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# Thiourea Coordination Complexes of Pb(II) Salts. III. Eightfold Coordination in $\frac{3}{4}$Pb(HCOO)$_2$. 4 Thiourea

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$\frac{3}{4}$Pb(HCOO)$_2$.4tu (tu = thiourea) is tetragonal with $a = 14{\cdot}286$ (2), $c = 16{\cdot}42$ (1) Å, $\varrho_{\text{meas}} = 2{\cdot}19$ g.cm$^{-3}$, $\varrho_{\text{calc}} = 2{\cdot}10$ g.cm$^{-3}$ for 8 formula units per cell. The structure was solved by Patterson and Fourier methods and refined by least-squares (isotropic temperature factors) to a conventional $R$ value of 10·2%. Choice of $I422$ as space group rather than $I4/mmm$ was based on comparison of observed and calculated (for both space groups) structure factors, especially for the weak reflexions. The structure found is similar to that of TlNO$_3$.4tu (J.C.A. Boeyens & F.H. Herbstein, *Inorg. Chem.* (1967). **6**, 1408). Lead ions lie along the $c$ axis, surrounded by twisted tetragonal prisms of sulphur atoms of thiourea molecules. Every fourth lead-ion position is vacant, the vacancies being fully ordered. The Pb$^{2+}$ ions are displaced from the centres of gravity of the prisms and Pb···S distances of 2·98, 3·38 and 3·85 Å are found. These distances correspond to ion–dipole interactions. The distances separating planes of sulphur atoms are virtually constant at 4·13 Å, irrespective of whether a prism is occupied or not. In $\frac{3}{4}$Pb(HCOO)$_2$.4tu both crystals and polymeric cation chains are non-centrosymmetric whereas in TlNO$_3$.4tu both are centrosymmetric. In $\frac{3}{4}$ Pb(HCOO)$_2$.4tu the chains have a body-centred arrangement, presumably in order to minimize cation–cation repulsions. The anions are disordered and lie in the channels enclosed by the cation chains. It seems probable that the unusual stoichiometry is determined by the space available in the channels for accommodation of the formate ions.

## Introduction

The thiourea (tu) coordination complexes of Pb(II) salts show many different compositions and structural types (see Goldberg & Herbstein (1972*a*) and Herbstein & Kaftory (1972) for examples and earlier references). The intrarelationships among the lead complexes themselves are as yet only hazily discernible but patterns have appeared in the interrelationships between some lead salt–thiourea complexes and the coordination complexes of other metals and/or ligands. For example, triclinic Pb(tu)$_6$(ClO$_4$)$_2$ (Goldberg & Herbstein, 1972*a*) is similar in both cation structure and overall crystal structure to a number of (M$^{\text{II}}$L$_6$)X$_2$ complexes, while Pb(tu)$_4$(picrate)$_2$ (Herbstein & Kaftory, 1972) has cationic polymeric chains similar to the molecular polymeric chains found in some M$^{\text{II}}$L$_2$X$_2$ complexes. Perhaps the closest resemblances are between complexes typified by $\frac{2}{3}$Pb(NO$_3$)$_2$.4tu† (Rosenheim & Meyer, 1906) and the ionic complexes of thiourea such as TlNO$_3$.4tu (Boeyens & Herbstein, 1967). These have a similar general structure but the relationship could not be demonstrated in detail because of disorder in the $\frac{2}{3}$Pb(NO$_3$)$_2$.4tu crystals. We have now determined the structure of the related complex, $\frac{3}{4}$Pb(HCOO)$_2$.4tu, which is fully ordered. This complex has eightfold coordination of thiourea about lead in infinite polymeric chains, but with every fourth lead position along the chain vacant. These ordered vacancies account for the unusual stoichiometric composition, which emerges from the crystal structure, chemical analyses having given ambiguous results.

The present paper supersedes earlier preliminary reports (Goldberg, Herbstein & Kaftory, 1968; Goldberg & Herbstein, 1969).

