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Thiourea Coordination Complexes of Pb(II) Salts. I. Octahedral Coordination in Triclinic Hexakis(thiourea)lead(II) Perchlorate

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The polymorph of $Pb(tu)_6(ClO_4)_2$ [tu = thiourea ($S=C(NH_2)_2$)] studied is triclinic with $a = 10{\cdot}83(2)$, $b = 12{\cdot}36\ (2)$, $c = 5{\cdot}86\ (2)$ Å, $\alpha = 102\ (1)^\circ$, $\beta = 95\ (1)^\circ$, $\gamma = 108{\cdot}3\ (8)^\circ$, space group $P\bar{1}$, 1 formula unit per cell. The structure was solved by Fourier methods and refined by full-matrix least-squares to a final conventional R value of 14·2 %. The crystal contains rather closely-packed $[Pb(tu)_6]^{2+}$ cations and ClO_4^- anions. The cation has sixfold coordination of S about Pb in a slightly distorted octahedral arrangement (all d(Pb–S) = 3·06 ± 0·01 Å but the S–Pb–S angles lie in the range 79–100°). The value obtained for d(Pb–S) indicates an ion-dipole interaction between metal and ligand. The anions are tetrahedral but with small deviations from regularity [d(Cl–O) in the range 1·41–1·50 Å (e.s.d. 0·05 Å), O–Cl–O angles in the range 100–114° (e.s.d. 2°)].

Introduction

This is the first of a series of papers on the crystal structures of thiourea coordination complexes of various lead(II) salts. Metal and ligand are being kept constant but anion and composition (salt:thiourea (tu) ratio) differ in the various complexes. Some complexes also contain additional components, such as water, which may or may not participate in the coordination to metal. The complexes studied so far are triclinic $Pb(ClO)_4)_2$.6tu (present paper), $Pb(picrate)_2$.4tu, $\frac{3}{4}Pb(HCOO)_2$.4tu and $Pb(HCOO)_2$.2tu.H_2O.

Mahr & Ohle (1939) prepared two different complexes of composition $Pb(ClO_4)_2$.6tu; yellow needles were obtained from acid solutions and white needles from neutral solutions. The yellow needles were found to be tetragonal by Boeyens & Herbstein (1967), who showed that their crystal structure was based on eightfold coordination of sulphur about lead in infinite polymeric chains. We now report the crystal structure of the second polymorph: the needles are triclinic and the crystals contain octahedral $[Pb(tu)_6]^{2+}$ and tetrahedral $(ClO_4)^-$ ions. These results have been described briefly (Goldberg, Herbstein & Reisner, 1967; Goldberg, Herbstein & Kaftory, 1968).

Experimental

White triclinic needles of $Pb(tu)_6(ClO_4)_2$ were precipitated on slow cooling of a saturated aqueous solution of thiourea to which the appropriate amount of $Pb(ClO_4)_2$ solution had been added (molar ratio $Pb(ClO_4)_2$:tu = 1:6). Chemical analysis confirmed the expected composition.

The crystal data (Table 1) were obtained from oscillation, Weissenberg and precession photographs. The intensities of 1752 reflexions (out of 1850 accessible to Cu $K\alpha$) were measured by the visual method from multiple-film equi-inclination Weissenberg photographs (l = 0,1,2,3) about the needle ([001]) axis. The intensities were corrected for Lorentz and polarization factors, for spot-shape (Phillips, 1956) and for absorption (using the approximation of a cylindrical crystal; $\mu R = 3{\cdot}16$ for the crystal used for intensity measurements). The reflexion intensities from the different layers were put on approximately the same scale by use of $0kl$ precession photographs (Mo $K\alpha$).

The following computational facilities were used:

(*a*) ALGOL programs for Elliott 503 written by one of us (I.G.) for data correction, Fourier syntheses, block-diagonal least-squares refinements and calculations of the geometry of the structure;

(*b*) Final full-matrix least-squares refinement was carried out at the Weizmann Institute on GOLEM, using FORTRAN programs written there.

