Molecular Adducts of Inorganic Salts. III. Non-Centrosymmetric $3Pb(ReO_4)_2.2tu.2H_2O$ (tu = Thiourea)

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Abstract

The non-centrosymmetric three-dimensional framework structure of lead perrhenate thiourea hydrate (space group $P\bar{4}2_1m$), $[\{Pb(ReO_4)_2\}_3(CH_4N_2S)_2].2H_2O$, is built up of two types of chains running along the c axis: $[Pb(ReO_4)_4]$ and $[Pb_2(ReO_4)_2tu_2](H_2O)_2$ (tu = thiourea). In the first type the Pb atom at the inversion point of the $\bar{4}$ axis is surrounded by a highly regular dodecahedron of two tetrads of ReO_4 groups, forming M—T—M (M = Pb, T = ReO_4) bridges. The second type of chain has $mm2$ symmetry and consists of $(PbO_7S_2)_2$ bipolyhedra with a common quadratic face of c-repeated pairs of ReO_4 corners; the next two O atoms in PbO_7S_2 are ReO_4 corners from the $[Pb(ReO_4)_4]$ chains and the last one belongs to H_2O. The S atoms of the tu molecules act as common vertices of the c-repeated lead bipolyhedra. An interesting feature of this structure is the arrangement of tu and H_2O molecules in an alternating sequence with short contacts between the C and O atoms $[C\cdots O$ 2.89 (5) and 2.91 (5) Å].

Comment

The first thiourea (tu) adducts of Pb salts for which the structure building role of tu was established were $PbCl_2.2tu$ (Nardelli & Fava, 1959) and $Pb(CH_3COO)_2.tu$ (Nardelli, Fava & Branchi, 1960). Herbstein and co-workers published a series of papers on the crystal chemistry of thiourea coordination complexes of Pb^{2+} salts (Herbstein & Reisner, 1984, and references therein). In these compounds the tu:Pb ratio (n) varies from 1 to 6 and the tu molecules act as monodentate ligands or form single, double or quadruple Pb—S—Pb bridges in the polymerized cationic complexes. The only two adducts of salts with tetrahedral anionic groups were $Pb(ClO_4)_2.6tu$, which crystallizes in white triclinic (Boeyens & Herbstein, 1967) and yellow tetragonal (Goldberg & Herbstein, 1972) modifications, and $Pb(ClO_4)_2.6tu.2H_2O$ (Boeyens & Herbstein, 1967) with a structure similar to that of the anhydrous tetragonal phase.

Recently, we started an investigation of the structure and properties of different perrhenates with the general formula $M(ReO_4)_2$ (M = Ca, Sr, Ba, Pb, Cd), their hydrates (Macíček & Todorov, 1992; Todorov & Macíček, 1995; for powder patterns see ICDD, 1994), and adducts (Macíček, Angelova & Petrova, 1995a,b: parts I and II of this series). In contrast to urea, which forms adducts with all of the above ions, thiourea compounds were obtained for Pb and Cd only. The title compound crystallizes from aqueous solutions of tu and $Pb(ReO_4)_2$ with tu:Pb ratios, n, of 1 and 2. The X-ray powder analysis of the solid residue, however, indicates that besides thiourea in this part of the $Pb(ReO_4)_2$–tu–H_2O system, other phases are also present.

$3Pb(ReO_4)_2.2tu.2H_2O$ is a new non-centrosymmetric phase containing $Pb(ReO_4)_2$ [lead perrhenate itself has space group $P31m$ (Picard, Besse, Baud, Chevalier & Gasperin, 1984)]. The two distinct Pb atoms in the structure are localized in special positions of the space group $P\bar{4}2_1m$: Pb1 lies on the inversion point of $\bar{4}$ [Wyckoff position 2(a)] and Pb2 on the diagonal mirror plane [4(e)]. The symmetry restricted coordination polyhedron of Pb1 is a highly regular dodecahedron of eight almost equidistant O atoms at $4 \times 2.592\,(16)$ (O11) and $4 \times 2.623\,(18)$ Å (O12). The α and β angles of 54.8 and 19.1° are very close to the angles of 51 and 19°, respectively, that correspond to minimum repulsivity among the ligands (King, 1969). The lengths of the 18 edges vary in the range $3.10\,(2)$–$4.04\,(2)$ Å. The ninefold coordinated Pb2 atom has four O atoms at $2 \times 2.891\,(15)$ (O21) and $2 \times 2.824\,(16)$ Å (O22), forming the basal square face of a tetra-monocapped tetragonal antiprism; two O atoms at $2 \times 2.564\,(14)$ Å; two S atoms at 2.973 (9) and 2.991 (9) Å, being the vertices of the upper rhombohedrally deformed square face; and a capping water O atom, OW, at 2.500 (10) Å. While the Pb1O$_8$ polyhedra are isolated, the Pb2O$_7$S$_2$ polyhedra share pairwise the basal tetragonal faces, thus forming $(Pb2O_7S_2)_2$ bipolyhedra. The $Pb2\cdots Pb2(-x, 1 - y, z)$ distance of 3.850 (1) Å across the shared face is comparable with the shortest $Pb\cdots Pb$ distances in PbO [litharge: 3.674 (1)–3.974 (1) Å (Boher, Garnier, Gavarri & Hewat, 1985); massicot: 3.536 (2)–3.856 (1) Å (Hill, 1985)].

