

Coordination Between Lead and Oxydiacetic Acid

Göran Svensson,* Solveig Olson and Jörgen Albertsson

Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

Svensson, G. Olson, S. and Albertsson, J., 1998. Coordination Between Lead and Oxydiacetic Acid. Acta Chem. Scand. 52: 868-872. © Acta Chemica Scandinavica 1998.

In tetralead(II) trisoxydiacetatodinitrate-water(1/1) there are three crystallographically independent lead atoms which are seven-, eight- and nine-coordinated, respectively, by oxydiacetate, water and nitrate oxygen atoms. For the seven- and eight-coordinated lead atoms, the position of the lone pair can be predicted from the coordination geometry, with lead-oxygen distances in the range 2.464(13)–2.890(13) Å. The lone pair of the nine-coordinated lead atom is inactive, with Pb-O distances in the range 2.593(14)–2.769(14) Å. The coordination polyhedron for the seven-, eight- and nine-coordinated lead atoms is described as part of a cubeoctahedron, a rectangular antiprism and a monocapped rectangular antiprism, respectively. The oxydiacetate ions are almost planar. The lead atoms are connected by nitrate and oxydiacetate to form a three-dimensional network.

The structure determination of the title compound is part of a general study of interactions between p-metals and small ligands of the type $O_2C-CH_2-X-CH_2-CO_2$, where X is nitrogen, oxygen or sulfur. This type of ligand can be mono-, bi- or tridentate, and can also form bridges between metal atoms. The title compound was synthesized in order to study the coordination between Pb^{II} and the potential tridentate ligand oxydiacetic acid. The coordination to Pb^{II} is of special interest because of the variation in the observed coordination numbers. By using a narrow-gap ligand the $6s^2$ lone pair is more likely to affect the geometry of the polyhedron around Pb^{II} . Several seven-, eight- and nine-coordinated Pb^{II} complexes with stereochemically active lone pairs are known from the literature. Two examples with O-ligands are Pb^{II} malonate¹ and Pb^{II} oxalate,² which are eight- and seven-coordinated, respectively. Sulfur-containing ligands such as, e.g., dialkyldithiophosphinates also form complexes with active lone pairs. One example is (diethyldithiophosphinato)lead(II), where six S atoms coordinate to lead in a pentagonal bipyramid with one of the equatorial positions occupied by a lone pair.³

Experimental

Colorless crystals of the title compound were prepared by mixing aqueous solutions of $Pb(NO_3)_2$ and oxydiacetic acid (molar ratio 1/1). Transparent crystals, suit-

able for single crystal diffraction, were grown from this acid solution (pH 1.1) by slow evaporation at room temperature.

Crystal data pertinent to the intensity data collection, structure solution and least-squares refinement are given in Table 1. Three intensity control reflections, measured every hour of X-ray exposure, varied within $\pm 2\%$. Data were corrected for Lorentz, polarization and absorption effects (numerical integration, using Xtal3.4⁴). The crystal structure was solved by direct methods and subsequent $\Delta\rho$ -maps (SHELXS-86⁵). The molar ratio between Pb and oxydiacetic acid was found to be 4/3, not 1/1 as expected, since one ligand is replaced by two nitrate groups. One Pb, one oxydiacetate and the nitrate group are in general positions, one Pb and the water oxygen in a mirror plane, and one Pb and one oxydiacetate ion on a twofold axis. The structure was refined by full-matrix least-squares (SHELXL-93⁶) minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$. The H atoms of the CH_2 groups were placed in calculated positions and refined riding on the parent atoms and using a common isotropic displacement parameter. Anisotropic displacement parameters were used for Pb, N and O atoms, while isotropic displacement parameters were used for C atoms. The final $\Delta\rho$ -maps showed remaining electron density in the vicinity of the Pb atoms. The magnitudes of the final displacement parameters for the nitrate and water molecules indicate disorder which could not be resolved. The large remaining electron density close to the Pb atoms and the

* To whom correspondence should be addressed.

Table 1. Crystal data and refinement parameters.