Table 1. *Crystal data*

$Pb(ClO_4)_2.[SC(NH_2)_2]_6$ $M = 862{\cdot}81$
$\mu = 182\ cm^{-1}$ for Cu $K\alpha$
Triclinic
Cell dimensions: $a = 10{\cdot}83\ (2)$, $b = 12{\cdot}36\ (2)$, $c = 5{\cdot}86\ (2)$ Å
$\alpha = 102\ (1)^\circ$, $\beta = 95\ (1)^\circ$ $\gamma = 108{\cdot}3\ (8)^\circ$
(Reciprocal cell dimensions:
$a^* = 0{\cdot}0971$ $b^* = 0{\cdot}0914$ $c^* = 0{\cdot}1746$ Å^{-1}
$\alpha^* = 79^\circ$ $\beta^* = 90^\circ$ $\gamma^* = 72^\circ$).
Volume of unit cell = 691 Å^3
$D_m = 2{\cdot}06\ g.cm^{-3}$, $D_x = 2{\cdot}01\ g.cm^{-3}$ for 1 formula unit per unit cell.
Laue group $P\bar{1}$; no systematic absences, hence space group $P1$ (No. 1) or $P\bar{1}$ (No. 2).

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Determination and refinement of structure

The crystals were assumed to be centrosymmetric and this was confirmed by the successful structure analysis. Symmetry requires the Pb atom to be at the origin; there are three independent thiourea groups and one independent perchlorate group in the asymmetric unit. A three-dimensional Fourier synthesis with all signs positive gave the approximate positions of all atoms (except hydrogen, which were not included at any stage of the analysis). The atomic coordinates, anisotropic Debye–Waller factors and 4 layer scale factors were refined by the full-matrix least-squares method. Atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964), dispersion corrections (real part only) being applied to the f-curves of Pb, S and Cl (*International Tables for X-ray Crystallography*, 1962). The quantity minimized was $\sum w_{hkl}(|F_o|-|F_c|)^2$ where $w_{hkl}=(1/|F_o|)$ for $|F_o|\geq 5$ and $w_{hkl}=\frac{1}{5}$ for $|F_o|\leq 5$. The refinement was stopped when the conventional R value equalled 14·2%, at which stage convergence appeared to have been attained. The three-dimensional difference synthesis based on the final calculated structure factors had no undulations larger than ±2 e.Å^{-3}. The atomic parameters are listed in Tables 2 and 3. The estimated standard deviations of Cl and S atoms are about 0·01 Å, and those of C, N, O range from 0·03 to 0·12 Å. It seems unlikely that the Debye–Waller factors are accurate enough to warrant discussion of their physical significance. 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.*

Table 2. *Fractional coordinates and e.s.d.'s of the atoms in the asymmetric unit*

	x	y	z
Pb	0	0	0
Cl	0·368 (1)	0·613 (1)	0·247 (2)
O(1)	0·422 (4)	0·552 (3)	0·395 (8)
O(2)	0·391 (5)	0·742 (3)	0·357 (8)
O(3)	0·232 (3)	0·546 (4)	0·234 (8)
O(4)	0·420 (5)	0·602 (5)	0·013 (9)
S(1)	0·282 (1)	0·020 (1)	−0·149 (2)
C(1)	0·327 (6)	−0·070 (4)	−0·020 (10)
N(1)	0·382 (4)	−0·159 (4)	−0·199 (9)
N(4)	0·317 (4)	−0·050 (4)	0·190 (20)
S(2)	0·119 (1)	0·121 (1)	0·479 (2)
C(2)	0·258 (4)	0·262 (4)	0·490 (20)
N(2)	0·271 (5)	0·349 (4)	0·670 (10)
N(5)	0·326 (3)	0·272 (3)	0·277 (7)
S(3)	−0·008 (1)	0·258 (1)	−0·017 (3)
C(3)	−0·061 (4)	0·333 (3)	0·240 (10)
N(3)	−0·116 (5)	0·427 (4)	0·231 (9)
N(6)	−0·072 (5)	0·298 (4)	0·450 (10)

Table 3. *Anisotropic temperature factors and their e.s. d's* (Å^2).