The bond lengths and angles in the ReO_4 tetrahedra have typical values (Lock & Turner, 1975; Picard, Baud, Besse, Chevalier & Gasperin, 1984; Macíček & Todorov, 1992). Three vertices of $Re1O_4$ take part in a simple mode of coordination with the Pb atoms, two to Pb1 and one to Pb2, the Pb—O bonds being of almost equal length (see Table 2) and the Re—O—Pb angles being 135.7 (8), 161 (1) and 170 (1)° for Re—O11—Pb1, Re—O12—Pb1 and Re—O13—Pb2, respectively. O11, in addition, is hydrogen bonded to an adjacent tu molecule and O14 is hydrogen bonded to a water molecule (see Fig. 1). Two vertices of $Re2O_4$ (O21 and O22) form bifurcated bonds with four Pb2 atoms, making the $O21\cdots O22$ edge a junction between four Pb2 atoms with angles Re—O—Pb and Pb—O—Pb
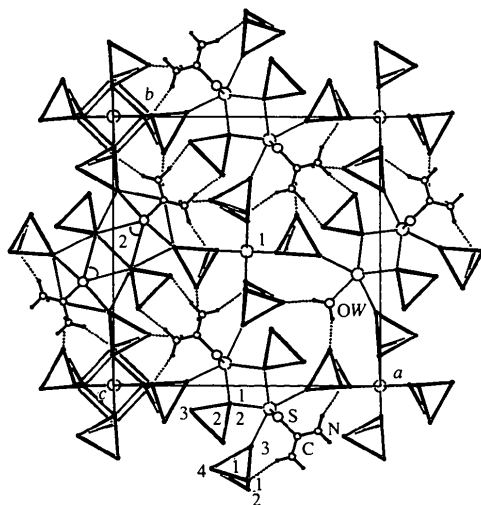
Fig. 1. Projection of the structure along the c axis with the atom numbering indicated. The Pb polyhedra are outlined on the left-hand side of the drawing. The Re atoms are omitted for clarity. Dotted lines represent hydrogen bonds.

of 136.8 (7) and 83.5 (5)°, respectively, for O21, and 136.0 (7) and 86.0 (5)°, respectively, for O22. The other two O atoms at Re2O$_4$ are only hydrogen bonded.

The geometry of the coordinated tu is featureless and is similar to that previously reported for the unco-ordinated (Elcombe & Taylor, 1968) and coordinated (Herbstein & Reisner, 1984) molecules. The amino H atoms, placed at calculated positions, conform to a reasonable hydrogen-bonding scheme as depicted in Fig. 1, with N$\cdots$O23(y, 1 $-$ x, $-z$) 2.94 (2) Å and N—H1$\cdots$O23 172 (1)°, and N$\cdots$O11 (x, y, z) 3.22 (2) Å and N—H2$\cdots$O11 146 (1)°.

The crystal has a three-dimensional framework structure formed by two types of chains running along the c axis: [MT_4] and [$M_2T_2\varphi_2$]φ'_2, in the revised notation of Hawthorne (Eby & Hawthorne, 1993; Hawthorne, 1994), where M = Pb, T = ReO$_4$, φ = bridging S atom of tu, and φ' stands for the flanking H$_2$O molecules. Similar fourfold bridges (as shown below)

$$M \underset{\diagdown T \diagup}{\overset{\diagup T \diagdown}{\diagdown T \diagup}} M$$
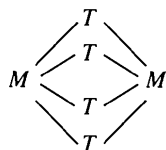
to those in the [MT_4] chains (Fig. 2a) exist in the structure of NaNd(ReO$_4$)$_4$.4H$_2$O (Slimane, Silvestre, Freundlich & Rimsky, 1982). In the structure of Ca(ReO$_4$)$_2$.urea.H$_2$O this kind of bridging alternates with double urea O-atom bridges of the type:

$$M \overset{\diagup O \diagdown}{\underset{\diagdown O \diagup}{}} M$$
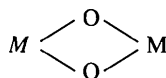
(Macíček, Angelova & Petrova, 1995). A rare case of square-face coupling of metal polyhedra is realised in the [$M_2T_2\varphi_2$]φ'_2 type chains; the Pb polyhedra are interconnected by S and T bridges (Fig. 2b) and the chains adopt $mm2$ symmetry.
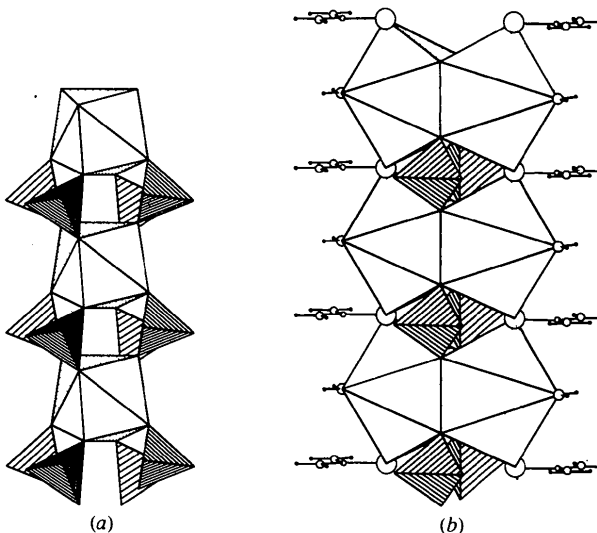
Fig. 2. Views of (a) the infinite [Pb(ReO$_4$)$_4$] chain and (b) the [Pb$_2$(ReO$_4$)$_2$tu$_2$].2H$_2$O ribbon.

The water molecule takes part in two short symmetrical hydrogen bonds: the OW$\cdots$O14($\frac{1}{2}$ $-$ x, $\frac{1}{2}$ $+$ y, 1 $-$ z)/O14(1 $-$ x, y, 1 $-$ z) distances are 2.843 (16) Å, and the OW—H$\cdots$O angles are 166.1 (5)°. The Pb2—OW and OW$\cdots$O bonds are coplanar (Fig. 1) with angles Pb2—OW$\cdots$O and O$\cdots$OW$\cdots$O of 134.0 (5) and 91.9 (5)°, respectively. This geometry is consistent with Class 1, Type D, of water according to Ferraris & Franchini-Angela (1972). Just above and below this plane are situated C atoms from the adjacent tu molecules, at the short distances of 2.89 (5) and 2.91 (4) Å for OW$\cdots$C(x, y, z) and OW$\cdots$C(x, y, 1 $+$ z), respectively. Such close disposition of H$_2$O and tu molecules in stacks may indicate that C and OW atoms are involved in a significant p_π–p_π interaction as the planar coordination environment of the water moiety facilitates the sp^2 hybridization of OW.

Experimental

Crystal data

[{Pb(ReO$_4$)$_2$}$_3$(CH$_4$N$_2$S)$_2$].- 2H$_2$O	Mo $K\alpha$ radiation
M_r = 2311.02	λ = 0.7107 Å
Tetragonal	Cell parameters from 22
$P\bar{4}2_1m$	reflections
a = 16.208 (2) Å	θ = 20.25–21.16°
c = 5.800 (2) Å	μ = 40.93 mm^{-1}
	T = 292 K

$V = 1523.5\ (8)\ \text{Å}^3$
$Z = 2$
$D_x = 5.037\ \text{Mg m}^{-3}$

Prismatic
$0.09 \times 0.07 \times 0.07$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Continuous scan profiles
Absorption correction:
  ψ scan
$T_{min} = 0.529,\ T_{max} = 0.998$
4712 measured reflections
2324 independent reflections

1317 observed reflections
  $[I > 3\sigma(I)]$
$R_{int} = 0.062$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 22$
$l = -8 \rightarrow 8$
3 standard reflections
  frequency: 120 min
  intensity decay: 3.9%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.049$
$S = 0.736$
1317 reflections
108 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F) + (0.040F)^2]$
$(\Delta/\sigma)_{max} = 0.279$

$\Delta\rho_{max} = 4.61\ \text{e Å}^{-3}$
$\Delta\rho_{min} = -2.88\ \text{e Å}^{-3}$
Extinction correction: Stout & Jensen (198)
Extinction coefficient: 2.751×10^7
Atomic scattering factors from *SDP/PDP* (Enraf–Nonius, 1985)

