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$Pb(NO_3)_2(EO3)$, where EO3 is Triethylene Glycol

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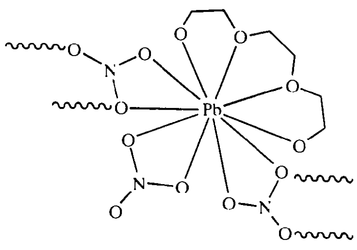
Abstract

A new polyglycol complex, *catena*-poly[[(3,6-dioxaoctane-1,8-diol-κ^4O)(nitrato-κ^2O,O')lead(II)]-μ-(nitrato-O,O':O',O'')], $[Pb(NO_3)_2(C_6H_{14}O_4)]_n$, has been synthesized and structurally characterized by single-crystal X-ray diffraction and IR spectroscopy. The Pb atom is coordinated by ten O atoms from the polyglycol and nitrate groups. The compound is polymeric along the *a* axis, through bridging nitrate groups.

Comment

New routes for synthesizing ferroelectric ceramics are of considerable interest and, of these methods, sol–gel processing using metal–organic precursors is one of the most potent and versatile (Chandler *et al.*, 1993; Schwartz, 1997). The title compound, (I), was prepared for use as a new type of precursor in sol–gel processing of ceramic films containing Pb, *e.g.* PZT $[Pb(Zr,Ti)O_3]$, PLZT $[(Pb,La)(Zr,Ti)O_3]$, PT ($PbTiO_3$) and PMN $[Pb(Mg_{0.33}Nb_{0.67}O_3]$ (Sayer & Sreenivas, 1990; Schwartz, 1997).



(I)

These Pb-based perovskites, and their solid solutions with other oxides, are of great importance in a number of ferroelectric devices. The increased need for fine-tuned and well defined complex ceramics of a small size for electronics applications gives impetus for research into solution-based routes. Metal–organic complexes dissolved in organic solvents are thus of general use in various sol–gel processes and, when used for film preparation, the solution is usually deposited by the spin-coating technique, *i.e.* the precursor solution is added to a spinning substrate. The gel film thereby obtained is subsequently heat treated to produce the final ceramic film.

The object of using the present $Pb(NO_3)_2(EO3)$ complex, where EO3 is triethylene glycol, was to obtain a precursor that is sufficiently soluble and stable during storage, as well as having a low organic content at higher temperatures. The weakly coordinating EO3 molecule was used to make insoluble $Pb(NO_3)_2$ soluble in solvents which are suitable for the other precursors, *i.e.* $Ti(O^iPr)_4$ and $Zr(O^iPr)_4$. Low organic content at the firing temperatures, where the gel is converted to oxide, should impede reduction of PbO to Pb, thus preventing damage to the Pt substrate which would hinder a good contact between the substrate and the PZT film. In a recent study, it was shown that the $Pb(NO_3)_2(EO3)$ precursor could be used for the preparation of PZT films and powders at 823–973 K (Lashgari & Westin, 1998). The Bi analogue, dimeric $[Bi(NO_3)_2(EO3)]_2$ (Rogers *et al.*, 1992), has also been used as a precursor in the preparation of ZnO-based varistors, with good results (Ekstrand *et al.*, 1997)

In the solid state, the title compound shows some similarities with its congeners having longer polyglycol ligands. In particular, the compound $Pb(NO_3)_2(EO4)$ (EO4 = tetraethyleneglycol; Rogers *et al.*, 1996) has structural features in common with $Pb(NO_3)_2(EO3)$. Both compounds are polymeric and both have polyethylene and nitrate groups coordinated to Pb^{2+}. The main difference between the two Pb coordination spheres is that the dissimilarity in chelating ability of the two

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polyethylene groups induces two distinct coordination modes of the nitrate groups.

In the present compound, the first coordination shell, consisting of ten O atoms around Pb^{2+}, is quite asymmetric, and therefore the ligand coordination mode cannot be described by a regular polyhedron (Fig. 1). A better way of describing the coordination is as an elongated bicapped distorted square prism (8 + 2 coordination). The two terminal alcohol O atoms, O1 and O2, are the capping atoms. Atoms O4, O6, $O9^i$ and O10, and atoms O3, O5, O7 and O9 constitute the two capped faces [symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$].

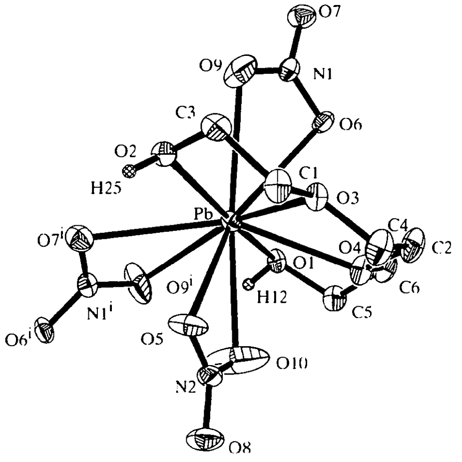

Fig 1. Perspective view and atomic numbering scheme of the title complex. Displacement ellipsoids are drawn at the 30% probability level. All H atoms, except those participating in hydrogen bonding, have been omitted for clarity. [Symmetry code: (i) $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.]