The appropriate expression for the temperature factor of atom r is

$$\exp\left(-2\pi^2\sum_{i=1}^{3}\sum_{j=1}^{3}U^r_{ij}h_ih_ja_j^*a_j^*\right)$$

where U^r_{ij} are the coefficients of the (symmetric) atomic thermal vibration tensors and a_i^* are the reciprocal lattice parameters

	U_{11}	U_{22}	U_{33}†	U_{12}	U_{13}	U_{23}
Pb	0·010 (1)	0·010 (1)	0·007	0·007 (1)	−0·014 (1)	−0·011 (1)
Cl	0·032 (4)	0·029 (4)	0·030	0·014 (3)	−0·007 (4)	−0·005 (4)
O(1)	0·07 (2)	0·07 (2)	0·06	0·03 (2)	0·03 (2)	−0·03 (2)
O(2)	0·13 (4)	0·05 (2)	0·07	0·04 (2)	0·00 (2)	0·00 (2)
O(3)	0·05 (2)	0·10 (3)	0·07	0·02 (2)	0·04 (3)	0·00 (2)
O(4)	0·11 (4)	0·06 (2)	0·07	0·03 (2)	0·03 (2)	0·04 (3)
S(1)	0·054 (6)	0·040 (5)	0·043	0·022 (5)	0·000 (5)	0·000 (5)
C(1)	0·09 (4)	0·02 (2)	0·03	−0·01 (2)	0·00 (2)	0·05 (3)
N(1)	0·05 (2)	0·05 (2)	0·05	0·01 (2)	0·00 (3)	0·00 (3)
N(4)	0·02 (2)	0·03 (2)	0·29	0·00 (2)	0·06 (4)	0·00 (3)
S(2)	0·034 (4)	0·019 (4)	0·029	0·003 (3)	−0·010 (4)	−0·005 (4)
C(2)	0·01 (2)	0·04 (3)	0·03	−0·02 (2)	−0·10 (3)	−0·03 (3)
N(2)	0·06 (3)	0·07 (3)	0·07	−0·01 (2)	−0·06 (3)	−0·02 (3)
N(5)	0·04 (2)	0·03 (2)	0·03	0·00 (2)	0·00 (3)	0·03 (2)
S(3)	0·044 (5)	0·039 (5)	0·041	0·012 (4)	−0·007 (5)	0·006 (5)
C(3)	0·04 (2)	0·03 (2)	0·03	0·02 (2)	−0·01 (2)	0·00 (3)
N(3)	0·10 (4)	0·07 (3)	0·04	0·07 (3)	−0·05 (2)	−0·04 (3)
N(6)	0·11 (4)	0·06 (3)	0·06	0·07 (3)	−0·02 (3)	−0·02 (3)

† The absolute values of U_{33} are in doubt because the inter-layer scale factors were not measured sufficiently accurately (Lingafelter & Donohue, 1966). The program used permitted refinement of both scale factors and U_{33} under these circumstances but did not give e.s.d.'s for the U_{33} values.

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* Table 4 has been deposited as Document NAPS 01654 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 cheques or money orders payable to: CCMIC-NAPS.

Description of the structure

The crystal consists of $[Pb(tu)_6]^{2+}$ octahedra and $(ClO_4)^-$ tetrahedra. The lead atoms of the octahedra are at the centres of symmetry at the corners of the unit cell. The two $(ClO_4)^-$ tetrahedra per unit cell are at general positions but arranged symmetrically about the symmetry centre at the (body) centre of the unit cell (Fig. 1).

