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Lead(II) oxydiacetate hydrate

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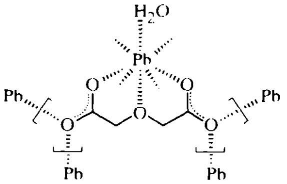
Abstract

The coordination polyhedron around the Pb atom in the title compound, poly[aqualead(II)-μ_5-oxydiacetato], [Pb(μ_5-$C_4H_4O_5$)(H_2O)]$_n$, is a distorted square antiprism formed by three O atoms from one oxydiacetate ligand, four O atoms from four other identical ligands and one water O atom, resulting in a three-dimensional network structure. The almost planar oxydiacetate ligand is disordered over two positions. The Pb lone-pair $6s^2$ electrons show stereochemical activity in the coordination sphere.

Comment

The structure determination of the title compound is part of a study of interactions between *p*-block metals and small ligands of the type $[O_2C\text{–}CH_2\text{–}X\text{–}CH_2\text{–}CO_2]^{2-}$, where *X* can be NH, O or S. This type of ligand can be mono-, bi- or tridentate and may form bridges between the metal atoms. A variety of solid-state complexes with the oxydiacetate ion, $O(CH_2COO^-)_2$, have been investigated, *e.g.* complexes with the trivalent lanthanoids (Albertsson, 1970; Albertsson & Elding, 1976), Rb^+ (Albertsson *et al.*, 1973) and Sr^{2+} (Baggio *et al.*, 1996). In complexes with Pb^{2+}, the $6s^2$ lone pair is likely to affect the coordination geometry, resulting in irregular coordination polyhedra with a large range of Pb—O distances. Several Pb^{2+} complexes with active lone pairs are known, *e.g.* [Pb($C_3H_2O_4$)] (Bensch & Günter, 1987) and [{HB(3,5-Me$_2$pz)$_3$}Pb(3,5-Me$_2$pzH)$_3$-Cl] (pz is pyrazolyl; Reger *et al.*, 1994).

Another reason for the present study was to compare the resulting structure with that of the related oxydiacetate double salt [$Pb_4(C_4H_4O_5)_3(NO_3)_2(H_2O)$] (Svensson *et al.*, 1998), which involves three independent Pb atoms with coordination numbers seven, eight and nine. At least, the surroundings of the seven- and eight-coordinated Pb atoms are influenced by stereochemically active lone pairs. In order to eliminate nitrate from the structure, lead acetate was used as a precursor instead of lead nitrate, resulting in the polymeric compound [{Pb(H_2O)}(μ_5-$C_4H_4O_5$)]$_n$, (I).



(I)

In the asymmetric unit of the title compound, the Pb atom, the water O atoms and the ether O1 atom of the oxydiacetate ligand are located on the $y = \frac{1}{4}$ mirror plane, with the acetate moieties distributed over two locations, *a* and *b*, with refined occupancies of 0.44 (3) and 0.56 (3), respectively (see *Experimental*). The differences between the *a* and *b* ligands are very small. They are almost planar, with r.m.s. deviations of 0.064 (for *a*) and 0.102 Å (for *b*), and have the expected overall geometry when compared with the