## Experimental

(*a*) $\frac{3}{4}$Pb(HCOO)$_2$.4tu

Although Pb(HCOO)$_2$ is only slightly soluble in water, it is easily soluble in saturated aqueous thiourea, giving greenish-yellow solutions. Acidification of these solutions with formic acid was necessary to prevent precipitation of a black powder, presumably PbS; slow evaporation led to crystallization of a small quantity of white needles. The best results were obtained using solutions prepared from 1g Pb(HCOO)$_2$ and 2g thiourea dissolved in 20 ml of 20% formic acid. The largest needles had a diameter of 0·06 mm. Repeated crystallizations gave a total amount of about 60 mg of material;* after selection of a number of crystals for X-ray photography, the remainder was used for

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* In part fulfilment of the requirements for the M.Sc. degree in Chemistry at Technion – Israel Institute of Technology.

† In order to emphasize the resemblance between the various complexes of this general family we express their compositions relative to 4tu molecules per formula unit, *e.g.* $\frac{2}{3}$Pb(NO$_3$)$_2$.4tu instead of Pb(NO$_3$)$_2$.6tu.

* We note that large triclinic rhombs were obtained by slow evaporation of mother liquors from these crystallizations; these crystals were shown to be Pb(HCOO)$_2$.2tu.H$_2$O and their structure is reported separately (Goldberg & Herbstein, 1972*b*).

chemical analysis. The results of the chemical analyses did not permit an unambiguous decision about the composition of the crystals. We shall use 6 $Pb(HCOO)_2$ .32tu for the unit-cell contents; this composition is based on the results of the crystal-structure analysis and will be justified later.

Cell dimensions were determined from back reflection Weissenberg photographs ([100]) and oscillation photographs ([001]). The Laue symmetry was $4/mmm$ and the reflexion condition $h+k+l=2n$. The possible space groups are therefore $I422$ (No. 97), $I4mm$ (No. 107), $I\bar{4}m2$ (No. 119), $I\bar{4}2m$ (No. 121) and $I4/mmm$ (No. 139). These results are summarized in Table 1.

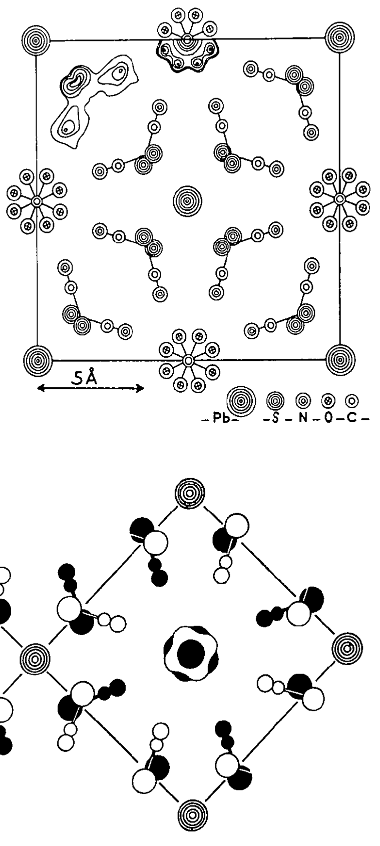

Fig. 1. Comparison of the structures of $\frac{3}{4}Pb(HCOO)_2.4tu$ and $TlNO_3.4tu$ shown in projection down [001]. The unit-cell axes have been oriented so as to emphasize the resemblance between the two structures.

Intensities of 470 independent reflexions were measured by the visual method from equi-inclination Weissenberg photographs (Cu $K\alpha$, $l=0-7$). Corrections were made for geometrical factors (Lp, spot-shape) and absorption (cylindrical-crystal approximation). Different layers were put on approximately the same scale *via* appropriate precession photographs (Mo $K\alpha$). This mutual scale was later improved by a least-squares technique. All calculations required in this structure analysis were carried out on the Technion's Elliott 503 computer, using ALGOL programs written by one of us (I.G.). The least-squares refinement was by the block-diagonal method, using Cruickshank & Pilling's (1961) weighting scheme.* Atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964), dispersion corrections (real part only) being applied to the $f$-curves of Pb and S (*International Tables for X-ray Crystallography*, 1962).

