The results of the present study support our earlier findings that this type of hydrazone prefers to maintain a nearly planar pentagonal configuration on coordination, leaving two vacant sites available for overall pentagonal bipyramidal coordination; these can be occupied by unidentate inorganic anions, σ-bonded organic groups or solvent molecules.

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References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Lorenzini, C., Pelizzi, C., Pelizzi, G. & Predieri, G. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2155–2158.

Mangia, A., Pelizzi, C. & Pelizzi, G. (1974). *Acta Cryst.* B**30**, 2146–2150.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nardelli, M., Pelizzi, C. & Pelizzi, G. (1977). *Transition Met. Chem.* **2**, 35–40.

Park, J. J., Collins, D. M. & Hoard, J. L. (1970). *J. Am. Chem. Soc.* **92**, 3636–3644.

Pelizzi, C. & Pelizzi, G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1970–1973.

Pelizzi, C., Pelizzi, G. & Predieri, G. (1984). *J. Organomet. Chem.* **263**, 9–20.

Pelizzi, C., Pelizzi, G., Predieri, G. & Resola, S. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1349–1354.

Pelizzi, C., Pelizzi, G., Predieri, G. & Vitali, F. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2387–2392.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Ugozzoli, F. (1983). *ASSORB*. A program for Walker and Stuart's absorption correction. Univ. of Parma, Italy.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1987). C**43**, 1505–1509

Structures of Two Dibutyldichlorotin(IV) Adducts with Diarsine and Diphosphine Oxides

By Giancarlo Pelizzi,* Pieralberto Tarasconi and Francesca Vitali

Istituto di Chimica Generale, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 *Parma, Italy*

and Corrado Pelizzi

Istituto di Chimica Biologica, Facoltà di Farmacia, Università di Sassari, Via Muroni 23/*a*, 07100 *Sassari, Italy*

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Abstract. (1): [1,2-Bis(diphenylarsoryl)ethane]di-*n*-butyldichlorotin(IV), $[Sn(C_{26}H_{24}As_2O_2)Cl_2(C_4H_9)_2]$, $M_r = 822{\cdot}14$, monoclinic, $C2/c$, $a = 10{\cdot}879\ (4)$, $b = 20{\cdot}751\ (8)$, $c = 16{\cdot}014\ (6)$ Å, $\beta = 98{\cdot}45\ (5)°$, $V = 3576\ (2)$ Å^3, $Z = 4$ (Sn on twofold axis), $D_x = 1{\cdot}527$ g cm^{-3}, D_m not measured, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 95{\cdot}17$ cm^{-1}, $F(000) = 1648$, $T = 298$ K, final $R = 0{\cdot}0407$ for 2114 unique observed reflections. (2): [Bis(diphenylphosphoryl)methane]di-*n*-butyldichlorotin(IV), $[Sn(C_{25}H_{22}O_2P_2)Cl_2(C_4H_9)_2]$, $M_r = 720{\cdot}22$, orthorhombic, $Pbca$, $a = 9{\cdot}80\ (1)$, $b = 19{\cdot}66\ (2)$, $c = 35{\cdot}36\ (3)$ Å, $V = 6813\ (11)$ Å^3, $Z = 8$, $D_x = 1{\cdot}404$ g cm^{-3}, D_m not measured, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 10{\cdot}29$ cm^{-1}, $F(000) = 2944$, $T = 298$ K, final $R = 0{\cdot}0822$ for 2716 unique observed reflections. Compound (1) has formula $SnBu^n_2Cl_2$(dpaoe)[dpaoe = 1,2-bis(diphenylarsoryl)ethane] and shows a polymeric nature as a result of the bridging action of the dpaoe ligand. The tin environment is that of a slightly distorted octahedron, the ligands being two Cl, two O and two butyl C atoms. The structure of (2) consists of discrete molecules of $SnBu^n_2Cl_2$(dppom) [dppom = bis(diphenylphosphoryl)methane] in which the metal atom is coordinated to two Cl and two butyl C groups and, more loosely to one than the other, to two O atoms from dppom. The coordination geometry about tin is highly distorted and does not exhibit the characteristics of an idealized polyhedron.