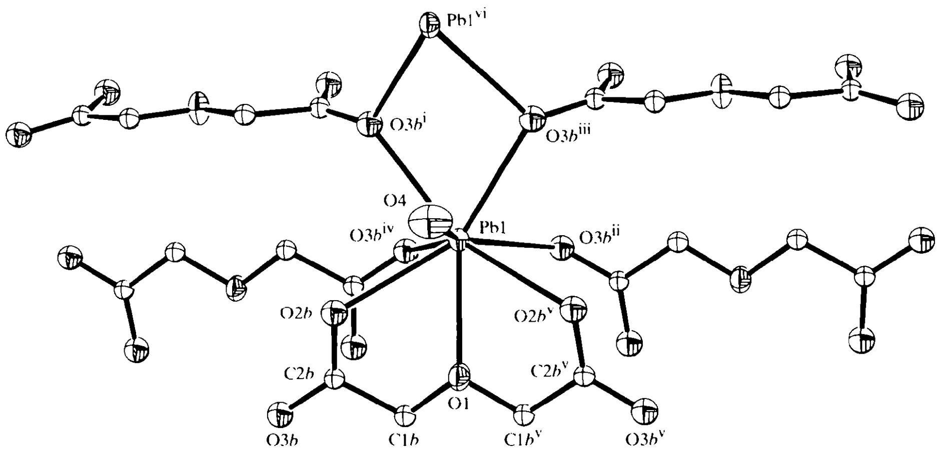


Fig. 1. A view (*ORTEP*III; Burnett & Johnson, 1996) of the crystal packing of the poly[aqualead(II)-μ_5-oxydiacetato] compound. Only *b* ligands are depicted, with the H atoms excluded. The bridging of the closest Pb atom (Pb^{vi}) is shown. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $1 - x, -\frac{1}{2} + y, 1 - z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x, \frac{1}{2} - y, z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$.]

pure acid (Herbertsson & Boman, 1973) and with other coordination compounds. The *b* ligand is shown in Fig. 1. Eight O atoms form a distorted square antiprism around the Pb atom (Fig. 2). One of the squares is composed of the water O4 atom and the O1, O2 and O2^{v} atoms of one oxydiacetate ligand acting in a tridentate manner with respect to this Pb atom. The other square is formed by four O3 atoms (O3^{i}, O3^{ii}, O3^{iii} and 3^{iv}) from four different oxydiacetate ligands (see Fig. 1 for symmetry codes). Thus, each ligand bridges five Pb^{2+} ions forming a three-dimensional network. The bonding distances between the Pb and the seven oxydiacetate O atoms are in the range 2.49 (3)–2.909 (17) Å for *a* and 2.554 (10)–2.787 (14) Å for *b*. The distance to the water O4 atom is slightly shorter, 2.451 (10) Å. The shortest Pb···Pb distance is Pb1···Pb1^{vi} of 4.334 (1) Å.

The distortion of the square antiprism may arise from a stereochemically active lone pair on Pb. The oxydiacetate ligand is bent upwards, as can be seen in Fig. 2, which indicates that the position of the lone pair is below the ligand in the direction of the triangle formed by atoms O1, O3^{ii} and O3^{iv}. The Pb1 atom is located 1.371 (5) Å above the O3*b* square and 1.436 (17) Å below the O2*b*/O2*b*^{v}/O4 triangle, the corresponding values for the *a* ligand being 1.515 (9) and 1.18 (3) Å, respectively. The angle between the O3 square and the ligand is 26 (1) (for *a*) or 30 (1)° (for *b*). The influence of the lone pair on the structure is small. It does not occupy a coordination site as in similar structures, *e.g.* lead(II) malonate, [Pb($C_3H_2O_4$)] (Bensch & Günter, 1987), which also has an antiprismatic coordination, although one corner is occupied by the lone pair; the resulting Pb—O distances are in the range 2.41 (1)–2.99 (2) Å. The lone-pair activity is also smaller in the title compound than in [$Pb_4(C_4H_4O_5)_3(NO_3)_2(H_2O)$] (Svensson *et al.*, 1998), especially if compared with the seven- and eight-coordinated Pb^{2+} ions in the latter compound.

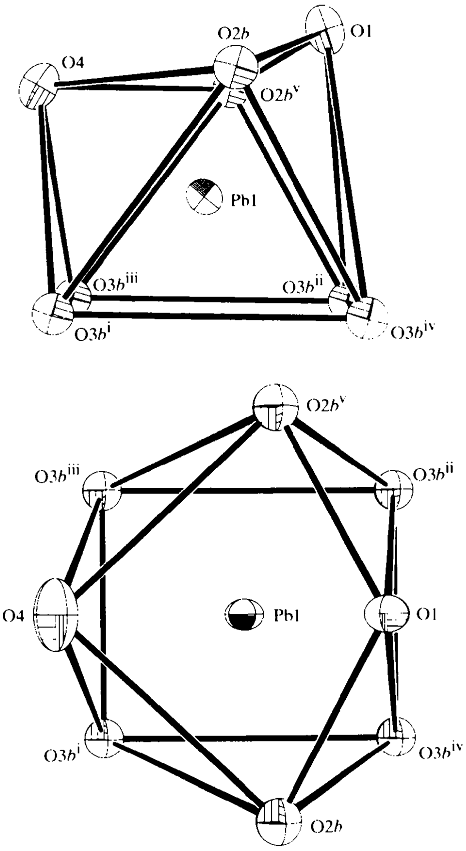


Fig. 2. Two views of the coordination polyhedron around Pb, showing the eight O atoms forming a distorted square antiprism (only atoms belonging to the *b* ligands are included, and symmetry codes and ellipsoid probability are as in Fig. 1).

