

Table 4. Comparison of relevant geometric parameters and rate constants for the displacement reaction $L\text{Co}(\text{chel})\text{Me} + \text{P}(\text{OMe})_3 \rightarrow \text{P}(\text{OMe})_3\text{Co}(\text{chel})\text{Me} + L$ (CH₂Cl₂ at 298 K) for (DO)(DOH)pn and (DH)₂ complexes (α is positive when the bending is towards the alkyl group)

	Reference	Co—C (Å)	Co—N (Å)	α (°)	k (s ⁻¹)
[PhNH ₂ Co(DO)(DOH)pnMe] ¹	(a)	1.991 (4)	2.147 (3)	-11.3	5.0 × 10 ⁻¹
[PhNH ₂ Co(DO)(DOH)pnEt] ¹	(e)	2.030 (4)	2.174 (3)	-7.1	—
[PhNH ₂ Co(DO)(DOH)pnCH ₂ CF ₃] ¹	(e)	2.009 (2)	2.130 (2)	-5.3	—
[PhNH ₂ Co(DO)(DOH)pnCH ₂ CO ₂ Me] ¹	(a)	2.038 (4)	2.126 (3)	-4.6	—
[PhNH ₂ Co(DH) ₂ Me] ¹	(b)	1.992 (2)	2.129 (4)	3.5	1.51
[PhNH ₂ Co(DH) ₂ Et] ¹	(b)	2.030 (3)	2.147 (2)	2.8	—
[pyCo(DO)(DOH)pnMe] ¹	(c)	2.003 (3)	2.106 (3)	6.9	3.4 × 10 ⁻²
[pyCo(DH) ₂ Me] ¹	(d)	1.998 (5)	2.068 (3)	3.2	8.0 × 10 ⁻²
[4C(OMe)NH-pyCo(DH) ₂ Et] ¹	(d)	2.035 (5)	2.081 (3)	9.1	—
[4CN-pyCo(DH) ₂ CH ₂ CF ₃] ¹	(d)	2.010 (3)	2.041 (4)	1.0	—
[pyCo(DH) ₂ CH ₂ CO ₂ Me] ¹	(d)	2.024 (6)	2.039 (6)	—	—

References: (a) Parker, Zangrando, Bresciani-Pahor, Randaccio & Marzilli (1986); (b) Marzilli, Bayo, Summers, Thomas, Zangrando, Bresciani-Pahor, Mari & Randaccio (1987); (c) Parker, Bresciani-Pahor, Zangrando, Randaccio & Marzilli (1986); (d) Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano (1985); (e) present work.

CH₂CO₂Me < Me < Et (electronic *trans* influence). Furthermore, while the Co—C bond length is unaffected by the change of the equatorial ligand, the Co—N axial bond varies significantly (electronic and steric *cis* influence) (Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985).

In the methyl cobaloximes (Table 4), the rate constant for PhNH₂ is 190 times larger than that for pyridine (py) in agreement with a longer (0.06 Å) Co—N distance in PhNH₂ with respect to pyridine. In the Co(DO)(DOH)pn complexes, this ratio is reduced to 15 and corresponds to a decreased difference in the Co—N axial bond length (0.04 Å).

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Structure of [Et₄N]₂[Sn₃Cl₁₀(μ-OH)₃(μ-OEt)]; a Trimeric Sn^{IV} Salt

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Abstract. Tetraethylammonium 1,1,1,2,2,2,3,3,3-decachloro-μ-2,3-ethoxo-tri-μ-1,2:1,3:2,3-hydroxo-trisnate(2-), [N(C₂H₅)₄]₂[Sn₃(C₂H₅O)Cl₁₀(OH)₃], $M_r = 1067.02$, monoclinic, $P2_1/c$, $a = 12.801$ (3), $b =$

19.412 (6), $c = 15.214$ (5) Å, $\beta = 93.60$ (2)°, $U = 3773$ (2) Å³, $Z = 4$, $D_x = 1.88$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 25.1$ cm⁻¹, $F(000) = 2088$, $T = 150$ K, $R = 0.040$ for 4333 [$I > 3\sigma(I)$] reflections. The [Sn₃Cl₁₀(μ-OH)₃(μ-OC₂H₅)]²⁻ anion has an isosceles triangle of six-coordinated Sn^{IV} ions. The base

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of the triangle is doubly bridged by OH^- and OC_2H_5^- groups, while the other two sides are each bridged by a single OH^- group. The apical Sn is bonded to four Cl^- , while the basal Sn atoms each have three Cl^- ligands.