### (*b*) $\frac{2}{3}Pb(CH_3COO)_2.4tu$†

An attempt was made to prepare an analogous lead acetate–thiourea complex, using the same techniques and relative concentrations of reagents. A few tiny needles were obtained; X-ray photography gave diffraction patterns identical with those of $TlNO_3.4tu$ (Boeyens & Herbstein, 1967) and it was inferred that the composition was $\frac{2}{3}Pb(CH_3COO)_2.4tu$. Enough material for chemical analysis was not obtained. We did not encounter the monoclinic crystals of $Pb(CH_3COO)_2.6tu$ reported by Nardelli & Chierci (1959). These results for $\frac{2}{3}Pb(CH_3COO)_2.4tu$, as well as earlier results for $\frac{2}{3}Pb(NO_3)_2.4tu$ and $TlNO_3.4tu$ are collected together in Table 1.

## Determination and refinement of structure

The $hk0$ Weissenberg photographs of the first four complexes listed in Table 1 are essentially identical; thus the structures in projection down [001] are the same (Fig. 1). As the $hkl$ photographs of $\frac{2}{3}Pb(CH_3COO)_2.4tu$ and $TlNO_3.4tu$ are the same, we infer that their three-dimensional structures are the same. Each metal ion position has an occupancy of 1

Table 1. *Crystallographic results for some related complexes*

| Formula unit of complex | $a$ (Å) | $c$ (Å) | Space group | $\varrho_{meas}$ (g.cm$^{-3}$) | $\varrho_{calc}$ (g.cm$^{-3}$) | Unit-cell contents (formula units) |
|---|---|---|---|---|---|---|
| $\frac{3}{4}Pb(HCOO)_2.4tu$ | 14·286 (2) | 16·42 (1) | $I422$* | 2·19 | 2·10 | 8 |
| $\frac{2}{3}Pb(CH_3COO)_2.4tu$ | 10·12 | 8·18 | $P4/mcc$ | 2·08 | 2·06 | 2 |
| $\frac{2}{3}Pb(NO_3)_2.4tu$† | 10·25 | 24·6 | $P4/mcc$ | 2·03 | 2·05 | 6 |
| $TlNO_3.4tu$ | 10·34 | 8·29 | $P4/mcc$ | 2·15 | 2·14 | 2 |
| $[Pb(CH_3COO)_2.6tu$‡ | $a=34{\cdot}25$, $b=8{\cdot}34$, $c=26{\cdot}62$ Å<br>$\beta=129{\cdot}5°$, $Z=8$, $\varrho_{calc}=1{\cdot}77$, $Cc$ or $C2/c]$ | | | | | |

* Reasons for choosing $I422$ from the five possible space groups are given in the text.
† Diffuse scattering not taken into account.
‡ Nardelli & Chierci (1959).

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* $w=(200+|F_o|+0{\cdot}02F_o^2)^{-1}$.

† We are grateful to Mr A. G. Nunn (IAESTE summer student, 1967) for his help with this part of the work.

in the thallium complex but of $\frac{2}{3}$ in the lead complex. No diffuse scattering or weak additional layer lines could be seen in the (rather poor) photographs of the lead acetate complex and thus the metal–atom vacancies appear to occur at random.

The $\frac{2}{3}Pb(NO_3)_2.4tu$ structure has not been studied further and the discussion given earlier (Boeyens and Herbstein, 1967) still delineates our knowledge of this material.

The virtual identity of the [001] projections of $TlNO_3.4tu$ and $\frac{3}{4}Pb(HCOO)_2.4tu$ indicates that similar structural principles hold in both crystals. We therefore expect $\frac{3}{4}Pb(HCOO)_2.4tu$ to have fourfold symmetry axes and reject space groups $I\bar{4}m2$ and $I\bar{4}2m$, which lack such axes. These interim conclusions were confirmed by the successful structure analysis. Despite their similarity in projection, the three-dimensional arrangements in $TlNO_3.4tu$ and $\frac{3}{4}Pb(HCOO)_2.4tu$ must be different, as the oscillation photographs about [001] have different intensity distributions. Those of $TlNO_3.4tu$ have alternating strong (even) and weak (odd) layer lines, a consequence of $z_{Tl}=\frac{1}{4}$; those of $\frac{3}{4}Pb(HCOO)_2.4tu$ have the intensity distribution shown schematically in Fig. 2. This pattern of strong and weak layer lines will be given by groups of three heavy atoms placed linearly along 00$z$, separated by less than $\frac{1}{3}c$ and repeated by the $c$ translation. A three-dimensional Patterson synthesis gave a strong peak at 0,0,0·295, corresponding to a Pb---Pb separation of 4·85 Å.