Introduction. Recent work in these laboratories has been directed towards an examination of organotin(IV) derivatives containing phosphorus or arsenic ligands (Harrison, Sharpe, Pelizzi, Pelizzi & Tarasconi, 1983*a*,*b*; Dondi, Nardelli, Pelizzi, Pelizzi & Predieri, 1985, 1986). Our interest in this research field arises from our awareness of the paucity of crystallographic studies on mixed organotin–organophosphorus and organotin–organoarsenic derivatives as revealed by a

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* To whom correspondence should be addressed.

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search carried out on the Cambridge Structural Database, as well as of the versatility shown by the diphosphine and diarsine oxides for binding metal centres.

In an attempt to provide further information in this field, an X-ray crystallographic study of $SnBu^n_2Cl_2$(dpaoe) (1) and $SnBu^n_2Cl_2$(dppom) (2) was undertaken, the results of which are presented in this paper.

Experimental. Crystals for X-ray work (colourless prisms in each case) obtained by evaporating a reaction mixture containing equimolar amounts of $SnBu_2Cl_2$ in anhydrous CH_3COCH_3 and dpaoe or dppom in $CHCl_3$. Crystal dimensions: (1) $0{\cdot}25 \times 0{\cdot}28 \times 0{\cdot}80$ mm, (2) $0{\cdot}42 \times 0{\cdot}50 \times 1{\cdot}20$ mm. Siemens AED three-circle diffractometer on line to a General Automation Jumbo 220 computer, room temperature, Ni-filtered Cu *K*α radiation for (1) and Nb-filtered Mo *K*α radiation for (2). Lattice parameters and their standard deviations determined for each compound from least-squares refinement of setting angles of 25 carefully centred reflections [(1) $19{\cdot}9 < \theta < 42{\cdot}1°$; (2) $10{\cdot}7 < \theta < 18{\cdot}0°$] chosen in diverse regions of reciprocal space. For (1) the systematic absences ($h + k$ odd for hkl, h odd for $h0l$ and k odd for $0k0$) indicate space groups *Cc* or *C*2/*c*. The choice of the centrosymmetric space group *C*2/*c* was dictated by the statistical distribution of the normalized structure factors *E* and the successful structure determination. For (2) the systematic absences (k odd for $0kl$, l odd for $h0l$ and h odd for $hk0$) uniquely indicate the space group *Pbca*. A summary of data collection and structural refinement for both (1) and (2) is given in Table 1. Intensity data collected by $\theta/2\theta$ scans with variable speed. Profile analysis according to Lehmann & Larsen (1974). Data corrected for Lorentz and polarization effects. Absorption corrections applied for (2) [but not for (1)] using the method of Walker & Stuart (1983); transmission factors: absorption: 0·490–1·350; extinction: 0·851–1·119.

Both structures solved by conventional Patterson and Fourier methods, and refined on *F* using full-matrix least-squares procedures. $\sum w|\Delta F|^2$ minimized, unit weights for (1). For (2) $w = 1/[\sigma^2(F_o) + 0{\cdot}003|F_o|^2]$. For (1) all non-H atoms refined anisotropically. The twelve H atoms of the dpaoe ligand located in an inner-data ΔF map and refined isotropically. Butyl H atoms ignored, in spite of the presence of some electron density in the expected regions. For (2) anisotropic thermal parameters only for Sn, Cl and the atoms from the dppom ligand except the phenyl ring C atoms, which were refined isotropically and treated as rigid groups with hexagonal symmetry. H atoms not included. Convergence at $R = 0{\cdot}0407$ and $R = 0{\cdot}0822$ for (1) and (2), respectively. The rather high *R* factor for (2) is mainly due to the low diffraction quality of the crystal and to significant deterioration in the X-ray beam (this effect was allowed for by appropriate scaling with respect to the standard), as well as disorder problems involving one of the two butyl chains. Scattering factors for neutral atoms and real and imaginary components of anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Calculations carried out with the *SHELX*76 set of programs (Sheldrick, 1976), partly on a Cyber 76 computer and partly on a Gould-SEL 32/77 computer. Other programs previously reported (Delledonne, Pelizzi & Pelizzi, 1987). Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 2 and 3. A selection of bond distances and angles is given in Tables 4 and 5.*

