $0, 0, z$  and the chain near  $\frac{1}{4}, \frac{1}{4}, z$ . The rotation increases the separation between the  $-\text{NH}_2$  groups of the thiourea molecule at  $z=0$  and the iodide ion at  $z=0$  ( $I$  in Fig. 6), but decreases the corresponding separation at  $z=\frac{1}{2}$  ( $D$  in Fig. 6). Since there is a fourfold axis along  $0, 0, z$  the sulphur atoms at  $z=\frac{1}{2}$  must move closer together to compensate for this effect and thus decrease their distance from the  $\text{Rb}^+$  ion at  $0, 0, \frac{1}{4}$ . To maintain the

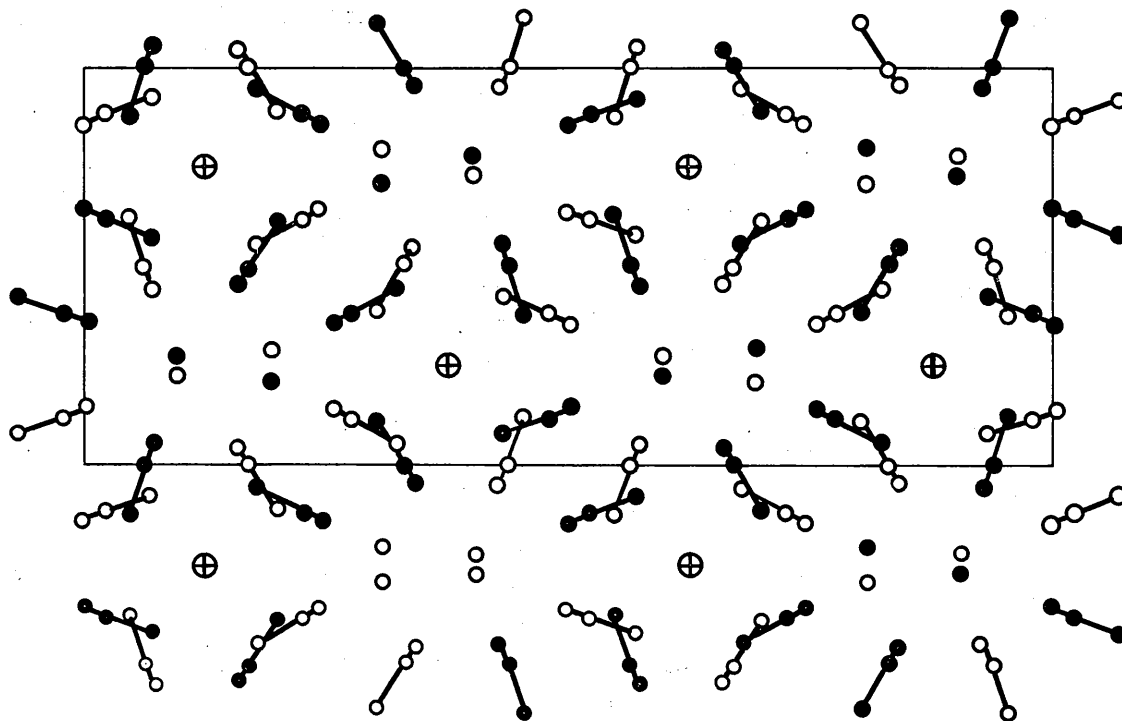


Fig. 7. Structure of the  $\text{CsCl} \cdot 4\text{thiourea} \cdot \text{H}_2\text{O}$  complex in projection along  $[001]$ . The same convention as in Fig. 3 is used.

proper Rb-S separations, the  $\text{Rb}^+$  ion moves away from  $0, 0, \frac{1}{4}$  towards  $z=0$ , ( $z=0.2435$  in the actual structure), thereby causing the sulphur square at  $z=0$  to expand.

It is significant that packing forces can produce these distortions and it shows conclusively that the tetragonal coordination column is not an absolute structure invariant in the thiourea complexes of a series of salts with a common cation.