We are now in a position to discuss the composition of the crystals and the choice between space groups $I422$, $I4mm$ and $I4/mmm$. The chemical analyses and density measurements limit the number of $Pb(HCOO)_2$ groups in the unit cell to 6; the lead ions go into positions (*a*) (000 *etc*) and (*e*) (00*z etc*); the formate ions go into positions (*f*) (0$\frac{1}{2}$*z etc*). The coordinates of these positions are the same in these space groups, while their different point symmetries are irrelevant because of the spherical symmetry of the lead ions, and the disorder of the formate ions. In $I422$ there remain only sixteenfold positions which can be used to accommodate the atoms of the thiourea molecules in a manner compatible with the projection shown in Fig. 1. Two independent thiourea molecules in these sixteenfold positions give 32 thiourea molecules per cell and hence unit-cell contents of 6 $Pb(HCOO)_2.32tu$. However the sixteenfold positions of $I4mm$ occur in pairs *xyz*, *yxz etc*., implying that thiourea molecules related by the $(1\bar{1}0)$ mirror planes must have the same $z$ coordinates. This requirement is not compatible with the arrangement of thiourea molecules indicated by the projection down [001] (Fig. 1). A similar difficulty occurs with the 16($l$) and thirtytwofold positions of space group $I4/mmm$ (the other sixteenfold positions of this space group are not at all compatible with Fig. 1). One possible solution would be to use four sets of sixteenfold positions, or two sets of thirtytwofold positions, each half-occupied in a random way. This random occupancy would apply to the long-range structure of the crystal; appropriate short-range order is essential.

Choice between an ordered arrangement (in $I422$) or a disordered arrangement (in $I4/mmm$) has been made by carrying out parallel refinements in these two space groups. The difference in overall $R$ value was small (12·4% for $I4/mmm$ and 10·3% for $I422$), as would be expected because of the identity of lead-ion contributions to both sets of structure factors. However, as Table 2 shows, there were striking differences for certain layer lines, especially for those with $l=2$ and 6. This eliminates the possibility of disorder and there seems no doubt that $I422$ is the correct space group. This is an unusual result in that centro-symmetric space groups have given satisfactory results in all previous structural work on crystals of this family.

Table 2. *The choice between space groups* $I422$ *and* $I4/mmm$: *the sums of real and imaginary parts of the structure factors for* $I422$ (*the real part is the structure factor for* $I4/mnm$), *and the R values for the individual reciprocal lattice levels with differing l*

| $l$ | Real part ($\sum\|A\|$) | Imaginary part ($\sum\|B\|$) | $\frac{\sum\|B\|}{\sum\|A\|}$ % | $R$ for $I4/mmm$ % | $R$ for $I422$ % |
|---|---|---|---|---|---|
| 0 | 14403 | 0 | 0 | 6·9 | 6·9 |
| 1 | 1970 | 86 | 4·4 | 14·6 | 14·5 |
| 2 | 4435 | 2554 | 57·6 | 36·7 | 16·5 |
| 3 | 10373 | 144 | 1·4 | 6·8 | 6·8 |
| 4 | 8222 | 127 | 1·5 | 9·9 | 9·9 |
| 5 | 4185 | 184 | 4·4 | 15·7 | 15·6 |
| 6 | 5389 | 2290 | 40·9 | 23·4 | 14·0 |
| 7 | 10902 | 241 | 2·2 | 10·2 | 10·2 |
| Totals | 59879 | 5545 | 9·3 | 12·4 | 10·3 |

The atomic coordinates and isotropic temperature factors for $I422$ are given in Table 3 and the following discussion is based on these results. Observed and calculated structure factors (Table 4) are not reproduced (the measured values were not considered accurate enough to warrant this) but can be obtained on request.*

A three-dimensional difference synthesis based on the final observed and calculated structure factors gave no regions of unexplained electron density. Hydrogen atoms were not visible in this difference synthesis. This result constitutes a confirmation of the proposed composition.

The estimated standard deviations of the atomic coordinates are Pb: $\sigma(z)\simeq0·007$; S: $\sigma(x)\simeq0·007$, $\sigma(z)\simeq0·04$; C, N: $\sigma(x)\simeq0·02$, $\sigma(z)\simeq0·1–0·15$ Å. Detailed coordinates for the atoms of the formate anions are not given (see next section).

