Skrzypczak-Jankun, E. & Smith, D. A. (1994*a*). *Acta Cryst.* **C50**, 91–93.
Skrzypczak-Jankun, E. & Smith, D. A. (1994*b*). *Acta Cryst.* **C50**, 1585–1588.
Skrzypczak-Jankun, E., Smith, D. A. & Maluszynska, H. (1994). *Acta Cryst.* **C50**, 1097–1099.
Smith, D. A., Sucheck, S., Cramer, S. & Baker, D. (1995). *Synth. Commun.* **25**, 4123–4132.
Smith, D. A., Sucheck, S., Cramer, S. & Skrzypczak-Jankun, E. (1992). *Tetrahedron Lett.* **33**, 7765–7768.
Smith, D. A., Sucheck, S. & Pinkerton, A. A. (1992). *J. Chem. Soc. Chem. Commun.* pp. 367–368.

Acta Cryst. (1997). **C53**, 581-583

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

ANTHONY M. J. LEES, ANDREW W. G. PLATT AND ROMAN A. KRESIŃSKI

School of Sciences, Staffordshire University, College Road, Stoke-on-Trent ST4 2DE, England. E-mail: sctrak@staffs.ac.uk

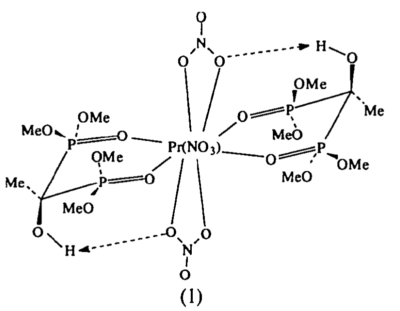
(*Received 12 November 1996; accepted 13 January 1997*)

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).

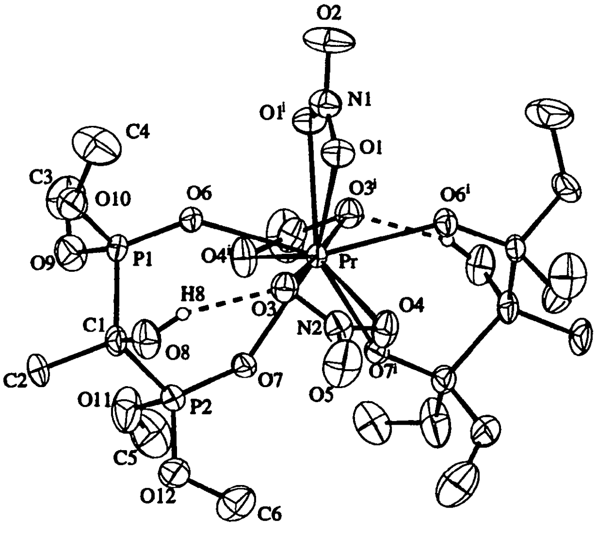


Fig. 1. *SNOOPI* (Davies, 1983) plot of the title complex with 30% probability ellipsoids and the atom-labelling scheme. H atoms have been omitted for clarity, except for the hydroxyl H atom. [Symmetry code: (i) $-x$, y, $\frac{1}{2}-z$.]

Experimental

Crystals of the title compound were crystallized from acetonitrile.

Crystal data

[Pr(NO$_3$)$_3$(C$_6$H$_{16}$O$_7$P$_2$)$_2$]
$M_r = 851.20$
Monoclinic
$C2/c$
$a = 20.860\,(4)$ Å
$b = 9.090\,(2)$ Å
$c = 17.202\,(3)$ Å
$\beta = 92.23\,(3)°$
$V = 3259.3\,(11)$ Å^3
$Z = 4$
$D_x = 1.735$ Mg m^{-3}
$D_m = 1.732$ Mg m^{-3}
D_m measured by flotation in CHCl$_3$/CH$_2$Br$_2$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2.4$–$25.0°$
$\mu = 1.780$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.35 \times 0.30 \times 0.30$ mm
Green

Data collection

Delft Instruments FAST TV diffractometer
Area detector scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.498$, $T_{\max} = 0.586$
6437 measured reflections