Table 1. *Summary of data collection and structure refinement*

	(1)	(2)
θ range (°)	3·0–65·0	3·0–25·0
hkl range	−12–12, 0–24, 0–18	0–11, 0–23, 0–42
Standard reflection	242	1,7,19
Frequency	Every 50 measurements	Every 75 measurements
Variation	Random fluctuations	Some deterioration
Reflections measured	3258	6703
Unique observed reflections $[I > 2\sigma(I)]$	2114	2716
R_{int}	0·0199	—
Parameters refined	234	165
Data-to-parameters ratio	9·0	16·5
Max. Δ/σ	0·87	0·85
Final max. and min. $\Delta\rho$ excursions (e Å^{-3})	0·43, −0·47[a]	0·77, −1·16[b]
R	0·0407	0·0822
wR	0·0532	0·0874

Notes: (*a*) close to Sn; (*b*) close to phenyl C atoms.

Discussion. As illustrated in the perspective drawing (Fig. 1), which also shows the atom-labelling scheme, compound (1) exists as a polymeric species with adjacent tin centres bridged through the O atoms of the dpaoe ligand. The compound has crystallographic twofold symmetry, and the Sn atom lies on a twofold axis in octahedral geometry, being coordinated to two *cis* O atoms from dpaoe, two *cis* Cl atoms and two butyl C atoms which are mutually *trans*. The ligand arrangement is not greatly distorted from a regular octahedral configuration, as indicated by the angles at Sn, all within 5° of 90 or 180°, and by least-squares calculations which show that the set of donor atoms forming the three coordination planes of the octahedron are coplanar to within 0·03 Å and that the planes intersect each other at 89°. The Sn—Cl bond distance of 2·594 (2) Å is among the longest reported for hexacoordinate tin complexes containing two Cl atoms in a *cis* disposition.

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* Lists of structure factors, H-atom coordinates for compound (1), thermal parameters, and non-essential bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43885 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* ($\times 10^5$ *for* Sn *and* As, *and* $\times 10^4$ *for* Cl, O *and* C) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$) *for compound* (1)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sn	50000	71735 (3)	25000	438 (2)
As	35436 (6)	83178 (3)	8428 (4)	417 (2)
Cl	5545 (2)	6303 (1)	3658 (1)	699 (7)
O	4591 (4)	7967 (2)	1555 (3)	512 (14)
C(1)	6914 (7)	7201 (4)	2310 (5)	708 (31)
C(2)	7249 (12)	7319 (9)	1504 (11)	1841 (88)
C(3)	8613 (12)	7400 (8)	1434 (10)	1503 (72)
C(4)	8979 (15)	8028 (8)	1238 (13)	1877 (98)
C(5)	4424 (6)	8728 (3)	29 (4)	477 (24)
C(6)	3862 (8)	8875 (4)	−780 (5)	646 (31)
C(7)	4537 (10)	9199 (5)	−1322 (6)	802 (35)
C(8)	5754 (11)	9377 (4)	−1044 (6)	887 (45)
C(9)	6312 (10)	9236 (5)	−245 (6)	963 (44)
C(10)	5650 (8)	8910 (4)	297 (5)	761 (33)
C(11)	2688 (6)	8972 (3)	1385 (4)	495 (22)
C(12)	1742 (8)	9321 (4)	929 (6)	650 (29)
C(13)	1154 (8)	9811 (4)	1312 (6)	780 (35)
C(14)	1522 (9)	9939 (4)	2141 (6)	752 (34)
C(15)	2479 (9)	9600 (4)	2598 (6)	693 (32)
C(16)	3062 (8)	9110 (3)	2222 (5)	574 (26)
C(17)	2250 (7)	7748 (3)	286 (5)	460 (20)

