the X-ray diffraction data and to Ms Fen-Ling Liao for plotting the figures.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1074). Services for accessing these data are described at the back of the journal.

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Tris(acetato-*O*,*O*′)(2,4-dimethoxyphenyl)-lead(IV)

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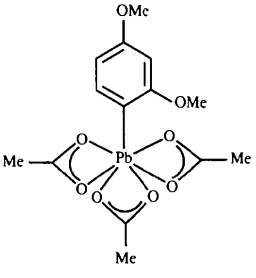
Abstract

The coordination around the Pb atom in the title compound, $[Pb(C_8H_9O_2)(C_2H_3O_2)_3]$, can be described as distorted dodecahedral with O atoms of the bidentate acetate groups occupying six of the coordination sites and the remaining sites occupied by the bonded C atom of the 2,4-dimethoxyphenyl group and a methoxy O atom.

Comment

Little data has been published on the coordination of lead in organolead compounds. The Pb atom has approximate trigonal bipyramidal coordination with bridging acetate groups in $[(CH_3)_3PbOAc]$ (Sheldrick & Taylor, 1975). In $[(CH_3)_4N][Ph_2Pb(OAc)_3]$, the metal atom is eight-coordinate with its ligands forming an approximate hexagonal bipyramid (Alcock, 1972). The O atoms around the Pb atom in $[Pb(OAc)_4]$ form a flattened trigonal dodecahedron with no bridging acetate groups (Kamenar, 1963). In the isostructural $[Sn(OAc)_4]$, the Sn atom has a pseudo-dodecahedral coordination with four bidentate acetate groups (Alcock & Tracy, 1979); the Sn—O distances are, however, variable. In order to determine the coordination of the Pb atom in the title compound, (I), the structure was investigated by single-crystal X-ray diffraction.



(I)

The molecular structure of (I) shows approximate mirror symmetry. All non-H atoms of the 2,4-dimethoxyphenyl group, Pb1 and one of the acetate groups lie in a plane [maximum deviation 0.114 (8) Å, unit weights] which bisects the plane occupied by the two other acetate groups and Pb1 [maximum deviation 0.166 (6) Å] with an interplanar angle of 89.8 (1)°. The coordination about Pb1 can be described as distorted rhombic dodecahedral with the O atoms of the acetate groups occupying six of the coordination sites and the remaining sites occupied by the bonded carbon (C5) of the phenyl group and a methoxy O atom (O2). The long Pb1—O2 bond [2.874 (5) Å] is facilitated by the significant distortion of the bond between Pb1 and the phenyl group such that the angles Pb1—C5—C4 and Pb1—C5—C6 are 125.9 (5) and 112.7 (4)°, respectively.

Each of the bidentate coordinated acetate ligands have unequal C—O bond distances with one longer (*ca* 2.5 Å) and one shorter (*ca* 2.2 Å). A similar but less pronounced effect observed for the Sn—O distances of $[Sn(OAc)_4]$ is attributed to overcrowding of the coordination about the Sn atom. The longer Pb1—O bond distances of (I) are similar to those found in the anion of $[(CH_3)_4N][Ph_2Pb(OAc)_3]$ which are in the range 2.48 (2)–2.63 (2) Å. The four shortest edges of the polyhedron are those of the bidentate atom pairs, the O···O distances of the acetate groups

[2.182 (7)–2.185 (8) Å] and O2· · ·C5 [2.309 (7) Å]. One edge distance [O4· · ·O5 2.802 (8) Å] is isolated with six edge distances in a group between 3.04 and 3.19 Å.

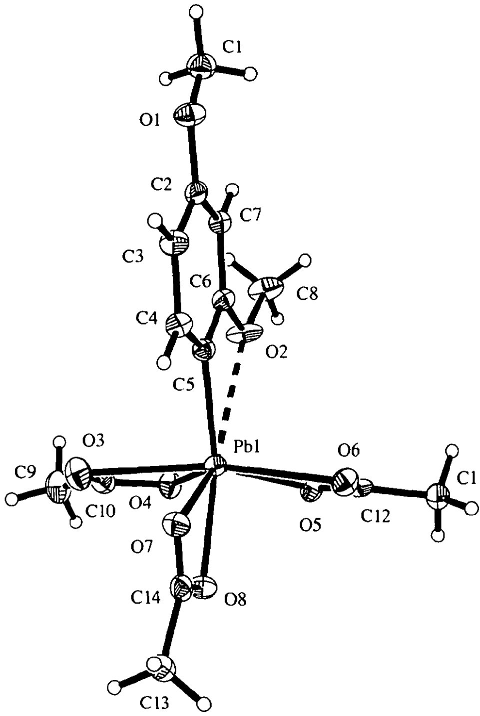


Fig. 1. Molecular structure of the title compound showing the atom numbering scheme and 30% displacement ellipsoids.