Formula	Pb ₄ (C ₄ H ₄ O ₅) ₃ (NO ₃) ₂ H ₂ O
M _r	1367.04
Crystal system	Orthorhombic
Space group	<i>Pbcm</i>
a/Å	9.309(2)
b/Å	8.4023(14)
c/Å	34.331(6)
V/Å ³	2685.4(8)
Z	4
D _x /g cm ⁻³	3.426(1)
μ/mm ⁻¹	25.2
Crystal size/mm ³	0.24 × 0.14 × 0.08
No. of faces	7
Absorption correction	Numerical integration, grid 12 × 6 × 6
Diffractometer	Enraf-Nonius CAD-4
Radiation/Å	0.71069 (Mo Kα)
Scan type	ω/2θ scan
Scan width/°	Δw = 0.48 + 0.48 tan θ
Maximum scan time/s	120
θ-Range for data collection/°	2 < θ < 35
θ-Range for unit-cell dimensions/°	15 < θ < 25 (25 reflections)
Transmission factor range	0.027–0.170
No. of reflections	
Measured	14759
Independent	5901
Observed, I > 2σ(I)	2701
R _{int}	0.071
hkl range	h 0–14 k 0–13 l 0–54 h –13–0 k –11–0 l 0–48
Refinement on	F ²
Least-squares weight	w = [σ ² (F) + 0.10P ²] ⁻¹ P = (F _o ² + 2F _c ²)/3
R [F, I > 2σ(I)]	0.055
R _w (F ²)	0.160
S	1.06
No. of reflections in refinement	2701
No. of parameters	154
(Δ/σ) _{max}	< 0.1
Δρ _{max} , Δρ _{min} /e Å ⁻³	4.2, –2.7
Extinction correction ¹⁴	0.00046(4)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (in Å²)

Atom	x/a	y/b	z/c	U _{eq} ^a
Pb1	0.06630(13)	0.07622(13)	3/4	0.0360(3)
Pb2	0.32015(8)	0.07376(8)	0.61852(2)	0.0310(2)
Pb3	0.43388(11)	3/4	1/2	0.0248(2)
O1	0.2060(15)	0.3492(16)	0.6153(4)	0.037(3)
O2	0.0396(16)	0.3139(17)	0.7086(4)	0.043(4)
O3	0.1495(17)	0.1418(16)	0.6704(4)	0.041(4)
O4	0.3633(19)	0.2375(15)	0.5592(4)	0.044(4)
O5	0.385(2)	0.4696(16)	0.5285(4)	0.049(4)
O6	0.136(2)	–1/4	1/2	0.054(6)
O7	0.1013(18)	–0.0073(18)	0.5823(5)	0.049(4)
O8	0.2905(16)	–0.1338(17)	0.5579(4)	0.042(4)
O9	–0.194(3)	0.135(5)	3/4	0.103(12)
O10	0.304(4)	–0.177(4)	0.6754(11)	0.21(2)
O11	0.479(3)	–0.198(3)	0.6425(10)	0.125(11)
O12	0.453(3)	–0.355(4)	0.6895(9)	0.142(12)
N1	0.410(3)	–0.246(2)	0.6695(8)	0.063(6)
C1	0.141(2)	0.4121(19)	0.6498(5)	0.027(3)
C2	0.108(2)	0.2818(19)	0.6776(5)	0.025(3)
C3	0.256(2)	0.467(2)	0.5878(5)	0.032(4)
C4	0.339(2)	0.386(2)	0.5566(6)	0.032(4)
C5	0.0564(16)	–0.1806(16)	0.5315(4)	0.042(5)
C6	0.1588(16)	–0.1026(16)	0.5588(4)	0.029(4)

$$^a U_{eq} = 8/3\pi^2 [U_{11}(aa^*) + U_{22}(bb^*) + U_{33}(cc^*)]$$

shape of the displacement parameters, elongated perpendicularly to the plane of the oxydiacetate groups, for the ligands also indicate some kind of disorder which could not be resolved. Diffraction data were therefore collected for three different crystals from two separate preparations. Refinement of these data sets resulted in a similar model with the same problems. Atomic scattering factors and anomalous dispersion factors were taken from Ref. 7.

Final atomic coordinates and equivalent displacement parameters are given in Table 2 and selected geometrical parameters in Table 3. Displacement ellipsoid plots

Table 3. Selected bond distances (in Å) and angles (in °) with e.s.d.s in parentheses.