Table 3. *Fractional atomic coordinates* ($\times 10^5$ *for* Sn *and* $\times 10^4$ *for* P, Cl, O *and* C) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$) *for compound* (2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Sn	7119 (12)	19180 (6)	13194 (3)	546 (4)
P(1)	4212 (5)	2337 (2)	1101 (1)	516 (15)
P(2)	4027 (5)	936 (2)	1485 (2)	577 (16)
Cl(1)	−1534 (5)	1499 (3)	1607 (2)	1017 (24)
Cl(2)	−271 (5)	2934 (3)	1053 (1)	732 (19)
O(1)	2685 (11)	2302 (6)	1046 (4)	683 (47)
O(2)	2468 (12)	994 (6)	1500 (4)	723 (49)
C(25)	4848 (17)	1765 (7)	1465 (4)	502 (56)
C(1)	4746 (11)	3160 (5)	1249 (3)	545 (44)
C(2)	6128 (11)	3300 (5)	1300 (3)	726 (53)
C(3)	6546 (11)	3953 (5)	1402 (3)	914 (61)
C(4)	5580 (11)	4467 (5)	1453 (3)	824 (57)
C(5)	4197 (11)	4327 (5)	1402 (3)	781 (54)
C(6)	3780 (11)	3674 (5)	1300 (3)	742 (53)
C(7)	5041 (12)	2127 (6)	670 (3)	655 (52)
C(8)	4221 (12)	2069 (6)	350 (3)	640 (47)
C(9)	4812 (12)	1938 (6)	−2 (3)	780 (52)
C(10)	6223 (12)	1864 (6)	−32 (3)	812 (56)
C(11)	7043 (12)	1922 (6)	288 (3)	808 (54)
C(12)	6452 (12)	2054 (6)	640 (3)	691 (54)
C(13)	4685 (14)	539 (7)	1901 (3)	756 (55)
C(14)	5606 (14)	1 (7)	1869 (3)	1378 (71)
C(15)	6186 (14)	−283 (7)	2192 (3)	1634 (84)
C(16)	5845 (14)	−30 (7)	2549 (3)	1256 (68)
C(17)	4923 (14)	507 (7)	2581 (3)	1383 (80)
C(18)	4343 (14)	792 (7)	2258 (3)	1252 (69)
C(19)	4603 (12)	477 (6)	1082 (3)	560 (47)
C(20)	3676 (12)	129 (6)	853 (3)	802 (59)
C(21)	4140 (12)	−244 (6)	543 (3)	972 (64)
C(22)	5531 (12)	−269 (6)	462 (3)	962 (61)
C(23)	6459 (12)	79 (6)	690 (3)	966 (62)
C(24)	5995 (12)	451 (6)	1000 (3)	742 (56)
C(26)	383 (21)	1223 (10)	892 (6)	922 (63)
C(27)	823 (20)	1359 (10)	501 (6)	780 (55)
C(28)	486 (20)	838 (10)	195 (6)	830 (56)
C(29)	824 (24)	1062 (11)	−198 (6)	1099 (67)
C(30)	1377 (19)	2257 (10)	1855 (5)	748 (55)
C(31)	666 (40)	2944 (19)	1977 (10)	1053 (110)
C(31′)	438 (60)	2627 (31)	2112 (18)	770 (171)
C(32)	1584 (45)	3316 (20)	2377 (11)	1419 (137)
C(32′)	839 (96)	3076 (46)	2466 (27)	1468 (256)
C(33)	937 (52)	2752 (24)	2640 (13)	1618 (151)
C(33′)	1870 (78)	2777 (38)	2624 (20)	1378 (230)

