Ionic Complexes of Thiourea. II.[1a] Chemical and Crystallographic Survey and Determination of the Crystal Structures of Some Representative Complexes

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Cell dimensions and space groups are given for about 30 complexes of thiourea with some alkali halides, many thallium(I) salts, and two lead(II) salts (complexes of lithium and sodium halides with thiourea could not be prepared). The complexes all have closely related structures and can be considered to belong to a single family. Similarities of space groups and molar volumes allow further subdivision of this family into a number of groups. The largest group comprises the tetragonal complexes of formula MX·4TU (TU = thiourea) and includes those formed by most alkali bromides and iodides, thallous bromide, and thallous iodide. These complexes all have $a \sim 21$ A, $c \sim 8.2$ A, and space group P4/mnc and have ordered structures. The complex TlClO₄·4TU is a typical representative of this group and its crystal structure has been determined by three-dimensional X-ray diffraction techniques. Each thallium is surrounded by eight sulfur atoms at the corners of a distorted cube and each sulfur bridges two thalliums. Thus there are chains ···4S···Tl···4S···Tl··· along [001], with $d(Tl···S) = 3.43$ A, corresponding to ion–dipole interaction between Tl and S. The polar and polarizable thiourea molecules act as bridges between the separated cations and anions, the latter being found in channels whose walls are formed by the amine groups of the thioureas. Adjacent cation–thiourea chains have slightly different orientations and dimensions. The TlNO₃·4TU complex has, at room temperature, $a \sim 10$ A, $c \sim 8.2$ A, and space group P4/mcc, and its structure is a partially disordered version of the TlClO₄·4TU structure, adjacent cation–thiourea chains appearing to be identical because of the partial disorder. However, at $-160°$, these complexes have similar ordered structures. The Pb(NO₃)₂·6TU complex has, at room temperature, $a \sim 10$ A, $c \sim 24.6$ A, and space group P4/mcc, and shows considerable diffuse scattering. Its structure is based on that of the TlNO₃·4TU complex but there is disorder in both cation and anion positions. The detailed nature of this disorder was not established. The tetragonal complexes Pb(ClO₄)₂·6TU and Pb(ClO₄)₂·6TU·2H₂O both have, at room temperature, $a = 18.64$ A and $c = 7.92$ A, and their space groups are, respectively, P4/mcc and I4/mcm. These two complexes are related by an order–disorder transformation in parts of their unit cells; other regions of the unit cells are disordered in both complexes at room temperature and complete refinement was not possible. Nevertheless it could be shown that, compared to the other structures, alternate cation–thiourea chains were absent. The complexes are more appropriately classified in terms of their structures than in terms of their compositions. In this sense there are two groups of related structures, with TlClO₄·4TU, Pb(NO₃)₂·6TU, and TlNO₃·4TU in the first group and Pb(ClO₄)₂·6TU and Pb(ClO₄)₂·6TU·2H₂O in the second. It is inferred that, given the general structure type, the detailed crystal structures depend mainly on anion shape and size.

1. Introduction

In 1888 Reynolds[3] reported a crystalline complex containing NH₄Br and thiourea in the ratio 1:4.[4] This was the first example of what is now known to be a large family in which some alkali halides and many thallium(I) salts can replace NH₄Br. When M and X are singly charged ions, the general formula of the complexes is MX·4TU (TU = thiourea). The same cation:thiourea ratio is retained when the anion is doubly charged, as in Tl₂SO₄·8TU. There are also a number of Pb(II) complexes of formula PbX₂·6TU which belong to the present family. Some hydrated complexes are also known.

Despite their relatively large number, nothing definite is known about the structure of these complexes nor about the nature of the bonding between their components. It will be noted that, apart from lead, the metals involved do not form coordination complexes. The present paper describes the results of a chemical and crystallographic study in which all of the preparations described in the literature have been repeated and a number of new complexes have been obtained and in-

vestigated. The family of complexes has been divided into smaller groups from both chemical and crystallographic points of view and the crystal structures of two typical MX·4TU complexes (TlNO₃·4TU and TlClO₄·4TU) have been determined to ascertain the main structural features of the family. Two Pb(II) complexes (Pb(NO₃)₂·6TU and Pb(ClO₄)₂·6TU) have also been studied by X-ray diffraction to determine how they differ from the MX·4TU complexes. Preliminary accounts of these results have been published.[1]

2. General Chemical and Crystallographic Survey

2.1. Experimental Work.—The complexes can be prepared from solution or in the solid state. The first method is simple and was standardized by the early workers in the field.[5,6] It consists of dissolving the constituents in either ethanol or water or in a mixture of these solvents. The complexes crystallize out on cooling. In some instances the nature of the products depends on whether free acid is present in the solution. All the complexes studied in the present paper were prepared from solution.

Preparation of complexes in the solid state is useful for special purposes but has the disadvantage that the samples are necessarily polycrystalline. The method is based on the observation of Stewart,[7] using infrared spectroscopic methods, that complexes are formed when mixtures of thiourea and appropriate alkali halides are compressed into pellets. Stewart used 20 tons/in.[2]

(1) (a) Part I: J. C. A. Boeyens and F. H. Herbstein, *Nature*, **211**, 588 (1966); (b) see also *Israel J. Chem.*, **3**, 8p (1966).
(2) To whom correspondence should be addressed at the Department of Chemistry, Technion—Israel Institute of Technology, Haifa, Israel.
(3) J. E. Reynolds, *J. Chem. Soc.*, **53**, 857 (1888).
(4) This complex was recently rediscovered by G. R. Shultze, J. Schellhorn, and F. Boberg, *Monatsh.*, **96**, 778 (1965).

(5) J. E. Reynolds, *J. Chem. Soc.*, **59**, 383 (1891).
(6) A. Rosenheim and W. Loewenstamm, *Z. Anorg. Allgem. Chem.*, **34**, 72 (1903).
(7) J. E. Stewart, *J. Chem. Phys.*, **26**, 248 (1957).

TABLE I

CRYSTALLOGRAPHIC RESULTS FOR METAL SALT–THIOUREA COMPLEXES OF THE PRESENT FAMILY

Space group[a]	Complex	Impurities in sample[b]	Ref[c]	Solvent[d]	a, A	b, A	c, A	Z	Vol./ formula unit, A³	Density, g cm⁻³ Calcd	Measd
Ibam	CsF·4TU·2H₂O[e]	...	...	W	17.02	12.50	8.45	4	450	1.82	1.84
Bbam	RbCl·4TU	RbCl	...	M	32.10	13.15	8.35	8	441		
	CsCl·4TU[e,f]	TU	h	A	32.10	13.22	8.51	8	451	1.74	1.75
	TlCl·4TU	...	h	W	32.10	13.03	8.57	8	448		
	NH₄Cl·4TU	TU	i	M	32.16	13.19	8.55	8	453		
P4/mnc	KBr·4TU	KBr, TU	...	M	19.84		8.28	8	408		
	RbBr·4TU	RbBr	...	M	19.87		8.36	8	413		
	CsBr·4TU	...	...	M	20.04		8.46	8	425		
	TlBr·4TU	TU	h	W	19.78		8.29	8	406		
	NH₄Br·4TU	...	i	A	19.88		8.31	8	411		
	KI·4TU	...	h, j	A	20.29		8.29	8	427		
	RbI·4TU[e]	...	k	M	20.35		8.30	8	430	2.00	2.00
	CsI·4TU	...	k	M	20.49		8.43	8	442		
	TlI·4TU	TU	h	W	20.25		8.27	8	424		
	NH₄I·4TU	NH₄I	i	M	20.33		8.31	8	429		
	NH₄NO₃·4TU	TU	h	A	20.65		8.29	8	442		
	TlClO₄·4TU[e]		l, m, n	W	21.07		8.28	8	459	2.20	2.19
P4/mcc	TlNO₃·4TU[e]		h	W	10.34		8.29	2	443	2.14	2.15
	Tl₂SO₄·8TU[e]		o	Acid	10.49		8.29	1	912	2.03	2.03
	Pb(NO₃)₂·6TU[e]		p	W	10.25		24.6	4	646	2.02	2.03
	Pb(ClO₄)₂·6TU[e]		l, m	Acid	18.64		7.92	4	688	2.08	2.10
I4/mcm	Pb(ClO₄)₂·6TU·2H₂O[e]	...		W	18.64		7.92	4	688	2.17	2.18
P4/m[g]	TlF·4TU·2H₂O[e]	...		W	14.65		8.22	4	441	2.12	2.15
Cccm	Tl₂CO₃·8TU		h	W	14.14	13.87	8.40	2	839		
	TlNO₂·4TU[e]		q	W	14.75	13.95	8.33	4	429	2.14	2.15
B2/m	TlClO₃·4TU[e]		m	W	22.33	10.00[r]	8.25	4	443	2.21	2.20
Pcnm	TlCNS·4TU	...		W	21.36	10.43	8.21	4	457	2.06	2.07

[a] The systematic absences allow both centrosymmetric and noncentrosymmetric space groups. As only centrosymmetric space groups have been found in the complexes whose structures have been determined, it has been assumed that all of the complexes are centrosymmetric. The standard settings of the space groups Bbam, Pcnm, and B/2m given in the table are Cmca (no. 64), Pnma (no. 53), and C2/m (no. 12), respectively. The transformed settings are used here to emphasize the resemblances among the various groups of complexes. [b] The following samples were analyzed here: CsF·4TU·2H₂O, CsCl·4TU, Pb(ClO₄)₂·6TU·2H₂O, TlF·4TU·2H₂O, TlCNS·4TU. The results were in agreement with the formulas listed except for CsCl·4TU (see footnote *f* below). Impurities were identified in precipitated polycrystalline samples from the diffractometer patterns (Cu Kα, Philips high-angle diffractometer). Indexed powder patterns of all samples mentioned *explicitly* in this column have been submitted to the American Society for Testing Materials for inclusion in the Powder Data File. [c] Dots in this column indicate that we have not been able to find a prior reference to the preparation of the complex. [d] W = water, A = absolute ethanol, M = water–ethanol mixture. [e] Single crystals were obtained for these complexes. [f] Chemical analysis of the precipitate obtained indicated the formula CsCl·6TU, in agreement with Rosenheim and Loewenstamm.[6] However, the X-ray powder pattern showed that free thiourea was present. Although the calculated density for 6 units of CsCl·6TU/ unit cell (1.725 g cm⁻³) is not far from the measured value, this composition is incompatible with the space group Bbam which has only fourfold and eightfold positions. [g] There are no systematic absences and eight different space groups are possible. However structural considerations make it probable that the correct space group is P4/m. [h] See ref 6. [i] See ref 5. [j] See ref 8a. [k] See ref 8b. [l] C. Mahr and H. Ohle, *Z. Anal. Chem.*, **115**, 254 (1938). [m] C. Mahr and H. Ohle, *Ann. Chem. Liebigs*, **542**, 44 (1939). [n] C. Mahr and H. Klamberg, *Mikrochem. Mikrochim. Acta*, **40**, 390 (1953). [o] See ref 9. [p] R. C. Haworth and F. G. Mann, *J. Chem. Soc.*, 661 (1943). [q] L. P. McHatton and M. J. Soulal, *ibid.*, 4095 (1953). [r] β = 105°.

while we obtained similar results when pressures of 100 tons/in.² were applied for 24-hr periods. The samples were held at room temperature in both sets of experiments.

In the present study the principal method used for characterizing and classifying the complexes prepared has been X-ray diffraction. Single-crystal methods were used where possible but most of the complexes crystallized in compact masses of minute fibrous needles too small for single-crystal methods. Single crystals cannot be grown from the melt because of the temperature-dependent equilibrium between thiourea and ammonium thiocyanate. All samples gave sharp and well-defined powder patterns and these were successfully indexed (see Table I, footnote *b*), generally with the help of information obtained from appropriate single-crystal patterns.

Although confident assignment of space groups on the basis of the powder patterns is possible by analogy with the space groups determined for isomorphous complexes for which single crystals are available, some minor errors may have been made. The powder patterns of the TlNO₃ and TlF complexes can for instance be indexed in the same way. The different space groups

and cell dimensions were derived from slightly different features of the single-crystal patterns. Powder patterns alone would not have revealed the correct cell dimensions for the Pb(NO₃)₂ complex. The only space group assigned on powder work alone is that for the Tl₂CO₃ complex. Crystals of this complex consist of composite bundles of small needles with parallel [001] axes. The *c* spacing can thus be determined from an [001] oscillation photograph, but it proved impossible to disentangle any of the other very complicated single-crystal patterns. The systematic absences in the powder pattern fortunately seem to define the space group uniquely.

Standard analytical techniques have been used where chemical analyses were required. It is essential to check samples by X-ray diffraction before chemical analysis as misleading results may be caused by coprecipitation of thiourea and/or metal salt with the complex.

Densities were determined by a flotation method using mixtures of methylene bromide and chloroform. No attempt was made to determine the density when only powdered samples were available.

2.2. Results.—The chemical and crystallographic results are summarized in Table I.

2.2.1. Complexes of Alkali Metal and Ammonium Salts.—Despite the statement[6] that complexes of salts from Li to Cs can be prepared, we have succeeded in obtaining only those complexes listed in Table I. Thus no lithium or sodium salts[8] give complexes with thiourea nor do KF, KCl, or RbF. The results obtained by working with solutions are in agreement with the results of solid-state preparations by Stewart[7] and ourselves. A number of complexes of ammonium salts have been prepared. In agreement with the earlier work[6] we did not succeed in preparing complexes of any alkali metal salt containing doubly or triply charged anions.