Experimental

Compound (I) was prepared by the method described by De Vos, Spierenberg & Wolters (1972). Crystals were obtained by recrystallization from dichloromethane and petroleum ether.

Crystal data

$[Pb(C_8H_9O_2)(C_2H_3O_2)_3]$
$M_r = 521.47$
Triclinic
$P\overline{1}$
$a = 8.123\ (1)$ Å
$b = 10.580\ (2)$ Å
$c = 10.981\ (2)$ Å
$\alpha = 98.52\ (1)°$
$\beta = 101.76\ (1)°$
$\gamma = 105.97\ (1)°$
$V = 867.1\ (3)$ Å^3
$Z = 2$
$D_x = 1.997$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 4.8–12.5°$
$\mu = 9.764$ mm^{-1}
$T = 190\ (2)$ K
Tablet
0.39 × 0.26 × 0.06 mm
Yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: analytical (*ABSC* in *SHELXTL/PC*; Sheldrick, 1990)
$T_{min} = 0.119$, $T_{max} = 0.545$
5829 measured reflections
4997 independent reflections

4175 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 30°$
$h = -1 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.102$
$S = 1.013$
4997 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.733$ e Å^{-3}
$\Delta\rho_{min} = -3.335$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.0010 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pb1—C5	2.143 (6)	Pb1—O7	2.496 (5)
Pb1—O8	2.177 (5)	Pb1—O6	2.511 (5)
Pb1—O4	2.198 (5)	Pb1—O3	2.587 (6)
Pb1—O5	2.201 (4)	Pb1—O2	2.874 (5)
C5—Pb1—O8	147.5 (2)	O7—Pb1—O6	82.7 (2)
C5—Pb1—O4	114.5 (2)	C5—Pb1—O3	91.4 (2)
O8—Pb1—O4	88.1 (2)	O8—Pb1—O3	83.6 (2)
C5—Pb1—O5	115.9 (2)	O4—Pb1—O3	53.6 (2)
O8—Pb1—O5	90.2 (2)	O5—Pb1—O3	132.4 (2)
O4—Pb1—O5	79.1 (2)	O7—Pb1—O3	85.0 (2)
C5—Pb1—O7	92.4 (2)	O6—Pb1—O3	166.8 (2)
O8—Pb1—O7	55.2 (2)	C5—Pb1—O2	52.37 (19)
O4—Pb1—O7	128.9 (2)	O3—Pb1—O2	96.77 (19)
O5—Pb1—O7	128.4 (2)	O4—Pb1—O2	76.40 (18)
C5—Pb1—O6	94.0 (2)	O5—Pb1—O2	74.82 (17)
O8—Pb1—O6	85.3 (2)	O6—Pb1—O2	96.13 (18)
O4—Pb1—O6	133.3 (2)	O7—Pb1—O2	144.66 (15)
O5—Pb1—O6	54.7 (2)	O8—Pb1—O2	160.10 (16)

A preliminary empirical absorption correction gave $R1_{(obs)} = 0.0452$ with residual electron density peaks of 2.30 and -2.54 e Å^{-3}. The full analytical absorption correction presented here gave lower *R* factors but higher residual electron density peaks (3.73 and -3.34 e Å^{-3}). The analytical correction has been chosen as the ratio T_{max}/T_{min} is closer to that quoted by the *Acta Crystallographica* CIF checking procedures (9.33) than the empirical T_{max}/T_{min} ratio (2.99).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1300). Services for accessing these data are described at the back of the journal.

