

The Crystal Structure of the 1:4 Caesium Chloride–Thiourea Complex

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(Received 30 August 1967)

The crystal structure of the complex, $\text{CsCl} \cdot 4(\text{SCN}_2\text{H}_4) \cdot \text{H}_2\text{O}$ has been determined by X-ray diffraction methods. The basic structure type was found to correspond to that of the alkali metal bromide, iodide and fluoride complexes of thiourea which are characterized by segregated columns of cations and anions, bridged by the polar thiourea molecules. In the present structure only the anionic environment differs from that found before and this shows that the structural details in this class of complex are determined by the anionic size, whereas the general structure type is determined by cation–sulphur interactions.

Introduction

A striking and so far unexplained feature of the series of ionic complexes formed between thiourea and ionic salts (Boeyens & Herbstein, 1966; Pfrepper, 1966) is the parallel between space group of the crystal and the anion involved (Boeyens & Herbstein, 1967). Whereas all the bromide and iodide complexes are tetragonal, all the chloride complexes are orthorhombic and isomorphous. These include the chlorides of Cs^+ , Rb^+ , NH_4^+ and Tl^+ , which represent a spread in cation radii from 1.75 to less than 1.49 Å. As shown by Boeyens & Herbstein (1967) the effective radius of thallium in these halide complexes is considerably less than 1.49 Å and probably very close to the value for K^+ , *viz.* 1.38 Å. Cationic size thus seems to have little effect on the details of the structure which are sensitive only to the size of the anion. This suggests that the arrangement of thiourea molecules around a cationic chain remains essentially the same in all structures and

that these ‘coordination’ columns arrange themselves so as to allow a best fit with the size of the accompanying anion. It was necessary to determine the structure of one of the chloride complexes to substantiate these ideas. Single crystals of only the caesium chloride complex were available.

Sample preparation

The isolation of a very low quality crystal of this complex has been reported before (Boeyens & Herbstein, 1967). Numerous attempts to repeat the preparation by crystallization from absolute alcohol ended in failure, yielding masses of satiny fibres which were much too delicate for crystallographic manipulation. An open test tube containing such material was left standing for eighteen months when it was found that solid state recrystallization had occurred. The density of these crystals was found to be slightly higher than that of the crystal described before (Boeyens & Herbstein,

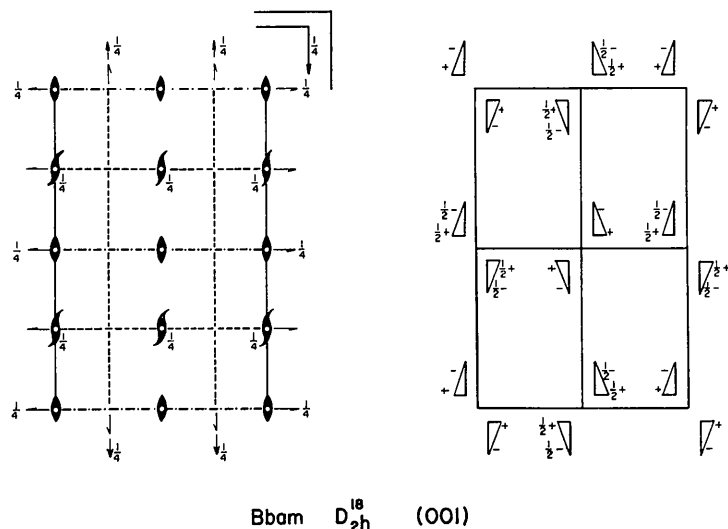


Fig. 1. Symmetry elements and operations of the space group $Cmca$ in the setting $Bbam$.