O12—Re1—O14	109.1 (9)	O23^{xiv}—Re2—O23^{iii}	107.8 (8)
O13—Re1—O14	109.0 (8)	N—C—N^{ix}	120 (2)
O21—Re2—O22	111.3 (8)		

Symmetry codes: (i) $1-x$, $1-y$, z; (ii) $1-y$, x, $-z$; (iii) y, $1-x$, $-z$; (iv) $x, y, z-1$; (v) $1-x$, $1-y$, $z-1$; (vi) $1-y$, x, $1-z$; (vii) y, $1-x$, $1-z$; (viii) $x, y, 1+z$; (ix) $y - \frac{1}{2}, \frac{1}{2}+x, z$; (x) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (xi) $x - \frac{1}{2}, \frac{3}{2} - y, -z$; (xii) $\frac{1}{2} - x, y - \frac{1}{2}, 1-z$; (xiii) $x - \frac{1}{2}, \frac{3}{2} - y, 1-z$; (xiv) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

The water H atoms were found from a difference Fourier map and the urea H atoms were placed in calculated positions (C—N—H 120°, N—H 0.95 Å). All H atoms were refined as riding with fixed $U_{iso} = 0.044\ \text{Å}^2$. The absolute configuration was elucidated by refinement of the two enantiomers with the same intensity data. The refinement of the alternative enantiomer converged at $R = 0.047$ and $wR = 0.056$, and one atom (O21) was non-positive definite. No other tests for the correctness of the absolute-configuration assignment were performed.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1988). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, unpublished).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pb1	1/2	1/2	0	0.0178 (2)
Pb2	0.08398 (5)	$x + 1/2$	0.5123 (2)	0.0183 (2)
Re1	0.31968 (5)	0.47198 (5)	0.4678 (1)	0.0167 (2)
Re2	0.39130 (5)	$x + 1/2$	−0.0020 (2)	0.0183 (2)
S	0.1143 (3)	$x + 1/2$	0.0139 (15)	0.025 (1)
O11	0.3584 (10)	0.5058 (11)	0.207 (3)	0.029 (5)
O12	0.3864 (12)	0.5041 (13)	0.678 (3)	0.037 (5)
O13	0.2267 (8)	0.5158 (10)	0.515 (3)	0.035 (4)
O14	0.3099 (10)	0.3684 (8)	0.482 (3)	0.034 (4)
O21	0.4328 (11)	$x + 1/2$	−0.252 (4)	0.031 (4)
O22	0.4350 (11)	$x + 1/2$	0.241 (4)	0.024 (4)
O23	0.2139 (10)	0.4078 (10)	0.005 (3)	0.038 (4)
OW	0.1931 (8)	$x + 1/2$	0.508 (4)	0.024 (4)
N	0.2689 (10)	0.6694 (11)	0.016 (3)	0.024 (4)
C	0.1903 (13)	$x + 1/2$	0.010 (8)	0.037 (7)

Table 2. *Selected geometric parameters* $(\text{Å}, °)$

Pb1—O11	2.592 (16)	Pb2—O22^{xii}	2.824 (12)
Pb1—O11^i	2.592 (16)	Pb2—O22^{xiii}	2.82 (2)
Pb1—O11^{ii}	2.592 (16)	Pb2—OW	2.500 (10)
Pb1—O11^{iii}	2.592 (16)	Re1—O11	1.727 (16)
Pb1—O12^{iv}	2.623 (18)	Re1—O12	1.711 (18)
Pb1—O12^v	2.623 (18)	Re1—O13	1.688 (14)
Pb1—O12^{vi}	2.623 (18)	Re1—O14	1.689 (13)
Pb1—O12^{vii}	2.623 (18)	Re2—O21	1.734 (19)
Pb2—S	2.973 (9)	Re2—O22	1.73 (2)
Pb2—S^{viii}	2.991 (9)	Re2—O23^{xiv}	1.729 (16)
Pb2—O13	2.564 (14)	Re2—O23^{iii}	1.729 (16)
Pb2—O13^{ix}	2.564 (14)	S—C	1.742 (16)
Pb2—O21^x	2.891 (11)	N—C	1.32 (3)
Pb2—O21^{xi}	2.891 (19)		
O11—Re1—O12	107.3 (8)	O21—Re2—O23^{xiv}	108.3 (9)
O11—Re1—O13	109.4 (9)	O21—Re2—O23^{iii}	108.3 (7)
O11—Re1—O14	113.1 (9)	O22—Re2—O23^{xiv}	110.5 (9)
O12—Re1—O13	108.7 (9)	O22—Re2—O23^{iii}	110.5 (7)

