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Structure of Lead(II) Oxalate Dihydrate

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Abstract

Lead(II) oxalate dihydrate, $PbC_2O_4.2H_2O$, has a polymeric structure. The channels formed by Pb^{2+} and oxalate ions are elongated along [001]. Within the channels there are water molecules of two sorts: (*a*) water weakly coordinated to lead ions and (*b*) water of crystallization.

Comment

Metal oxalates and metal oxalate crystal hydrates have been used for studies of various aspects of solid-state reactivity since the early 1940's; crystal structures of many of them remain unknown, probably because of the experimental difficulties in obtaining single crystals. The crystal structure of anhydrous lead oxalate has been studied by powder techniques (Noerlund, Cox & Lehmann, 1989; Palade, 1985). Recently, the structure of $PbC_2O_4.3H_2O$ was solved (Huang, Wang & Mak, 1990). No structural data on lead oxalate dihydrate have been reported.

The structure of lead oxalate dihydrate was found to be polymeric, with different types of Pb—O bonds. The oxalate anion is practically flat and bound to four Pb^{2+} cations, two of the coordinating cations forming chelate cycles with mirror symmetry (Pb—O distances approximately 2.5 Å, Pb···Pb distances 6.47 Å). In addition, two O atoms of one of the chelate cycles are more weakly bound to two other mirror-symmetrical Pb^{2+} cations (Pb—O distances 2.75 Å, Pb···Pb distance equal to *c*/2). Thus, each Pb^{2+} cation coordinates four O atoms belonging to two mutually perpendicular oxalate anions, related by an *n*-plane reflection. The O atoms form a square parallel to (010). The coordination sphere of Pb^{2+} comprises two more oxalate O atoms, which are weakly bound, and one water O atom. All seven O atoms coordinated to the Pb^{2+} cation form a distorted square antiprism without a vertex, and it is most probable that the unshared electron pair of lead is directed towards this absent vertex (Fig. 1).

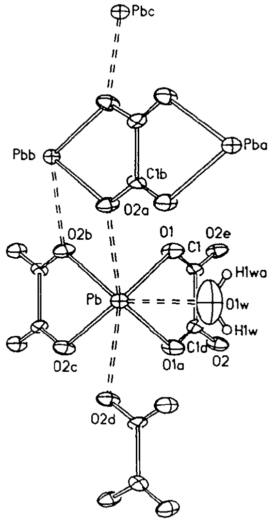

Fig. 1. Diagram showing the nearest neighbours of the Pb^{2+} cations and the $C_2O_4^{2-}$ anions in the structure of $PbC_2O_4.2H_2O$.

The coordination number of Pb in the structure of $PbC_2O_4.2H_2O$ is the same as in the structure of $PbC_2O_4.3H_2O$ (Huang, Wang & Mak, 1990), but the coordination polyhedra are different. The oxygen antiprisms surrounding different cations have common edges (Pb—Pb = 4.39 Å) and form the walls of the channels with the minimal diameter 4.54 Å, elongated along [001] (Fig. 2). The water molecules are located within these channels. The water molecule not coordinated to the lead cation forms a weak hydrogen bond with an oxalate O atom [O(2*w*)··· O(1) = 2.93 Å]. The location of both types of water molecules within the channels may explain the ease with which the crystals lose water when stored under ambient conditions. A preliminary comparison of the crystal structure of lead oxalate dihydrate with the structure reported for the anhydrous lead oxalate (Noerlund, Cox & Lehmann, 1989; Palade, 1985) allows us to suppose that the dehydration proceeds topotactically [the majority of the atomic positions in the original and the transformed material are substantially the same and there is an accord in three dimensions between initial and final lattices (Bernal, 1960)], *via* the formation of a 'vacancy structure'. The vacancy structure has been reported previously to be formed as a result of the dehydration of a number of metal oxalate crystal hydrates (Chaix-Pluchery, Mutin, Bouillot & Niepce, 1989, and references therein).

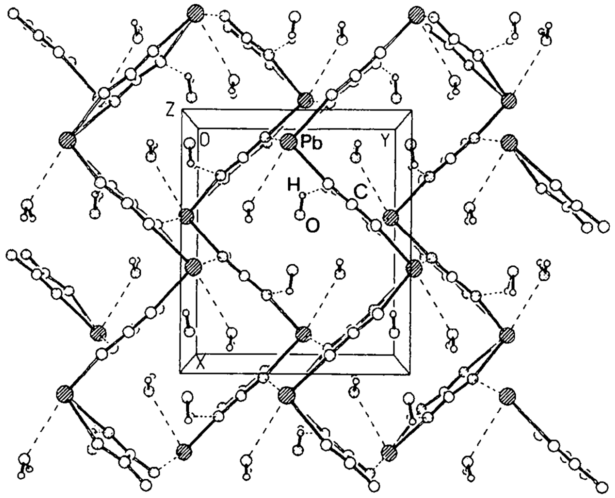

Fig. 2. Crystal packing in $PbC_2O_4.2H_2O$ projected along [001].