The packing is most dense in the [001] direction and somewhat less dense in [010] and, especially, [100] directions. The structure can be described in terms of cations with their centres in the (100) planes, interleaved by anions approximately in alternate (200) planes. As the cations are much larger than the anions, it is the former which determine the packing. The crystal should be considered formally as an ionic crystal, but dispersion forces undoubtedly make a much larger relative contribution to the lattice energy than in ionic crystals with smaller ions. Although the perchlorate ions are surrounded by $-NH_2$ groups of thiourea molecules (Fig. 1), there is little evidence for N···O hydrogen bonding (the shortest *d*(N···O) is 3·04 Å). The distance Pb···S(7) [Fig. 1(*b*)] is 3·74 Å, which may indicate a weak Pb···S interaction. More significantly, we note that some S···S distances, where the sulphur atoms are in different cations, do fall below Pauling's (1960) value of the van der Waals diameter of sulphur (3·70 Å; see Fig. 1(*b*) for details). An alternative explanation, following Nardelli, Fava Gasparri, Giraldi Battistini & Domiano (1966), is that a more appropriate value for the van der Waals diameter of sulphur is about 3·45 Å.

The dimensions of the PbS_6 octahedron are given in Fig. 2. The Pb–S distances are all essentially equal at 3·06 (1) but the three independent angles differ significantly (e.s.d. ~ 1°) and this leads to appreciable distortion from a regular octahedron. The angles that