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Tetrakis(N,N'-diphenylbenzamidinato)-dicopper(II) Dichloromethane Solvate

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Abstract

The title compound, [Cu$_2$(C$_{19}$H$_{15}$N$_2$)$_4$].2CH$_2$Cl$_2$, forms a cage structure with fourfold symmetry. The cage comprises two Cu atoms lying on the axis and four bridging ligand units related by the fourfold rotation. The ligand units also have approximate twofold axial symmetry. The Cu1—Cu2 separation of 2.460 (2) Å is consistent with a single-bond distance. The metal–ligand distances, Cu1—N1 of 2.020 (5) and Cu2—N2 of 2.027 (4) Å, are effectively equal. A cavity within the structure is occupied by disordered molecules of dichloromethane solvent.

Comment

As part of a study of amidino complexes of Cu^I and Cu^{II}, the title compound, (I), was prepared from anhydrous copper(II) chloride and lithio(N,N'-diphenylbenzamidine) in monoglyme solution (Kilner &

Pietrzykowski, 1983), and recrystallized from dichloromethane.

In the structure, the two non-equivalent Cu atoms lie on the same fourfold axis of the space group and are bridged by four ligand molecules forming a binuclear cage (Figs. 1 and 2). The ligand has approximate twofold symmetry about an axis in the C1—C8···C11 direction, which relates the two halves of the molecule. The point-group symmetry of the molecule is thus approximately 422 (D_4), the fourfold symmetry, of course, being exact. The two Cu atoms are sufficiently close [2.460 (2) Å] to be regarded as single bonded and the two Cu—N distances [2.020 (5) and 2.027 (4) Å] are very similar. In the ligand, the distances C1—N1 and C1—N2 of 1.327 (8) and 1.335 (8) Å, respectively, are virtually identical, indicating that delocalization has occurred, which is in contrast to the significantly different mean values of 1.360 (8) and 1.302 (7) Å found for C—N and C=N, respectively, in the free uncoordinated ligand dimer (Alcock, Barker & Kilner, 1988). These workers considered there to be a marked interaction between the C—N(amine) part of the skeleton and its associated phenyl ring, with a tendency towards planarity. This effect is absent in the present structure where the dihedral angles between the N1—C1—N2 plane and the planes of the phenyl groups at C2 and C14 are nearly equal at 63.7 (5) and 65.2 (5)°, respectively. This feature is evidenced also by the pseudosymmetry of the ligand moiety. The increased C1—C8 length of 1.524 (6) Å, compared with the mean value 1.485 Å in the free ligand, is evidence of the loss of conjugation with the phenyl group in that structure in favour of delocalization
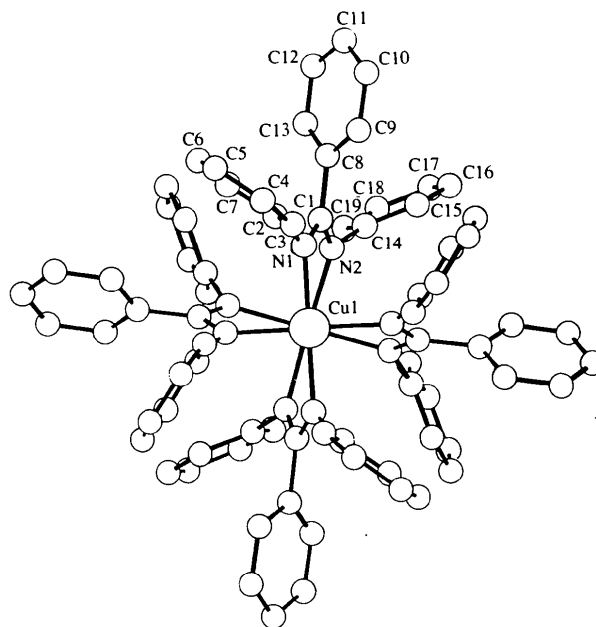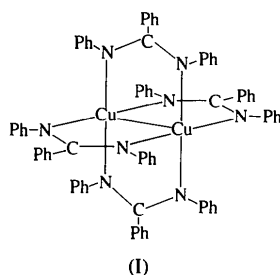

Fig. 1. The title molecule viewed along the fourfold axis, with independent atoms labelled. Atom Cu2 is overlapped exactly by Cu1.