Further, in analogy with the EO4 ligand in $Pb(NO_3)_2$EO4, the chelating tetradentate EO3 group could be viewed as defining an incomplete equatorial girdle around Pb (Rogers *et al.*, 1996). The Pb—O distances of the EO3 O atoms range from 2.62 (1) to 2.77 (1) Å (Table 1).

The significant elongation of the Pb—O2 distance, compared with the other Pb—O contacts, can be attributed to the fact that O2 is involved in two types of hydrogen bonding, namely, between EO3 and EO3, and between EO3 and nitrate. Accordingly, the O1 atom in one complex acts as the donor atom and the O2 atom in the adjacent coordination sphere acts as the acceptor atom (Table 2). The other hydrogen-bonding contact is between an O2 donor atom and an O5 acceptor atom belonging to the terminal nitrate group. This terminal nitrate group is unsymmetrically bidentate and coordinates Pb with O5 and O10, leaving O8 as the only non-coordinating O atom.

The bridging nitrate group is also unsymmetrically bidentate, but to two different Pb atoms. Atom O9 bridges two neighbouring Pb atoms, which makes the compound polymeric along the crystallographic *a* axis. The remaining two O atoms of this bridging nitrate group, O6 and $O7^i$, complete the Pb^{2+} coordination sphere in an alternating way. Here, $O7^i$ is rather loosely bonded to Pb, at a distance of 2.93 (1) Å. Such long Pb—O contacts, with relatively weak and labile interactions, are commonly found in crown ethers (Shin *et al.*, 1993; Rogers *et al.*, 1996). A similar bonding situation between the Pb atom and the bridging nitrate group is probably operating in the present compound. The structural motif of doubly-bidentate nitrate groups bridging Pb atoms has also been observed in the linear polyamine *catena*-bis[(μ_2-nitrato-*O*,*O*,*O*′,*O*″)(μ_2-nitrato-*O*,*O*,*O*′)(ethylenediamine)-lead(II)], $[Pb_2\{(NO_3)_2[C_2H_4(NH_2)_2]\}_2]_n$ (Harrowfield *et al.*, 1996).

In the crystallographic *b* direction, there is an apparent cavity that could be a potential site for a stereochemically active lone pair. However, the presence of such a lone pair on Pb^{2+} is difficult to establish, since Pb strongly absorbs X-rays, *i.e.* it is difficult to distinguish between lone-pair and absorption correction effects. Another, complementary, indication of a possible lone pair on Pb would be to look for isostructural compounds with a stereochemically inactive closed shell cation at the Pb-atom position. A database search was therefore undertaken [Cambridge Structural Database (1997); 167 000 entries]. Complexes containing Sr and triethylene glycol were among the possible candidates, and $Sr(NO_3)_2(EO3)_2$ was found (Rogers *et al.*, 1994). Although no clarity about the lone-pair issue was obtained, some questions arose which could be addressed in future work; for example, despite the similarity in size between the Sr^{2+} and Pb^{2+} ions, the two compounds have different EO3 and nitrate-group coordination modes.

Experimental

$Pb(NO_3)_2$ (p.a., Riedel–Haen) and anhydrous EO3 (Fluka, $> 99\%$ puriss, $< 0.08\%$ H_2O) were used as received. EO3 (10 ml, 74.9 mmol) was added to $Pb(NO_3)_2$ (4.14 g, 12.5 mmol) and stirred for 3 h at 323–328 K in a closed flask. After cooling and storage at room temperature, well formed colourless tetragonal crystals of $Pb(NO_3)_2(EO3)$ were formed. The compound decomposes at 377 K. The FT–IR spectrum in KBr of the title compound, in the region 1500–400 cm^{-1}, has been deposited. Peaks were found at: 1432 (*sh*), 1414 (*sh*), 1382 (*s*), 1355 (*sh*), 1302 (*sh*), 1247 (*w*), 1220 (*w*), 1133 (*sh*), 1111 (*s*), 1072 (*s*), 1032 (*sh*), 934 (*w*), 923 (*sh*), 883 (*sh*), 873 (*sh*), 835 (*sh*) and 825 (*w*) (cm^{-1}) (*s* = strong, *w* = weak, *sh* = shoulder).