Table 2. Fractional coordinates of the atoms in the asymmetric unit for an overall temperature factor of 3.62 \AA^2 and $R_{hkl} = 0.14$

	x	y	z
Cs	0.3761	$\frac{1}{4}$	$\frac{1}{4}$
Cl	0.5970	0.2751	0
S(1)	0.3224	0.0546	0
S(2)	0.3013	0.1110	$\frac{1}{2}$
S(3)	0.4320	0.0792	$\frac{1}{2}$
S(4)	0.4527	0.1235	0
N(1)	0.2579	0.1426	0.1363
N(2)	0.3408	-0.0428	0.6363
N(3)	0.5009	0.1460	0.6363
N(4)	0.4264	-0.0496	0.1363
C(1)	0.2752	0.1182	0
C(2)	0.3304	-0.0042	$\frac{1}{2}$
C(3)	0.4791	0.1176	$\frac{1}{2}$
C(4)	0.4377	-0.0009	0
O	0.6925	0.2075	0

projection. The partially overlapping circles represent chloride ions and the isolated circles represent oxygen atoms associated with water molecules. Open and full circles represent atoms associated with molecules in the mirror planes at $z=0$ and $\frac{1}{2}$ respectively. The struc-

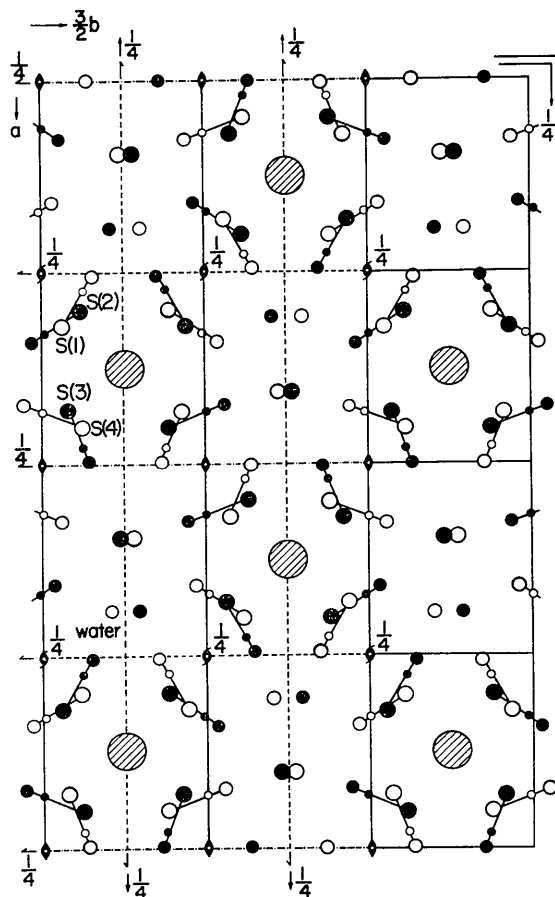


Fig. 2. Projection of the structure along [001]. Open circles indicate atoms belonging to molecules lying in the mirror plane in the paper and full circles refer to the mirror $c/2$ above the plane of the paper.

ture can be considered as columns consisting of thiourea molecules coordinated around a linear array of caesium ions, packed parallel to [001] in such a way as to leave elliptical channels for occupation by chloride ions and water molecules. Although not demanded by space group symmetry the axis of a column is, within experimental error, a fourfold rotation axis with respect to the thiourea molecules. This arrangement occurs in all ionic thiourea complexes investigated to date. Although the data are not reliable enough to allow calculation of accurate molecular parameters, it is clear that the Cs^+ -thiourea columns in this structure are almost identical with those in the $\text{CsF} \cdot 4(\text{thiourea}) \cdot 2\text{H}_2\text{O}$ structure (Boeyens, 1968) with a Cs^+ -S approach of 3.76 \AA and S-S distances of $\sim 4.28 \text{ \AA}$ within a column compared with 3.70 and 4.25 \AA in the CsF complex.