Introduction. Partial hydrolysis or alcoholysis of Sn^{IV} halides gives a variety of interesting species (Zubieta & Zuckerman, 1978). Neutral dimers of formula $[\text{Cl}_3\text{-Sn}(\text{OR})(\text{HOR})]_2$ ($R = \text{H, Me, Et}$ etc.) are commonly isolated and these have been shown to have double OR^- bridges between two six-coordinate Sn centres (Tudela, Fernandez & Vegas, 1986, and references therein). We now report an anion with an unprecedented trimeric structure, held together by an ethoxy and three hydroxy groups.

Experimental. Transparent six-sided plates were obtained on recrystallizing a sample of $\text{Et}_4\text{N}[\text{SnCl}_3]$ (prepared in ethanol from $\text{Et}_4\text{NCl}\cdot\text{H}_2\text{O}$ and SnCl_2) from $\text{CH}_2\text{Cl}_2/\text{hexane}$ in air. Precession photographs showed monoclinic symmetry with systematic absences $h0l \neq 2n$, $0k0 \neq 2n$ uniquely defining space group $P2_1/c$. Nicolet R3m automated diffractometer, graphite monochromator, lattice parameters from 25 high-angle reflections automatically centred; 5589 reflections, 4963 unique ($R_{\text{int}} = 0.0125$), $3 < 2\theta < 45^\circ$, collected with a θ - 2θ scan, $0 < h < 16$, $0 < k < 24$, $-19 < l < 19$, three standard reflections monitored regularly showed no significant variation; 4333 data [$I > 3\sigma(I)$] corrected for Lorentz and polarization effects; empirical absorption corrections applied based on φ scans of each of three reflections, crystal size $0.5 \times 0.5 \times 0.12$ mm, transmission factors between 0.75 and 0.44. Structure solved by direct methods; full-matrix least-squares refinement based on F with all ordered non-H atoms anisotropic. The methylene C atoms of one Et_4N^+ were disordered and were included with isotropic temperature factors and with tied site-occupancy factors which refined to 0.72 and 0.28 for the major/minor orientations. Ordered ethyl group H atoms were included in calculated positions with common temperature factors, hydroxide H atoms were not located. $R = 0.0409$, $wR = 0.0460$ with $w = [\sigma^2(F) + 0.001F^2]^{-1}$, $(\Delta/\sigma)_{\text{max}} = 0.1$, final difference Fourier peaks $< 1.3 \text{ e } \text{\AA}^{-3}$, three reflections (110, 020, 011) appeared to suffer from extinction and were omitted; atomic scattering factors and f' and f'' values from *International Tables for X-ray Crystallography* (1974).^{*} Main calculations using *SHELX76* (Sheldrick, 1976), least-squares planes using *PARST* (Nardelli, 1985).

^{*} Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, calculated H-atom positions and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44228 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The asymmetric unit comprises two discrete Et_4N^+ cations (one of which is partially disordered), and an $[\text{Sn}_3\text{Cl}_{10}(\text{OH})_3(\text{OEt})]^{2-}$ anion which is illustrated in Fig. 1. Atomic parameters are given in Table 1, and selected bond data in Table 2. The three Sn atoms of the anion are each six-coordinate and in oxidation state IV. They lie at the apices of an isosceles triangle, linked by O atoms. Two sides of the triangle are bridged by single OH^- ligands, while the third is doubly bridged by OH^- and OEt^- ligands. The coordination about the unique Sn(1) is completed by four Cl^- , giving an overall *cis*- SnCl_4O_2 environment, while the other Sn atoms have three Cl^- and exhibit *fac*- SnCl_3O_3 local geometry. The two hydroxy groups bridging to Sn(1) are essentially symmetrically positioned with average Sn—O distances of 2.100 (4) Å, despite joining inequivalent Sn centres. In contrast, both bridging groups between Sn(2) and Sn(3) are significantly closer to Sn(2). Possibly to compensate for this the Sn—Cl bonds on Sn(2) are significantly longer [av. 2.371 (2) Å] than those of Sn(3) [av. 2.359 (2) Å]; these differences can only be attributed to crystal-packing effects since Sn(2) and Sn(3) are otherwise chemically identical. The Sn—Cl bonds on Sn(1) are longer still [av. 2.389 (2) Å], but all lie within the normal range for Cl bonded to six-coordinate Sn^{IV} .

The ethoxide ligand lies across one face of the triangle, which directs the CH_3 group towards the axial Cl(11) on Sn(1). This appears to cause a bending of the core about the O(12)—O(13) vector to give a dihedral angle between the planes defined by O(12)Sn(1)O(13) and by O(12)Sn(2)Sn(3)O(13) of $13.7 (1)^\circ$, while the ethoxide is bent away from the triangular face so that the C(1)—O(231) vector is displaced $16.4 (3)^\circ$ from the Sn(2)O(231)Sn(3) plane.