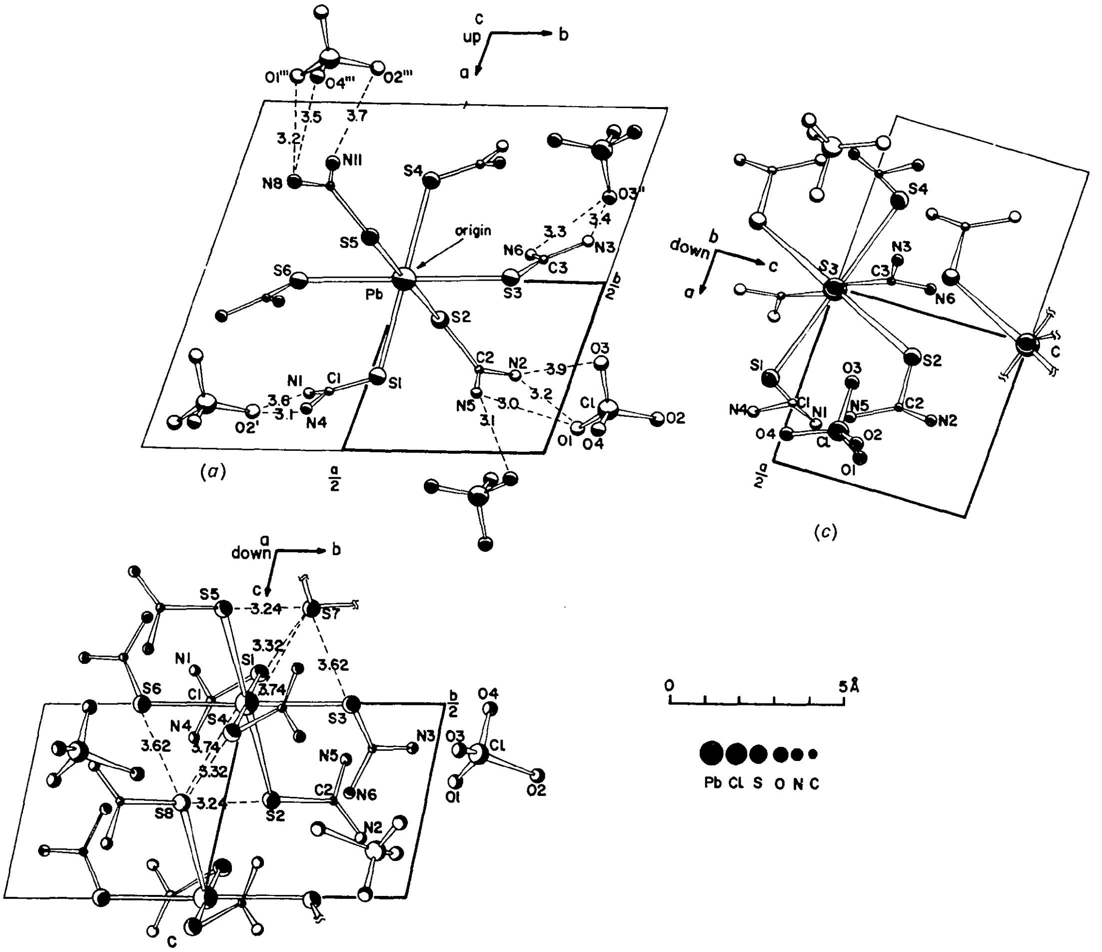

Fig. 1. Oblique projections of the crystal structure on to the three principal planes: (*a*) on to (001), (*b*) on to (100), (*c*) on to (010). The numbering of the atoms corresponds to the asymmetric unit given in Tables 2 and 3, with some additions of symmetry-related atoms. The shorter interatomic distances have been inserted. In (*c*) the labels N4 and N1 should be interchanged.

specify the orientations of the thiourea groups relative to the planes defined by Pb and S atoms are given in the caption to Fig. 2.

The ClO_4^- ion is tetrahedral but with small deviations from regularity, particularly with regard to the bond angles [d(Cl–O) = 1·42 (4), 1·46, 1·41, 1·50 Å, O–Cl–O = 112 (2), 100, 110, 108, 110, 114°]. The thiourea molecules have dimensions which are compatible with standard values; the accuracy of our results is too small to warrant detailed reproduction here.

Discussion

(*a*) *Crystal structure*

Rather similar cation–anion arrangements are found in other formally ionic $[ML_6]^{2+}X_2^-$ crystals where there is an appreciable disparity in the ionic sizes. Examples of such crystals with octahedral cations include lead(II), magnesium and calcium hexa-antipyrine perchlorates, which are isomorphous in space group $P\bar{3}$ (Vijayan & Viswamitra, 1966, 1967, 1968) and nitropentamminocobalt(III) bromide (Cotton & Edwards, 1968). Hydrogen bonds between cations and anions appear to be absent in these crystals. Similar packing is found in hexakis(thiourea)nickel(II) bromide (Weininger, O'Connor & Amma, 1969) where there is hydrogen-bonding between bromide ions and NH_2 groups of thiourea, and in hexakis(pyrazole)Ni(II) nitrate (Reimann, Santoro & Mighell, 1970) where there is hydrogen bonding between pyrrole-type nitrogen atoms (> N–H) and nitrate groups.

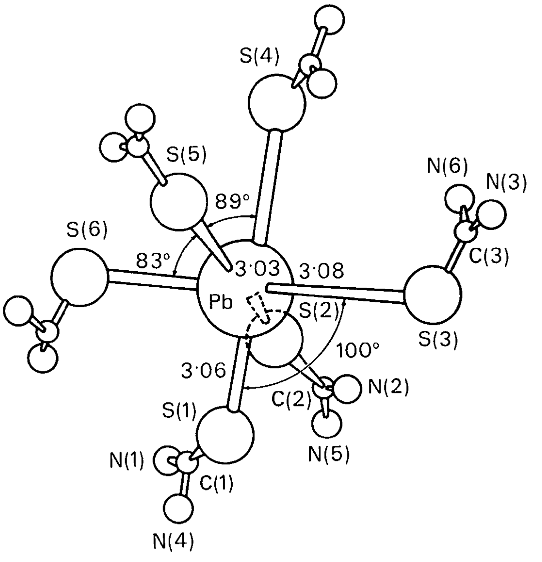

Fig. 2. Geometrical structure of $[Pb(tu)_6]^{2+}$ cation (symmetry $\bar{1}$). The bond angles at the sulphur atoms are: Pb–S(1)–C(1) = 103 ± 1°; Pb–S(2)–C(2) = 110 ± 5°; Pb–S(3)–C(3) = 115 ± 1°. The tilt angles of the three independent thiourea molecules are given by the angles between the planes defined by: S(3)–Pb–S(1) and Pb–S(1)–C(1); 29°; S(3)–Pb–S(1) and Pb–S(3)–C(3), 53½°; S(3)–Pb–S(2) and Pb–S(2)–C(2), 48¾°. The twist angles of the three thiourea molecules are given by the angles between the planes defined by

