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Hexakis(2-chloroethylammonium) Hexachloroplumbate(II) Chloride

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Abstract

The crystal structure of $6(C_2H_7ClN)[PbCl_6]2Cl$ consists of discrete $[PbCl_6]^{4-}$ octahedra and Cl^- anions to which the $ClCH_2CH_2NH_3^+$ cations are hydrogen bonded. Due to intramolecular hydrogen bonding, the cations adopt conformations with N—C—C—Cl torsion angles ranging from 59.4 (6) to 72.4 (6)°.

Comment

Alkylammonium haloplumbates(II) form structures which have not been observed for other alkylammonium halometallates(II). The methylammonium trihaloplumbates, for example, are the only alkylammonium trihalometallates(II) known to have an anionic partial structure analogous to the octahedral network of cubic perovskite (Knop, Wasylishen, White, Cameron & van Oort, 1990). The same workers were also the first to report on an alkylammonium hexahaloplumbate(II): they obtained tetrakis(methylammonium) hexaiodoplumbate(II) dihydrate as a byproduct of the synthesis of the corresponding triiodoplumbate(II) (Vincent, Robertson, Cameron & Knop, 1987). The present work is part of a systematic investigation on alkylammonium haloplumbates(II) and is the first report on a hexachloro derivative.

(I)
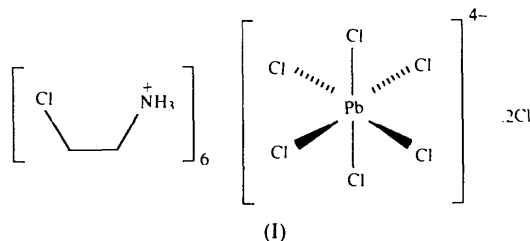
Hexakis(2-chloroethylammonium) hexachloroplumbate(II) chloride, (I), was prepared by slow evaporation of a concentrated hydrochloric acid solution containing lead(II) chloride and 2-chloroethylamine hydrochloride in stoichiometric quantities. Its crystal structure consists of alternating layers parallel to (010) of discrete centrosymmetric $[PbCl_6]^{4-}$ octahedra and Cl ions. Each octahedron forms hydrogen bonds to four cations, two of which are each connected to a Cl ion *via* another hydrogen bond. The units thus built are linked to each other *via* hydrogen bonds between one cation and two Cl ions to yield a network which can be described as hydrogen-bonded ribbons along [010] of alternating tetrakis(2-chloroethylammonium) hexachloroplumbate(II) and dimeric 2-chloroethylammonium chloride units. Cl···H distances are 2.30 (2)–2.45 (3) Å for Cl belonging to $[PbCl_6]^{4-}$ and 2.18 (2)–2.46 (3) Å for the Cl ion. N—H···Cl angles are in the range 131 (2)–163 (2)°.
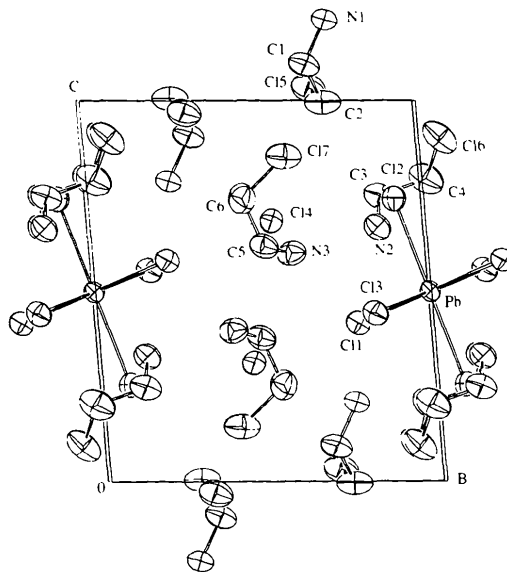
Fig. 1. *ORTEP* view (Johnson, 1965; Hall, Flack & Stewart, 1992) along [100] with H atoms omitted for clarity. The displacement ellipsoids are plotted at the 50% probability level.