Pb1–O2	(.2)	2.464(13)	Pb2–O7	2.487(17)	
Pb1–O9		2.51(3)	Pb2–O3	2.467(13)	
Pb1–O2_3	(.4)	2.798(14)	Pb2–O4	2.493(12)	
Pb1–O3	(.4)	2.890(13)	Pb2–O1	2.549(13)	
Pb3–O5	(.8)	2.592(13)	Pb2–O8	2.732(4)	
Pb3–O8_6	(.7)	2.593(14)	Pb2–O11_5	2.78(2)	
Pb3–O5_5	(.9)	2.673(15)	Pb2–O10	2.86(2)	
Pb3–O6_7		2.77(2)	Pb2–O11	2.87(2)	
Pb3–O4_5	(.9)	2.769(14)			
C1–O1	1.44(2)	O1–C3	1.44(2)	C5–O6	1.44(2)
C1–C2	1.48(2)	C3–C4	1.48(7)	C5–C6	1.49(2)
C2–O2	1.26(2)	C4–O4	1.28(2)	C6–O7	1.26(2)
C2–O3	1.26(2)	C4–O5	1.28(2)	C6–O8	1.24(2)
N1–O10	1.19(3)	N1–O11	1.22(3)	N1–O12	1.23(3)
C1–O1–C3	115.3(13)	C5–O6–C5_10	117.5(18)	O6–C5–C6	108.7(9)
O1–C1–C2	110.6(13)	O1–C3–C4	109.1(15)	C5–C6–O7	113.9(10)
C1–C2–O2	119.0(15)	C3–C4–O4	119.5(7)	C5–C6–O8	120.9(9)
C1–C2–O3	119.8(15)	C3–C4–O5	118.7(16)	O7–C6–O8	125.1(16)
O2–C2–O3	121.2(16)	O4–C4–O5	121.7(18)		

Symmetry transformations used:

- (2) $x, y, 3/2-z$; (3) $-x, -1/2+y, z$; (4) $-x, -1/2+y, 3/2-z$; (5) $1-x, 1/2+y, z$; (6) $x, 1/2-y, 1-z$; (7) $x, 1+y, z$; (8) $x, 3/2-y, 1-z$; (9) $1-x, 1-y, 1-z$; (10) $x, -1/2-y, -z+1$.

(ORTEP-3⁸) of the Pb coordination are shown in Figs. 1a–1c. The geometry around the lead atoms are shown in Figs. 2a–2c and a packing stereo-diagram in Fig. 3.

A list of observed and calculated structure factors, anisotropic displacement parameters and hydrogen atom parameters is available from one of the authors (G.S.)

Description of the structure

In the title compound the Pb atoms are coordinated by oxydiacetate, water and nitrate O atoms. The three

crystallographically independent Pb atoms are seven-, eight- and nine-coordinated, respectively. To the best of our knowledge this is the first compound where seven-, eight- and nine-coordinated lead have been found in the same structure.

Pb1 is seven-coordinated by four oxydiacetate ions and the water molecule, with Pb1 and the water oxygen in a mirror plane. Two of the planar organic ligands are bidentate and two are unidentate (Fig. 1a). The seventh position in the coordination shell is occupied by the water molecule O9. The range of the Pb1–O distances is 2.464(13)–2.890(13) Å with a Pb1–O9 (water) distance