Experimental

Crystal data

$PbC_2O_4.2H_2O$
$M_r = 331.2$
Orthorhombic
Pnam
$a = 9.053$ (1) Å
$b = 8.036$ (1) Å
$c = 7.834$ (1) Å
$V = 569.9$ (2) Å^3
$Z = 4$
$D_x = 3.860$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 20 reflections
$\theta = 16\text{-}23.2°$
$\mu = 57.3$ mm^{-1}
$T = 296$ K
Needle
0.75 × 0.006 × 0.005 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 1.00$, $T_{max} = 1.38$
490 measured reflections
490 independent reflections
378 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0$
$\theta_{max} = 57.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 97 reflections
intensity variation: $\leq 7\%$

Refinement

Refinement on F
Final $R = 0.0270$
$wR = 0.0280$
$S = 1.210$
378 reflections
55 parameters
All H-atom parameters refined
$w = 1/[\sigma(F_o)^2 + 0.0004F_o^2]$
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 0.486$ e Å^{-3}
$\Delta\rho_{min} = -0.513$ e Å^{-3}
Secondary-extinction correction: Larson (1967)
Extinction coefficient: 3.5×10^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *XTL Structure Determination System* (Syntex, 1973). Cell refinement: *XTL Structure Determination System.* Data reduction: *XTL Structure Determination System.* Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *YANX* (Gerr, Yanovskii & Struchkov, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976).

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

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

	x	y	z	U_{eq}
Pb	0.3957 (1)	−0.0377 (1)	0.2500	0.0187 (5)
C(1)	0.146 (1)	0.244 (1)	0.148 (1)	0.019 (6)
O(1)	0.224 (1)	0.137 (1)	0.079 (1)	0.031 (5)
O(2)	0.065 (1)	0.350 (1)	0.422 (1)	0.028 (5)
O(1*w*)	0.138 (2)	−0.214 (2)	0.2500	0.07 (1)
O(2*w*)	0.386 (2)	−0.484 (2)	0.2500	0.043 (9)

Table 2. *Geometric parameters* (Å, °)

Pb—O(1)	2.489 (7)	Pb—O(2*A*)	2.748 (7)
Pb—O(2*B*)	2.540 (8)	Pb—O(1*w*)	2.73 (2)
C(1)—O(1)	1.24 (1)	C(1)—O(2)	1.25 (1)
C(1)—C(1)*	1.60 (2)	O(1*w*)—H(1*w*)	0.9 (2)
O(2*w*)—H(2*w*)	0.9 (1)		
O(1*A*)—Pb—O(1)	65.3 (3)	O(2*A*)—Pb—O(1)	76.3 (2)
O(2*B*)—Pb—O(1)	75.7 (3)	O(2*C*)—Pb—O(1)	109.0 (3)
O(2*D*)—Pb—O(1)	140.5 (3)	O(2*B*)—Pb—O(2*A*)	67.8 (2)
O(2*C*)—Pb—O(2*A*)	127.9 (3)	O(2*D*)—Pb—O(2*A*)	138.5 (3)
O(2*C*)—Pb—O(2*B*)	64.1 (3)	O(1)—Pb—O(1*w*)	76.2 (4)
O(2*A*)—Pb—O(1*w*)	86.5 (2)	O(2*B*)—Pb—O(1*w*)	145.6 (5)
O(2*E*)—C(1)—O(1)	127.8 (9)	C(1*A*)—C(1)—O(1)	116.1 (8)
Pb—O(1)—C(1)	120.7 (7)	Pb—O(2*A*)—C(1*B*)	124.0 (7)
Pb—O(1*w*)—H(1*w*)	116 (11)	H(1*wA*)—O(1*w*)—H(1*w*)	114 (18)
H(2*wA*)—O(2*w*)—H(2*w*)	76 (11)		

Crystals of $PbC_2O_4.2H_2O$ were grown using the technique described by Boldyrev (1963). Aqueous solutions of $Na_2C_2O_4$ (0.1 *M*) and $Pb(NO_3)_2$ (0.1 *M*) were allowed to diffuse slowly into the reactor filled with an aqueous solution of $NaNO_3$ (0.1 *M*). Although the technique was described earlier as a method of obtaining anhydrous lead oxalate, it was shown in the present study to give single crystals of lead oxalate dihydrate, easily losing water when stored.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71366 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1074]

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Structure of *trans*-Dichlorobis[1,2-bis(diphenylphosphino)ethane]osmium(II) Dichloromethane Solvate

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Abstract

The structure consists of discrete *trans* octahedral molecules with Os—Cl = 2.434 (1) Å and Os—P = 2.372 (1) and 2.348 (1) Å.