Table 4. *Selected bond distances* (Å) *and angles* (°) *for* $\text{SnBu}^n_2\text{Cl}_2$(dpaoe)

Sn—Cl	2·594 (2)	As—C(5)	1·925 (7)
Sn—O	2·236 (4)	As—C(11)	1·924 (7)
Sn—C(1)	2·149 (8)	As—C(17)	1·951 (7)
O—As	1·657 (4)	C(17)—C(17$^{\rm ii}$)	1·530 (11)
Cl—Sn—O	176·6 (1)	Sn—O—As	146·9 (3)
Cl—Sn—C(1)	89·7 (2)	O—As—C(5)	107·4 (3)
O—Sn—C(1)	89·2 (2)	O—As—C(11)	109·2 (2)
Cl—Sn—Cl$^{\rm i}$	91·73 (7)	O—As—C(17)	115·2 (2)
Cl—Sn—O$^{\rm i}$	91·6 (1)	C(5)—As—C(11)	108·4 (3)
Cl—Sn—C(1$^{\rm i}$)	92·4 (2)	C(5)—As—C(17)	110·8 (3)
O—Sn—O$^{\rm i}$	85·2 (2)	C(11)—As—C(17)	105·6 (3)
O—Sn—C(1$^{\rm i}$)	88·6 (2)	As—C(17)—C(17$^{\rm ii}$)	112·7 (5)
C(1)—Sn—C(1$^{\rm i}$)	177·0 (3)		

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

Table 5. *Selected bond distances* (Å) *and angles* (°) *for* $\text{SnBu}^n_2\text{Cl}_2$(dppom)

Sn—Cl(1)	2·560 (6)	Sn—Cl(2)	2·410 (5)
Sn—O(1)	2·290 (11)	Sn—O(2)	2·582 (12)
Sn—C(26)	2·062 (21)	Sn—C(30)	2·110 (19)
P(1)—O(1)	1·510 (12)	P(2)—O(2)	1·533 (13)
P(1)—C(1)	1·779 (10)	P(2)—C(13)	1·788 (14)
P(1)—C(7)	1·775 (11)	P(2)—C(19)	1·778 (12)
P(1)—C(25)	1·821 (16)	P(2)—C(25)	1·818 (16)
O(1)—Sn—O(2)	76·9 (4)	O(1)—Sn—Cl(1)	178·2 (3)
Cl(2)—Sn—C(26)	101·6 (6)	O(2)—Sn—Cl(2)	161·1 (3)
Cl(1)—Sn—Cl(2)	94·5 (2)	C(26)—Sn—C(30)	156·2 (8)
Cl(2)—Sn—C(30)	102·2 (6)	P(1)—C(25)—P(2)	115·4 (9)
Sn—O(1)—P(1)	142·8 (8)	Sn—O(2)—P(2)	135·1 (7)
O(1)—P(1)—C(1)	111·8 (6)	O(2)—P(2)—C(13)	111·3 (7)
O(1)—P(1)—C(7)	109·3 (6)	O(2)—P(2)—C(19)	112·5 (7)
O(1)—P(1)—C(25)	113·7 (7)	O(2)—P(2)—C(25)	112·0 (7)
C(1)—P(1)—C(7)	109·2 (6)	C(13)—P(2)—C(19)	108·9 (6)
C(1)—P(1)—C(25)	104·7 (7)	C(13)—P(2)—C(25)	105·2 (7)
C(7)—P(1)—C(25)	107·9 (7)	C(19)—P(2)—C(25)	106·6 (7)