$$\mathrm{Pb{-}S(1){-}C(1)\ and\ S(1){=}C(1)}\!<\!\begin{matrix}\mathrm{N(1)}\\ \mathrm{N(4)}\end{matrix}\quad 54^\circ$$

$$\mathrm{Pb{-}S(2){-}C(2)\ and\ S(2){=}C(2)}\!<\!\begin{matrix}\mathrm{N(2)}\\ \mathrm{N(5)}\end{matrix}\quad 31^\circ$$

$$\mathrm{Pb{-}S(3){-}C(3)\ and\ S(3){=}C(3)}\!<\!\begin{matrix}\mathrm{N(3)}\\ \mathrm{N(6)}\end{matrix}\quad 14^\circ$$

A rather different type of packing is found in hexakis(imidazole)nickel(II) nitrate, where cations and anions are packed one above the other along the trigonal axis of the crystal (Santoro, Mighell, Zocchi & Reimann, 1969) rather than roughly side by side in the basal plane, as in the other examples considered above.

(*b*) *Structure of the cation*

Crystals containing octahedral $[Pb(tu)_6]^{2+}$ cations do not appear to have been studied previously. The lead–sulphur distance is compatible with ionic bonding between these atoms (Table 5). There are appreciable distortions of the cations from regular octahedral symmetry. One would hope to learn something about the bonding at the metal atoms by comparison of these distortions with the results available for the geometrical structures of other $[ML_6]^{2+}$ cations and ML_4X_2 molecules where L is a ligand and X a counterion. The following survey shows that many difficulties beset this path, presumably because the factors affecting metal–ligand bond angles are many and varied and no single factor seems to predominate.

Table 5. *Radii of* Pb *and* S (*Pauling*, 1960)

	Radius (Å)		
	van der Waals	Ionic	Covalent
Pb	1·53	1·20 (2+)	1·50
S	1·85	1·74 (2−)	1·00
Sum	3·38	2·94	2·50

The metal–ligand bond vectors are almost exactly mutually orthogonal in the following complexes with nickel–nitrogen bonds: hexakis(pyrazole)Ni(II) nitrate (Reimann *et al.*, 1970), hexakis(imidazole)Ni(II) nitrate (Santoro *et al.*. 1969), tetrakis(pyrazole)Ni(II) chloride (Reimann, Mighell & Maurer, 1967) and bromide (Mighell, Reimann & Santoro, 1969). The deviations from orthogonality do not exceed 1°. A regular octahedron is also found in $Mg[antipyrine]_6^{2+}$ (Vijayan & Viswamitra, 1967) where the Mg–O distance (2·06 Å) is the same as in magnesium oxide. Metal–ligand directional bonding is presumably important in the $[NiL_6]^{2+}$ and NiL_4X_2 complexes but not in Mg $[antipyrine]_6ClO_4$. The non-bonded N···N and O···O distances of adjacent ligands are close to the appropriate van der Waals distances in all these complexes and this may also play a role.

The other $[ML_6]^{2+}$ cations and ML_4X_2 molecules that have been studied are much less regular, especially insofar as metal–ligand bond angles are concerned. Distortion of the cation towards a trigonal antiprism configuration (three of the six ligands distorted towards each other and away from the other three) has already been demonstrated in $Ni(tu)_6Br_2$ (Weininger *et al.*, 1969; cation symmetry $\bar{1}$) and in Ca(antipyrine)$_6$ (ClO$_4$)$_2$ and Pb(antipyrine)$_6$(ClO$_4$)$_2$ (Vijayan & Viswamitra, 1968, 1966; both cations have symmetry $\bar{3}$). Near-equality of metal–sulphur and metal–chlorine distances in many ML$_4$Cl$_2$ complexes makes it worthwhile investigating whether a similar sort of distortion is found in these molecules. A distortion towards a trigonal antiprism configuration is found in Co(tu)$_4$Cl$_2$ (O'Connor & Amma, 1969), Ni(tmtu)$_4$Cl$_2$ (Luth & Truter, 1968; tmtu = tetramethylenethiourea) and Ni(etu)$_4$Cl$_2$ (Robinson, Holt & Carpenter, 1967; triclinic and monoclinic polymorphs; etu = ethylenethiourea). These molecules are all centrosymmetric.