Crystal data

$[Pb(NO_3)_2(C_6H_{14}O_4)]$
$M_r = 481.38$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
Pbca
$a = 8.935\,(2)$ Å
$b = 15.733\,(7)$ Å
$c = 18.372\,(4)$ Å
$V = 2582.9\,(12)$ Å^3
$Z = 8$
$D_x = 2.476$ Mg m^{-3}
D_m not measured

Cell parameters from 24 reflections
$\theta = 9.2$–$12.3°$
$\mu = 13.115$ mm^{-1}
$T = 223\,(1)$ K
Irregular
$0.58 \times 0.43 \times 0.31$ mm
Colourless

Data collection

Stoe four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (*XSHAPE*; Stoe & Cie, 1996*c*)
$T_{\min} = 0.049$, $T_{\max} = 0.218$
3784 measured reflections
2969 independent reflections

2170 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 27.54°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 20$
$l = -1 \rightarrow 23$
3 standard reflections
frequency: 240 min
intensity decay: 19.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.111$
$S = 1.076$
2969 reflections
174 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 15.956P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.092$ e Å^{-3}
$\Delta\rho_{\min} = -1.616$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.00231 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pb—O1	2.623 (7)	Pb—O9	2.864 (12)
Pb—O2	2.765 (7)	Pb—O10	2.652 (13)
Pb—O3	2.680 (6)	O5—N2	1.236 (12)
Pb—O4	2.662 (7)	O6—N1	1.243 (10)
Pb—O5	2.707 (9)	O7—N1	1.232 (11)
Pb—O6	2.809 (8)	O8—N2	1.203 (11)
Pb—O7^{i}	2.932 (8)	O9—N1	1.241 (12)
Pb—O9^{i}	2.695 (10)	O10—N2	1.175 (14)
O1—Pb—O2	170.1 (2)	O5—Pb—O9	132.7 (3)
O1—Pb—O3	124.2 (2)	O5—Pb—O7^{i}	67.0 (2)
O1—Pb—O4	62.9 (2)	O6—Pb—O7^{i}	136.8 (2)
O1—Pb—O5	118.7 (2)	O6—Pb—O9	44.2 (3)
O1—Pb—O6	72.5 (2)	O9^{i}—Pb—O2	108.9 (3)
O1—Pb—O7^{i}	111.1 (2)	O9^{i}—Pb—O5	81.7 (4)
O1—Pb—O9	108.6 (3)	O9^{i}—Pb—O6	125.9 (3)
O1—Pb—O9^{i}	67.6 (2)	O9^{i}—Pb—O7^{i}	44.1 (3)
O1—Pb—O10	73.8 (3)	O9^{i}—Pb—O9	120.9 (3)
O2—Pb—O6	104.1 (2)	O10—Pb—O2	113.8 (3)
O2—Pb—O9	64.7 (3)	O10—Pb—O3	95.5 (5)
O2—Pb—O7^{i}	64.8 (2)	O10—Pb—O4	67.5 (5)
O3—Pb—O2	62.7 (2)	O10—Pb—O5	45.1 (3)
O3—Pb—O5	74.4 (2)	O10—Pb—O6	133.0 (4)
O3—Pb—O6	77.7 (2)	O10—Pb—O7	86.0 (5)
O3—Pb—O7^{i}	122.8 (2)	O10—Pb—O9^{i}	66.5 (6)
O3—Pb—O9^{i}	156.2 (3)	O10—Pb—O9	172.5 (5)
O3—Pb—O9	77.3 (3)	N2—O5—Pb	96.8 (6)
O4—Pb—O2	125.0 (2)	N1—O9—Pb^{i}	100.5 (7)
O4—Pb—O3	62.5 (2)	O7—N1—O9	118.6 (9)
O4—Pb—O5	92.6 (3)	O7—N1—O6	122.9 (8)
O4—Pb—O6	68.3 (2)	O9—N1—O6	118.4 (9)
O4—Pb—O7^{i}	153.5 (2)	O10—N2—O8	120.9 (12)
O4—Pb—O9^{i}	119.2 (3)	O10—N2—O5	116.8 (11)
O4—Pb—O9	107.0 (3)	O8—N2—O5	122.3 (10)
O5—Pb—O2	68.8 (2)	N2—O10—Pb	101.4 (9)
O5—Pb—O6	151.4 (2)		

Symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H12···O2^{i}	0.95 (8)	1.89 (8)	2.855 (10)	180 (8)
O2—H25···O5^{ii}	0.85 (10)	2.03 (10)	2.857 (11)	179 (11)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.

All H atoms, except those participating in hydrogen bonding, were refined with fixed and isotropic displacement parameters using a riding model. The positions of the H atoms involved in hydrogen bonding were determined from the final difference Fourier map and refined isotropically. Soft geometrical restraints were also applied to these H atoms. The large thermal motion of O10 was attributed to partial disorder of the weakly coordinating nitrate group. The largest peak and deepest hole in the final difference Fourier map were located 0.97 and 0.99 Å from Pb, respectively.

