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2:1 Complex of *N*,*N*′,*N*″-Trimethylnitrilotriacetamide and Pb(NO$_3$)$_2$

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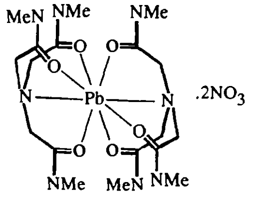
Abstract

N,*N*′,*N*″-Trimethylnitrilotriacetamide, like underivatized nitrilotriacetamide, forms a 2:1 complex with lead nitrate, namely bis(*N*,*N*′,*N*″-trimethylnitrilo-κN-triacetamide-$\kappa^3 O,O',O''$)lead(II) dinitrate, [Pb(C$_9$H$_{18}$N$_4$O$_3$)$_2$](NO$_3$)$_2$. Increasing the bulk of the organic ligands through methylation of the amide N atoms leads to a reduction in the coordination number of the Pb^{II} atom from ten to nine and eliminates the nitrate anions from the coordination sphere.

Comment

The present report is part of a continuing study of the synthesis (Smith, Sucheck, Cramer & Baker, 1995; Smith, Sucheck, Cramer & Skrzypczak-Jankun, 1992), structure (Skrzypczak-Jankun & Smith, 1994*a*; Skrzypczak-Jankun, Smith & Maluszynska, 1994) and metal-coordinating properties (Skrzypczak-Jankun & Smith, 1994*b*; Smith, Sucheck & Pinkerton, 1992) of novel amide ligands. These compounds are of interest due to their propensity to form intricate hydrogen-bonding networks, their highly polydentate metal-complexing ability, their potential for use in starburst-dendrimer formation and as the materials for toxic waste remediation. This paper describes the three-dimensional structure of the 2:1 complex of *N*,*N*′,*N*″-trimethylnitrilotriacetamide and Pb^{II}(NO$_3$)$_2$, (I).



(I)

The X-ray analysis has proven (I) to be a nine-coordinate Pb^{II} complex, with the Pb^{II} atom coordinated by six O atoms, one N atom (N17) and the O20′ atom from a symmetry-related molecule forming a distorted cube around the central Pb ion, edge shared with another distorted cube by the center of symmetry through the bridging O20 and O20′ atoms. The other nitrilo N atom (N1) is within bonding distance of the Pb^{II} atom, capping a cube face made by other coordinated atoms. The details of the Pb coordination are given in Table 2.

There are only several other organic ligand complexes of nine-coordinate lead (Herbstein, 1981; Kepert, Patrick, Skelton & White, 1988; Engelhardt, Kepert, Patrick & White, 1989; Byriel *et al.*, 1992; von Arnim, Dehnicke, Maczek & Fenske, 1993). In the previously reported complex of bis(nitrilotriacetamide) [(ntam)$_2$] with lead nitrate (Smith, Sucheck & Pinkerton, 1992), the Pb^{II} atom was ten-coordinate and one of the nitrate groups participated in the coordination. In the title compound, the ligand is the same except that the amide groups of ntam are methylated. The nitrate anions are not bound to the Pb atom. All available N—H groups, together with both nitrate anions, participate in the three-dimensional hydrogen-bonding network (Table 3). The Pb—N distances of 2.848 (4) and 2.783 (4) Å, and the coordination of lead indicate that in this complex, like in (ntam)$_2$Pb(NO$_3$)$_2$, the lone electron pair on the Pb atom is also stereochemically inactive.

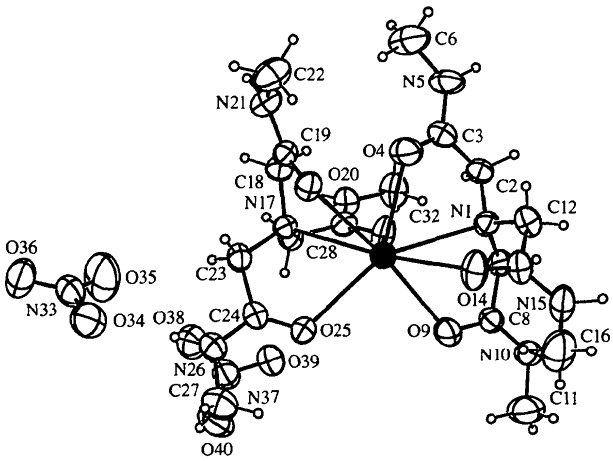


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the title molecule with 50% probability displacement ellipsoids.