2.2.2. Complexes of Thallium(I) Salts.—We were able to prepare thiourea complexes of all of the thallium(I) salts available to us. Crystallographic examination showed these complexes to be isostructural with the alkali halide complexes. The thallium(I) salt complexes thus provide a means of investigating the structural influence of the anion.

The complexes of all of the thallous halides were prepared as well as the complexes of thallous nitrate, nitrite, sulfate, carbonate, chlorate, perchlorate, and thiocyanate (see Table I for results and references to earlier work). Recently Pfrepper[9] has reported preparation of many of these complexes.

The instructions of Golovnia and Prokofieva[10] for the preparation of the 2:7 halide and nitrate complexes as well as the 1:6 and 1:7 sulfate complexes were followed carefully, but the products obtained were not found to be crystallographically different from the normal ones listed in Table I, except for coprecipitated impurities. It thus seems probable that the analytical figures of these authors refer to mixtures.

The sulfate complex prepared in sulfuric acid medium has a 1:8 ratio[10] while that prepared in neutral aqueous medium has the composition $Tl_2SO_4 \cdot 7TU \cdot 2H_2O$.[6] There is an interesting relationship between these two complexes. Both are obtained as good single crystals. Weissenberg photographs of the 1:8 complex show regular patterns of spots which give the cell dimensions and space group of Table I. The Weissenberg photograph of the hydrated 1:7 complex has an intricate pattern of sharp and diffuse reflections which in part shows a close resemblance to the corresponding Weissenberg photograph of the anhydrous complex. This suggests that there are similar arrangements of thallium atoms in the two complexes whereas the regular thiourea arrangement of the 1:8 complex is disturbed in the hy-

drated 1:7 complex. Neither of these complexes has been studied in detail.

2.2.3. Complexes of Calcium Salts.—An attempt was made to prepare the complexes $CaCl_2 \cdot 6TU$ and $CaI_2 \cdot 6TU$ described by Greenbaum[11] but no complexes could be obtained.

2.2.4. Complexes of Pb(II) Salts.—The well-known chemical similarities between compounds of lead and thallium suggested that some of the numerous lead salt–thiourea complexes reported in the literature may also belong to the present family. The structures of some 1:1 and 1:2 complexes formed by lead salts have been found to be of a different type.[12–14] There are however some 1:4 and 1:6 complexes which have not yet been investigated structurally. Five of these were prepared, of which two 1:6 complexes proved to belong to the present family. One of these is $Pb(NO_3)_2 \cdot 6TU$,[15] which has been studied previously and is discussed in more detail later in this paper. The second is tetragonal $Pb(ClO_4)_2 \cdot 6TU$, which crystallizes as yellow crystals from an aqueous solution of the components acidified with perchloric acid.[16] (We note here that Mahr and Ohle describe crystals obtained under these conditions as "white compact needles." The reason for the difference in color is not known. Mahr and Ohle give analytical figures but no other information whereby their material could be identified.) Our yellow complex had an initial density of 2.1 g cm⁻³; after exposure to the atmosphere for several days the density increased to 2.18 g cm⁻³ but there were no visible changes in the crystals. The density increase was accompanied by a change of space group although the cell dimensions remained the same, the increase in density being consistent with the uptake of two molecules of water per formula unit. All diffraction studies of the anhydrous material were made on crystals sealed into thin-walled Lindemann glass tubes. The structures of both hydrated and anhydrous crystals are described later in this paper.

The lead salt–thiourea complexes which do not belong to the present family are $PbCl_2 \cdot 4TU$, $Pb(CNS)_2 \cdot 4TU$, and triclinic $Pb(ClO_4)_2 \cdot 6TU$.

The $PbCl_2 \cdot 4TU$ complex has been prepared by the method of Walter and Storfer.[17] The crystallographic results are: $a = 19.35$, $b = 30.60$, $c = 5.82$ A, space group Pnma or Pn2₁a, observed density 2.23 g cm⁻³, calculated density for 8 formula units/cell 2.22 g cm⁻³. Nardelli, Cavalca, and Braibanti,[18] who used a different method of preparation, have reported that a complex of this composition has monoclinic symmetry and cell dimensions different from those given above.

The $Pb(CNS)_2 \cdot 4TU$ complex has been prepared by

(8) (a) E. A. Werner [*Proc. Chem. Soc.*, **22**, 245 (1906)] was the first to show that a sodium iodide complex could not be prepared; (b) W. R. G. Atkins and E. A. Warner [*J. Chem. Soc.*, **101**, 1167 (1912)] showed that a lithium iodide complex could not be prepared.

(9) G. Pfrepper, *Z. Anorg. Allgem. Chem.*, **347**, 160 (1966). The complexes prepared were characterized by chemical analyses; in some instances this appears to have led to erroneous conclusions, *e.g.*, formulation of thallium(I) iodide complex as TlI·6TU (*cf.* footnote *f* to Table I).

(10) V. A. Golovnia and I. V. Prokofieva, *Izv. Sektora Platiny i Drug. Blagorodn. Met., Inst. Obshch. i Neorgan. Khim., Akad. Nauk SSSR*, **27**, 62 (1952); *Chem. Abstr.*, **50**, 16526d (1956).

(11) F. R. Greenbaum, *J. Am. Pharm. Assoc., Pract. Pharm. Ed.*, **18**, 784; *Chem. Zentr.*, **100**, II, 2344 (1929).

(12) M. Nardelli, G. Fava, and G. Branchi, *Acta Cryst.*, **13**, 898 (1960).

(13) M. Nardelli and G. Fava, *ibid.*, **12**, 727 (1959).

(14) L. Bru Villaseca and F. R. Fernandez, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **54A**, 311 (1958).

(15) See footnote *p* in Table I.

(16) See footnote *m* in Table I.

(17) G. Walter and E. Storfer, *Monatsh.*, **65**, 53 (1935).

(18) M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 867 (1956).

the method of Rosenheim and Meyer.[19] The diffraction photographs have proved to be complicated and have not yet been interpreted; however, it is clear that there is no structural relationship to the complexes of interest here.

The triclinic $Pb(ClO_4)_2 \cdot 6TU$ complex is prepared by dissolving the components in hot water and allowing the solution to cool slowly (the black precipitate, presumably PbS, which forms initially should be filtered off). Our chemical analysis shows the colorless crystals deposited to have a molar ratio of 1:6. The crystallographic results are: $a = 11.08$, $b = 12.03$, $c = 5.86$ A, $\alpha = 102°$, $\beta = 94°$, and $\gamma = 108°$. The measured density is 2.06 g cm^{-3} while that calculated for 1 formula unit/cell is 2.01 g cm^{-3}; the space group is P$\bar{1}$. Structural analysis[20] has shown that these crystals contain octahedral $Pb(TU)_6{}^{2+}$ cations and this is thus a normal coordination complex.

2.3. Discussion.—It will be seen from Table I that the c axes all lie in the range 7.92–8.57 A (except for $Pb(NO_3)_2 \cdot 6TU$ which has a trebled c spacing) and that the various sets of a and b axes also have dimensional resemblances which are shown diagrammatically in Figure 1. These close relationships among the unit cell dimensions strongly suggest that all of the structures are similar despite the occurrence of two different cation: thiourea ratios (1:4 and 1:6) and the presence of water molecules in some complexes. Further classification into smaller groups can be made in terms of common space groups and similar formula-unit volumes and this enables choice of strategic complexes for more detailed crystal structure analyses.

We consider first the complexes with four thiourea molecules per metal ion. Twelve of these have space group P4/mnc with $a \sim 21$ A and two have space group P4/mcc with $a \sim 10$ A. The extra reflections which lead to the doubling of the a axis and the different systematic absences are all weak and this at once suggests that the larger unit cell is derived from the smaller unit cell by an increase in the degree of order of the structural arrangement, the cell edges remaining in the same directions for both structures. This has been established qualitatively by photographing $TlNO_3 \cdot 4TU$ at $-160°$ where the a axis was found to have doubled and the space group changed to P4/mnc. Detailed structure analyses of $TlClO_4 \cdot 4TU$ and $TlNO_3 \cdot 4TU$ at room temperature provide a quantitative confirmation of this conclusion. The $TlF \cdot 4TU \cdot 2H_2O$ crystals have a tetragonal cell with $a = 14.65$ and $c = 8.22$ A and this is clearly derived from the partially disordered structure with $a \sim 10$ A resulting from the previous cell diagonals becoming the cell edges of the ordered unit cell. The structure thus lies between those of $TlNO_3 \cdot 4TU$ and $TlClO_4 \cdot 4TU$. In $TlNO_2 \cdot 4TU$ and $Tl_2CO_3 \cdot 8TU$ a different type of distortion, unspecified as yet in detail, leads also to lowering of symmetry; in these complexes the cell diagonals of the disordered
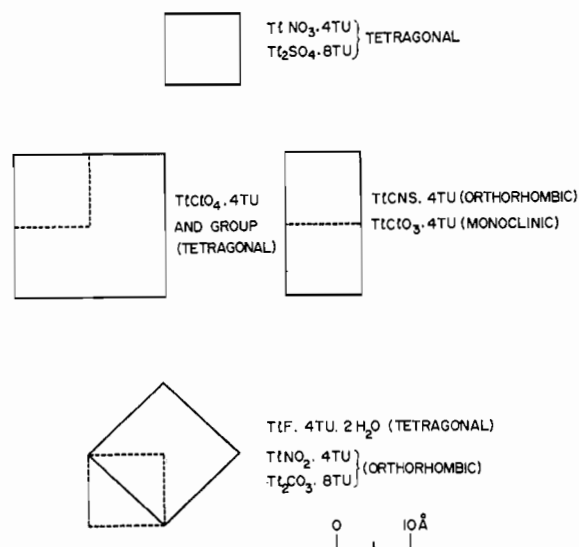
(19) A. Rosenheim and V. J. Meyer, *Z. Anorg. Allgem. Chem.*, **49**, 13 (1906).

(20) (a) F. H. Herbstein and M. Reisner, unpublished results, 1966; (b) J. C. A. Boeyens, submitted for publication.

Figure 1.—The relationship between the various ordered unit cells and the partially disordered unit cell with $a \sim 10$ A from which they are derived. The outline of the 10-A cell is indicated with broken lines in the other diagrams. Only the projection down [001] is given and minor distortions leading to lowering of symmetry have been disregarded in the diagrams but not in the legends.

unit cell become the edges of the ordered orthorhombic unit cell and this leads to fairly complicated domain structures in the ordered crystals.

The two complexes $TlClO_3 \cdot 4TU$ and $TlCNS \cdot 4TU$ both have $a \sim 2b \sim 21$ A and it seems reasonable to suppose that here the ordering has taken place in one direction only and that a resultant distortion had led to a lowering of the unit cell symmetry. Thus examples of all possible ways in which ordering can occur in a tetragonal cell with $a \sim 10$ A have been found among the complexes so far examined. This is illustrated in Figure 1.

Five other complexes with a metal ion–thiourea ratio of 1:4 have been prepared and studied. Some special remarks are required here. The $CsCl \cdot 4TU$ complex is definitely anhydrous, as proved by measurement of the density of a single crystal (the unreliability of analytical figures has already been mentioned). No such unambiguous claims can be made for the other chloride complexes because (a) their densities could not be measured because of their fibrous nature; (b) analytical figures (which are available only for Tl$^+$ and NH$_4{}^+$ complexes) can be misleading; and (c) their apparent isomorphism with $CsCl \cdot 4TU$ is not unassailable (space groups cannot be determined unambiguously from powder patterns; water molecules, as in the $Pb(ClO_4)_2$ complex, do not necessarily alter cell dimensions). However, the close relationship within this group of four chloride complexes is demonstrated by the closeness of the volumes per formula unit which lie in the range 441–453 A^3 and by the fact that the chloride complexes all have the same (or nearly the same) space group, different from that of the majority of the complexes. Another indication of a fairly substantial difference between the two groups is obtained by com-

parison of the volumes per formula unit for, say, CsCl·4TU and CsBr·4TU. The volume per formula unit is 26 Å³ *less* for the bromide than for the chloride complex, a situation that would be inconceivable for isostructural complexes.

Two lead salt complexes with a metal ion:thiourea ratio of 1:6 have been obtained and their cell dimensions show that both are related, but in different ways, to the first group of 1:4 complexes discussed above.

Four hydrated complexes have been prepared in the course of the present work. The $Pb(ClO_4)_2 \cdot 6TU$ complex can take up two molecules of water without change in cell dimensions and the structure analyses reported later in this paper show that this water is zeolitic. In the $CsF \cdot 4TU \cdot 2H_2O$ complex it has been found that the water molecules have an important structural role.[20b] The complicated diffraction patterns found for $Tl_2SO_4 \cdot 7TU \cdot 2H_2O$ have been mentioned earlier. Nothing is yet known in detail about the structure of $TlF \cdot 4TU \cdot 2H_2O$.

A striking feature of Table I is the parallel between space groups and the anions involved: for example, all of the chlorides and only the chlorides have space group Bbam. There are also parallels between the nature of the anions and cations involved and the dimensions and volumes of the unit cells. However these points are more conveniently dealt with during the discussion of the results of the structure determinations.