Discussion

In the ideal case the fourfold column axis is also a crystallographic fourfold 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 1:4 TlNO_3 and 1:8 Tl_2SO_4 -thiourea complexes (Boeyens & Herbstein, 1966). 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 directions normal to the chain to make close-packed contacts with the walls of the retaining channel. In the TlNO_3 -4(thiourea) room temperature structure both conditions are satisfied, the latter due to the disc-like nature of the rotationally disordered flat nitrate groups. In the Tl_2SO_4 -8(thiourea) structure there are only half as many sulphate as thallous ions in the parallel chains. The tetrahedral sulphate groups are large enough to buttress 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 equilibrium separation of thallous ions, would have occurred.

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 arrangement whereby the tetragonal symmetry of the channel is destroyed. To accommodate such a staggered chain, adjacent coordination 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 orthorhombic symmetry and is exemplified by the $\text{CsF} \cdot 4(\text{thiourea}) \cdot 2\text{H}_2\text{O}$ structure (Boeyens, 1968). In this structure the included anion is the elongated $(\text{F} \cdot 2\text{H}_2\text{O})^-$ hydrogen bonded unit. A somewhat similar situation is encountered in the present structure. In this case, however, the chloride is not hydrogen bonded to the water in the channel ($d(\text{Cl}-\text{O}) = 3.2 \text{ \AA}$) and the complex can also occur anhydrous with the same structure. 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 axis 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 $z=0, \frac{1}{2}$. 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 alcoholic solutions.

This structure therefore confirms that the basic structure type of the ionic thiourea complexes depends on cation-sulphur ion-dipole interactions which lead to the occurrence of linear coordination columns which arrange themselves in various ways to accommodate best the anion involved. This determines the space group. In the arrangement of such columns around chlorate ions a further factor, not yet described, seems to play a role since the 1:4 TlClO_3 -thiourea complex is monoclinic, space group $C2/m$ (Boeyens & Herbstein, 1967).

In this discussion the role of the cation has been largely ignored. It is however clear that the size of the anionic channel will depend directly on the cation-sulphur distances. No reliable data for these approaches are as yet available, but there is qualitative evidence that the range of existence of these complexes is defined by an interplay of cationic and anionic size factors.

Table 3. *Alkali halide-thiourea complexes existing in the solid state*

The thiourea complexes of the salts represented by circles exist as solids – the others not.

	Li	Na	K	Rb	Cs
F	×	×	×	×	0
Cl	×	×	×	0	0
Br	×	×	0	0	0
I	×	×	0	0	0

The only complexes of the alkali metal halides so far reported to exist in the solid state are those represented by circles in Table 3.

The lithium and sodium ionic radii are apparently too small to allow the type of eightfold coordination encountered in these complexes to occur. The remainder of Table 3 seems to represent a curious anomaly. One would expect the smaller cations to form more compact coordination columns. The more compact the columns, the smaller one would expect the diameter of the channels between them to be and hence the smaller the anions that can be included. Exactly the reverse is found experimentally. The only tentative explanation that suggests itself is that the stability of this type of complex depends on the total degree of close packing in the structure. For a cation of less than critical size perfect close packing in the column can never occur, irrespective of the size of the anion. The same applies to an anion of less than critical size in the channel. If both anion and cation are below the critical size, e.g. Cl^- and K^+ , the complex with thiourea can never attain sufficient rigidity to crystallize. In the case of Tl^+ the Tl-S bonding has more covalent character and this probably provides sufficient stabilization to permit the crystallization of both chloride and fluoride complexes. In the purely ionic complexes, however, the combined sizes of cation and anion seem to be the decisive factor.

A deeper understanding of this aspect is expected to be gained by a structure analysis of the $\text{RbI} \cdot 4(\text{thiourea})$ complex, which is now in progress.

I am indebted to Miss J. Hewitt of the National Research Institute of Mathematical Sciences for intricate alteration of the Gantzel and Hope Fourier program to allow its use on the 360/40 computer; likewise to H. J. Messerschmidt of IBM (SA) for his modifications to the Busing, Martin & Levy *ORFLS* program.

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