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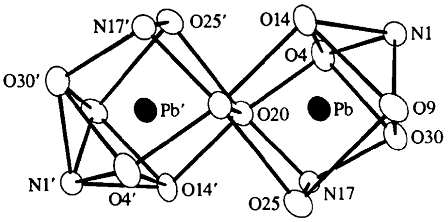

Fig. 2. Coordination sphere of Pb^{II}.

Experimental

The title compound was crystallized from water.

Crystal data

$[Pb(C_9H_{18}N_4O_3)_2](NO_3)_2$
$M_r = 791.74$
Monoclinic
$P2_1/c$
$a = 12.148\,(2)$ Å
$b = 20.749\,(3)$ Å
$c = 13.026\,(2)$ Å
$\beta = 113.68\,(1)°$
$V = 3007\,(1)$ Å^3
$Z = 4$
$D_x = 1.75$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–14°$
$\mu = 5.72$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.18 × 0.05 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.454$, $T_{max} = 0.751$
6349 measured reflections
6060 independent reflections

4109 reflections with $I > 3\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.99°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 25$
$l = -16 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: −6.03%

Refinement

Refinement on F
$R = 0.028$
$wR = 0.035$
$S = 1.114$
4109 reflections
370 parameters
H atoms riding

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.425$ e Å^{-3}
$\Delta\rho_{min} = -0.186$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

N1—C2	1.471 (7)	N17—C23	1.469 (5)
N1—C7	1.469 (7)	N17—C28	1.472 (7)
N1—C12	1.462 (7)	C19—O20	1.243 (7)
C3—O4	1.237 (5)	C19—N21	1.315 (7)
C3—N5	1.328 (7)	C24—O25	1.233 (6)
C8—O9	1.245 (5)	C24—N26	1.317 (5)
C8—N10	1.299 (7)	C29—O30	1.232 (6)
C13—O14	1.228 (5)	C29—N31	1.328 (7)
C13—N15	1.315 (8)	N31—C32	1.466 (6)
N17—C18	1.464 (7)		
C2—N1—C7	109.6 (4)	C18—N17—C23	111.7 (4)
C2—N1—C12	110.7 (4)	C18—N17—C28	110.2 (4)
C7—N1—C12	111.8 (4)	C23—N17—C28	110.8 (4)
C3—N5—C6	122.9 (4)	C19—N21—C22	122.9 (5)
C8—N10—C11	122.5 (4)	C24—N26—C27	122.8 (5)
C13—N15—C16	120.9 (4)	C29—N31—C32	122.2 (5)

Table 2. *Coordination sphere of lead(II) (Å)*

Pb···N1	2.848 (4)	Pb···O20	2.740 (3)
Pb···O4	2.588 (4)	Pb···O20^{i}	2.989 (3)
Pb···O9	2.677 (4)	Pb···O25	2.683 (3)
Pb···O14	2.738 (4)	Pb···O30	2.566 (4)
Pb···N17	2.783 (4)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N5—HN5···O36^{ii}	1.02	1.88	2.867 (5)	158.5
N10—HN10···O38^{iii}	0.98	2.00	2.945 (5)	159.8
N15—HN15···O40^{iii}	0.95	2.11	2.993 (6)	155.4
N21—HN21···O36^{iv}	0.94	2.08	2.956 (7)	154.1
N26—HN26···O34	0.95	2.19	3.099 (6)	160.1
N31—HN31···O40^{i}	1.03	2.06	3.085 (7)	168.5
N31—HN31···O39^{i}	1.03	2.29	3.053 (7)	129.3

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

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974).