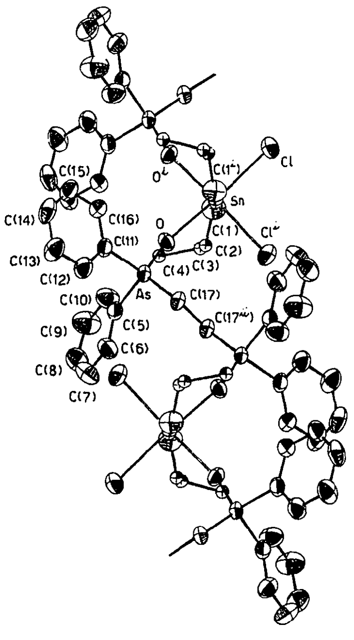

Fig. 1. Perspective view of the structure of $\text{SnBu}^n_2\text{Cl}_2$(dpaoe) with the numbering scheme used. Thermal ellipsoids are drawn at the 40% probability level. The butyl C atoms are represented by arbitrarily small spheres, except that bonded to Sn. The following equivalent positions generate the coordinates of the atoms so marked: (i) = $1-x, y, \tfrac{1}{2}-z$; (ii) = $\tfrac{1}{2}-x, \tfrac{3}{2}-y, \bar{z}$.

The structure of (1) is basically similar to that of the analogous phosphorus adduct, $SnBu^n_2Cl_2$(dppoe) (Harrison, Sharpe, Pelizzi, Pelizzi & Tarasconi, 1983*a*) which is also polymeric. In comparison to (1), however, the dppoe derivative does not possess any crystallographically imposed symmetry and exhibits a much less regular coordination geometry, in accordance also with the strong dissimilarity in the two Sn—O linkages. Furthermore, on going from the phosphorus to the arsenic complex, one finds a small, but significant, lengthening of the Sn—Cl bonds and, concomitantly, a shortening of the Sn—O bonds. Bond distances and angles involving the dpaoe ligand are unexceptional and agree closely with those reported for the other two tin–dpaoe complexes characterized by X-ray diffraction, namely $[SnPh_3Cl]_2$(dpaoe) (Pelizzi & Pelizzi, 1983) and $[SnPh_3(NO_3)]_2$(dpaoe) (Dondi, Nardelli, Pelizzi, Pelizzi & Predieri, 1986). Unlike the present compound, the latter molecules adopt trigonal bipyramidal structures consisting of binuclear monomeric units in which the dpaoe ligand bridges two adjacent metal atoms.

The crystal structure of (2) is built up of discrete monomeric $SnBu^n_2Cl_2$(dppom) molecules which are separated by normal van der Waals interactions. A perspective view of the compound along with the atom-labelling scheme is shown in Fig. 2. The Sn atom is surrounded by two O atoms from the dppom ligand (bound more loosely to one than the other), two Cl atoms and two butyl C atoms in a *cis–cis–trans* arrangement. The coordination polyhedron, as is apparent from the bond distances and angles quoted in Table 5, is highly distorted, no doubt reflecting in part the predominantly unidentate coordination of dppom, and cannot be adequately described by any idealized geometry. If only the five nearest neighbours are considered, the tin environment can be viewed as a distorted trigonal bipyramid, whose equatorial plane is formed by Cl(2), C(26) and C(30), while the axial sites are occupied by Cl(1) and O(1). The principal angular distortions that occur in such a description are in the equatorial plane being caused by the opening of the C—Sn—C angle to 156·2 (8)° along with the associated closing of the two C—Sn—Cl angles to 101·6 (6) and 102·2 (6)°. Alternatively, if the more weakly bonded O atom is also included, the ligand configuration may be described as a very distorted octahedron, the *trans* angles being 156·2 (8), 161·1 (3) and 178·2 (3)°, while the angles between neighbouring atoms range from 76·9 (4) [O(1)—Sn—O(2)] to 104·4 (3)° [Cl(1)—Sn—O(2)]. The disparity of the two Sn—O linkages (0·15 Å) is reflected in the two Sn—Cl bonds, which are even more unequal, the difference being *ca* 0·29 Å, with the longer *trans* to the more strongly bound O atom.