3. Crystal Structure Analyses of Representative Complexes with $M^+:TU = 1:4$

3.1. Choice of Complexes for Structure Analysis.—
The structural basis for understanding the cohesion in these complexes is to be provided by analysis of the crystal structures of representative examples. It has already been pointed out that the 1:4 complexes studied here can apparently be classified into various ordered and partially disordered structure types on the basis of their various cell dimensions. It has also been shown that $TlNO_3 \cdot 4TU$ is partially disordered at 25° and ordered at −160° but the extra reflections found at −160° are too weak for their intensities to be measured accurately. Thus it was decided to choose the complex $TlClO_4 \cdot 4TU$ as a representative of one of the ordered structure types and $TlNO_3 \cdot 4TU$ as a representative of the partially disordered type;[21] analysis of their crystal structures should reveal most of the general features of this portion of the family of complexes. An additional reason for choosing the nitrate and perchlorate complexes was to simplify comparison between the $MX \cdot 4TU$ complexes on the one hand and $Pb(NO_3)_2 \cdot 6TU$ and $Pb(ClO_4)_2 \cdot 6TU$ on the other.

The chloride complexes and those of CsF and TlF fall into different groups. The structure of $CsF \cdot 4TU \cdot 2H_2O$ has been determined by J. C. A. B. and will be reported later,[20b] and work on the structures of $CsCl \cdot 4TU$ and $TlF \cdot 4TU \cdot 2H_2O$ is planned for the future.

3.2. Experimental Work.—
The methods used for all of the structure analyses described in this paper will be summarized here. Cell dimensions were measured from oscillation and Weissenberg photographs by visual estimation, the usual multiple-film technique[22] being used. Cu Kα radiation was used exclusively. Absorption corrections were applied for cylindrical samples,[23] care being taken to choose crystals that satisfactorily fulfilled this requirement. Unobserved reflections were given a value of $1/3I_{min}$;[24] corrections were also made for $\alpha_1-\alpha_2$ splitting. These values were then corrected for Lorentz, polarization, and spot-shape factors. In some instances the corrected intensities for individual layer lines were put on an approximately absolute scale by Wilson's[25] method but no attempt was made to put the various layer lines on the same scale experimentally. The scale factors of the individual layer lines were, however, among the adjustable parameters of the full-matrix, least-squares refinement program used.

The structures were generally determined by Patterson methods and refined by Fourier, difference-synthesis, and least-squares methods. The computer programs used for these methods, for the correction of intensities, and for the analysis of the results have been listed elsewhere.[26] The atomic-scattering factors of Cromer, *et al.*,[27] were used for Tl⁺ and those of Hanson, *et al.*,[28] were used for all other atoms. Appropriate corrections were applied for anomalous scattering.[29]

3.3. Determination of the Structure of $TlNO_3 \cdot 4TU$.
—A batch of yellow tetragonal needles bounded by [100] faces was obtained from aqueous solution and a crystal of average diameter 0.007 cm was selected for measurement of intensities. A total of 362 independent *hkl* reflections (41 with $I_{obsd} = 0$) was included in the analysis; this is 77% of the total number of reflections within the sphere of reflection for Cu Kα.

A three-dimensional Patterson synthesis showed that the sulfur atoms (and by implication also the carbons) must lie in the mirror planes at $z = 0, 1/2$ (*i.e.*, at the eightfold positions m $(x, y, 0)$, etc.). This in turn means that the two thallium atoms in the unit cell must lie at positions a $(0, 0, 1/4; 0, 0, 3/4)$. The positions of the nitrogen atoms above and below the mirror planes were then deduced from the Patterson map and found to be compatible with the known geometry of the thiourea molecule. At this stage there were no clear indications of the positions of the atoms of the nitrate ions. A set of structure factors was calculated from the available atomic positions and the signs obtained used in the calculation of a three-dimensional electron-density map which showed the positions of all atoms except those of the nitrate ions.

The only indication of the presence of the nitrate group was a pillar of electron density along $[1/2, 1/2, z]$ with local maxima at $z = 1/4$ and $1/2$. Further local maxima occurred in 16-fold general positions just off the fourfold axis near $z = 3/8$. The atoms of the nitrate

(21) This complex was first studied crystallographically by E. G. Cox, A. J. Shorter, and W. Wardlaw [*J. Chem. Soc.*, 1886 (1938)], who did not obtain the correct cell dimensions and space group.

(22) M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, p 86.

(23) See ref 22, p 204.

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

(25) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(26) J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.*, **69**, 2160 (1965).

(27) D. T. Cromer, A. C. Larson, and J. T. Waber, *Acta Cryst.*, **17**, 1044 (1964).

(28) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, **17**, 1040 (1964).

(29) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 213.

groups were distributed among these positions in a statistical manner. Refinement was now continued by least squares, all atoms being given individual isotropic temperature factors. The final R factor ($R = \Sigma|\Delta F|/\Sigma|F_o|$) was 0.079; the final atomic coordinates are given in Table II and the observed and calculated structure factors on an absolute scale are given in Table III. The Debye–Waller factors of the four atoms of the nitrate ion are so large that it is clear that their positional parameters have no physical significance.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS WITH THEIR ESTIMATED STANDARD DEVIATIONS FOR $TlNO_3\cdot 4TU$

	Atom	x	y	z	B, A^2
	Tl	0	0	$^1/_4$	5.8
					0.1
	S	−0.0411	0.2614	0	5.1
		0.0006	0.0006		0.2
	C	0.107	0.334	0	5.6
		0.002	0.002		0.6
	N	0.168	0.367	0.147	5.4
		0.001	0.001	0.002	0.3
Disordered	O	0.398	0.458	0.125	22.1
		0.006	0.010	0.009	3.5
	$^1/_2$N(1)	0.5	0.5	0.25	14.1
					5.4
	$^1/_2$N(2)	0.5	0.5	0	10.5
					3.8

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS ON AN ABSOLUTE SCALE FOR $TlNO_3\cdot 4TU$

H	F_o	F_c
L = 0, K = 0		
2	134	134
3	162	159
4	108	106
5	112	99
6	89	78
7	56	53
8	59	55
9	15	15
10	7	7
11	16	20
12	11	11
13	1	2
L = 0, K = 1		
1	139	136
2	61	63
3	206	198
4	139	133
5	79	78
6	55	49
7	64	55
8	61	60
9	34	31
10	16	16
11	19	21
12	13	13
13	3	5
L = 0, K = 2		
2	64	64
3	80	85
4	122	132
5	63	64
6	50	50
7	73	69
8	63	54
9	29	33
10	25	25
11	20	23
12	16	19
13	4	8
L = 0, K = 3		
3	55	61
4	113	122
5	58	66
6	44	49
7	71	70
8	34	36
9	24	22
10	14	17
11	15	16
12	10	14
L = 0, K = 4		
4	123	131
5	59	62
6	33	32
7	41	44
8	39	35
9	14	19
10	14	13
11	5	8
12	4	5
L = 0, K = 5		
5	58	65
6	40	46
7	40	40
8	32	34
9	20	17
10	12	15
11	13	16
12	5	9
L = 0, K = 6		
6	37	40
7	23	29
8	31	33
9	18	20
10	16	17
11	13	15
L = 0, K = 7		
7	17	19
8	16	19
9	13	15
10	7	10
11	2	5
L = 0, K = 8		
8	7	7
9	8	9
10	3	6
L = 0, K = 9		
9	11	14
L = 1, K = 1		
2	42	36
3	41	−39
4	47	−45
5	12	−14
6	41	−38
7	19	−20
8	6	−6
9	9	−9
10	6	−5
11	2	−2
12	1	8
L = 1, K = 2		
3	34	−36
4	15	9
5	36	41
6	1	−3
7	10	−9
8	9	8
9	2	2
10	2	0
11	2	−0
12	1	0
L = 1, K = 3		
4	13	15
5	40	40
6	7	12
7	7	6
8	20	19
9	11	12
10	2	−2
11	2	−1
12	1	2
L = 1, K = 4		
5	1	3
6	6	−7
7	18	−20
8	2	1
9	5	6
10	6	−6
11	2	−2
12	3	3
L = 1, K = 5		
6	12	−13
7	20	−23
8	2	−5
9	2	3
10	6	−6
11	4	−3
L = 1, K = 6		
7	2	−0
8	7	8
9	7	7
10	3	−2
L = 1, K = 7		
8	6	6
9	6	6
10	1	1
L = 1, K = 8		
9	3	0
L = 2, K = 0		
1	66	−82
2	114	−127
3	69	−67
4	53	−52
5	109	−99
6	101	−87
7	59	−48
8	42	−35
9	43	−37
10	38	−32
11	21	−18
12	13	−11
L = 2, K = 1		
1	128	−141
2	169	−175
3	106	−99
4	71	−65
5	94	−87
6	80	−75
7	47	−42
8	33	−32
9	38	−35
10	29	−28
11	14	−12
12	6	−6
L = 2, K = 2		
2	179	−185
3	112	−113
4	82	−79
5	85	−85
6	72	−73
7	43	−39
8	24	−22
9	26	−27
10	24	−20
11	4	−6
12	3	−4
L = 2, K = 3		
3	83	−80
4	69	−68
5	75	−76
6	75	−74
7	45	−42
8	28	−24
9	30	−29
10	25	−22
11	14	−11
12	10	−9
L = 2, K = 4		
4	44	−46
5	47	−51
6	53	−55
7	37	−37
8	33	−30
9	37	−34
10	28	−25
11	17	−13
12	12	−10
11	17	−13
12	12	−10
L = 2, K = 5		
5	49	−51
6	49	−49
7	29	−29
8	21	−22
9	22	−21
10	13	−13
11	9	−8
L = 2, K = 6		
6	39	−40
7	23	−24
8	16	−17
9	10	−12
10	6	−7
11	5	−5
L = 2, K = 7		
7	27	−23
8	23	22
9	19	−15
10	14	−11
L = 2, K = 8		
8	24	−18
9	13	−11
10	11	−9
L = 3, K = 1		
2	43	−42
3	8	−11
4	7	−5
5	16	−16
6	17	−14
7	38	−31
8	14	−15
9	3	−1
10	4	−5
11	1	1
L = 3, K = 2		
3	7	−7
4	12	−14
5	1	−2
6	9	10
7	1	0
8	12	11
9	7	8
10	7	−8
11	1	−2
L = 3, K = 3		
4	24	27
5	37	40
6	11	11
7	17	−2
8	14	12
9	8	10
10	1	0
11	1	1
L = 3, K = 4		
5	17	19
6	19	−18
7	15	−14
8	1	2
9	1	0
10	1	−1
11	1	−1
L = 3, K = 5		
6	17	−20
7	10	−9
8	1	2
9	1	−1
10	6	−5
11	4	−5
L = 3, K = 6		
7	4	−6
8	1	2
9	5	6
10	1	0
L = 3, K = 7		
8	4	5
9	10	8
L = 3, K = 8		
9	2	2
L = 4, K = 0		
1	112	124
2	91	89
3	111	104
4	121	113
5	39	35
6	26	24
7	43	41
8	30	31
9	20	19
10	7	9
11	6	7
12	5	7
L = 4, K = 1		
1	91	87
2	45	45
3	72	71
4	92	84
5	51	53
6	42	39
7	49	47
8	32	31
9	16	16
10	10	10
11	13	14
12	9	12
L = 4, K = 2		
2	33	32
3	67	63
4	65	66
5	46	45
6	34	36
7	37	39
8	37	40
9	20	20
10	16	15
11	18	18
12	8	12
L = 4, K = 3		
3	85	89
4	60	60
5	42	44
6	23	23
7	27	29
8	33	36
9	16	17
10	10	11
11	10	12
L = 4, K = 4		
4	58	63
5	47	52
6	33	36
7	28	29
8	22	22
9	4	6
10	4	5
11	5	8
L = 4, K = 5		
5	34	34
6	19	22
7	26	28
8	21	21
9	13	15
10	12	12
11	7	8
L = 4, K = 6		
6	16	20
7	23	25
8	19	18
9	17	16
10	12	13
L = 4, K = 7		
7	15	17
8	7	8
9	8	7
10	3	6
L = 4, K = 8		
8	7	8
9	7	8
L = 5, K = 1		
2	10	−5
3	12	−13
4	12	−12
5	10	−9
6	15	−14
7	19	−15
8	6	−6
9	3	−3
10	4	−3
L = 5, K = 2		
3	9	−9
4	2	−1
5	8	10
6	3	1
7	1	−2
8	6	5
9	3	3
10	4	−2
L = 5, K = 3		
4	12	13
5	21	23
6	7	7
7	1	1
8	10	9
9	6	7
10	1	−0
L = 5, K = 4		
5	8	7
6	9	−8
7	9	−10
8	1	1
9	1	2
10	2	−2
L = 5, K = 5		
6	9	−10
7	8	−10
8	1	−0
9	1	0
10	3	−4
L = 5, K = 6		
7	1	−2
8	1	3
9	3	4
L = 5, K = 7		
8	2	3
9	3	4

Projections of the structure of $TlNO_3\cdot 4TU$ down [001] and [010] are shown in Figure 2. The nitrate ions are enclosed in a roughly cylindrical channel whose walls consist of the amine groups of the thiourea molecules and the hypothetical position of one NO_3^- group is marked. The three-dimensional arrangement of sulfur atoms about each thallium atom is shown in Figure 3. The thallium atom has eight equidistant sulfur neighbors at distances of 3.43 ± 0.015 A. These are related in groups of four by the fourfold axis passing through the thallium atom. Within one of these groups the S···S distance is 3.87 A whereas that between sulfurs along [001] is 4.14 A. The thallium atom environment is an almost tetragonal prism slightly distorted toward an antiprism. More detailed diagrams of the cation and anion environments are given in Figures 4 and 5.