2569 independent reflections
2437 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0474$
$\theta_{\max} = 25.02°$
$h = -24 \rightarrow 16$
$k = -6 \rightarrow 10$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.0348$
$wR(F^2) = 0.0868$
$S = 0.836$
2569 reflections
203 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2)]$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 1.03$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Extinction correction: none
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	$U_{\rm eq}$
Pr†	0	0.33359 (3)	1/4	0.03098 (14)
O1	0.0293 (2)	0.5882 (3)	0.2007 (2)	0.0543 (8)
O2†	0	0.7941 (6)	1/4	0.094 (2)
O3	0.1130 (2)	0.3458 (3)	0.1840 (2)	0.0501 (8)
O4	0.0364 (2)	0.2537 (4)	0.1128 (2)	0.0614 (9)
O5	0.1347 (2)	0.2397 (6)	0.0757 (2)	0.1001 (15)
O6	0.08667 (13)	0.4078 (3)	0.3460 (2)	0.0436 (7)
O7	0.06439 (13)	0.1149 (3)	0.2813 (2)	0.0421 (7)
O8	0.2079 (2)	0.2348 (5)	0.2826 (2)	0.0645 (9)
O9	0.1231 (2)	0.2960 (4)	0.4760 (2)	0.0671 (10)
O10	0.1957 (2)	0.4631 (4)	0.4090 (2)	0.0734 (11)
O11	0.1018 (3)	−0.0175 (5)	0.4052 (3)	0.101 (2)
O12	0.1528 (2)	−0.0746 (5)	0.2848 (3)	0.111 (2)
N1†	0	0.6598 (6)	1/4	0.055 (2)
N2	0.0954 (2)	0.2790 (5)	0.1220 (2)	0.0549 (10)
P1	0.14118 (6)	0.34983 (12)	0.39440 (7)	0.0391 (3)
P2	0.11830 (6)	0.05037 (13)	0.32622 (7)	0.0506 (3)
C1	0.1793 (2)	0.1883 (5)	0.3519 (3)	0.0470 (12)
C2	0.2330 (3)	0.1259 (6)	0.4060 (3)	0.068 (2)
C3	0.0828 (3)	0.3747 (8)	0.5257 (3)	0.088 (2)
C4	0.1997 (3)	0.6040 (7)	0.3758 (5)	0.106 (3)
C5	0.0471 (4)	−0.0978 (10)	0.4222 (4)	0.112 (3)
C6	0.1453 (3)	−0.1070 (7)	0.2034 (4)	0.082 (2)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Pr—O1	2.547 (3)	O1—N1	1.248 (4)
Pr—O3	2.658 (4)	O2—N1	1.221 (7)
Pr—O4	2.611 (3)	O3—N2	1.268 (5)
Pr—O6	2.494 (3)	O4—N2	1.256 (5)
Pr—O7	2.448 (3)	O5—N2	1.218 (5)
O7^{i}—Pr—O7	71.34 (13)	O7^{i}—Pr—O3	115.34 (10)
O7^{i}—Pr—O6	137.97 (9)	O7—Pr—O3	68.89 (9)
O7—Pr—O6	72.34 (9)	O6^{i}—Pr—O3	109.73 (10)
O6^{i}—Pr—O6	148.61 (13)	O6—Pr—O3	68.89 (10)
O7^{i}—Pr—O1	143.29 (10)	O1—Pr—O3	65.89 (10)
O7—Pr—O1	132.41 (10)	O4—Pr—O3	48.01 (10)
O6^{i}—Pr—O1	73.20 (10)	O4^{i}—Pr—O3	133.81 (10)
O6—Pr—O1	78.32 (10)	O3^{i}—Pr—O3	175.22 (13)
O1^{i}—Pr—O1	49.40 (15)	N1—O1—Pr	96.8 (3)
O7^{i}—Pr—O4	75.64 (11)	N2—O3—Pr	96.2 (3)
O7—Pr—O4	78.24 (11)	N2—O4—Pr	98.8 (2)
O6^{i}—Pr—O4	72.87 (10)	O2—N1—O1	121.5 (2)
O6—Pr—O4	116.42 (10)	O1—N1—O1^{i}	117.1 (5)
O1—Pr—O4	82.50 (11)	O5—N2—O4	123.0 (5)
O1—Pr—O4^{i}	129.47 (11)	O5—N2—O3	120.7 (5)
O4—Pr—O4^{i}	147.7 (2)	O4—N2—O3	116.3 (4)
O1—Pr—O3^{i}	109.43 (10)		

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

Data were collected using previously described procedures (Darr, Drake, Hursthouse & Malik, 1993) for triclinic symmetry and subsequently transformed. The position of the Pr atom was estimated using Patterson methods (*SHELXS*86; Sheldrick, 1990) and all remaining non-H-atom positions were obtained using subsequent Fourier syntheses (*SHELXL*93; Sheldrick, 1993). All non-H atoms were refined anisotropically. The hydroxyl H atom was located close to its final refined position (O—H 0.82 Å). Other H atoms were introduced at calculated positions (C—H 0.96 Å) and all H atoms were assigned a common refined isotropic displacement parameter. Three aberrant low-angle reflections with $F_o << F_c$ were suppressed and an absorption correction was applied (Walker & Stuart, 1983) based on the converged model. On reconvergence, the H-atom displacement parameter was 0.144 (8) Å^2.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1990). Cell refinement: *MADNES*. Data reduction: *MADNES*. Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL*93.

The authors wish to acknowledge the use of the EPSRC Chemical Database Service at Daresbury (Fletcher, McMeeking & Parkin, 1996) and the EPSRC X-ray Crystallography Service, Cardiff, Wales.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.

Davies, K. (1983). *SNOOPI. Molecular Plotting Program.* Chemical Crystallography Laboratory, University of Oxford, England.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Leroux, Y., El Manouni, D., Safsaf, A., Neuman, A., Gillier, H. & Burgada, R. (1991). *Phosphorus Sulfur Silicon*, **56**, 95–103.