Data collection: *STADI*4 (Stoe & Cie, 1996*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1021). Services for accessing these data are described at the back of the journal.

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Di-μ-oxo-bis[bis(bipyridine-*N*,*N'*)-manganese(III,IV)] Triperchlorate Bis(nitrobenzene) Hemihydrate

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Abstract

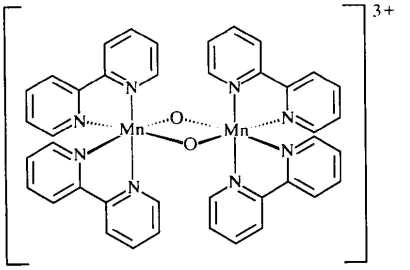
The title compound, $[Mn_2O_2(C_{10}H_8N_2)_4](ClO_4)_3.2C_6H_5NO_2.0.5H_2O$, retains a half water molecule and incorporates two nitrobenzene molecules in the structure when recrystallized from a mixture of nitrobenzene and nitromethane. The two manganese sites have differing geometries suggestive of oxidation states Mn^{III} and Mn^{IV}. The supposed d^4 configuration of Mn^{III} implies a Jahn–Teller distortion, which is observed.

Comment

Oxo-bridged mixed-valence manganese compounds provide important small molecule model compounds for the metalloenzyme OEC (oxygen evolving complex) of Photosystem II in photosynthesis; for a recent review, see Manchanda *et al.* (1995). The first experimental charge–density study of such a compound was recently carried out on the tetrafluoroborate salt of bis(μ-oxo)-tetrakis(2,2'-bipyridine)dimanganese(III,IV) (Jensen *et al.*, 1995) and revealed a substantial accumulation of charge density in a deformation map between the μ-O atoms in the Mn_2O_2 plane. The current study was undertaken to follow up this work with a combined X-ray and neutron study of the perchlorate salt of this cation. Different crystal growth media were tested with the aim of growing large crystals suitable for neutron work and resulted in the surprising incorporation of nitrobenzene molecules in the crystal.

The asymmetric unit contains one cation, three perchlorate anions, two nitrobenzene molecules and one half water molecule. All perchlorate ions were disordered. Two ions were modelled with all O atoms occupying two sites equally and one ion was modelled with only two of the O atoms occupying two sites. All groups were restrained to have tetrahedral geometry with a Cl—O bond length of 1.414 Å. The geometry around the metal sites determined at room temperature and at 200 K do not differ significantly. Details given in the text refer to the room-temperature results.

The cation, (I), has two crystallographically independent metal sites with clearly differing geometries suggestive of its description as a localized $Mn^{III}Mn^{IV}$ dimer. The Mn1—O bond lengths are longer relative to those of Mn2—O, which suggests that Mn1 may be assigned as the Mn^{III} site and Mn2 as Mn^{IV}. The Mn1—N(axial) bond lengths [average 2.170 (6) Å] are longer than the Mn1—N(equatorial) bond lengths [average 2.117 (6) Å], which may be explained as Jahn–Teller distortion of a d^4 Mn^{III} ion.



(I)

The distortion is probably reduced somewhat by the competing effect of the bridging O atoms resulting in an elongation of the equatorial Mn—N bonds. This same effect may explain the observed elongation of the Mn2—N(equatorial) bond lengths [average

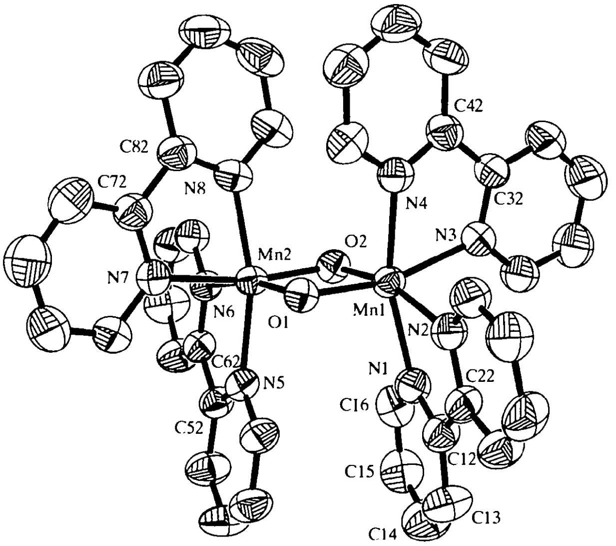


Fig. 1. Cation (I) drawn with atomic displacement parameters at the 50% probability level and showing the atom-labelling scheme.