In Cs_4PbCl_6 [the only hexachloroplumbate(II) reported previously], Petrov *et al.* (1987) found almost ideal $[PbCl_6]^{4-}$ octahedra with Pb—Cl bond lengths between 2.882 (3) and 2.889 (3) Å and Cl—Pb—Cl bond angles deviating from ideal values by no more than 0.42°. In the title compound the octahedron is slightly distorted. Pb—Cl1 is *ca* 0.05 Å shorter than the other two Pb—Cl bond lengths. The distortion can be accounted for by scrutiny of the hydrogen bonding. Cl1 forms a hydrogen bond with a Cl···H distance of 2.45 (3) Å, whereas for Cl2

and Cl3 the corresponding distances are 2.31 (2) and 2.30 (2) Å, respectively. The Cl1···H bond thus seems to be rather weak. Cl2 forms two further hydrogen bonds with Cl···H distances of 2.41 (6) and 2.45 (3) Å. Despite this, the Pb—Cl2 and Pb—Cl3 bond lengths differ by only 0.002 Å. Apart from the axial distortion of Pb—Cl1, the octahedron shows an angular distortion as a consequence of the bridging of Cl1 and Cl2 by two H atoms bonded to N1. The maximum deviation of the octahedral angles from ideal values is 3.04 (4)°.

The cations each adopt an unusual conformation in which one N—H bond is almost exactly coplanar with the corresponding C—Cl bond, leading to N—C—C—Cl torsion angles of 59.4 (6)–72.4 (6)°. The intramolecular N···Cl distances of 3.065 (5)–3.196 (6) Å are considerably shorter than the sum of the van der Waals radii (3.30 Å) of Cl and N (Pimentel & McClellan, 1960).

Experimental

Crystal data

6(C$_2$H$_7$ClN)[PbCl$_6$]2Cl
$M_r = 974.05$
Triclinic
$P\overline{1}$
$a = 8.175$ (1) Å
$b = 10.150$ (2) Å
$c = 11.254$ (1) Å
$\alpha = 83.28$ (1)°
$\beta = 81.07$ (1)°
$\gamma = 74.30$ (1)°
$V = 885.3$ (2) Å^3
$Z = 1$
$D_x = 1.827$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.89–16.68°$
$\mu = 5.88$ mm^{-1}
$T = 298$ K
Prism
$0.175 \times 0.175 \times 0.100$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.852$, $T_{max} = 0.998$
4031 measured reflections
3105 independent reflections
3036 observed reflections
[$F > 2\sigma(F)$]

$R_{int} = 0.015$
$\theta_{max} = 24.97°$
$h = -9 \rightarrow 2$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.029$
$wR = 0.039$
$S = 1.06$
3007 reflections
223 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{max} = 0.058$
$\Delta\rho_{max} = 1.33$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV, Tables 2.2B and 2.3.1)

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}
Pb	1/2	1	1/2	0.0354 (2)
Cl1	0.6525 (2)	1.2215 (1)	0.4190 (1)	0.0486 (9)
Cl2	0.5536 (2)	0.9145 (1)	0.2567 (1)	0.0513 (9)
Cl3	0.8307 (2)	0.8287 (1)	0.5547 (1)	0.0521 (9)
Cl4	0.3372 (2)	0.5454 (1)	0.3147 (1)	0.060 (1)
Cl5	0.7122 (2)	0.3087 (2)	0.0313 (2)	0.078 (1)
Cl6	1.1372 (3)	1.0715 (2)	0.0972 (2)	0.085 (2)
Cl7	0.8964 (3)	0.5916 (2)	0.1451 (2)	0.086 (2)
N1	0.4136 (6)	0.2482 (5)	0.2104 (4)	0.051 (3)
C1	0.3729 (7)	0.3200 (6)	0.0926 (5)	0.065 (5)
C2	0.5221 (9)	0.2731 (7)	-0.0050 (5)	0.081 (7)
N2	1.1654 (6)	0.8625 (5)	0.3326 (5)	0.058 (4)
C3	1.0331 (7)	0.8772 (6)	0.2508 (5)	0.063 (5)
C4	0.9727 (6)	1.0228 (7)	0.2057 (6)	0.083 (6)
N3	0.6704 (7)	0.5943 (6)	0.4004 (4)	0.063 (4)
C5	0.8477 (7)	0.5114 (6)	0.3810 (5)	0.061 (5)
C6	0.8850 (9)	0.4572 (5)	0.2556 (7)	0.083 (6)

Table 2. *Selected geometric parameters* (Å, °)

Pb—Cl1^i	2.850 (1)	Cl6—C4	1.804 (6)
Pb—Cl2^i	2.902 (1)	N2—C3	1.492 (8)
Pb—Cl3^i	2.904 (1)	C3—C4	1.481 (9)
Cl5—C2	1.803 (9)	Cl7—C6	1.747 (6)
N1—C1	1.476 (7)	N3—C5	1.463 (7)
C1—C2	1.521 (8)	C5—C6	1.531 (9)
Cl1^i—Pb—Cl2^i	91.08 (4)	N2—C3—C4	110.1 (5)
Cl1^i—Pb—Cl3^i	89.71 (4)	Cl6—C4—C3	109.8 (4)
Cl2^i—Pb—Cl3^i	93.04 (4)	N3—C5—C6	109.7 (5)
N1—C1—C2	110.1 (4)	Cl7—C6—C5	109.8 (4)
Cl5—C2—C1	110.0 (5)		

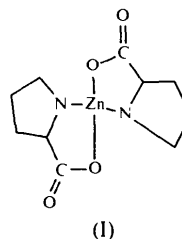Symmetry code: (i) $1-x$, $2-y$, $1-z$.