Pflugrath, J. W. & Messerschmidt, A. (1990). *MADNES. Program for Area-Detector Data Interpretation.* Delft Instruments, Delft, The Netherlands.
Platt, A. W. G., Simpson, D., Fawcett, J. & Russell, D. R. (1994). *Inorg. Chim. Acta*, **223**, 45–53.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–164.

Acta Cryst. (1997). C**53**, 583-585

Bis(ethylxanthato)phenylantimony(III)

ALEXANDER J. BLAKE, MATTHEW PEARSON, D. BRYAN SOWERBY AND PETER P. WOODHEAD

Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England. E-mail: a.j.blake@nottingham.ac.uk

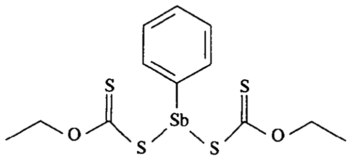
(*Received 7 November 1996; accepted 16 January 1997*)

Abstract

The Sb atom in the title compound, bis(*O*-ethyl dithiocarbonato-*S*)phenylantimony(III), [Sb(C_6H_5)($C_3H_5OS_2$)$_2$], is in sixfold coordination to the C atom of the phenyl group [Sb—C 2.163 (3) Å] and five S atoms of three xanthate ligands. Of these, two S atoms form primary bonds [Sb—S 2.5377 (19) and 2.4987 (17) Å] and there are two intramolecular secondary bonds [Sb···S 3.1051 (15) and 2.9981 (16) Å], making the ligands asymmetrically chelating. The final contact is a weak intermolecular secondary bond [Sb···S 3.905 (2) Å]. The geometry thus described can best be considered as distorted pentagonal pyramidal, but if the antimony lone pair of electrons is stereochemically active, the arrangement becomes pseudo-pentagonal bipyramidal.

Comment

If only short primary bonds (Table 1) are considered, the basic structure of the title compound, (1), is trigonal pyramidal as would be expected for an AB_2E molecule. The two Sb—S separations [2.538 (2) and 2.499 (2) Å to the S1 and S3 atoms, respectively] (Fig. 1) are, however, slightly different and the S1—Sb—S3 angle [77.52 (6)°)] is unusually small. Angles subtended at antimony between sulfurs and the bonding carbon of the phenyl group are more normal with values of 95.89 (8) and 95.22 (8)°.



(1)

As with other dithio ligands of this type (Tiekink & Winter, 1992; Haiduc, Sowerby & Lu, 1995; Haiduc & Sowerby, 1995), there is the possibility of further ligand interaction as the formally non-bonded S atoms may also enter into coordination. If this occurs, ligands can become either bridging or chelating, with each mode leading to symmetric and asymmetric variants. A result of this added bonding will be an increase in the antimony coordination number and distortion of the pyramidal geometry.

Such interactions occur in compound (1), resulting in secondary Sb···S intramolecular separations of 3.1051 (15) and 2.9981 (16) Å to the S2 and S4 atoms, respectively, these being the S atoms which are formally doubly bonded to C atoms. It is also clear that there is the expected partial delocalization of the C=S double bond as the 'short' C—S separations (*ca* 1.65 Å) are slightly longer than double bonds (*ca* 1.62 Å), while the 'long' C—S bonds (*ca* 1.73 Å) are shorter than a conventional single bond (*ca* 1.81 Å). There is also the expected inverse correlation between Sb—S and C—S distances at a given S atom. If these interac-

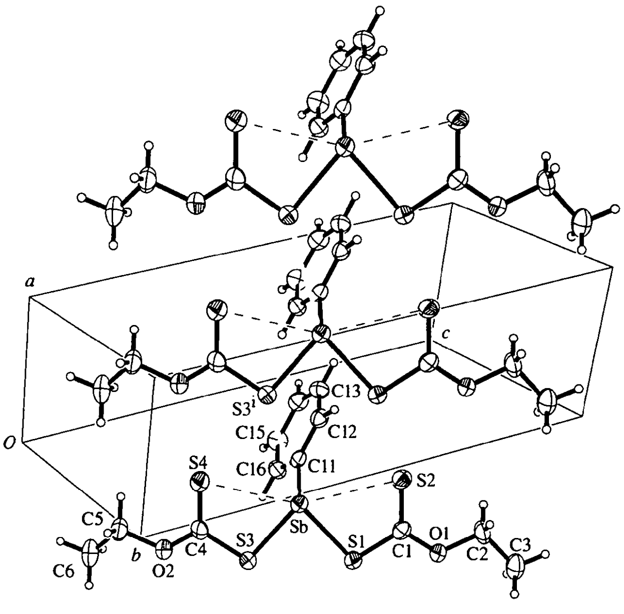


Fig. 1. A view of the structure of (1) with the atom-numbering scheme. Displacement ellipsoids enclose 70% probability surfaces and H atoms are shown as spheres of arbitrary radii. Dashed and dotted lines represent intra- and intermolecular Sb···S interactions, respectively. The latter link molecules into chains running parallel to the crystallographic *a* axis [symmetry code: (i) 1 + *x*, *y*, *z*].

Acta Crystallographica Section C
ISSN 0108-2701 © 1997