Experimental

The title compound was prepared by dissolving stoichiometric amounts of oxydiacetic acid and lead acetate in water. A precipitate was formed when these solutions were mixed. Colourless crystals suitable for X-ray measurements were grown by slow recrystallization from a water solution at room temperature.

Crystal data

[Pb(C$_4$H$_4$O$_5$)(H$_2$O)]
M_r = 357.28
Orthorhombic
Pnma
a = 6.9403 (5) Å
b = 9.9480 (7) Å
c = 9.5931 (7) Å
V = 662.33 (8) Å^3
Z = 4
D_x = 3.583 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 19–30°
μ = 25.452 mm^{-1}
T = 293 (2) K
Prism
0.13 × 0.11 × 0.08 mm
Clear, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: Gaussian (Hall *et al.*, 1995)
$T_{\rm min}$ = 0.089, $T_{\rm max}$ = 0.194
2166 measured reflections
1006 independent reflections
729 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.0441
$\theta_{\rm max}$ = 30°
$h = -9 \rightarrow 0$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 0$
3 standard reflections frequency: 60 min intensity decay: −2.0%

Refinement

Refinement on F^2
$R(F)$ = 0.044
$wR(F^2)$ = 0.112
S = 1.197
1006 reflections
53 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.017
$\Delta\rho_{\rm max}$ = 4.287 e Å^{-3}
$\Delta\rho_{\rm min}$ = −3.698 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Pb1	0.26026 (6)	1/4	0.61467 (5)	0.0189 (3)
O1	0.3837 (14)	1/4	0.3638 (11)	0.027 (2)
O4	−0.0763 (14)	1/4	0.5373 (13)	0.042 (3)
C1*a*†	0.441 (4)	0.386 (3)	0.311 (3)	0.022 (4)
C2*a*†	0.344 (4)	0.493 (3)	0.391 (3)	0.018 (3)
O2*a*†	0.247 (3)	0.470 (3)	0.491 (3)	0.027 (3)
O3*a*†	0.376 (3)	0.6104 (18)	0.343 (2)	0.022 (3)
C1*b*‡	0.475 (3)	0.363 (2)	0.309 (2)	0.014 (3)
C2*b*‡	0.374 (3)	0.486 (2)	0.360 (2)	0.016 (3)
O2*b*‡	0.251 (2)	0.475 (2)	0.459 (2)	0.026 (3)
O3*b*‡	0.426 (2)	0.5955 (15)	0.3013 (19)	0.025 (3)

† Site occupancy = 0.44 (3). ‡ Site occupancy = 0.56 (3).

Table 2. *Selected bond lengths (Å)*

Pb1—O1	2.554 (10)	Pb1—O3*a*$^{\rm ii}$	2.91 (2)
Pb1—O4	2.451 (10)	Pb1—O2*b*	2.69 (2)
Pb1—O2*a*	2.49 (3)	Pb1—O3*b*$^{\rm i}$	2.689 (13)
Pb1—O3*a*$^{\rm i}$	2.76 (2)	Pb1—O3*b*$^{\rm ii}$	2.787 (14)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $1 - x, y - \frac{1}{2}, 1 - z$.

After the first few cycles of least-squares refinement, the anisotropic displacement ellipsoids for C1, C2, O2 and O3 were very elongated, indicating some kind of disorder of the ligand. Refinement of two positions for each of these atoms resulted in a lowering of the r.m.s. deviation from the mean of the $\Delta\rho$ maps from 0.57 to 0.50 e Å^{-3}. The number of parameters decreased from 56 to 53 since the atoms were refined with isotropic displacement parameters because of the closeness of the a and b positions. Attempts to refine the structure in the non-centrosymmetric space group $Pna2_1$ were unsuccessful. The relatively high residual electron density is located near the Pb atom, the maximum 0.83 Å and the minimum 0.71 Å from the Pb1 atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *Xtal*3.4 (Hall *et al.*, 1995). Data reduction: *Xtal*3.4. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *TEXSAN for Windows* (Molecular Structure Corporation, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1511). Services for accessing these data are described at the back of the journal.

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