3.4. Determination of the Structure of $TlClO_4\cdot 4TU$.—The crystals are light yellow tetragonal needles elongated along [001] and showing {100} and {130} faces. The average diameter of the crystal used for intensity photographs was 0.01 cm and the intensities of 1611 *hkl* reflections (581 with $I_{obsd} = 0$) were measured; this is 78% of the reflections within the sphere of reflection for Cu Kα.

The structure was determined by analysis of the three-dimensional Patterson function, bearing in mind the necessarily close resemblance to the structure of $TlNO_3\cdot 4TU$. The three-dimensional Patterson did not reveal the differences in the atomic arrangements about the fourfold axis at [0, 0, z] and the twofold axis at [0, $^1/_2$, z] but did confirm that, as in the $TlNO_3$ complex, the thiourea molecules must all lie in the mirror planes at z = 0 and $^1/_2$ with the nitrogen atoms related by the mirror planes. The perchlorate groups were also seen to lie in the same mirror planes with their chlorine atoms slightly off [$^1/_4$, $^1/_4$, z].

A structure factor calculation based on the atomic positions derived from the Patterson synthesis gave R = 0.39. Least-squares refinement of atomic coordinates and individual isotropic temperature factors ceased at R = 0.122. A three-dimensional difference synthesis showed three of the oxygen atoms of the perchlorate group to be vibrating anisotropically. As the least-squares program available to us did not allow isotropic and anisotropic Debye–Waller factors to be refined simultaneously, we first refined anisotropically
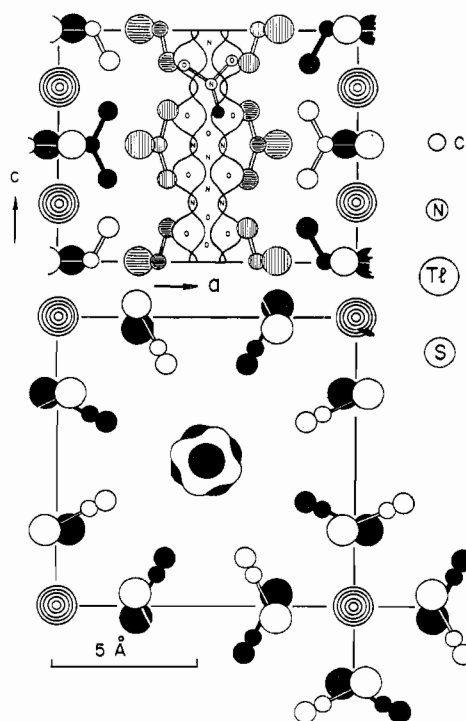
Figure 2.—The structure of the $TlNO_3 \cdot 4TU$ complex is shown in projection down [001] and [010]. Atoms represented by filled circles in the projection down [001] are in the mirror plane in the plane of the paper, while those represented by open circles are in the mirror plane lying $c/2$ above or below the plane of the paper. The nitrogen atoms of a thiourea molecule are related by the mirror planes and coincide in the projection. The full-circle molecules in the [010] projection lie about $a/4$ below the plane of the paper and 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.

the motion of the two independent oxygen atoms (one of these lies in the mirror plane), convergence being reached at $R = 0.118$. A further slight improvement was obtained by refining (with individual isotropic temperature factors) the positional and thermal parameters of all atoms other than the two anisotropic oxygens. Convergence was considered complete when all parameter shifts were less than 10% of the estimated standard deviations. At this stage $R = 0.117$ and $R_1 = 0.098$ ($R_1 = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2}$. Because of the approximate nature of the absorption corrections, the high number of unobserved reflections included in the treatment, and the high atomic number of thallium no attempt was made to weigh the observed structure factors differentially and unit weights were assigned to all reflections.

The final atomic parameters are given in Tables IV and V and observed and calculated structure factors are compared in Table VI.

The final structure is shown in projection down [001] in Figure 6, which should be compared with the analogous projection in Figure 2. The two thallous ions have slightly different environments which are conveniently discussed by reference to Figure 3. The details of the interatomic distances are given in the cap-
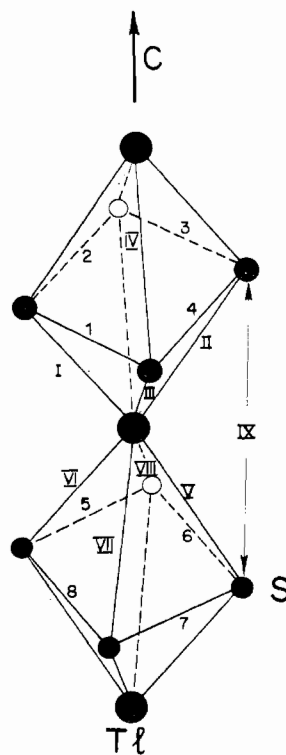
Figure 3.—The arrangement of sulfur atoms about the thallium in a thallium–thiourea chain. Similar arrangements are found in the $TlNO_3 \cdot 4TU$ and $TlClO_4 \cdot 4TU$ structures but there are small differences in interatomic distances which are detailed below. In both structures $\sigma(Tl \cdots S) \sim 0.009$ A and $\sigma(S \cdots S) \sim 0.015$ A. (1) In $TlNO_3 \cdot 4TU$: All $d(Tl \cdots S)$ are equivalent and equal 3.43 A; all $d(S \cdots S)$ in (001) are equivalent and equal 3.87 A; IX $= c/2 = 4.14_5$ A. (2) In $TlClO_4 \cdot 4TU$: (a) The chain along [0, 0, z]: 1–2–3–4 = 3.82 A; 5–6–7–8 = 3.98 A; I–II–III–IV = 3.43 A; V–VI–VII–VIII = 3.46 A; IX = 4.14 A. (b) The chain along [0, $^1/_2$, z]: 1–3–6–8 = 3.87 A; 2–4–5–7 = 3.91 A; I–II–VII–VIII = 3.44 A; III–IV–V–VI = 3.44 A; IX = 4.13 A.

Figure 4.—A perspective view of the cation–thiourea chain in $TlNO_3 \cdot 4TU$. The central black atoms are the thalliums while the other spheres, in order of decreasing radius, represent sulfur, nitrogen, and carbon. All molecules lying across the same mirror plane are marked in the same way.

TABLE IV

FRACTIONAL ATOMIC COORDINATES AND INDIVIDUAL
TEMPERATURE FACTORS FOR TlClO₄·4TU AND THEIR
ESTIMATED STANDARD DEVIATIONS FOR THE ATOMS WITH
ISOTROPIC TEMPERATURE VIBRATIONS[a]

Atom	x	y	z	B, A^2
Tl$_A$	0	$^1/_2$	$^1/_4$	3.42
				0.04
Tl$_B$	0	0	0.2441	3.56
			0.0003	0.04
S$_A$	0.1221	-0.0536	0	2.5
	0.0003	0.0003		0.1
S$_B$	-0.0187	0.3707	0	2.7
	0.0003	0.0003		0.1
S$_C$	0.5210	0.1284	0	3.1
	0.0003	0.0003		0.1
S$_D$	0.3726	0.4875	0	3.3
	0.0003	0.0003		0.1
C$_A$	0.172	0.014	0	1.8
	0.001	0.001		0.4
C$_B$	0.056	0.330	0	1.6
	0.001	0.001		0.4
C$_C$	0.447	0.165	0	2.1
	0.001	0.001		0.4
C$_D$	0.345	0.409	0	1.6
	0.001	0.001		0.4
N$_A$	0.189	0.039	0.141	3.1
	0.0006	0.0006	0.002	0.3
N$_B$	0.081	0.315	0.141	3.4
	0.0007	0.0007	0.002	0.3
N$_C$	0.419	0.178	0.139	3.0
	0.0006	0.0006	0.002	0.3
N$_D$	0.333	0.382	0.138	3.2
	0.0007	0.0007	0.002	0.3
Cl	0.2444	0.2138	0	3.0
	0.0003	0.0003		0.1
O	0.304	0.249	0	3.0
	0.001	0.001		0.4

[a] The letter subscripts refer to the lettering of the molecules in Figure 6. The oxygen atom lies on the perchlorate threefold axis shown in Figure 6.

Figure 5.—A perspective view of the idealized anion environment in TlNO₃·4TU. The black spheres are purely schematic representations of the disordered anions.

plane nearer to the thallium is larger than that further from it (d(S···S) = 3.98 and 3.82 A, respectively), and consequently the thallium–sulfur distances are nearly the same at 3.43 and 3.46 A. The top and bottom squares of the sulfur atoms have a relative rotation of 18.1°. Thus the angles of twist in the two chains are very close to one another.

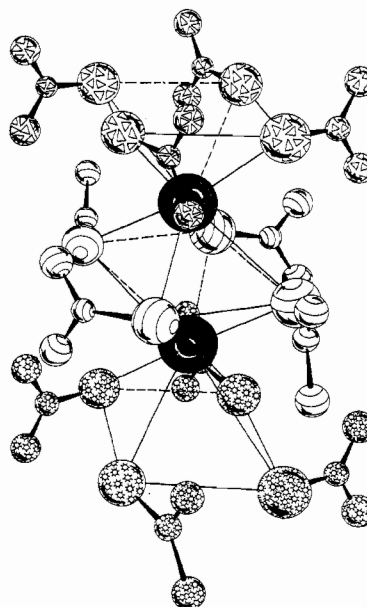Because of the highly anisotropic vibrations of the perchlorate ion, it is difficult to assign errors to the positions found for its atoms, but the separation of 1.46

TABLE V

FRACTIONAL COORDINATES AND VIBRATION PARAMETERS FOR OXYGENS WITH ANISOTROPIC DISPLACEMENTS FOR TlClO₄·4TU[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
1	0.196	0.249	0	0.002	0.010	0.19	0.002	0	0
	0.001	0.002	...	0.001	0.002	0.05	0.001	...	...
2	0.244	0.168	0.128	0.008	0.005	0.029	-0.004	-0.003	0.003
	0.001	0.001	0.004	0.001	0.001	0.006	0.001	0.002	0.002

[a] The anisotropic Debye–Waller factors are given by: $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviations are given below each value.

tion to this figure. The environment of the thallous ion on the twofold axis is very similar to that in TlNO₃· 4TU. The eight sulfur atoms surrounding the thallous ion are at the corners of a twisted rhombic prism with the thallous ion at its center. The sulfur–sulfur distance along the chain is 4.14 A, while normal to the chain axis the two values are 3.87 and 3.91 A. The thallium–sulfur distances are 3.44 and 3.43 A. The top and bottom halves of the prism are rotated by 17.6° with respect to one another and do not deviate significantly from squareness although this is not required by the space group. The thallous ion on the fourfold axis is also surrounded by eight sulfurs but it is displaced from the center of its coordination polyhedron by 0.05 A. The square of sulfur atoms in the mirror

A between the chlorine atom and the isotropic oxygen is similar to the Cl–O distance of 1.48 ± 0.03 A found by Gluyas in lithium perchlorate.[30]

The separation of the nitrogen and oxygen atoms is of particular importance because of possible hydrogen bonding. Unfortunately the only N···O distances for which reliable values can be obtained are those from the isotropic oxygen to N$_C$ and N$_D$. These distances are 3.06 and 3.10 A and are not less than the van der Waals separation between nitrogen and oxygen given by Pimentel and McClellan.[31] The TlNO₃·4TU complex was examined by infrared spectroscopy but there

(30) R. E. Gluyas, *Dissertation Abstr.*, **17**, 2800 (1957).

(31) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 292.

Table VI

Observed and Calculated Structure Factors on an Absolute Scale for TlClO$_4$·4TU[a]

Figure 6.—The structure of the TlClO₄–TU complex shown in projection down [001]. Only one-fourth of the unit cell is shown, but the symmetry elements inserted permit generation of the rest of the structure. Except for the thallium atoms which lie at $z \sim 1/4$, all of the atoms shown as full circles lie in the mirror plane at $z = 0$ and those shown as open circles are in the mirror plane at $z = 1/2$. A double circle represents two atoms related by a mirror plane coinciding in projection.

was no evidence for the formation of NH···O bonds.[32]

A rigid-body analysis[33] of the motion of the perchlorate group has been made. The vibration about the axis shown in Figure 6 for the perchlorate group at $z = 1/2$ is of the order of 30° but all of the other tensor elements are insignificant. It is not possible from the available evidence to decide whether this is entirely a thermal effect or whether there is an appreciable contribution from static disorder.