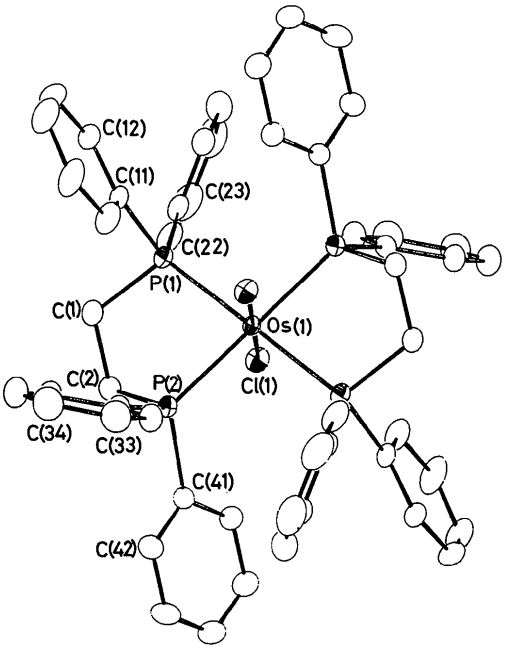

Fig. 1. View of $[OsCl_2(C_{26}H_{24}P_2)_2].CH_2Cl_2$ showing the atom-labelling scheme. H atoms are excluded and the thermal ellipsoids are drawn at the 30% probability level.

Comment

Crystals of the title compound were obtained during studies of the effects of ligand set and metal stereochemistry on the relative stabilities of osmium(II), -(III) and -(IV) complexes (Champness, Levason, Pletcher, Spicer & Webster, 1992). The structure consists of discrete *trans* octahedral molecules with the Os atom located on a centre of symmetry. The geometry is very similar to that of *trans*-$[Ru(Ph_2PCH_2CH_2PPh_2)_2Cl_2]$ (Lobana, Singh & Tiekink, 1990), for which Ru—Cl = 2.436 (1), Ru—P = 2.389 (1), 2.369 (1) Å and P—Ru—P = 82.1 (1)°. Comparison may also be made with an Os complex containing a four-membered chelate ring, $[Os\{H_2C{=}C(PPh_2)_2\}_2Cl_2]$, for which Os—Cl = 2.431 (1), Os—P = 2.343 (1), 2.330 (1) Å and P—Os—P = 72.74 (3)° (Cotton, Diebold & Matusz, 1987).

Experimental

Crystal data

$[OsCl_2(C_{26}H_{24}P_2)_2].CH_2Cl_2$
$M_r = 1142.9$
Triclinic
$P\bar{1}$
$a = 10.065$ (2) Å
$b = 10.437$ (2) Å
$c = 12.974$ (4) Å
$\alpha = 68.22$ (2)°
$\beta = 70.69$ (2)°
$\gamma = 88.31$ (2)°
$V = 1187.6$ (6) Å^3
$Z = 1$

$D_x = 1.597$ Mg m^{-3}
$D_m = 1.57$ (2) Mg m^{-3}
Density measured by flotation in CCl_4-C_6H_{14}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 13.0 - 17.3°$
$\mu = 3.08$ mm^{-1}
$T = 293$ (3) K
Air-stable blocks
0.40 × 0.22 × 0.18 mm
Pale yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.91$, $T_{max} = 1.00$
4947 measured reflections
4666 independent reflections
4644 observed reflections
$[F > 3\sigma(F)]$

$R_{int} = 0.011$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
1 standard reflection
frequency: 60 min
intensity variation: 3.5%

Refinement

Refinement on F
Final $R = 0.0231$
$wR = 0.0313$
$S = 1.27$
4639 reflections
278 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{max} = 0.2$
$\Delta\rho_{max} = 1.32$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}
Atomic scattering factors from *SHELX76* (Sheldrick, 1976) (C, H, P, Cl) and *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1) (Os)