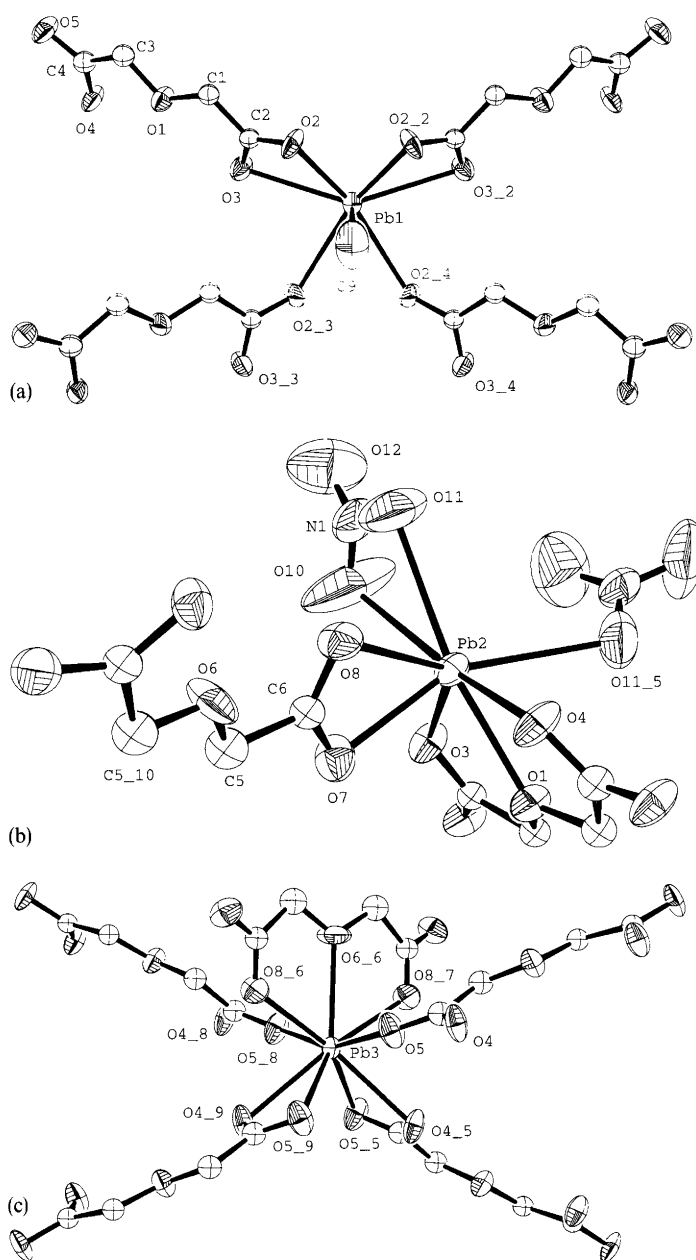


Fig. 1. The coordination of the lead atoms in tristetralead(II) oxydiacetatedinitrate–water (1/1). Lead is seven-coordinated in (a), eight-coordinated in (b) and nine-coordinated in (c). Symmetry related oxygen atoms are generated by the symmetry operations given in Table 3. Thermal ellipsoids are scaled to include 50% probability.