The [Ti(urea)$_6$]$^{3+}$ cation in hexakis(urea)titanium(III) iodide (Davis & Wood, 1970) is also distorted from an octahedral towards a trigonal prism shape. However this distortion occurs as a rotation of 5·6° about the threefold axis (cation symmetry 32) instead of an elongation along a threefold axis (cation symmetry $\bar{3}$) as in the other examples discussed above. The Ti–O–C angle is 138°, considerably greater than the corresponding angles in the octahedral thiourea complexes.

There are exceptions: Ni(tu)$_4$Cl$_2$ (Lopez-Castro & Truter, 1963) does not have a centre of symmetry and is 'umbrella-shaped'. The [Pb(tu)$_6$]$^{2+}$ cation is centrosymmetric but no regularity can be discerned in the way in which it is distorted from an ideal octahedral configuration. The non-bonded S···S distances are close to the van der Waals diameter of sulphur in the complexes with Ni–S and Co–S bonds but interactions of this kind cannot be important in [Pb(tu)$_6$]$^{2+}$, [Pb(antipyrine)$_6$]$^{2+}$ and [Ca(antipyrine)$_6$]$^{2+}$.

The mean coordinate-bond dissociation energies in octahedral second-row transition metal [M(tu)$_6$]Cl$_2$ complexes have recently been measured by Ashcroft (1970) and compared with values for other complexes: $\bar{D}$(M–S) ranges around 30 kcal. mole^{-1} (seven different complexes) whereas $\bar{D}$(M–S) is 56 kcal.mole^{-1} (for [Fe(H$_2$O)$_6$]$^{2+}$ and $\bar{D}$(M–N) ranges around 65 kcal. mole^{-1} (for five different hexammine complexes). The greater bond-strength of metal–nitrogen than metal–sulphur bonds is one of the reasons why the pyrazole and imidazole complexes are more resistant to bond-angle distortion than thiourea complexes.

The dispositions of the thiourea groups in transition metal–thiourea complexes have been reviewed by Berta, Spofford, Boldrini & Amma (1970). The metal–sulphur–carbon angles are between 106 and 116°; the rotation (tilt) of the thiourea molecule about the M–S bond is in the range 30–57° and the twist of the thiourea about the S–C bond is in the range 14–35°. These tilts and twists occur irrespective of the nature of the transition metal or its coordination number in the complex, and are not influenced by the nature of the anion. Although hydrogen bonding, van der Waals forces and packing considerations could influence the exact orientation of the ligand, nevertheless the tilt and twist were considered to be fundamental consequences of the metal–thiourea interaction, and it was suggested that low-energy sulphur *d* orbitals that do not mix with the thiourea π orbitals act as acceptors for the metal electrons. The Pb–S–C tilt and twist angles found in [Pb(tu)$_6$]$^{2+}$ fall within or close to the limits given above, and it is reasonable to assume that much the same factors operate in determining the thiourea conformation in all these metal–thiourea complexes; it is not necessary that the metal atom should belong to the transition series, only that it should form an octahedral thiourea coordination complex.

We conclude, from the Pb···S distances, that the bonding in the cations is a result of ion–dipole interactions. This leads to the further conclusion that the irregular distortions found from the regular octahedron expected on the basis of ligand repulsions, are due to packing effects. However the orientations of the ligands about the metal ion are so similar to those found in other metal–thiourea coordination complexes that we conclude that they are determined primarily by the bonding characteristics of the sulphur atoms, with only secondary perturbations from packing effects.