3.5. The Crystal Structures of TlNO₃·4TU and TlClO₄·4TU. 3.5.1. Mutual Relationship.—The structure of the perchlorate complex differs from that of the nitrate complex in that the arrangements of thallium atoms and thiourea molecules about $[0, 0, z]$ and $[0, 1/2, z]$ are not equivalent. Although not required by the space group, the thiourea molecules around $[0, 1/2, z]$ are almost related by a fourfold axis. The difference in the arrangements around $[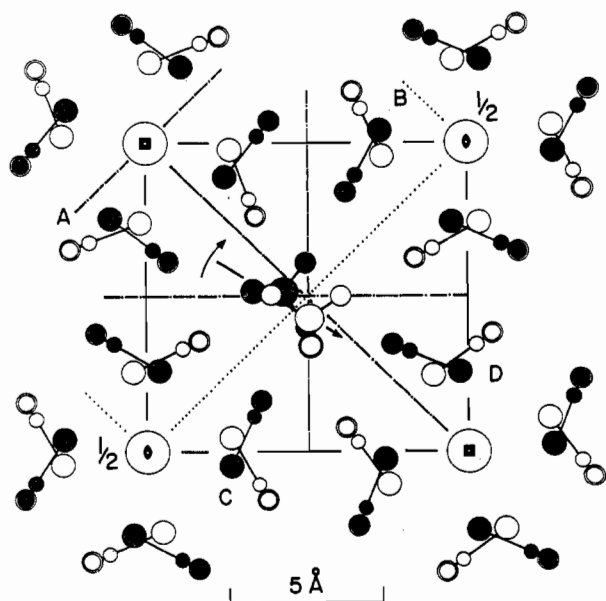0, 0, z]$ and $[0, 1/2, z]$ can thus be ascribed to two factors: a small relative rotation of the two sets of thiourea molecules and a shift of the thallium atoms on the fourfold axis along $[0, 0, z]$. It has been pointed out earlier that at $-160°$ the TlNO₃ complex has the same type of structure as the TlClO₄ complex but that the superlattice reflections are exceedingly weak. This may be due either to closely similar arrangements around $[0, 0, z]$ and $[0, 1/2, z]$ or else simply to a transformation temperature only slightly above $-160°$. Nothing is yet known about the nature of the transformation.

The Debye–Waller factors of the atoms of the thiourea molecules in the TlNO₃ complex are all consider-

(32) We are indebted to Mr. G. N. Krynauw for this work.
(33) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754 (1956).

ably higher than those in the TlClO₄ complex even though both structures were determined at room temperature. The higher Debye–Waller factors probably result from the occurrence of two slightly different orientations for the thiourea molecules distributed approximately at random through the TlNO₃ complex crystals. The atoms in the average orientation obtained from the structure analysis therefore have higher Debye–Waller factors than normal, but the atomic displacements are static rather than dynamic.

The essential difference between the two structures is in the positions occupied by the anions. In the TlNO₃ complex the nitrate groups are disordered along the fourfold axis which is also the axis of the cylindrical channel enclosed by NH₂ groups. In the perchlorate complex this channel has an elliptical rather than a circular cross section because of the different orientations of the thiourea molecules about $[0, 0, z]$ and $[0, 1/2, z]$. The perchlorate ions lie across at the mirror planes at $z = 0$ and $z = 1/2$ and are related by a c glide; the anions thus need not have the same x and y coordinates. The arrangement of the anions seems to be the reason why the low-temperature ordered structure has space group P4/mnc and doubled a axis compared to the higher temperature, partially disordered structure with space group P4/mcc. It is true that the latter situation is the less complicated but it requires not only the cations but also the anions to have the same x and y coordinates and to be exactly $c/2$ apart. However the equilibrium separation between anions can only fortuitously equal the distance between cations. Thus one would expect successive anions, which are larger than the cations and far less constrained by their surroundings, to have different x, y coordinates and thus to be shifted off the channel axis. This destroys the symmetry required by P4/mcc, the a axis doubles, and the space group changes to P4/mnc. The temperature (or temperature range) at which the partial disordering takes place presumably depends on the shape and size of the anion and the degree of its interaction with the amine groups of the surrounding thiourea molecules. It also seems possible that the displacement of the thallium atoms on the fourfold axes from $z = 1/4$ may be due ultimately to the slight bulging of the anion channels approximately along [110].

The Tl₂SO₄·8TU complex is a special case. Here the average separation of sulfur atoms (of sulfate groups) in the channel is 8.3 A: there would thus seem to be sufficient space for sulfate ions to arrange themselves linearly in an undistorted channel. The fact that the sulfate group has no fourfold axis is therefore the only reason why this complex should avoid the space group P4/mcc. By taking up two different orientations statistically, the crystallographic symmetry demands can however be met. The Tl₂SO₄ complex may therefore have the space group P4/mcc and $a \sim 10.5$ A even at low temperatures.

3.5.2. Interatomic Distances and Molecular Dimensions.—The most important facts for assessing the nature of the bonding in these complexes are the dis-

TABLE VII

DEPENDENCE OF CELL DIMENSIONS OF THIOUREA COMPLEXES OF VARIOUS METAL BROMIDES AND
IODIDES ON NATURE OF CATIONS AND ANIONS (SOME RELEVANT DATA FOR THE SALTS ARE ALSO INCLUDED)

| Cation in complex | r^+ for C.N. 8,[a] A | —— c of complex, A —— | | ——Cell vol., A³—— | | | Diff between iodide and bromide complexes | | Vol. diff per ion between MI and MBr,[c] A³ |
		Bromide	Iodide	Bromide complexes	Iodide complexes	Δa, A	¹/₈ × (diff in unit cell vol.), A³	
K⁺	1.38	8.28	8.29	3260	3414	0.45	19	16.3
Tl⁺	1.49	8.29	8.27	3245	3392	0.47	18	*11.4*
NH₄⁺	1.53	8.31	8.31	3286	3434	0.45	18	*16.6*
Rb⁺	1.53	8.36[b]	8.30	3302	3438	0.48	17	18.5
Cs⁺	1.75	8.46	8.43	3396	3538	0.45	17	16.5

[a] See footnote 34. [b] This value is probably too high. [c] The values for salts with B2 (CsCl) structure are italicized; the other salts have the B1 (NaCl) structure.

tances between thallium and sulfur atoms and the shape of the coordination polyhedron of sulfurs about thallium. The variations in $d(Tl\cdots S)$ found here in both complexes are probably not significant and it is sufficient to consider only the single value $d(Tl\cdots S) = 3.43$ A. Similarly, it is adequate for the present discussion to take the coordination polyhedron as a tetragonal prism with $c/a \sim 1.1$.

The covalent radii for thallium and sulfur can be taken as 1.5 and 1.0 A, respectively, whereas the corresponding ionic radii are 1.49 and 1.84 A.[34] Thus the Tl$\cdots$S distance found in the two complexes studied here corresponds to ionic and not to covalent interaction. The experimental value for $d(Tl\cdots S)$ is about 0.10 A longer than the value obtained by summing the ionic radii. A similar lengthening of the Na$\cdots$O distances is found in some of the complexes of sodium iodide with oxygen-containing molecules to be discussed later (section 3.5.4). However the appropriateness of the ionic radii of oxygen and sulfur used in these calculations is not established and so the significance of the bond lengthening is not certain.

The shape and size of the coordination polyhedron of sulfur about thallium can be compared with similar situations in other crystals. The closest comparison is probably with thallosothallic sulfide Tl⁺(Tl³⁺S₂).[35,36] Here the Tl(III) atoms are linked by sulfur atoms to form chains of tetrahedra sharing faces $(d(Tl\cdots S) = 2.6$ A) and the interactions are essentially ionic. The Tl(I) atoms lie between the chains in positions of eight-coordination $(d(Tl\cdots S) = 3.3$ A) and these interactions are also ionic. Similar comparisons can be made between the alkali halide complexes of thiourea and various thio salts.[37] A rather similar environment is found in NH₄Cu₇S₄,[38] where the NH₄ ion is in the middle of a tetragonal prism of sulfur atoms. Dimensions of the prism are 3.93 × 3.93 × 3.84 A and $d(N\cdots S) = 3.38$ A, a little larger than that (3.30 A) found in NH₄SH.[39] In KFeS₂[40] the potassium ion is surrounded

in an irregular way by eight sulfur atoms and $d(K\cdots S) = 3.35$ A.

The dimensions of the three independent thiourea molecules in TlClO₄·4TU do not differ significantly among themselves, nor significantly from those of thiourea in the TlNO₃·4TU complex nor indeed from those of thiourea itself,[41] nor from those of thiourea in various covalently bonded complexes.[42] The presence of the relatively heavy metal atoms makes it difficult to validate small differences in the dimensions of thiourea molecules in different environments and earlier speculations about the effects of complex formation are as yet unsubstantiated.

3.5.3. Variation of Cell Dimensions in the Isomorphous Complexes with TlClO₄·4TU Structure.— The complexes of formula MX·4TU (with M⁺ = K⁺, Tl⁺, NH₄⁺, Rb⁺, and Cs⁺ and X⁻ = Br⁻, I⁻, and some other anions) are isomorphous with TlClO₄·4TU. The regular variation in their cell dimensions has already been noted (section 2.3) and can be largely explained using the present results for the TlClO₄·4TU structure. Most of the relevant experimental facts are summarized in Table VII which is based on the results given in Table I. Similar features hold for the NH₄Br–NH₄NO₃ and TlBr–TlI–TlClO₄ complexes.

It has been pointed out earlier that, in the TlClO₄·4TU structure, the anions are related only by a c glide and thus need not have the same x and y coordinates. The separation of two neighboring anions in the z direction is therefore not determined by the interionic distance, since there may be appreciable differences in the other two coordinates. This explains why the c spacings of the series of complexes depend only on the nature of the cation, while the a spacings depend on the size of the anion (see Table VII).

Comparison of unit cell volumes shows that the volume occupied by an iodide ion is about 18 A³ larger than that occupied by a bromide ion. The volume differences for the bromides and iodides of the cations of Table VII are also listed in this table.[43] Except for thallium, which is mentioned again below, the volume

(34) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Clarendon Press, Oxford, 1962 p 71. The radius for C.N. 8 has been obtained by multiplying that for C.N. 6 by 1.036. (C.N. = coordination number.)
(35) H. Hahn and W. Klinger, *Z. Anorg. Chem.*, **260**, 110 (1949).
(36) V. Scatturin and E. Frasson, *Ric. Sci. Suppl.*, **26**, 3382 (1956).
(37) See ref 34, pp 534–539, for review.
(38) G. Gattow, *Acta Cryst.*, **10**, 549 (1957).
(39) C. D. West, *Z. Krist.*, **88**, 97 (1934).
(40) J. W. Boon and C. H. MacGillavry, *Rec. Trav. Chim.*, **61**, 910 (1942).

(41) N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 2551 (1958).
(42) Bis(thiourea)–cadmium formate: M. Nardelli, G. F. Gaspari, and P. Boldrini, *Acta Cryst.*, **18**, 618 (1965), and the references contained therein.
(43) A compilation of cell dimensions of the alkali and thallium halides is given by R. W. G. Wyckoff, "Crystal Structures," Vol. 1, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1963.

increments obtained by replacing bromide with iodide ions appear to be very similar for salts and complexes. The limited data do not suggest any particular dependence on coordination number (C.N.). As polarization effects are likely to be small in the complexes, one may take 18 A³/ion as a reasonable average value of the bromide–iodide volume increment.

An equally detailed comparison of any two cationic radii in the complexes is not possible since only bromide and iodide complexes can be compared. The fluorides and chlorides have different space groups and their molecular volumes show little dependence on cation type. The following observations can however be made: for both bromide and iodide complexes the Rb^+ and NH_4^+ complexes have virtually identical cell volumes. This is in satisfactory agreement with the same ionic radii usually assigned to Rb^+ and NH_4^+. Unfortunately, this comparison cannot be extended to the salts because of the different crystal structures of rubidium and ammonium halides.

The position of thallium(I) in Table VII requires some comment. The TlBr·4TU and TlI·4TU complexes have slightly *smaller* unit cell volumes than the corresponding KBr and KI complexes; further, the c axes of all of these complexes are very similar. Nevertheless the ionic radius of Tl^+ is given as 1.49 A and that of K^+ as 1.38 A, while the present results show that the measured value $d(Tl \cdots S)$ in the TlClO₄·4TU complex would not be compatible with an ionic radius for Tl^+ of less than 1.49 A. These facts suggest that the effective radius of Tl^+ is less in the halide complexes than in the perchlorate complex, leading to the conclusion that the halide complexes have more covalent character than the perchlorate complex. It is interesting to note that the thallium(I) halides are practically insoluble in water but dissolve in aqueous thiourea solutions and this may be due to formation of complexes in solution, although probably with structures somewhat different from those of the solid complexes.

3.5.4. Comparison with Other Complexes.—Members of the present family of thiourea complexes are formulated as ionic complexes with the polarizable thiourea molecules acting as bridges between the separated cations and anions. The main cohesive forces are therefore due to ion–dipole interactions. Although the cations and, particularly, the anions are contained in channels of thiourea molecules, these thiourea molecules are not bonded to one another as they are in the thiourea–hydrocarbon channel inclusion complexes and description of the present complexes in terms of thiourea channels does not seem to have adequate physical basis.

The crystal structures of a number of other complexes have been determined where the components are ionic salts and neutral, but polar, molecules. One family in particular shows close resemblances to the present family of thiourea complexes. These are the 1:3 complexes of NaI with $(CH_3)_2NCHO$,[44] $(CH_3)_2CO$,[45] and

CH_3OH;[46] the structure of $LiClO_4 \cdot 3H_2O$[47,48] is also similar in many ways. In $NaI \cdot 3(CH_3)_2CO$, for example, there are chains of composition $Na^+ \cdot 3(CH_3)_2CO$ with the chain axis along the hexagonal axis of the crystal. Each Na^+ ion is surrounded by an octahedral arrangement of oxygen atoms of the carbonyl groups. The iodide ions are not in contact with one another in the channels between the methyl groups but appear to be bonded to the methyl groups by van der Waals forces. Thus the cations have analogous environments in both families of complexes but the anions are much less strongly bound to the rest of the structure in the thiourea complexes than in the sodium iodide complexes of the oxygen-containing molecules.