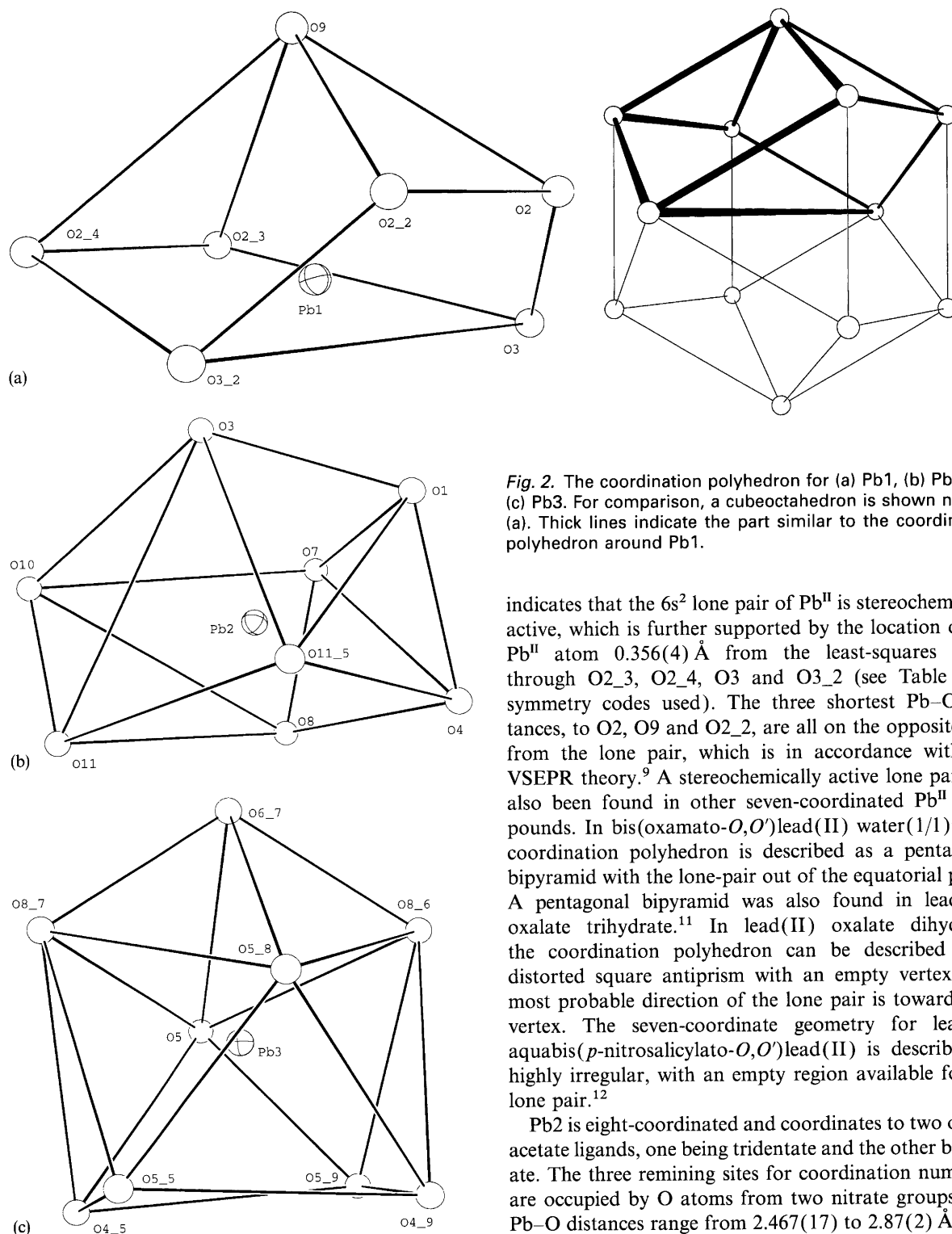


Fig. 2. The coordination polyhedron for (a) Pb1, (b) Pb2 and (c) Pb3. For comparison, a cubeoctahedron is shown next to (a). Thick lines indicate the part similar to the coordination polyhedron around Pb1.

indicates that the $6s^2$ lone pair of Pb^{II} is stereochemically active, which is further supported by the location of the Pb^{II} atom $0.356(4)$ Å from the least-squares plane through O2_3, O2_4, O3 and O3_2 (see Table 3 for symmetry codes used). The three shortest Pb–O distances, to O2, O9 and O2_2, are all on the opposite side from the lone pair, which is in accordance with the VSEPR theory.⁹ A stereochemically active lone pair has also been found in other seven-coordinated Pb^{II} compounds. In bis(oxamato- O,O')lead(II) water(1/1)¹⁰ the coordination polyhedron is described as a pentagonal bipyramid with the lone-pair out of the equatorial plane. A pentagonal bipyramid was also found in lead(II)-oxalate trihydrate.¹¹ In lead(II) oxalate dihydrate² the coordination polyhedron can be described as a distorted square antiprism with an empty vertex. The most probable direction of the lone pair is towards this vertex. The seven-coordinate geometry for lead in aquabis(*p*-nitrosalicylato- O,O')lead(II) is described as highly irregular, with an empty region available for the lone pair.¹²

Pb2 is eight-coordinated and coordinates to two oxydiacetate ligands, one being tridentate and the other bidentate. The three remaining sites for coordination number 8 are occupied by O atoms from two nitrate groups. The Pb–O distances range from $2.467(17)$ to $2.87(2)$ Å, with the nitrate O atoms forming the longest bond. The coordination polyhedron is highly irregular. To accommodate the lone-pair as a ninth vertex, it may be described as a rectangular antiprism with O4, O8, O11 and O11_5 forming one of the rectangles and O1, O3, O10 and O7 the other (Fig. 2b). The stereochemically active lone-pair may then be located in the first of these faces, in this way completing a severely distorted mono-

of $2.51(3)$ Å. The coordination polyhedron is shown in Fig. 2a compared with a cubeoctahedron, which indicates that the polyhedron formed around Pb1 may be interpreted as a part of that polyhedron. As can be seen from Fig. 2a, the coordination is rather one-sided, with ample space available where the lone-pair can be located. This