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Steric Hindrance in a Mixed Solvated Nickel(II) Complex: Bis(acetonitrile-*N*)-tetrakis(*N*,*N*-dimethylacetamide-*O*)-nickel(II) Bis(tetrafluoroborate)

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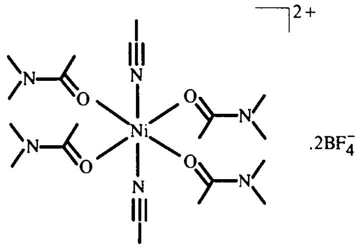
Abstract

The title compound, $[Ni(CH_3CN)_2\{(CH_3)_2NCOCH_3\}_4](BF_4)_2$, has an octahedral coordination structure with the centre of symmetry at the Ni atom. Both of the two crystallographically inequivalent *N*,*N*-dimethylacetamide (DMA) molecules have normal coordination Ni—O bond lengths and Ni—O—C angles, but one of the Ni—O—C—N torsion angles deviates from 180°, indicating that the Ni—O bond is displaced from the direction of the lone pair of the sp^2-O atom. This is ascribed to the steric hindrance of DMA coordination in an octahedral environment, which is imposed by the non-bonding contact of the acetyl methyl group with the ligating O atom of the adjacent DMA molecule.

Comment

Our thermodynamic studies of complexation equilibria in DMA solution have revealed activation of the solvated metal ions (Suzuki & Ishiguro, 1992). Unusual coordination structures such as five-coordinate $[NiCl(DMA)_4]^+$ are also found in DMA. Because this solvent effect is encountered in various metal–ligand systems but never observed in an analogous solvent *N*,*N*-dimethylformamide (DMF), we have ascribed it to the steric hindrance of the acetyl methyl group of DMA, which may destabilize the solvation structure and cause the less-crowded complexes to emerge in solution. The difference between DMA and DMF disappears in the case of tetrahedral complexes, which also supports the idea (Koide, Suzuki & Ishiguro, 1995).

An EXAFS study in DMF and DMA solutions, however, showed no difference in the solvation structures of bivalent transition metal ions except for Zn^{2+}; all the ions but Zn^{2+} have an octahedral coordination structure $[M^{II}(solvent)_6]^{2+}$ (M = Mn, Co, Ni, Cu) and the M—O bond lengths are almost identical in the two solvents (Ozutsumi, Koide, Suzuki & Ishiguro, 1993). To clarify detailed structural features of the steric hindrance in DMA coordination, we have isolated a hygroscopic crystal of the title compound, (I), from a mixture of acetonitrile and diethyl ether, and performed an X-ray diffraction analysis on the single crystal.



(I)

The structure (Fig. 1) shows that the Ni^{2+} ion has a centrosymmetric octahedral coordination environment in which both acetonitrile and DMA coordinate. Both of the crystallographically inequivalent DMA molecules have normal bond lengths (Ni—O) and angles (Ni—O—C) (Herceg & Fischer, 1974; Lemoine & Herpin, 1980; Ozutsumi *et al.*, 1993). Nevertheless, the Ni—O—C—N (τ) torsion angles in Table 2, which serve as a measure of coplanarity between the metal and the molecular plane of DMA, indicate that the coordinating conformation of the two DMA molecules is clearly distinguishable: 'regular' and 'twisted'. One of the DMA molecules (O1–C14) is almost coplanar with Ni ($\tau = -170°$), and the coordination occurs approximately in the direction of the lone pair of the sp^2-O atom. The other (O2–C24), however, has $\tau = -113°$; thus, the metal is largely out of the DMA molecular plane, *i.e.* the coordinated DMA is twisted around the O2—C21 bond.

Similar distortion is found in $[Cu(DMA)_4(ClO_4)_2]$, where two of the DMA molecules have τ(Cu—O—C—N) = −165° and the other two have τ = 125° (Lemoine & Herpin, 1980). On the other hand, all the τ(M—O—C—N) torsion angles are 172–176° in tetrahedral coordination structures $[M^{II}Cl_2(DMA)_2]$ (M = Co, Zn) (Lindner, Perdikatsis & Thasitis, 1973; Herceg & Fischer, 1974). In DMF solvates, the torsion angles are 161–179° both in octahedral (Baumgartner, 1986; Young, Walters & Dewan, 1989) and tetrahedral structures (Suzuki, Fukushima, Ishiguro, Masuda & Ohtaki, 1991). Accordingly, the acetyl methyl group of DMA

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