Various features of the structures of the two related families of complexes can be usefully discussed in terms of some of Pauling's rules.[49] It has already been shown that, in the family of thiourea complexes, the cations are surrounded by eight sulfur atoms in a distorted cubic arrangement and that a similar arrangement is found about potassium and ammonium ions in $KFeS_2$ and $NH_4Cu_7S_4$, respectively. On the other hand, the complexes of NaI with oxygen-containing molecules have a distorted octahedral arrangement of oxygen atoms about the cation. Sodium ions appear generally to have an octahedral environment of oxygen atoms and, in $NaCrS_2$,[37] there is also an octahedral environment of sulfur atoms about sodium. These facts are in harmony with Pauling's first rule, in terms of which the radius ratio determines the coordination. The radius ratios for various cations, oxygen, and sulfur are given in Table VIII. As a rough guide it is found that octahedral arrangements are favored for $r^+/r^- < 0.732$ and cubic arrangements for $r^+/r^- > 0.732$, and the results for the complexes are in agreement with this. It seems probable that, if a complex of a sodium halide with thiourea is prepared, then it will not belong to the present family but will have an octahedral arrangement of sulfur about the sodium ion.

TABLE VIII
VALUES OF RADIUS RATIO r^+/r^- FOR VARIOUS CATIONS
WITH OXYGEN AND SULFUR[a]

	Na⁺ (0.95)	K⁺ (1.33)	Rb⁺ (1.48)	Cs⁺ (1.69)	Tl⁺ (1.44)
O²⁻ (1.40)	0.68	0.95	1.06	1.20	1.03
S²⁻ (1.84)	0.52	0.72	0.81	0.92	0.78

[a] The ionic radii in angstroms (C.N. 6) are given in parentheses. The singly underlined r^+/r^- values indicate where octahedral arrangements have been reported and those doubly underlined indicate a cubic arrangement of anions about cation. No underlining means that a complex of this general type has not been reported.

In both families of complexes the coordination polyhedra about the cations are joined by shared faces. As would be expected, both coordination polyhedra are distorted so as to increase the distance between ad-

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

(45) P. Piret, Y. Gobillon, and M. van Meerssche, *ibid.*, 205 (1963).
(46) P. Piret and G. Mesureur, *J. Chim. Phys.*, **62**, 287 (1965).
(47) C. D. West, *Z. Krist.*, **88**, 198 (1934).
(48) R. C. Evans, "Crystal Chemistry," 2nd ed, Cambridge University Press, London, 1964, pp 291–292.
(49) See ref 34, pp 83–86.

jacent 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).

It seems probable that the symmetries of typical crystals of the two families of complexes—the tetragonal symmetry of the thiourea complexes and the hexagonal symmetry of the crystalline complexes studied by Piret and his co-workers—must be attributed to the symmetries of the respective arrangements of polar molecules about the cations of the cation–molecule chains.

It should be noted that not all complexes of salts and neutral polar molecules are built up on the same principles as the two families discussed above. Some of these complexes (*e.g.*, sucrose–sodium bromide dihydrate[50] and bis(cysteylglycine)–sodium iodide[51]) have quite complicated structures with hydrogen bonding playing an important role while in the tetraethylammonium bromide–bis(succinimide) complex[52] the general constructional principle has been described as one of "local neutralization of charge"—not only are the positive (NH) and negative (oxygen) ends of the polar succinimide molecules directed toward anions and cations, respectively, but anions and cations are themselves in contact.

4. Crystal Structure Analyses of Two Complexes with $Pb^{2+}:TU = 1:6$

There are two tetragonal 1:6 complexes of Pb(II) salts—$Pb(NO_3)_2 \cdot 6TU$ and $Pb(ClO_4)_2 \cdot 6TU$, which appear to belong to the present family. Their cell dimensions show that their structures are different and both structures have been determined in order to establish the relationship of these $PbX_2 \cdot 6TU$ complexes to the $MX \cdot 4TU$ and $M_2Y \cdot 8TU$ complexes.

4.1. The Lead Nitrate–Thiourea Complex.

The $Pb(NO_3)_2 \cdot 6TU$ complex was first prepared by Rosenheim and Meyer[19] and its chemical formula has been the subject of some controversy. Rosenheim and Meyer gave the stoichiometric formula as $2Pb(NO_3)_2 \cdot 11TU$ and this result was supported by Mahr and Ohle.[16] However, Haworth and Mann[15] preferred the composition $Pb(NO_3)_2 \cdot 6TU$. These formulas are all based on the results of chemical analyses. Our own conclusions come from crystallographic considerations and are most conveniently discussed at the end of this part of this paper. In agreement with Haworth and Mann we prefer $Pb(NO_3)_2 \cdot 6TU$ and we shall continue to use this formulation, deferring justification until later. The complex was first studied by X-ray diffraction by Bru and his co-workers,[53] who gave the correct space group but used as composition $6Pb(NO_3)_2 \cdot 32TU$; the structure briefly described by Bru[54] is not in accordance with our present results. A [001] rotation photograph shows both sharp and diffuse layer

lines. The sharp layer lines correspond to a spacing of 24.6 A, layer lines with $l = 1, 2, 5, 7$, and 11 being absent or very weak. Zero and upper layer Weissenberg and precession photographs show that the crystals are tetragonal with $a = 10.25$ A; the systematic absences show that the space group is P4/mcc (No. 124) (assuming a center of symmetry as explained in footnote *a* to Table I). This description is oversimplified as it takes no account of the diffuse layer lines. A Weissenberg photograph of such a layer shows some structure consisting of diffuse spots with the correct tetragonal symmetry. The only interpretation is long-range disorder but appreciable short-range order in the structure.

This complicated situation has deterred us from attempting a three-dimensional analysis of the structure and also makes it difficult to establish the chemical composition of the complex by arguments based on space group symmetry alone. For our present purposes it is sufficient to note that the subcell 10.3 $\times$ 10.3 $\times$ 8.2 A has virtually the same dimensions as the unit cell of $TlNO_3 \cdot 4TU^1$ and that there is no evidence for any disorder in the (001) projection of the $Pb(NO_3)_2$ complex. Thus a two-dimensional analysis using $hk0$ reflections should indicate any differences between the two structures *in projection*. A total of 79 $hk0$ reflections was used in constructing a Fourier projection down [001], all signs being taken as positive. This agreed almost exactly with the corresponding projection of the $TlNO_3$ complex. Least-squares refinements of the x, y, and B parameters of the atoms ceased at $R = 0.109$. In this refinement the thallium atoms of the $TlNO_3 \cdot 4TU$ structure were replaced with atoms with $f = {}^2/_3 f_{Pb}$; there were also twice as many nitrate groups as before but the positions obtained for their atoms are unlikely to have much physical significance because of the disorder, which was also shown in the Fourier projection by a relatively featureless plateau of electron density near $^1/_2$, $^1/_2$, $-$. The final atomic parameters are given in Table IX. The observed and calculated structure factors are compared in Table X.

TABLE IX

Fractional Atomic Coordinates and Isotropic Temperature Factors with Their Estimated Standard Deviations for the Structure of $Pb(NO_3)_2 \cdot 6TU$ in [001] Projection

Atom	x	y	B, A^2
Pb	0	0	2.8 (0.2)
S	−0.036 (0.002)	0.246 (0.002)	5.8 (0.8)
C	0.135 (0.008)	0.345 (0.008)	2.9 (1.8)
N	0.173 (0.004)	0.372 (0.004)	6.9 (1.3)
O	0.35 (0.01)	0.45 (0.01)	16.0 (5.6)
N	0.5	0.5	5.0 (1.2)

The over-all agreement is sufficient to confirm the general similarity of the $Pb(NO_3)_2 \cdot 6TU$ and $TlNO_3 \cdot 4TU$ structures. The variation in individual Debye–Waller factors is caused by the fact that in the proper unit cell ($c = 24.6$ A) three sets of crystallographically independent thiourea molecules are in positions of near overlap in projection but in the refine-

(50) C. A. Beevers and W. Cochran, *Proc. Roy. Soc.* (London), **A190**, 257 (1947).
(51) H. B. Dyer, *Acta Cryst.*, **4**, 42 (1951).
(52) H. M. Powell and E. Wait, *J. Chem. Soc.*, 1866 (1958).
(53) L. Bru, M. P. Rodriguez, M. Cubero, and E. Moreno, *Anales. Real Soc. Espan. Fis. Quim.* (Madrid), **53A**, 59 (1957).
(54) L. Bru, *Acta Cryst.*, **10**, 798 (1957).

TABLE X

OBSERVED AND CALCULATED STRUCTURE FACTORS ON AN
ABSOLUTE SCALE FOR Pb(NO₃)₂·6TU

H	F_o	F_c		H	F_o	F_c		H	F_o	F_c		H	F_o	F_c
L = 0, K = 0				7	48	44		6	41	44		10	17	25
1	75	91		8	63	61		7	73	70		11	21	22
2	88	85		9	48	45		8	44	45		12	14	18
3	112	111		10	26	26		9	38	37		L = 0, K = 6		
4	84	83		11	25	29		10	26	27		6	47	45
5	104	106		12	21	25		11	25	21		7	32	37
6	82	80		13	13	17		12	19	21		8	46	42
7	48	45		L = 0, K = 2				L = 0, K = 4				9	32	30
8	65	65		2	31	17		4	124	124		10	24	22
9	31'	35		3	49	47		5	82	60		11	22	20
10	13	16		4	99	107		6	36	35		L = 0, K = 7		
11	18	23		5	61	52		7	43	44		7	19	27
12	22	22		6	37	43		8	48	43		8	32	29
13	10	15		7	51	50		9	33	32		9	25	28
L = 0, K = 1				8	63	56		10	26	28		10	15	21
1	89	106		9	41	44		11	12	20		11	7	21
2	70	44		10	37	33		12	9	18		L = 0, K = 8		
3	145	146		11	25	29		L = 0, K = 5				8	18	23
4	107	110		12	29	27		5	81	68		9	15	21
5	76	80		L = 0, K = 3				6	54	45		10	11'	16
6	51	32		3	15	15		7	51	43		L = 0, K = 9		
				4	104	106		8	47	39		9	20	19
				5	59	67		9	-37	29				

ment each of these sets of three molecules was treated as a single molecule. The Debye–Waller factor of the carbon atom is normal because the three C atoms seem to coincide fortuitously in projection.

Some of the interatomic distances in the structure using the average atomic positions are: $d(\text{Pb}\cdots\text{S}) = 3.29 \pm 0.03$ A and $d(\text{S–C}) = 1.97 \pm 0.15$ A. A C–N distance cannot be calculated from the results.

The Pb(NO₃)₂·6TU complex has much the same arrangement of thiourea molecules as TlNO₃·4TU, although there must be some differences in detail in the [001] direction. The nitrate ions are in disordered positions in the channels formed by the amine groups of the thiourea molecules while the cations partially fill the positions corresponding to those occupied by Tl⁺ ions in TlNO₃·4TU. Absences among the thiourea molecules seem improbable and we shall assume that there are 24 thiourea molecules per unit cell. The chemical formula is most logically expressed in terms of unit cell contents: Table XI contains the various proposed compositions expressed in these terms and the corresponding calculated crystal densities. The composition Pb(NO₃)₂·6TU gives the best agreement between observed and calculated densities and it is for this reason that we favor it. These arguments do not require the Pb(NO₃)₂:TU ratio to be integral, whereas, in TlNO₃·4TU, for example, symmetry considerations demand (effects of crystal defects being ignored) an integral TlNO₃:TU ratio. At present the accuracy with which the chemical composition can be expressed depends on the accuracy of the experimental chemical analyses and density measurements. Greater accuracy will only be attainable if the lead nitrate complex forms a completely ordered phase, perhaps at lower temperatures.

TABLE XI

DENSITIES CALCULATED FOR VARIOUS PROPOSED
COMPOSITIONS OF THE LEAD NITRATE–THIOUREA COMPLEX

Proposed compn (unit cell contents in formula units)		Calcd density,[a]	Ref
Pb(NO₃)₂	TU	g cm⁻³	
4.36	24	2.13	16, 19
4	24	2.05	15
4.5	24	2.16	53

[a] Measured density 2.03 g cm⁻³.

The 1:6 molar ratio means that there must be eight nitrate ions per unit cell and the separation along [001] between these will be about 3.1 A. As this is the approximate thickness of a nitrate ion, these ions must have their planes nearly parallel to (001) and are probably mainly azimuthally disordered. In TlNO₃·4TU the density of nitrate ions is only three-fourths as large and there are fewer restrictions on their positioning. *Given the general structure type*, it appears that the chemical composition of the lead nitrate–thiourea complex is determined by the space requirements of the nitrate ions.

4.2. The Lead Perchlorate–Thiourea Complexes.
4.2.1. Determination of Structures.—Diffraction photographs of the hydrated and anhydrous Pb(ClO₄)₂·6TU complexes differ only in the presence of a set of very weak hkl reflections with $h + k + l = 2n + 1$ on the photographs of the anhydrous complex; otherwise the reflections match in both position and intensity. Thus the anhydrous and hydrated complexes are ordered and partially disordered phases of the same structure; in contrast to the better known situation where increase in temperature causes the order–disorder transformation, here it is attack by water vapor. The hydrated complex has the higher symmetry, body-centered space group I4/mcm (No. 140). There is no difference in their cell dimensions.