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* Table 4 has been deposited as Document NAPS 10656 with the National Auxiliary Publications Service, CCM Information Corporation, 866 Third Avenue, New York, N.Y. 10022, U.S.A. A copy may be secured by citing the Document No. and remitting $5·00 for photocopy or $2.00 for microfiche copy. Advance payment is required. Make checks or money payable to: CCMIC-NAPS.

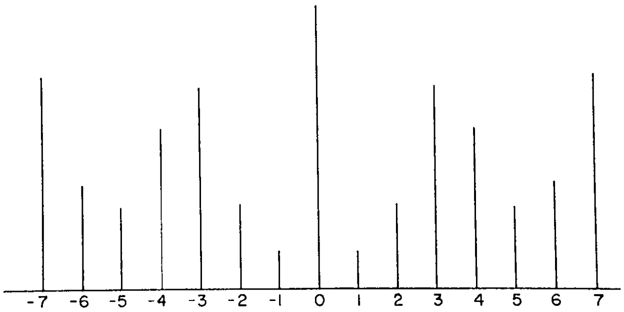

Fig. 2. Schematic representation of the mean intensity of the layer lines in [001] oscillation photographs of $\frac{3}{4}$Pb(HCOO)$_2$.4tu.

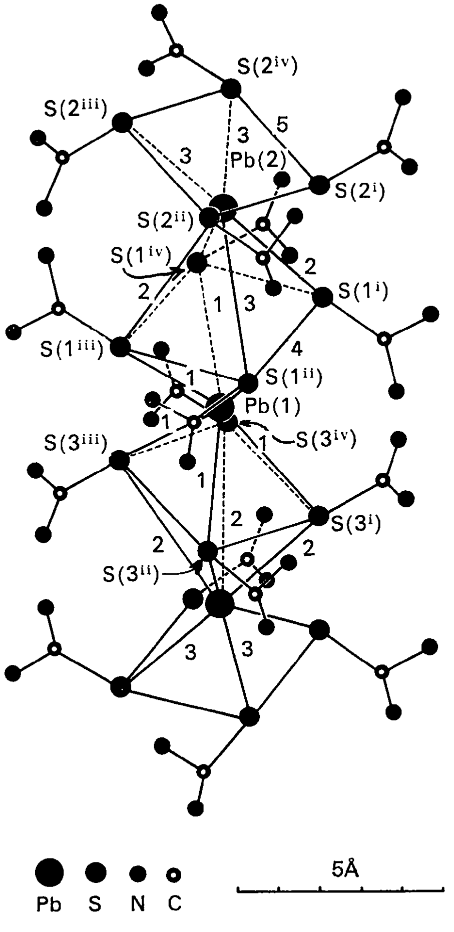

Fig. 3. The structural motif (anions not shown). The distances are:

Pb–S, 1=3·38, 2=3·85, 3=2·98, S···S, 4=3·78,5=3·80 Å.

The angles in the coordination spheres about the lead ions are:

S(1$^{\rm i}$)–Pb(1)–S(3$^{\rm i}$) = 77° (1)
S(1$^{\rm i}$)–Pb(1)–S(3$^{\rm ii}$) = 124 (1)
S(1$^{\rm i}$)–Pb(1)–S(3$^{\rm iii}$) = 166 (1)
S(1$^{\rm i}$)–Pb(1)–S(3$^{\rm iv}$) = 101 (1)
S(1$^{\rm i}$)–Pb(1)–S(1$^{\rm ii}$) = 68 (1)
S(1$^{\rm i}$)–Pb(1)–S(1$^{\rm iii}$) = 104 (1)
S(1$^{\rm i}$)–Pb(2)–S(1$^{\rm iii}$) = 89 (1)

S(2$^{\rm i}$)–Pb(2)–S(1$^{\rm i}$) = 73° (1)
S(2$^{\rm i}$)–Pb(2)–S(1$^{\rm ii}$) = 120 (1)
S(2$^{\rm i}$)–Pb(2)–S(1$^{\rm iii}$) = 156 (1)
S(2$^{\rm i}$)–Pb(2)–S(1$^{\rm iv}$) = 97 (1)
S(2$^{\rm i}$)–Pb(2)–S(2$^{\rm ii}$) = 72 (1)
S(2$^{\rm i}$)–Pb(2)–S(2$^{\rm iii}$) = 129 (1)