The structure was solved by direct methods and subsequent difference syntheses. Near the end of the refinement some H atoms could be located from a difference synthesis. All other H atoms were positioned geometrically. The positional parameters of all atoms and anisotropic (H atoms isotropic) displacement parameters were refined by full-matrix least squares on F. The bond lengths and angles involving the H atoms were restrained to 1.01 (C—H) and 1.03 Å (N—H), and 109.5°, respectively. *CAD*-4 *Diffractometer Control Software* (Enraf–Nonius, 1991) was used for cell refinement and data collection. All other calculations and the preparation of the material for publication were performed using the *Xtal*3.2 (Hall, Flack & Stewart, 1992) program package.

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(I)

The Zn atom is pentacoordinate, the fifth coordination site being occupied by the symmetry related atom O(4^i) [symmetry code: (i) 2−x, y−½, −z] of a neighbouring proline molecule so that an infinite polymeric chain is generated. The polymer shows a helical structure along the 2₁ direction. The zinc coordination here is unique, as most zinc–amino acid complexes are hexacoordinate (Freeman, 1976).
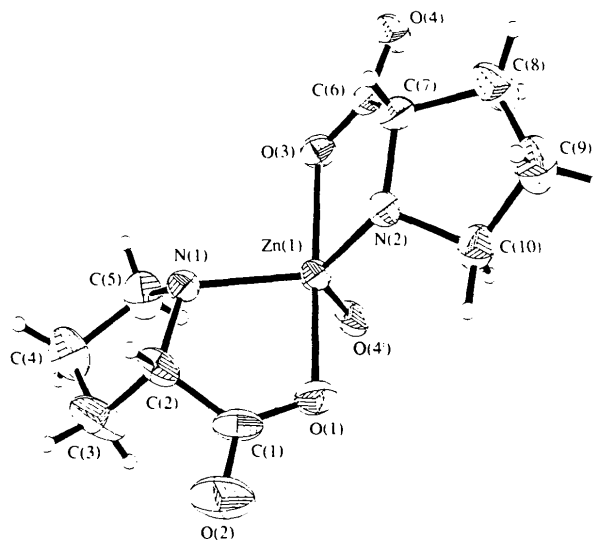
Acta Cryst. (1995). C51, 244–245

Bis(L-prolinato-*N,O*)zinc(II)

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Abstract

The title *trans* complex, [Zn(C₅H₇NO₂)₂], forms a polymer and shows a helical structure along the 2₁ direction with atoms O4(2−x, y−½, −z), Zn, N(2), C(7) and C(6) forming the repeating unit. The Zn atom has trigonal bipyramidal geometry and the pyrrolidine rings adopt envelope conformations.

Fig. 1. View of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

Comment

The title complex results from the reaction of zinc oxide with L-proline. The two L-proline molecules in the complex are coordinated to the Zn atom *via* their N and carboxylic O atoms. The two bidentate ligands are *trans* with respect to each other, as in the case of the hexacoordinate complex bis(L-prolinato)copper(II) dihydrate (Mathieson & Welsh, 1952). The two pyrrolidine rings adopt envelope conformations with best mirror planes bisecting the N(1)—C(2) and N(2)—C(7) bonds, and passing through the C(4) and C(9) atoms, respectively.

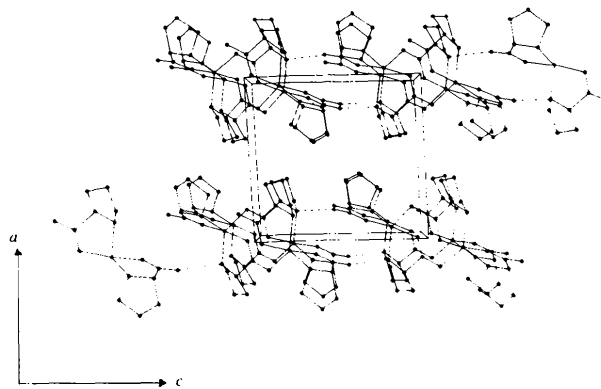† Post Doctoral Research Fellow. Permanent address: Department of Physics, Anna University, Madras 600025, India.

Fig. 2. Projection of the unit cell along the *b* axis.