#### Effect of a small anion

Anions as small as chloride and fluoride will not fill a channel between four tetragonally close-packed coordination columns. As a result it is found that complexes containing these anions show a high tendency to take up water with the anions into the structure. A detailed study of an anhydrous complex has never been reported but it was demonstrated that the hydrated and anhydrous complexes of  $\text{CsCl}$  are isomorphous (Boeyens, 1968*b*). On this basis, one can assume that the space occupied by the water molecules in the hydrated structure is void in the anhydrous form. Calculation of the lattice energy for this structure (Boeyens, 1968*c*) showed that in the absence of other interactions these voids do not necessarily render the structure electrostatically labile.

The structure of the hydrated  $\text{CsCl} \cdot 4\text{thiourea}$  complex is shown in projection along  $[001]$  in Fig. 7. It is interesting to note that although the chloride ions are too large to follow the pitch of the thallos chain, they

are too small to fit tightly into a channel of the same geometry as found in the structure of the  $\text{RbI}$  complex. Considering the space occupied by water to be a void, one sees that the staggered chain of chloride ions is in contact with three rather than four coordination columns. The  $-\text{NH}_2$  ends of the three columns enclose the anions almost completely and prevent the close approach of the anions by a fourth. The fourth column therefore packs so as to make maximum contact with the two columns on the open side of the channel. As a consequence, it relates to these two by  $2_1$  axes and not by twofold axes as in the ideal structure. The resulting channel has as cross section a highly eccentric ellipse with the chain of anions at one focal axis. It was found experimentally that zeolitic water can diffuse into the structure to occupy the void near the other focal axis without forming any hydrogen bonds.

Anhydrous complexes containing the fluoride anion are not known. In the  $\text{CsF}$  complex, the anion is doubly hydrated through hydrogen bonds as shown in Fig. 8 which shows the  $(001)$  projection of the structure (Boeyens, 1968*a*). For the sake of argument the positions occupied by water molecules can once more be considered as voids. The anion is then seen to be so small that its chain has the same pitch as the cations and it is completely surrounded by four  $-\text{NH}_2$  groups or only two coordinated columns instead of the four in the model structure. By analogy with the chloride structure, it is found that both the other neighbouring columns are close-packed with the first two and related

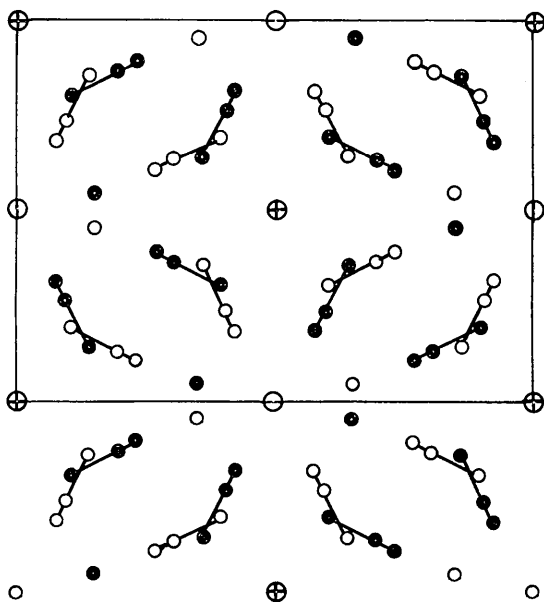


Fig. 8. Structure of the  $\text{Cs}(\text{F} \cdot 2\text{H}_2\text{O}) \cdot 4\text{thiourea}$  complex in projection along  $[001]$ . The same convention as in Fig. 3 is used.

to them by  $2_1$  axes. Hence there are two voids per channel and they occur on opposite sides of the chain of anions. This structure was shown by lattice energy calculations (Boeyens, 1968c) to be inherently unstable, except when each anion is hydrogen bonded to two water molecules in the voids.

#### Effect of unsymmetrical anions

As indicated before, an almost limitless variety of structures can be envisaged if not only the size but also the shape of the anions is varied. An interesting type was encountered recently in the structure of  $\text{TlClO}_3 \cdot 4\text{thio}$ -

urea (Mitchell & Boeyens, 1970), where the packing of coordination columns was found to be such that the symmetry of the anionic channel, as shown in Fig. 9, is  $2_1/m$ . Although this is the symmetry of the now familiar staggered chain, this is the first example of an anion which is sufficiently irregularly shaped to induce this symmetry through chemical interactions at the walls of the channel. Apart from minor distortions such as a displacement of the cation as in the  $\text{RbI}$  complex, the symmetry of the coordination columns is still of the  $4/m$  type. Only the packing of neighbouring columns is changed in such a way as to optimally enclose the irregularly shaped anions.