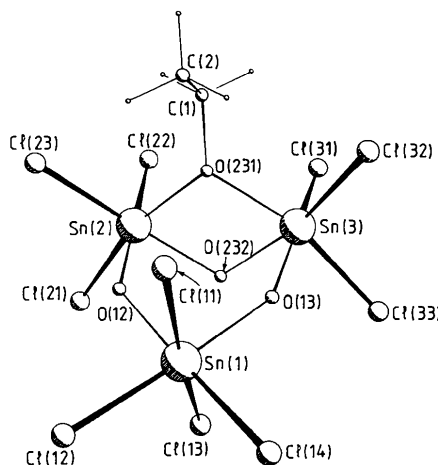


Fig. 1. The structure of the $[\text{Sn}_3\text{Cl}_{10}(\text{OH})_3(\text{OEt})]^{2-}$ anion showing atom labelling; H atoms on the bridging hydroxy groups are not shown.

Table 1. Final positional and equivalent isotropic thermal parameters for [Et₄N]₂[Sn₃Cl₁₀(OH)₃(OEt)]

Atoms marked ' or '' have site occupancies of 0.72 or 0.28 respectively.

	x	y	z	U _{eq} * (Å ²)
Sn(1)	0.41401 (3)	0.39536 (2)	0.22037 (3)	0.023
Sn(2)	0.22816 (3)	0.55442 (2)	0.16650 (2)	0.020
Sn(3)	0.15081 (4)	0.44999 (2)	0.32554 (3)	0.023
Cl(11)	0.3242 (1)	0.3193 (1)	0.1179 (1)	0.032
Cl(12)	0.5588 (1)	0.4068 (1)	0.1318 (1)	0.034
Cl(13)	0.4799 (1)	0.4795 (1)	0.3268 (1)	0.036
Cl(14)	0.4866 (1)	0.3020 (1)	0.3056 (1)	0.040
Cl(21)	0.3583 (1)	0.6403 (1)	0.1771 (1)	0.030
Cl(22)	0.0897 (1)	0.6347 (1)	0.1786 (1)	0.029
Cl(23)	0.2057 (1)	0.5499 (1)	0.0100 (1)	0.031
Cl(31)	0.0165 (1)	0.5234 (1)	0.3657 (1)	0.038
Cl(32)	0.0445 (1)	0.3506 (1)	0.3098 (1)	0.040
Cl(33)	0.2201 (2)	0.4341 (1)	0.4723 (1)	0.044
N(2)	0.2614 (4)	0.1252 (3)	0.3080 (4)	0.028
C(211)	0.3772 (5)	0.1143 (4)	0.3333 (5)	0.031
C(212)	0.4013 (6)	0.0821 (4)	0.4225 (5)	0.038
C(221)	0.2019 (6)	0.0579 (3)	0.3018 (5)	0.032
C(222)	0.2360 (6)	0.0087 (4)	0.2333 (5)	0.043
C(231)	0.2555 (6)	0.1629 (4)	0.2221 (5)	0.043
C(232)	0.1465 (6)	0.1832 (4)	0.1861 (5)	0.042
C(241)	0.2104 (6)	0.1669 (4)	0.3795 (5)	0.034
C(242)	0.2561 (7)	0.2367 (4)	0.3986 (6)	0.045
N(3)	0.2451 (5)	0.7077 (3)	0.4601 (4)	0.031
C(311)'	0.3514 (9)	0.7419 (6)	0.4832 (7)	0.042
C(311)''	0.339 (2)	0.665 (2)	0.416 (2)	0.042
C(312)	0.4421 (7)	0.7048 (6)	0.4367 (7)	0.070
C(321)'	0.2424 (9)	0.6337 (6)	0.4815 (7)	0.042
C(321)''	0.272 (2)	0.707 (2)	0.565 (2)	0.042
C(322)	0.2663 (9)	0.6226 (6)	0.5878 (7)	0.073
C(331)'	0.1667 (9)	0.7491 (6)	0.5115 (7)	0.042
C(331)''	0.152 (2)	0.663 (2)	0.438 (2)	0.042
C(332)	0.0517 (7)	0.7190 (7)	0.4913 (7)	0.078
C(341)'	0.2138 (9)	0.7118 (6)	0.3603 (7)	0.042
C(341)''	0.240 (2)	0.780 (2)	0.438 (2)	0.042
C(342)	0.2097 (8)	0.7851 (5)	0.3268 (6)	0.063
O(231)	0.1275 (3)	0.4741 (2)	0.1910 (3)	0.021
O(232)	0.2486 (4)	0.5337 (2)	0.3004 (3)	0.024
O(12)	0.3421 (3)	0.4781 (2)	0.1514 (3)	0.025
O(13)	0.2804 (4)	0.3906 (2)	0.2924 (3)	0.034
C(1)	0.0346 (5)	0.4565 (4)	0.1343 (5)	0.029
C(2)	0.0559 (6)	0.3968 (4)	0.0774 (5)	0.042