It was decided first to determine the structure of the hydrated complex by three-dimensional methods in an attempt to locate the water molecules, not previously encountered in a structure of this type. The additional order in the anhydrous complex was then to be studied by two-dimensional methods. Quasi-cylindrical crystals of average diameter 0.01 cm were used and the intensities of 345 hkl ($l = 0, 1, 2$) reflections were measured for the hydrated complex and of 218 $hk0$ reflections for the anhydrous complex. Only sharp reflections were measured, but it should be noted that the [001] oscillation photographs, which were indistinguishable for the anhydrous and hydrated complexes, showed weak diffuse layer lines corresponding to a periodicity along [001] of 4 A. There were also indications of diffuse regions joining sharp reflections on the Weissenberg photographs. Quantitative treatment of these effects is difficult and they were ignored in the present structure analysis. However the detailed structures must be more complicated than those reported here.

The structure of the hydrated complex was solved by using the three-dimensional Patterson function. The thiourea molecules surrounding the chains of cations as well as the chlorine atoms were fully resolved in the Patterson, but little detail was discernible in the region around [0, ¹/₂, z]. A structure factor calculation based on the positions of the resolved atoms gave a residual $R = 0.28$. Least-squares refinement of these atomic positions ceased at $R = 0.14$, the final coordinates and Debye–Waller factors being given in Table XII. The observed and calculated structure factors on an approximately absolute scale are given in Table XIII.

TABLE XII

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC
TEMPERATURE FACTORS FOR $Pb(ClO_4)_2 \cdot 6TU \cdot 2H_2O$[a]

Atom	x	y	z	B, Å²
Pb	0	0	0.25	4.8 (0.1)
S	-0.0119 (0.0007)	0.1281 (0.0006)	0	3.3 (0.3)
C	0.060 (0.003)	0.181 (0.003)	0	4.0 (1.3)
N	0.091 (0.002)	0.202 (0.002)	0.12 (0.01)	5.6 (0.9)
Cl	0.3	0.2	0	7.0 (0.8)
Disordered atoms				
S	0.40	-0.10	0	19
O	0.26	0.14	0	16
O	0.26	0.24	0.07	26
O (water)	0.37	0.02	0	15

[a] Estimated standard deviations are given only where parameters have been refined by the method of least squares.

A three-dimensional Fourier synthesis, calculated using the refined coordinates, gave very little additional resolution. The [001] projection of this Fourier is shown in Figure 7. The sharp but elongated peaks on the (220) plane represent chlorine atoms. The surrounding diffuse region must be associated with the oxygen atoms of the perchlorate group, which are ob-
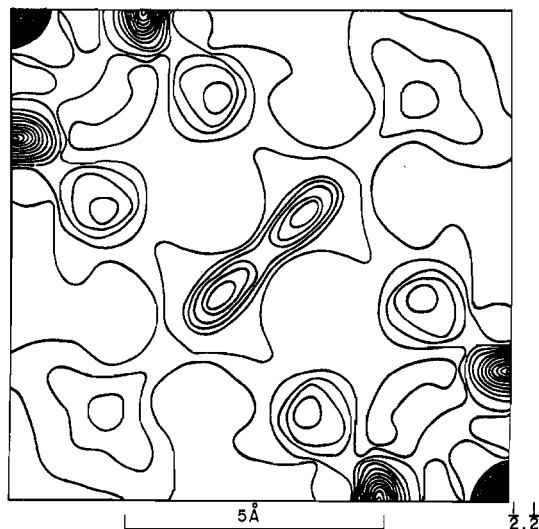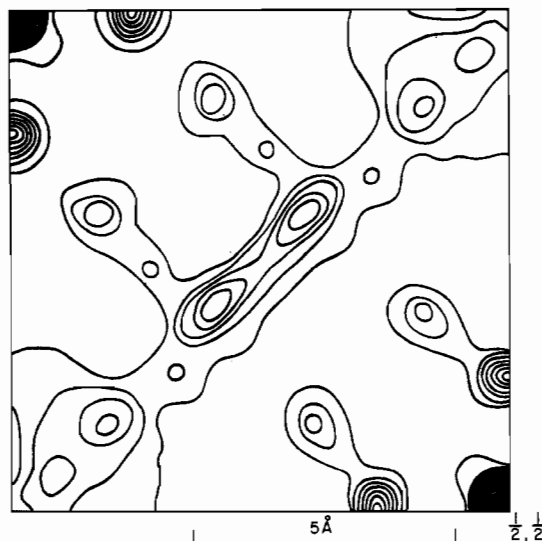

Figure 7.—Electron density projection down [001] with contours at arbitrary intervals for four asymmetric units of the anhydrous lead perchlorate–thiourea complex. The $^1/_2$, $^1/_2$ diagonal is a mirror plane. The space group is I4/mcm. Contours are at arbitrary intervals.

meaningless. All that can be said is that they must be in the general region where they have been placed.

The structure of the anhydrous complex was investigated two-dimensionally only. This limitation was unavoidable because the weakness of the extra

TABLE XIII

OBSERVED AND CALCULATED STRUCTURE FACTORS ON AN APPROXIMATELY ABSOLUTE SCALE FOR $Pb(ClO_4)_2 \cdot 6TU \cdot 2H_2O$

```
L = 0, K = 0        L = 0, K = 3        L = 0, K = 6        L = 0, K = 9        L = 0, K = 14       L = 1, K = 3 (cont)
 H   Fo   Fc        3   30   63         6  273  213         9  169  191        14  76   50          8   7  -12
 2  275  171        5  324  286         8  255  237        11  143  101        16  40   45         10  25   15
 4  246  299        7  227  237        10  122  123        13   93   94        18  29   23         12  31  -20
 6  234  228        9  189  209        12  107   97        15  103   93       L = 0, K = 15        14  39  -37
 8  256  299       11   73   87        14   99  113        17   58   55        14  39  -37         16  17  -13
10  273  322       13   67   58        16  120  102        19   28   30        16  17  -13         18  18  -14
12  102  109       15  119  129        18   47   54        21   24   25        18  18  -14         20  10  -12
14  134  151       17   75   76        20   30   26       L = 0, K = 10        20  10  -12         22  13  -13
16  117  140       19   30   28        22   28   34        10  206  162        22  13  -13        L = 1, K = 4
18   44   44       21   31   31       L = 0, K = 7         12   48   46       L = 0, K = 16         5  37  -35
20   41   44       23   27   39         7  281  281        14  103   89        16  59   44          7  28  -42
22   34   37      L = 0, K = 4          9  260  217        16   75   67       L = 1, K = 1          9 110  125
L = 0, K = 1        4   42   59        11   94  100        18   33   26         2  39   -2         11  38  -29
 3  220  259        6  147  171        13  100   95        20   28   32         4 236  236         13   9   -7
 5  386  366        8  227  232        15  128  129       L = 0, K = 11         6 152 -118         15  10   -1
 7  313  301       10   83   98        17   70   77        11   25   46         8  31  -39         17  10   -9
 9  245  241       12   65   68        19   35   36        13   67   52        10  48  -47         23   6   -2
11  153  161       14  108   98        21   29   25        15   73   74        12  38  -47        L = 1, K = 5
13  117  117       16   86   96       L = 0, K = 8         17   48   44        14   9   10          6  18  -19
15  144  151       18   44   45         8  362  332        19   29   26        16  38  -40          8  26   11
17   88   95       20   25   24        10  115  114       L = 0, K = 12        18  10  -12         10  59   62
19   39   35       22   31   41        12  122  106        12   64   31        20  10  -15         12  34   17
21   39   35      L = 0, K = 5         14  119  109        14   56   57        22   8  -13         14  17   21
23   29   40        5  172 -103        16   96   92        16   67   58       L = 1, K = 2         16  30   26
L = 0, K = 2        7  250  250        18   53   54        18   31   33         3  39  -73         18  30   22
 2  436  398        9  159  170        20   22   19        20   9   17          5   4   18         20   9   12
 4  124  116       11  103   97        22   19   28       L = 0, K = 13         7  55  -58         22   7    5
 6  310  356       13  111  128                           13   30   33          9  43  -30        L = 1, K = 6
 8  268  286       15   78   70                           15   76   64         11  53  -58          7  22   26
10  143  153       17   86   86                           17   39   35         13  48  -52          9   8  -15
12   68   91       19   29   27                           19   17   20         15  29  -32         11  83   83
14   94  110       21   29   31                                                17  18  -24         13   9    5
16  104  122       23   23   43                                                19  25  -24         15  38   34
18   51   62                                                                   21  16  -16         17  39   39
20   26   18                                                                   23  11  -13         19  10   13
22   35   41                                                                  L = 1, K = 3         21  20   17
                                                                               4  17   15
                                                                               6 106 -110
```

```
L = 1, K = 7        L = 1, K = 12       L = 2, K = 1        L = 2, K = 4        L = 2, K = 7        L = 2, K = 11
 8  18   31        12  17  -17          3 234 -250          4 397 -397          7 137 -114         11 179 -133
10  47   41        14  18  -15          5 234 -207          6 254 -233          9  58  -71         13  94  -85
12  22   -6        16  25  -15          7 270 -108          8 170 -179         11 142 -125         17  47  -37
14  10    2        18   9    7          9 141 -153         10 186 -198         13  94 -103         19  41  -39
16  31   20        20  17  -16         11 142 -161         12 190 -202         15  28  -29        L = 2, K = 12
18  18   23       L = 1, K = 13        13 104 -119         14  80 -101         17  58  -51         12 112  -97
20   9   11        13  18  -13         15  44  -53         16  57  -57         21  33  -34         14  93  -63
22   7    4        15  18   -9         17  36  -41         18  58  -72        L = 2, K = 8         16  44  -39
L = 1, K = 8       17  32   20         19  68  -72         20  47  -57          8  28    0         18  44  -35
 9  39   26        19  12    9         21  36  -42         22  20  -22         10 138 -119         20  23  -34
11   9    5       L = 1, K = 14        23  12  -13        L = 2, K = 5         12 108  -94        L = 2, K = 13
13  10  -28        14  18  -10        L = 2, K = 2          5 372 -396         14  58  -57         13 108  -77
15  36  -16        16  24   16          2 190 -187          7 175 -155         16  51  -42         15  51  -35
17  30   25        18  24   31          4 399 -397          9 177 -167         18  41  -45         17  41  -37
19  16   24       L = 1, K = 15         6 209 -201         11 175 -196         20  39  -47         19  31  -34
L = 1, K = 9       16  13    9          8 118 -110         13 122 -115         22   9  -20        L = 2, K = 14
16  13    9        18  19   18         10 145 -180         15  61  -79        L = 2, K = 9         14  54  -43
18  19   18       L = 2, K = 0         12 130 -152         17  47  -44          9 121  -76         16  39  -27
L = 1, K = 10      12  10   -9         14  93 -108         19  56  -64         11 126 -119         18  28  -31
11  10   -3        14  68  -65         16  40  -54         21  33  -40         13  97  -77        L = 2, K = 15
13  74  -37        16  10   -1         18  57  -62         23   8  -10         15  51  -44         15  35  -29
15  18  -31        18  10   -8         20  53  -69        L = 2, K = 6         17  49  -43         17  19  -17
17  17   -5        20  20  -17         22  15  -19          6 189 -176         19  51  -46        L = 2, K = 16
19  15  -15        22  11  -17        L = 2, K = 3          8 138 -130         21  25  -31         16  13  -13
21  20  -24       L = 2, K = 1        21  29  -39         10 141 -147        L = 2, K = 10
L = 1, K = 11      1 106 -198         23  11  -11         12 158 -155         10 126  -88
                                                          14  66  -69         12 157 -128
                                                          16  36  -39         14  68  -55
                                                          18  57  -56         16  47  -37
                                                          20  40  -48         18  51  -48
                                                          22  21  -25
```

viously seriously disordered in agreement with the results of the least-squares refinement. The broad peak on the same plane must be associated with the thiourea molecule outside the cationic chain and the water molecule, only a disordered arrangement being compatible with the mm symmetry required by the space group. In agreement with this, the Debye–Waller factors obtained by least squares for the atoms of the water and thiourea molecules are so large as to make the coordinates assigned to them physically

reflections on the photographs of the anhydrous complex made it very difficult to measure their intensities accurately; it was acceptable because, the z coordinates of the atoms being known from the structure of the hydrated complex, the projection on (001) would give the additional information required.

Positions for all of the atoms, except oxygen and carbon, could be derived from the Patterson, which showed considerably better resolution in the region around $^1/_2$, 0. These positions were used for a structure factor

calculation followed by a Fourier synthesis and the electron density map obtained is shown in Figure 8. Only the carbon atoms and one oxygen are not resolved on this map, but their positions can be inferred graphically.

An attempt was made to refine the positions so obtained by the method of least squares, but this proved largely unsuccessful. The Debye–Waller factors of the atoms in the molecule near $1/2$, 0 were so high as to be not physically meaningful unless interpreted as indicative of disorder. For the best fit obtained $R = 0.165$ (for the observed reflections only $R = 0.105$). The final atomic parameters are given in Table XIV and observed and calculated structure factors, on an approximately absolute scale, are given in Table XV.