#### The effect of hydrogen bonds

The complexes formed by thallos carbonate, nitrite and dihydrogen phosphate are isomorphous, orthorhombic and very nearly tetragonal. Their  $a$  and  $b$  cell dimensions, with  $a$  slightly larger than  $b$ , are approximately equal to  $a/2$  of the model structure. Since these salts all derive from comparatively weak acids or strong hydrogen bonding anions, it is not surprising to find that the deviation from ideal structure is caused by hydrogen bonding between the included anions and  $-\text{NH}_2$  groups at the walls of the channel.

The projection along  $[001]$  of the structure of  $\text{TlH}_2\text{PO}_4 \cdot 4\text{thiourea}$  (Verhoef & Boeyens, 1968) is shown in Fig. 10. The unsymmetrical anion occupies a position of  $222$  symmetry, so that oxygen atoms and hydroxyl groups are statistically superimposed to appear as a tetrahedral arrangement. At first glance it might seem anomalous that phosphate groups [ $d(\text{P}-\text{O}) = 1.45 \text{ \AA}$ ] can repeat with the same pitch as thallos ions, whereas the thallos perchlorate complex [ $d(\text{Cl}-\text{Cl}) = 1.46 \text{ \AA}$ ] has the same structure as the  $\text{RbI}$  complex. The explanation lies in the fact that the phosphate tetrahedra are compressed normal to  $[001]$

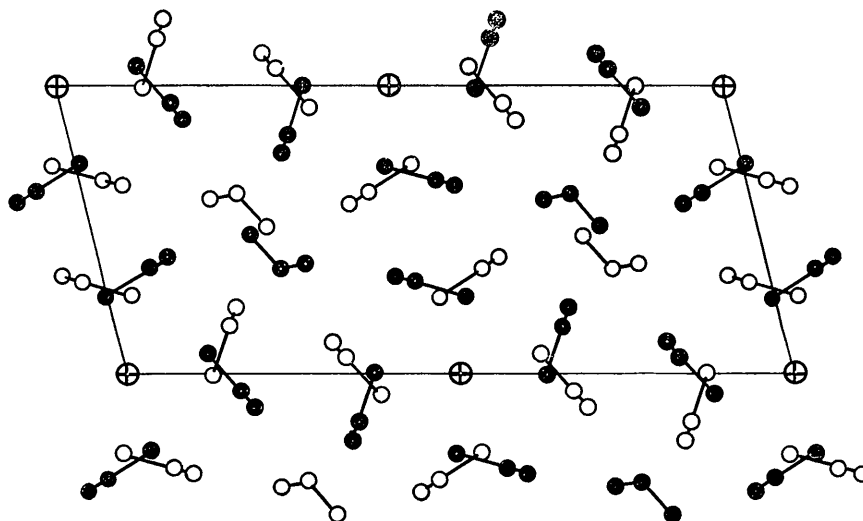


Fig. 9. Structure of the  $\text{TlClO}_3 \cdot 4\text{thiourea}$  complex shown in projection along  $[001]$ . The same convention as in Fig. 3 is used.

as evidenced by two O-P-O angles of 103 and 114°. Another interesting feature of the structure is that the phosphate ions do not lie in the same mirror planes as the thiourea molecules, but halfway between these. Although the positions of the hydrogen atoms in the structure were not determined experimentally, it appears that these positions are more favourable for hydrogen bonding with the -NH<sub>2</sub> groups than the positions in the mirror planes.

As already indicated, the orthorhombic rather than tetragonal symmetry of this complex is due to hydrogen bonding. As is obvious from Fig. 10, the oxygen atoms of the phosphate tetrahedra are all directed towards thiourea molecules which lie roughly parallel to [100] and away from the thiourea molecules which are roughly parallel to [010]. Hydrogen bonds therefore only occur parallel to [100]. This means that in (001) projection larger overlap between the phosphate and -NH<sub>2</sub> groups is possible with the thiourea molecules lying along [010] than with those along [100]. The *b* axis is therefore somewhat shorter than the *a* axis. It follows that the only reason why orthorhombic rather than tetragonal symmetry prevails is the fact that the phosphate group does not have the full fourfold symmetry required to form hydrogen bonds along both [100] and [010].