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF IN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[1-hydroxyethane-1,1-diylbis(dimethyl phosphonate-*O*)]tris(nitrato-*O*,*O*′)-praseodymium

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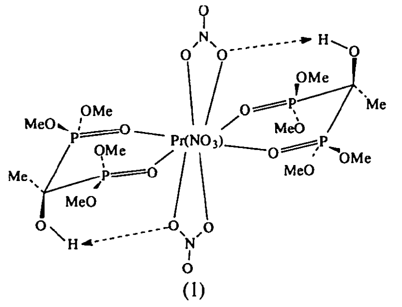
Abstract

The structure of $[Pr(NO_3)_3(C_6H_{16}O_7P_2)_2]$ consists of discrete molecules in which the Pr atom is ten coordinate, with both nitrate and diphosphonate ligands chelating through two O atoms.

Comment

Crystals of $[Pr\{[(CH_3O)_2P(O)]_2C(OH)CH_3\}_2(NO_3)_3]$, (1), form spontaneously on mixing solutions of $[(CH_3O)_2P(O)]_2C(OH)CH_3$ and $Pr(NO_3)_3$ hydrate in acetonitrile.



(1)

The structure of the title compound is similar to that of $[Pr\{[(CH_3O)_2P(O)]_2C(OH)Ph\}_2(NO_3)_3]$, (2) (Platt, Simpson, Fawcett & Russell, 1994), wherein distortions of coordinated nitrate ligands were attributed to intramolecular hydrogen bonding. Similar distortions were observed in (1), the non-hydrogen-bonded nitrate O atoms residing symmetrically at distances of 2.547 (3) Å from the Pr atom, while those of the hydrogen-bonded nitrate ligand lie at distances of 2.658 (4) and 2.611 (3) Å. The longer of these corresponds to the O3 atom, which is directly involved in hydrogen bonding [O3···O8 2.748 (5) Å]. Analogous bond lengths in (2) range from 2.531 (12) to 2.659 (14) Å. In contrast to (2), the hydroxyl H atom in compound (1) is clearly located. The Pr—O(P) distances in (1) are 2.448 (3) and 2.494 (3) Å, which lie within the range 2.434 (9)–2.498 (9) Å observed in compound (2). The largest residual peak in the final difference Fourier map ($1.03\ e\ Å^{-3}$) lies at 1.762 Å from the O7 and O7^{i} atoms [symmetry code: (i) $-x, y, \frac{1}{2}-z$] and 1.882 Å from the O2^{ii} atom [symmetry code: (ii) $x, y-1, z$]. The possibility that this corresponds to a H atom disordered between this site and the hydroxyl position was ruled out because, when refined as such, the occupancy at this position is negligible. The structures of the free ligands, $[(CH_3O)_2P(O)]_2C(OH)CH_3$ and $[(CH_3O)_2P(O)]_2C(OH)Ph$, have been determined previously (Leroux *et al.*, 1991).

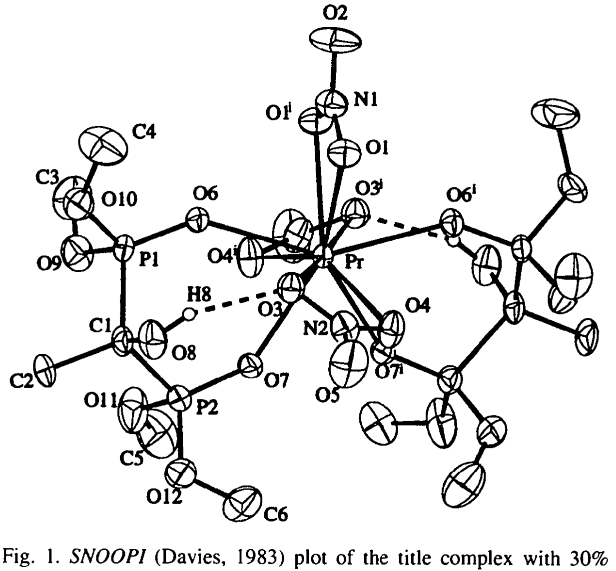


Fig. 1. *SNOOPI* (Davies, 1983) plot of the title complex with 30% probability ellipsoids and the atom-labelling scheme. H atoms have been omitted for clarity, except for the hydroxyl H atom. [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

Experimental

Crystals of the title compound were crystallized from acetonitrile.