Table 3. *Fractional coordinates of the atoms* ($\times 10^4$) *and their e.s.d's, and isotropic temperature factors* (*results for space group I*422)

No attempt has been made to give parameters for the atoms of the anions, which are disordered.

| | *x* | *y* | *z* | *B* Å$^2$ |
|---|---|---|---|---|
| Pb(1) | 0 | 0 | 0 | 2·1 |
| Pb(2) | 0 | 0 | 2948 (4) | 2·1 |
| S(1) | 1512 (5) | 1116 (5) | 1275 (30) | 3·1 |
| S(2) | 1122 (7) | 1516 (5) | 3736 (31) | 3·2 |
| C(1) | 1205 (15) | 2227 (17) | 1254 (90) | 3·7 |
| C(2) | 2222 (16) | 1167 (17) | 3755 (95) | 3·5 |
| N(1) | 0936 (12) | 2711 (11) | 0334 (50) | 5·6 |
| N(3) | 0993 (14) | 2725 (10) | 2331 (45) | 5·6 |
| N(2) | 2725 (10) | 0938 (13) | 2797 (35) | 5·5 |
| N(4) | 2705 (11) | 1061 (15) | 4602 (40) | 5·6 |

## Description of the structure

The projection on (001) is shown in Fig. 1, and the structural motif in the cation chains in Fig. 3. The arrangement of the motifs in the unit cell is shown in Fig. 4. The motif itself consists of three lead ions in twisted tetragonal prisms (twist angle $\simeq 18°$) formed by the sulphur atoms of thiourea molecules. One lead ion is at the centre of gravity (not a centre of symmetry) of the central prism, while the two outer lead ions are displaced from the centres of the two adjacent prisms. Successive motifs along a lead–thiourea chain are separated by empty prisms. Two adjacent chains are shown in Fig. 4 and their mutual displacement along [001] will be noticed. The parallel chains enclose a roughly cylindrical channel which contains the anions. Some indications of the HCOO$^-$ anions appear in the electron-density projection (Fig. 1) where six equivalent positions related by rotations through 45° are shown. This could be interpreted as due directly to formate groups but the apparent bond angle is 135° in projection, rather larger than the true bond angle of about 120°. Furthermore, definite positions for the atoms of the anions could not be found in the three-dimensional electron-density synthesis and it is inferred that these are considerably disordered.

The interatomic distances in the cation motif are shown in Fig. 5. Despite the considerable variation in Pb–S distances, the distance between successive squares of sulphur atoms (these four sulphur atoms are related by a fourfold axis and hence are necessarily in one plane) is essentially equal, irrespective of whether the prism is occupied by a lead atom or not. This distance of 4·15 Å is the same as the corresponding distance found in TlNO$_3$.4tu and similar complexes. The regular vacancies along the chains of $\frac{3}{4}$Pb(HCOO)$_2$.4tu result in these chains being non-centrosymmetric. Chains with all cation sites occupied are centrosymmetric.

Space group *I*422 is chiral and it should be possible, at least in principle, to determine the absolute configuration studied. There will undoubtedly be difficulties in practice as the chirality is a consequence of the arrangement of the lighter atoms, the lead ions taken by themselves having a centrosymmetric arrangement.

There are close approaches between amine groups of thiourea molecules in the [110] direction (caption to Fig. 4). The distance between nitrogen atoms are a little less than the van der Waals diameter of nitrogen (3·0 Å). Detailed analysis of the implications of these close approaches requires knowledge of the actual hydrogen positions, which cannot be obtained from the present set of experimental measurements.

## Discussion

The $TlNO_3$.4tu and the $\frac{3}{4}Pb(HCOO)_2$.4tu structures have overall similarities but differ in important details. The polymeric cation chains are almost identical in regard to the arrangement of the thiourea molecules. This is shown rather neatly by the relation between the coordinates of analogous atoms in the two crystallographically independent thiourea molecules (Table 3): for example the coordinates of the two sulphur atoms have very nearly the relation $x, y, z$; $y, x, \frac{1}{2}-z$. This means that there are pseudo twofold axes in the [110] direction (and related directions) at $z=\frac{1}{4}$. The $TlNO_3$.4tu structure has true twofold axes in these positions.