A further effect of the hydrogen bonding is apparent in the Tl---S separations in the structure, but this is illustrated more strikingly in the structure of the thallos benzoate.4thiourea complex (Verhoef & Boeyens, 1969) which is shown in Fig. 11. The -NH<sub>2</sub> groups of all thiourea molecules are seen to be directed towards the ends of benzoate ions containing carboxyl groups. This represents a drastic departure from the model structure since no conceivable arrangement of tetragonal coordination columns can lead to this configuration. The symmetry of the columns therefore changes from 4/*m* to *mm*. It is further found that, of the four thiourea molecules surrounding a carboxyl group, only the two lying nearly parallel to [100] are hydrogen bonded through their -NH<sub>2</sub> groups to the carboxyl oxygen atoms. These hydrogen bonds seem to enhance the dipole moment of the thiourea molecules and this leads to stronger Tl-S attractions and hence smaller Tl-S separations. For thiourea molecules involved in hydrogen bonding,  $d(\text{Tl} \cdots \text{S}) = 3.38 \text{ \AA}$  and for those not hydrogen bonded it is 3.45 Å. Similarly it is found that the sulphur atoms of neighbouring thiourea molecules which are both involved in hydrogen bonding are only 3.36 Å apart and for those not involved in hydrogen bonding this separation is 4.54 Å. The nature of this interaction is not known and it may be due to weak  $\pi$ -bonding.

#### Ionicity of the complexes

The structural studies outlined above prove conclusively that the cohesion in the thiourea complexes with ionic salts is largely due to ion-dipole attractions.

Using the calculable volumes occupied by ions in these complexes, it is possible to assess the degree of ionicity more quantitatively.

After a critical examination of the literature, Heide (1955) concluded that ionic radii represent physically

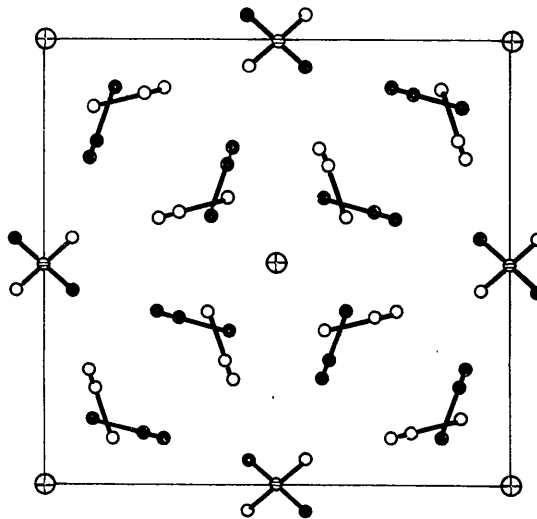


Fig. 10. Structure of the  $\text{TIH}_2\text{PO}_4 \cdot 4\text{thiourea}$  complex shown in projection along [001]. The shaded oxygen atoms have *z* coordinates of less than  $\frac{1}{4}$  for anions centred at  $\frac{1}{4}$  and the others have  $z > \frac{1}{4}$ .