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Thiourea Coordination Complexes of Pb(II) Salts.
II. Octahedral Coordination in Tetrakis(thiourea)lead(II) Picrate

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Pb(tu)$_4$(picrate)$_2$ is monoclinic with $a=39{\cdot}51$ (8), $b=4{\cdot}74$ (5), $c=20{\cdot}13$ (8) Å, $\beta=125$ (1)°, space group *Cc* or *C*2/*c* (latter established by successful structure analysis), 4 formula units per cell. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to a final conventional *R*-value of 12·4%. The crystal contains polymeric chains of edge-sharing distorted Pb(tu)$_6$ octahedra and stacks of picrate ions. Both the polymeric chains and the stacks of anions are arranged in infinite sheets parallel to (100), the crystal structure thus being made up of interleaved parallel cationic and anionic sheets with hydrogen bonds between them. The distances from Pb to shared S are 2·87 and 3·23 Å and the distance of Pb to unshared S is 2·96 Å. The analogous polymeric chains of edge-sharing octahedra found in Cd(tu)$_2$(HCOO)$_2$, Ni(tu)$_2$(NCS)$_2$ and Pb(tu)$_2$Cl$_2$ are more regular than the polymeric chains in Pb(tu)$_4$(picrate)$_2$. The overall packing is similar to that found in the equimolar molecular complex of hexabromobenzene and 1,2,4,5-tetrabromobenzene.

Introduction

The coordination complexes of Pb(II) salts with thiourea (tu) show a variety of compositions and types of coordination but no clear principles have yet emerged allowing one to connect composition and coordination type. Sixfold coordination of thiourea about lead has been found in triclinic Pb(ClO$_4$)$_2$.6tu (Goldberg & Herbstein, 1972), eightfold coordination in tetragonal Pb(ClO$_4$)$_2$.6tu (Boeyens & Herbstein, 1967) and sevenfold (mixed ligand) coordination in PbCl$_2$.2tu (Nardelli & Fava, 1959). Although some PbX$_2$.4tu complexes are known (Boeyens & Herbstein, 1967) on structures have yet been reported. We have determined the crystal structure of tetrakis(thiourea)lead(II) picrate (Yatsimirsky & Astasheva, 1952) and find that there is octahedral coordination of sulphur about lead, the octahedra being arranged in infinite polymeric chains and joined by shared edges. Preliminary reports have been published (Goldberg, Herbstein & Kaftory, 1968; Herbstein & Kaftory, 1969). It would be premature to generalize from this result as the cell dimensions and space groups of the PbX$_2$.4tu complexes investigated so far do not show any marked similarities.

Experimental

Yellow needles, elongated along [010], were obtained by slow cooling of an aqueous solution containing thiourea and lead(II) picrate.

Crystal data (*from oscillation and Weissenberg photographs*)

Pb(C$_6$H$_2$N$_3$O$_7$)$_2$ [SC(NH$_2$)$_2$]$_4$,
m.p. 159° (decomp.), $M=963{\cdot}6$, $\mu=134$ cm^{-1} (for Cu $K\alpha$),
monoclinic, $a=39{\cdot}51(8)$, $b=4{\cdot}74(5)$, $c=20{\cdot}13(8)$ Å, $\beta=125(1)°$,
$U=2918$Å^3,
$D_m=2{\cdot}09$ g.cm^{-3}, $D_x=2{\cdot}07$ g.cm^{-3} for $Z=4$.
Reflexion conditions hkl for $h+k=2n$, $h0l$ for $l=2n(h=2n)$, $0k0$ for $(k=2n)$.
Possible space groups: *Cc* (No. 9) or *C*2/*c* (No. 14) (*C*2/*c* was confirmed by the structure analysis).

Intensities of 1842 $h0l$, $h1l$ and $h2l$ independent reflexions were measured by the visual method from equi-inclination Weissenberg photographs (Cu $K\alpha$). Geometrical corrections were applied by standard programs; an absorption correction was not made ($\mu R=1{\cdot}07$ for the crystal used).

Computing facilities used and other details are described in part I (Goldberg & Herbstein, 1972).

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