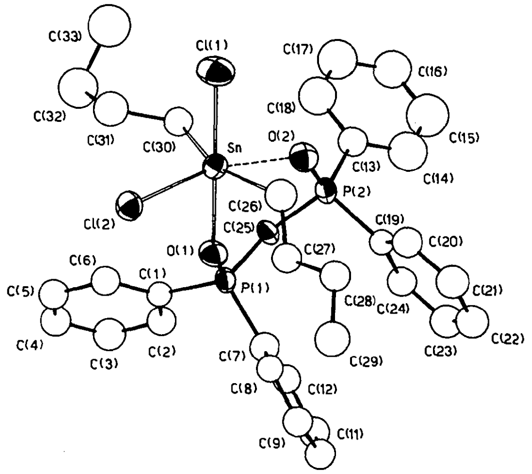

Fig. 2. Perspective view of the structure of $SnBu^n_2Cl_2$(dppom) with the numbering scheme used. Thermal ellipsoids are drawn at the 30% probability level. Anisotropic thermal parameters were only used for shaded atoms. For clarity, the disorder in the C(30)—C(31)—C(32)—C(33) butyl chain is not shown.

As regards the metal-atom environment and the arrangement of the ligands, a similar situation has been previously observed in the structure of the above mentioned $SnBu^n_2Cl$(dppoe) derivative, which also contains highly irregular coordinated Sn atoms, with much of distortion arising from the weaker coordination of one of the two O=P groups. Both these compounds can be seen as intermediate in the range of Sn^{IV} compounds which span from purely tetrahedral towards octahedral, as extra ligands become involved with the metal centre. Unlike the present compound, the whole crystal structure of the dppoe adduct is polymeric and this is, in fact, the only significant difference between the two compounds. The structural parameters observed for the dppom ligand agree fairly well with those reported for the only other known tin–dppom complex, namely $SnPh_2(NO_3)_2$(dppom) (Dondi, Nardelli, Pelizzi, Pelizzi & Predieri, 1986), in which, unlike those in (2), the two Sn—O bonds are nearly equal in length.

References

Delledonne, D., Pelizzi, G. & Pelizzi, C. (1987). *Acta Cryst.* C**43**, 1502–1505.

Dondi, S., Nardelli, M., Pelizzi, C., Pelizzi, G. & Predieri, G. (1985). *J. Chem. Soc. Dalton Trans.* pp. 487–491.

Dondi, S., Nardelli, M., Pelizzi, C., Pelizzi, G. & Predieri, G. (1986). *J. Organomet. Chem.* **308**, 195–206.

Harrison, P. G., Sharpe, N. W., Pelizzi, C., Pelizzi, G. & Tarasconi, P. (1983*a*). *J. Chem. Soc. Dalton Trans.* pp. 921–926.

Harrison, P. G., Sharpe, N. W., Pelizzi, C., Pelizzi, G. & Tarasconi, P. (1983*b*). *J. Chem. Soc. Dalton Trans.* pp. 1687–1693.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht).

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Pelizzi, C. & Pelizzi, G. (1983). *J. Chem. Soc. Dalton Trans.* pp. 847–849.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1987). C**43**, 1509–1511

Structure of Tripotassium Aquabis(nitrilotriacetato)neodymate(III) Pentahydrate

By P. Starynowicz

Institute of Chemistry, University of Wrocław, 14 *F. Joliot-Curie Street,* 50-383 *Wrocław, Poland*

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Abstract. $K_3[Nd(C_6H_6NO_6)_2H_2O].5H_2O$, $M_r = 745\cdot9$, monoclinic, $C2/c$, $a = 15\cdot43$ (3), $b = 12\cdot93$ (2), $c = 26\cdot14$ (3) Å, $\beta = 96\cdot58$ (15)°, $V = 5181$ (15) Å^3, $Z = 8$, $D_m = 1\cdot93$, $D_x = 1\cdot912$ (6) Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot57$ mm^{-1}, $F(000) = 2968$, $T = 302$ (2) K, final $R = 0\cdot039$ for 5044 reflections. The Nd ion is nine-coordinate (seven O and two N atoms), forming an approximate tricapped trigonal prism. The analogous compounds of Eu and Ho are probably isomorphic.