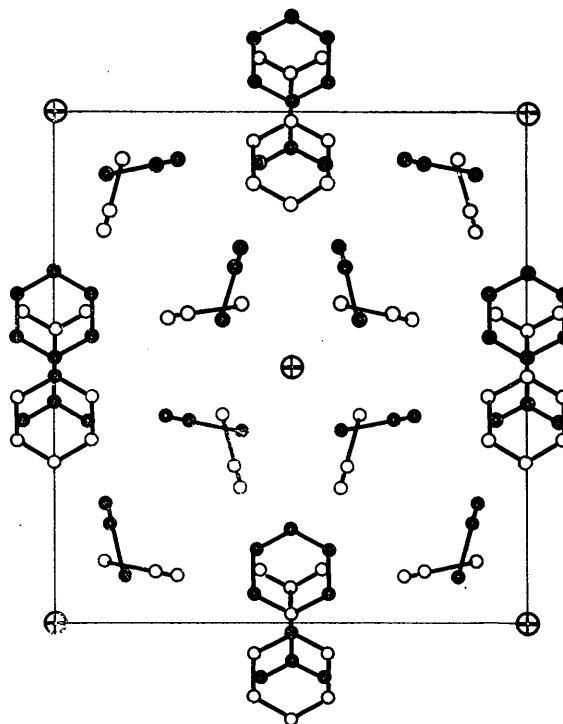


Fig. 11. Structure of the thallos benzoate.4thiourea complex according to the convention of Fig. 3, except that the mirror planes now occur at  $z = \frac{1}{4}, \frac{3}{4}$  and the cations at  $z = 0, \frac{1}{2}$ .



real quantities only if they are given as the sum of two such radii which defines the separation of two ionic centres of gravity. The ionic radii proposed by Pauling (1927, 1928), Goldschmidt (1926) and Zachariassen (1931) are of this type and thus based on crystallographic interionic distances. Born & Huang (1954) showed that these additive radii can also be derived from the radii of free ions obtained theoretically by Jensen (1936), by defining a penetration distance. The radii calculated by Jensen for free ions are usually thought of (Born & Huang, 1954) as not having any particular significance, as the real wave-mechanical electron densities have no uniquely definable radii. Since they do give a rough idea of ionic volumes it is nevertheless instructive to compare them with the additive radii. As can be expected, they are somewhat larger, as seen from Table 2 which gives the ratios of free radii to additive radii.

Table 2. Ratios of free ionic to additive radii

Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
1.37	1.41	1.44	1.45	1.26	1.21	1.19	1.16

In the case of the thiourea complexes it was demonstrated (Boeyens & Herbstein, 1967) that the iodide-complexes have cell volumes of 18 Å<sup>3</sup> per anion larger than the corresponding bromide complexes. Since the additive radii of an iodide ion (2.16 Å) and a bromide ion (1.95 Å) are not very different, it is reasonable to assume that, if both species are approximately spherical (negligible polarization), voids in the two lattices will be of about the same size in isomorphous complexes of a single cation. The difference in cell volumes can thus largely be ascribed to the difference in ionic volumes.

In order to obtain an estimate of actual atomic volumes, it is assumed that the effective radii differ from the additive radii by a constant factor,  $x$ , for both anions in their complexes.

Then

$$\frac{4}{3}\pi x^3[(2.16)^3 - (1.95)^3] = 18,$$

or

$$x = 1.17.$$

This factor agrees with the ratios of free to additive radii in Table 2. It can be concluded that the anions in the complexes are more 'free' than in ordinary ionic lattices and that Jensen's calculated radii may have some physical meaning.

### Cohesion in the complexes

It seems appropriate to assume that the free ions in alkali halide-thiourea complexes have unit charges, while the sulphur atoms and -NH<sub>2</sub> groups have charges determined by the dipole moment of thiourea polarized in the field of the free ions. Considering these partial charges to reside on the S and N atoms, calculations

(Boeyens & Gafner, 1968) have shown them to be -0.66e and 0.33e respectively. In terms of these charge distributions the Madelung energies of the model structure (Boeyens & Gafner, 1968), the RbI complex (Kruger & Boeyens, 1968) and the CsCl and CsF complexes (Boeyens, 1968c) were calculated. All these structure types were found to have lattice energies of approximately 179 kcal.mole<sup>-1</sup>. Since the electrostatic attractions between four moles of thiourea amount to approximately 17 kcal (Boeyens & Gafner, 1968), it follows that thiourea can form solid complexes of the present type only with alkali halides with lattice energies of less than approximately 162 kcal.mole<sup>-1</sup>. This prediction is borne out accurately by experiment. The only exception is CsF with a lattice energy of 173 kcal.mole<sup>-1</sup>. It has, however, been shown that its complex has two hydrogen bonds per formula unit which amounts to an energy contribution of 14 kcal.mole<sup>-1</sup> (Boeyens, 1968c). Although these results seem to rule out the possibility of complexing between thiourea and those alkali halides with lattice energies larger than 162 kcal.mole<sup>-1</sup>, there is the possibility that some or all of them might form thiourea complexes with different composition and/or of a different crystal-chemical class.

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