In $TlNO_3$.4tu all metal-ion sites are occupied whereas in $\frac{3}{4}Pb(HCOO)_2$.4tu every fourth site is vacant. In both complexes the chains are arranged in a square pattern insofar as the *ab* plane is concerned but, in $\frac{3}{4}Pb(HCOO)_2$.4tu, the four chains surrounding a particular reference chain are displaced from it by $c/2$, leading to a body-centred tetragonal structure. The possible configurations of adjacent chains in the (110) plane are shown in Fig. 6. The electrostatic repulsive interaction between triads of $Pb^+$ ions will be least for the body-centred arrangement found in the crystals.

It has been argued earlier (Boeyens & Herbstein, 1967) that, given the general structural arrangement, the actual composition $\frac{2}{3}Pb(NO_3)_2$.4tu is determined by the number of nitrate ions that can be accommodated per repeat unit in the channels between the cation chains. As the thickness of a nitrate ion is about 3 Å, only 8 nitrate ions can be accommodated per 24·6 Å repeat unit along [001]. Acetate and nitrate ions have rather similar shapes and so the same compositions are obtained for their thiourea-rich lead salt–thiourea complexes. The formate ion is a little smaller than the nitrate and acetate ions and 6 formate ions can be accommodated per repeat unit of 16 Å (equivalent to 9 per 24 Å). Lead-ion vacancies remain in the cation chains of all these complexes but cannot be filled because of the lack of space for their accompanying anions.

The unsymmetrical arrangement of the lead ions within the sulphur-atom framework of the cation chain is due to electrostatic repulsion between adjacent positive ions. The shortest Pb–S distance of 2·98 Å is appropriate to ion–dipole interaction, similar to that found in other lead salt–thiourea complexes. The Pb–S distance of 3·38 Å corresponds to a rather weak interaction of this kind, while the Pb–S distance of 3·85 Å would ordinarily be neglected in considering lead-thiourea ion-dipole interactions. The central $Pb^{2+}$ ion must be symmetrically situated, and its interactions with the surrounding sulphurs are rather weak. Presumably it is energetically more favourable for the other two lead ions to interact maximally with the further thiourea groups and at the same time reduce their interaction with the nearer thiourea groups because this arrangement leads to an appreciable reduction of $Pb^{2+} \cdots Pb^{2+}$ repulsions. The metal ions appear

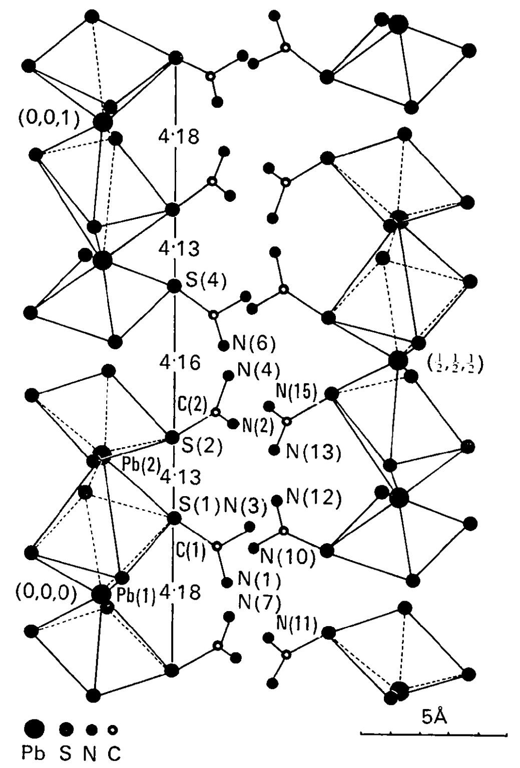

Fig. 4. Arrangement of two parallel lead–thiourea chains in the (110) plane of the unit cell. The closest distances between nitrogen atoms are: N(1)–N(11) 2·87, N(10)–N(7) 2·87, N(2)–N(12) 2·86, N(3)–N(13) 2·86, N(6)–N(15) 2·87 Å.