TABLE XIV

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR $Pb(ClO_4)_2 \cdot 6TU$

Atom	x	y	B, $Å^2$
Pb	0	0	6.1
Pb	$1/2$	$1/2$	5.9
S	-0.0084	0.1258	4.7
S	0.3687	0.5146	3.8
S	0.588	0.104	9.0
C	0.059	0.181	6.5
C	0.323	0.433	6.0
C	0.50	0.07	15.0
N	0.093	0.205	5.0
N	0.302	0.405	5.0
N	0.46	0.06	10.0
Cl	0.306	0.197	8.0
O	0.255	0.141	7.4
O	0.36	0.17	10.0
O	0.28	0.23	9.0

Figure 8.—Electron density projection down [001] with contours at arbitrary intervals for two asymmetric units of the anhydrous lead perchlorate–thiourea complex. The $1/2$, $1/2$ diagonal is an n-glide plane. The space group is P4/mcc. Contours are at arbitrary intervals.

tures of the structures of the anhydrous (ordered) and hydrated (partially disordered) complexes are very similar. Thus there is a centered array of cation–thiourea chains in both complexes, with the anions between the chains while the disordered molecules of thiourea (and water for the hydrated complex) are in the channels of the cation chain–anion network. The order–disorder transformation that occurs on absorption of water vapor affects the structures in two ways:

TABLE XV

OSERVED AND CALCULATED STRUCTURE FACTORS ON AN APPROXIMATELY ABSOLUTE SCALE FOR $Pb(ClO_4)_2 \cdot 6TU$

L 0, K 0 H F_o F_c															

(table of structure factors)

The arrangement of thiourea molecules found for the anhydrous complex around $1/2$, 0 cannot occur if the molecules do, in fact, lie in the (001) mirror planes, since this would mean an approach of 2.5 A between non-bonded nitrogen atoms. The thiourea molecules around the twofold axis should be considered as disordered on the two sides of the mirror plane. This is plausible because the Fourier peak associated with this arrangement was found to be isotropically broadened in the hydrated complex. This type of disorder may be the cause of the diffuse-layer line of spacing 4 A.

4.2.2. Comparison of Structures.—The major ea-

(i) in the hydrated complex the cation–thiourea chains along the edges and central axis of the unit cell are identical whereas they differ slightly in orientation in the anhydrous complex, as can be seen in Figure 9; (ii) in the hydrated complex the perchlorate ions are so oriented that their two orthogonal mirror planes coincide with the mirror planes of positions h of the space group. In the anhydrous complex the mirror plane parallel to (220) has disappeared and the perchlorate ion is only constrained to lie with one of its mirror planes in the (001) mirror plane of the unit cell.

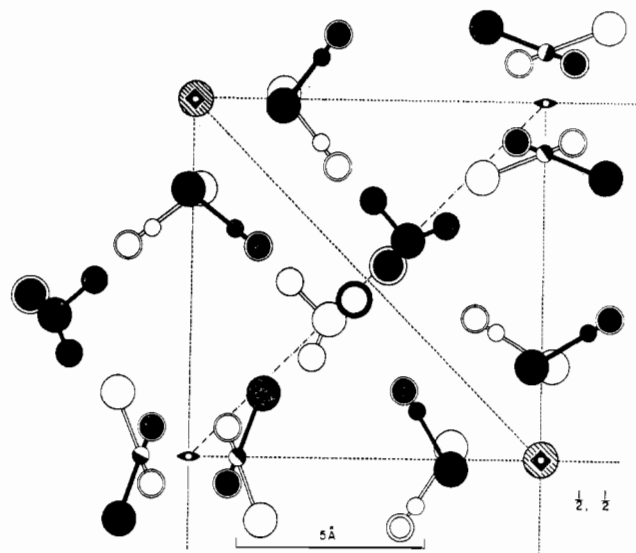**4.2.3. Interatomic Distances.**—Although all the

Figure 9.—The structure of the anhydrous lead perchlorate–thiourea complex in projection along [001]. The z coordinates were obtained from the three-dimensional analysis of the structure of the hydrated complex. The atoms shown as full circles lie in the mirror plane at $z = 0$ and the atoms shown as open circles lie in the mirror plane at $z = 1/2$. Double circles represent pairs of atoms related by the appropriate mirror plane. The shaded (lead) atoms lie in special positions at $z = 1/4$. The thiourea molecules around the twofold axis are located in idealized rather than actual positions and this region is, in fact, considerably disordered.

interatomic distances are close to standard values, only the Pb–S distances are sufficiently accurate to warrant discussion. In the hydrated complex these are all crystallographically equivalent and equal to 3.11 ± 0.02 A. In the anhydrous structure there are two independent sets of 3.07 and 3.16 A. Because of the incomplete refinement of the latter structure, it is not possible to say whether these differences are significant and we shall assume here a mean value of 3.11 A for the Pb···S separation in the $Pb(ClO_4)_2$ complexes. In $Pb(NO_3)_2 \cdot 6TU$ the mean value of the Pb···S separation has been given earlier as 3.29 ± 0.03 A but the significance of this value is doubtful as no account was taken of the disorder in that structure. The Pb···S distances found in other lead salt–thiourea complexes are as follows. (1) Mono(thiourea)–lead(II) acetate:[12] within chains the Pb···S distance is 3.10 ± 0.01 A, while the chains are linked in pairs through weaker Pb···S links of length 3.34 ± 0.01 A. (2) Bis(thiourea)–lead(II) chloride:[13] within chains four Pb···S distances are found: 2.92 ± 0.03, 3.02 ± 0.03, 3.04 ± 0.03, 3.10 ± 0.03 A. Thus the Pb···S bond lengths in the $Pb(ClO_4)_2 \cdot 6TU$ complexes are somewhat larger than the coordinate bonds found in bis(thiourea)–lead(II) chloride but not longer than those found in mono(thiourea)–lead(II) acetate. There is clearly a relatively stronger interaction between Pb and S than between Tl and S, and this is in agreement with the ability of lead to form both mainly ionic complexes of the present type and ordinary coordination complexes.

5. General Discussion of the Structures of the MX·4TU and PbX₂·6TU Complexes

In the $TlNO_3 \cdot 4TU$ complex the cation–thiourea chains are complete and packed in regular array. However the space in the channels between the chains is not completely filled, there being only two nitrate ions in each channel for each repeat distance of 8.2 A along [001]. In the $Pb(NO_3)_2 \cdot 6TU$ complex the number of nitrate ions has increased to eight per repeat distance of 24.6 A (or $2^2/_3$ per 8.2 A), which is about the maximum number that can be packed into the available space. There are now four lead ions (per 24.6 A) to be distributed among the six cation sites of the one independent cation–molecule chain in the unit cell; the fact that layer lines hkl appear for certain values only of l suggests that the distribution of the lead ions among available sites is not random but no detailed information is available on this point. Another possible arrangement would be for alternate cation–molecule chains to become nonequivalent, with complete filling of the cation sites in one set of chains and filling of one-third of the cation sites in the other set of chains. Presumably both energetic and entropy factors militate against this possibility. Thus essentially similar arrangements are found in $TlNO_3 \cdot 4TU$ and $Pb(NO_3)_2 \cdot 6TU$ except for incomplete occupation of the space available for anions and cations, respectively, in the two structures.

In the $TlClO_4 \cdot 4TU$ complex the large perchlorate ions fill the channels between the cation–molecule chains, there being two perchlorate ions per channel for each repeat distance of 8.2 A along [001]. In the $Pb(ClO_4)_2 \cdot 6TU$ complex the [001] axis is only slightly shorter at 7.92 A and again two perchlorate ions can be accommodated in each channel in the repeat distance along [001]. There is now one Pb^{2+} ion per channel repeat unit instead of two Tl^+ ions; instead of half-filling the cation sites of all of the cation–molecule chains, it is now possible to fill all of the cation sites of half the chains without there being any extra cations and this is the essential difference between the $Pb(ClO_4)_2$ and $Pb(NO_3)_2$ complexes. The unfilled chain disappears and is replaced by disordered thiourea and water molecules. One may consider that the filled chains, together with the perchlorate ions, form a loose ionically bonded framework surrounding channels within which the disordered thiourea molecules (for the anhydrous complex) or the disordered thiourea and water molecules (for the hydrated complex) are contained. Because of space limitations, there are only half as many thiourea molecules in these channels as participate in the cation–thiourea chains and this leads to a ratio of 1:6 and a contraction of the unit cell in the [100] direction from about 21 A (for the ordered $TlClO_4 \cdot 4TU$ structure type) to 18.64 A. The thiourea and water molecules contained in the channels appear to play no other structural role than to fill space.

Thus, as one may indeed already infer from the cell dimensions, the complexes $TlClO_4 \cdot 4TU$, $Pb(NO_3)_2 \cdot 6TU$,

and $TlNO_3 \cdot 4TU$ belong to the same group of structures within the family, despite the differences in stoichiometry. In $TlClO_4 \cdot 4TU$ the space available to both cations and anions is fully occupied; in $Pb(NO_3)_2 \cdot 6TU$ the space available to the anions is fully occupied but there are now only half as many cations per anion and so only two-thirds of the cation positions are occupied (the absence of random occupancy of these sites indicates that chemical factors also play a role); in $TlNO_3 \cdot 4TU$ the cation sites are fully occupied and it is the requirement of electrical neutrality which prevents more anions from entering the structure even though there is space available for their accommodation. On the other hand the $Pb(ClO_4)_2 \cdot 6TU$ complex is appreciably different; the first type of structural arrangement (like that in $Pb(NO_3)_2 \cdot 6TU$) is not possible because the perchlorate ions are too large to allow insertion in the interchain channels of the additional anions needed to compensate for the extra positive charge of Pb^{2+} compared to M^+. Thus a considerable change of structure is required and this occurs by omission of alternate cation–thiourea chains, the anion arrangements being similar in $TlClO_4 \cdot 4TU$ and $Pb(ClO_4)_2 \cdot 6TU$. From these results we infer that, given the general structure type, the detailed crystal structures depend mainly on anion size and shape.

Notes

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Preparation of Co(dipy)₂X₂⁺ Complexes (X⁻ = Cl⁻, Br⁻, I⁻, NO₂⁻) by Controlled Oxidative Processes

By A. A. Vlček[1]

In the series $Co(dipy)_2X_2^+$ only substances with $X^- = Cl^-$,[2] NO_2^-,[3,4] acetate,[5] and $Co(dipy)_2CO_3^+$,[2] as well as $Co(dipy)_3^{3+}$,[2,6] have been described. In most preparations of these complexes the main step consists of the oxidation of divalent cobalt complexes with hydrogen peroxide or oxygen. However, this method is not suitable for preparation of other complexes (*e.g.*, for $X^- = I^-$), and the reaction with oxygen or hydrogen peroxide as oxidation agents is not a straightforward operation.

A recent study of complexes of the general type $Co(dipy)_2X_2$[7] has shown that these complexes undergo, in most cases, a very easy oxidation and that they can be used as starting material for the preparation of the corresponding series of trivalent cobalt complexes. In case an oxidation agent is used, the reduced form of which enters the coordination sphere, the desired complex is formed in one step without any formation of intermediates.

(1) On leave of absence from the J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague, Czechoslovakia; recipient of a Senior Foreign Scientist National Science Foundation fellowship, 1964–1965.
(2) F. M. Jaeger and J. A. van Dijk, *Z. Anorg. Allgem. Chem.*, **227**, 273 (1936).
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(6) F. H. Burstal, and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).
(7) A. A. Vlček, submitted to be published.

Results and Discussion

Bis-Halogeno Complexes.—The previous studies on $[Co(dipy)_2Cl_2]Cl^{2-4a}$ have shown that this complex undergoes extremely rapid hydrolysis in aqueous solution. However, the solutions in alcohol are much more stable than the aqueous solutions.

The general method for the preparation of bis-halogeno complexes of the type $[Co(dipy)_2X_2]^+$ makes use of the fact that the solubility of the corresponding divalent complex in methanol is rather high and that the divalent complex undergoes an immediate and clean oxidation with the corresponding halogen. The resulting trivalent complex, being much less soluble than the starting material, separates from solution. In this way the previously known $[Co(dipy)_2Cl_2]Cl$, as well as the new complexes $[Co(dipy)_2I_2]I$ and $[Co(dipy)_2Br_2]Br$, has been prepared.

The chloro complex results in the form of a mixture of *cis* and *trans* isomers which can be separated by fractional crystallization from boiling ethanol. Upon reaction with water, both forms dissolve to give red-violet solutions and spectrophotometric studies show the presence of the bis-aquo form in solution (see Table I). Both isomers dissolve in methanol and ethanol without decomposition.

$[Co(dipy)_2I_2]I$ and $[Co(dipy)_2Br_2]Br$ complexes precipitate in the form of dark violet and brownish green crystalline powders, respectively. They are slightly soluble in methanol and ethanol and almost insoluble in water. The solubility in alcohols can be enhanced by adding lithium or sodium perchlorate or lithium chloride.

When a mixture of $CoCl_2$ and dipyridyl in the ratio 1:3 or 1:4 is oxidized with the halogen (in the presence of the corresponding lithium halogenide) the bis-halogeno species is formed (in yields of 30–40%) together with tris-dipyridyl complex.

The polarographic behavior of the system cobalt(II)–dipyridyl shows that there exists a rather rapid equilibrium between various cobalt(II)–dipyridyl com-