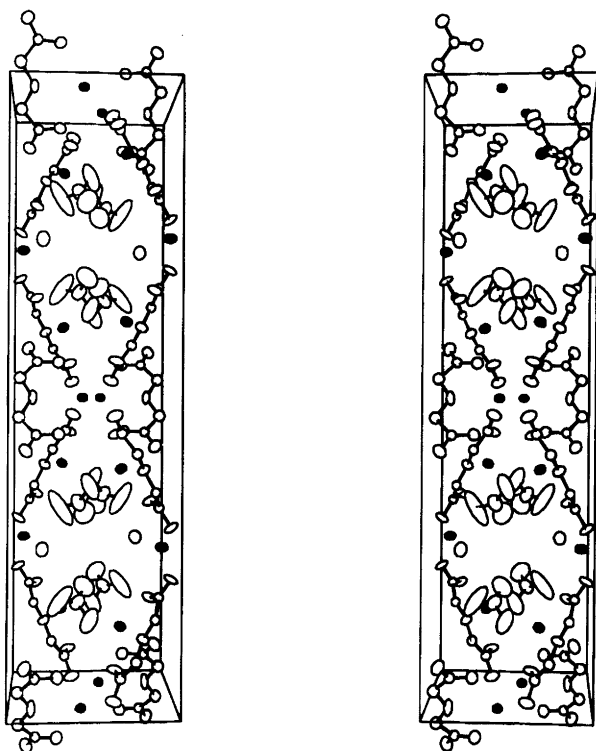


Fig. 3. Crystal packing projected along [100].

capped rectangular antiprism, which is one of the regular geometries for nine-coordination. The distance from Pb2 to the plane formed by O4, O8, O11 and O11_5 is 1.074(10) Å, which is the shortest distance between Pb2 and any possible boundary plane of the polyhedron. A monocapped rectangular antiprism is also found in lead(II)malonate,¹ where the lone-pair also occupies one vertex.

Pb3 is nine-coordinated by five oxydiacetate ligands. One acts as a tridentate ligand, two as bidentate and two as monodentate ligands (Fig. 1c). The Pb–O distances range from 2.593(14) to 2.769(14) Å. The geometry of the PbO₉ polyhedron can be described as a monocapped square antiprism, with O6_7 as the capping atom (Fig. 3c), or with the alternative description as a tri-capped trigonal prism, with O6_7, O4_9 and O4_5 as capping atoms. These two polyhedra are closely related, with symmetry C_{4v} and D_{3h} , respectively. The position of the lone pair is not obvious from the geometry of the coordination polyhedron. The high coordination number makes it less likely that the lone pair should influence the

geometry. This is also indicated by the closer range of Pb–O distances for the nine-coordination compared to what is found for the seven- and eight-coordinated Pb1 and Pb2. In lead acetate trihydrate¹³ nine oxygen atoms form a monocapped square antiprism. One of the Pb–O distances is elongated, 3.09(4) Å, while the others are in the range 2.47(3) to 2.85(5) Å. The most likely position for the lone pair is, therefore, along this elongated bond.

One of the ligands (O1–O5, C1–C4) coordinates to nine Pb atoms and the other (O6–O8, C5–C6) to seven. The carboxylate oxygen atoms interact with two Pb atoms each, except for O7, which has one interaction only. Each ether oxygen interacts with one lead atom, only. In this way a three-dimensional network is formed (Fig. 3). The oxydiacetate ligands form wave-like chains along *c* with the Pb atoms, water molecules and nitrate ions in between chains.

Acknowledgment. Financial support by the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

References

1. Bench, W. & Günter, J. R. *Z. Kristallog.* 178 (1987) 257.
2. Virovets, A. V., Naumov, D. Y., Boldyreva, E. V. and Podberezskaya, N. V. *Acta Crystallogr., Sect. C* 49 (1993) 1882.
3. Svensson, G. and Albertsson, J. *Acta Chem. Scand.* 45 (1991) 820.
4. Hall, S. R., King, G. S. D. and Stewart, J. M., Eds. *Xtal3.4 User's Manual*. University of Western Australia, Lamb, Perth 1995.
5. Sheldrick, G. M. *SHELXS-86. A Program for Crystal Structure Solution*. University of Göttingen, Germany 1986.
6. Sheldrick, G. M. *SHELXL-93. A Program for Refinement of Crystal Structures*. University of Göttingen, Germany 1993.
7. *International Tables for X-Ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands 1992.
8. Farrugia, L. J. *J. Appl. Crystallogr.* (1997). *In press*.
9. Gillespie, R. J. and Nyholm, R. S. *Quart. Rev. Chem. Soc.* 11 (1957) 339.
10. Skoulika, S., Michaelides, A. and Aubry, A. *Acta Crystallogr., Sect. C* 44 (1988) 808.
11. Sheng-Hua, H., Ru-Ji, W. and Mak, T. C. W. *J. Crys. Spectrosc. Res.* 20 (1990) 99.
12. Tahir, M. N., Ülkü, D. and Móvsümov, E. M. *Acta Crystallogr., Sect. C* 52 (1996) 2436.
13. Rajaram, R. K. and Rao, J. K. M. *Z. Kristallog.* 160 (1982) 225.

Received January 23, 1998.