Introduction. It is known from spectroscopic investigations (Bukietyńska & Mondry, 1985, 1987) that nitrilotriacetic acid (NTA) may form at least two different complexes with a lanthanide ion, depending on stoichiometry. The 1:1 complexes for light (Pr–Tb) and heavy (Dy–Lu) lanthanides have been described previously (Martin & Jacobson, 1972*a*,*b*). They display certain features common in the complexes of rare earths with aminopolycarboxylic acids (Sinha, 1976; Fuller, Molzahn & Jacobson, 1978; Nesterova, Porai-Koshits, Mitrofanova & Filippova, 1980): (*a*) the metal–nitrogen distance is 0·2–0·3 Å longer than the shortest metal–carboxylic oxygen bond; (*b*) waters or hydroxyl groups are often more remote than carboxyl oxygens; (*c*) the metal–carboxylic oxygen distance may be increased if the carboxyl group is involved in bridge formation [this is not limited to aminopolycarboxylates only (Đào, 1987)]. The present work aims to determine the structures of the lanthanide–NTA 1:2 complexes.

Experimental. The title compound was prepared by addition of NTA to a suspension of freshly precipitated $Nd_2(CO_3)_3$ in a hot aqueous solution of K_2CO_3. The resulting solution was allowed to evaporate at ambient temperature, until large well-formed pink parallelepipeds were formed. Anal.: calc.: Nd 19·3, K 15·7, C 19·3, N 3·8, H 3·2, water of coordination and crystallization 14·5%; found: Nd 18·7, K 17·2, C 17·3, N 3·7, H 3·2, water (thermogravimetrically) 14·4%. A parallelepiped 0·2 × 0·2 × 0·15 mm was cut from a larger crystal, D_m by flotation in $C_2H_4Br_2/CHCl_3$. Systematic absences indicated two possible space groups, Cc or $C2/c$, of which the latter was successfully attempted. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflections, $19 < 2\theta < 24°$), variable $\theta/2\theta$ scan, $4 < 2\theta < 60°$, three standards every 100 reflections, mean variance 6·0%, 7780 intensities measured, index range h 0→20, k 0→18, l −36→36, no corrections for absorption or extinction. 5247 reflections with $I > 3\sigma(I)$ were averaged to 5050 unique reflections, $R(F^2)$ and $wR(F^2)$ were 0·0220 and 0·0201 respectively. Most calculations were performed with locally modified *XTL/XTLE* programs (Syntex, 1976). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), real and imaginary components of anomalous dispersion included for all non-H atoms. The Nd atom was located from a Patterson map, the remaining non-H atoms from subsequent difference syntheses; C-bonded hydrogens placed geometrically, water hydrogens from difference syntheses, not all of them found. During structure solution it was necessary to interchange the positions of K4 and O*W*6 because of an abnormally large temperature factor for K4. The occupancy factor of K4 in its new position was set to 0·5 in accordance with stoichiometry, O*W*7 was also found to be disordered with site occupancy 0·5. Final full-matrix least-squares refinement based on F (non-H atoms anisotropic, except O*W*7 isotropic, hydrogens with fixed parameters), $R = 0\cdot039$, $wR = 0\cdot045$, $S = 2\cdot47$, $\Delta\rho$ between −0·63 and 1·30 e Å^{-3}, the highest peaks around Nd and K atoms, $w = 1/\sigma^2(F)$. Oscillation and Weissenberg photographs, as well as the infrared spectra, suggest isomorphism of the analogous compounds of Eu and Ho.

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