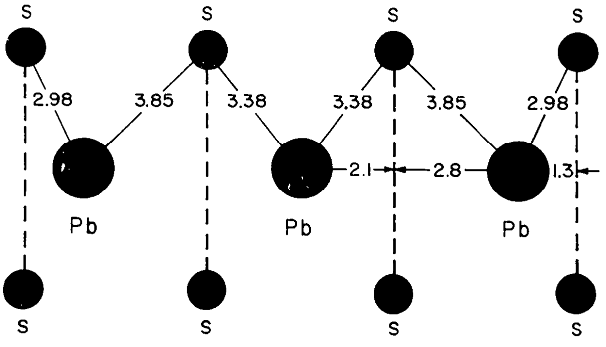

Fig. 5. Interatomic distances in the cation motif.

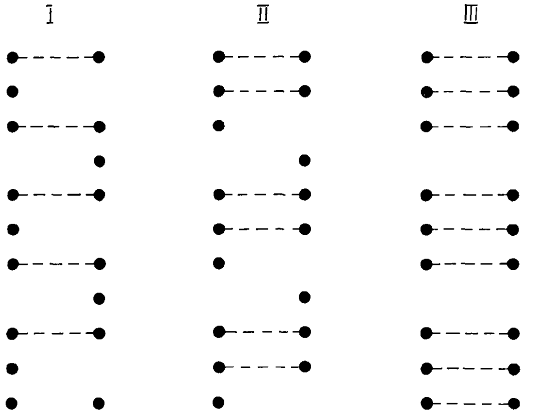

Fig. 6. The three possible topological arrangements of cations in adjacent polymeric chains in the (110) plane. The shortest $Pb^{2+} \cdots Pb^{2+}$ distances are shown by broken lines.

to play a smaller role than had been expected in the maintenance of a regular periodicity of thiourea groups along the direction of the chain axis. The important factor here seems to be the close packing of the amine groups of adjacent chains and interactions with the disordered anions in the channels between cation chains.

*Note added in proof*: – Truter & Vickery (1972) have suggested that $NH \cdots S$ hydrogen bonding between successive thioura molecules stacked along the [001] axis is responsible for the integrity of the columns in this family of complexes, and have shown that the appropriate interatomic distances and angles are compatible with this proposal. Hydrogen bonding within the columns could provide a neat answer to the question why the presence or absence of lead ions has so little effect on the column dimensions.

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# Die Kristallstruktur des Phtalimids (Kladnoit)

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Phthalimide, $C_8O_2NH_5$, occurring as the mineral kladnoite, is monoclinic with $a_0 = 22{\cdot}83$, $b_0 = 7{\cdot}651$, $c_0 = 3{\cdot}810$ Å, $\beta = 91{\cdot}36°$, space group $P2_1/n$, $Z = 4$. The crystal structure has been determined from three-dimensional diffractometer data. The final $R$ index for 1058 reflexions is 0·094. Two plane molecules are centrosymmetrically hydrogen bonded. These groups are stacked parallel to either $(\bar{2}11)$ or $(\bar{2}\bar{1}1)$ in the **c** direction.

## Experimentelles

Das von Rost (1942) beschriebene Mineral Kladnoit mit der chemischen Zusammensetzung des Phtalimids ($C_8O_2NH_5$), (Probe Nr. 34199 des Nationalmuseums Prag) wurde auf einem Zweikreisdiffraktometer (STADI-2-System der Fa. STOE) vermessen. Aus den systematischen Auslöschungen ($0k0$, $k = 2n+1$; $h0l$, $h+l = 2n+1$) ergab sich die Raumgruppe $P2_1/n$. Folgende Daten wurden ermittelt:

$$
\begin{aligned}
Z &= 4,\\
a_0 &= 22{,}83 \pm 0{,}01\ \text{Å},\\
b_0 &= 7{,}651 \pm 0{,}004\ \text{Å},\\
c_0 &= 3{,}810 \pm 0{,}002\ \text{Å},\\
\beta &= 91{,}36 \pm 0{,}02°,\\
D_m &= 1{,}47\ \text{g.cm}^{-3},\\
D_c &= 1{,}469\ \text{g.cm}^{-3},\\
\mu\text{Cu}\ K\alpha &= 9{,}15\ \text{cm}^{-1};
\end{aligned}
$$

sie stehen in guter Übereinstimmung mit den von Bagchi & Kasem (1945) bestimmten Werten.