* The equivalent isotropic temperature factor U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The anion can be regarded as a derivative of the commonly observed dimeric compounds [Cl₆Sn₂(OR)₂L₂] in which L₂ is Cl₄Sn(OH)₂²⁻. The Sn(2)Sn(3) end of the anion has similar geometry to that observed in simpler dimers such as [SnCl₂Br(OH)(thf)]₂·2thf (Tudela *et al.*, 1986), [SnCl₃(OH)(OH₂)₂] (Barnes, Sampson & Weakley, 1980) and [SnCl₃(OEt)(HOEt)]₂ (Webster & Collins, 1974), while the Sn(1) fragment obviously relates structurally to *cis*-SnCl₄(OH₂)₂ (Cusack, Patel, Smith, Allen & Nowell, 1984; Valle, Cassol & Russo, 1984). The combination of the two units imposes wide Sn—O—Sn angles at the three-coordinated O(12) and O(13) atoms [140.4 (2) and 141.6 (2)° respectively], compared with corresponding angles of *ca* 106° in the four-membered Sn₂O₂ subunit. A six-membered (—Sn—O—)₃ ring related to that in the [Sn₃Cl₁₀(OH)₃(OEt)]²⁻ anion has recently been found as part of the complicated structure of [PhSn(O)—O₂CC₆H₁₁]₆ (Chandrasekhar, Day & Holmes, 1985).

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Table 2. Selected bond lengths (Å) and angles (°)

Sn(1)—Cl(11)	2.389 (2)	Sn(1)—Cl(12)	2.370 (2)
Sn(1)—Cl(13)	2.414 (2)	Sn(1)—Cl(14)	2.383 (2)
Sn(1)—O(12)	2.099 (4)	Sn(1)—O(13)	2.090 (5)
Sn(2)—Cl(21)	2.355 (2)	Sn(2)—Cl(22)	2.376 (2)
Sn(2)—Cl(23)	2.382 (2)	Sn(2)—O(12)	2.101 (4)
Sn(2)—O(231)	2.071 (4)	Sn(2)—O(232)	2.077 (4)
Sn(3)—Cl(31)	2.344 (2)	Sn(3)—Cl(32)	2.364 (2)
Sn(3)—Cl(33)	2.370 (2)	Sn(3)—O(13)	2.107 (5)
Sn(3)—O(231)	2.103 (4)	Sn(3)—O(232)	2.100 (4)
C(1)—O(231)	1.465 (7)	C(1)—C(2)	1.48 (1)
Sn(1)···Sn(2)	3.952 (1)	Sn(1)···Sn(3)	3.964 (1)
Sn(2)···Sn(3)	3.353 (1)		
Cl(11)—Sn(1)—Cl(12)	92.8 (1)	Cl(11)—Sn(1)—Cl(13)	171.6 (1)
Cl(11)—Sn(1)—Cl(14)	92.3 (1)	Cl(11)—Sn(1)—O(12)	88.2 (1)
Cl(11)—Sn(1)—O(13)	86.6 (1)	Cl(12)—Sn(1)—Cl(13)	93.7 (1)
Cl(12)—Sn(1)—Cl(14)	95.1 (1)	Cl(12)—Sn(1)—O(12)	88.7 (1)
Cl(12)—Sn(1)—O(13)	175.7 (1)	Cl(13)—Sn(1)—Cl(14)	92.4 (1)
Cl(13)—Sn(1)—O(12)	86.6 (1)	Cl(13)—Sn(1)—O(13)	86.6 (1)
Cl(14)—Sn(1)—O(12)	176.1 (1)	Cl(14)—Sn(1)—O(13)	89.2 (1)
O(12)—Sn(1)—O(13)	87.0 (2)	Sn(1)—O(13)—Sn(3)	141.7 (2)
Cl(21)—Sn(2)—Cl(22)	93.4 (1)	Cl(21)—Sn(2)—Cl(23)	97.8 (1)
Cl(21)—Sn(2)—O(231)	165.0 (1)	Cl(21)—Sn(2)—O(232)	91.4 (1)
Cl(21)—Sn(2)—O(12)	90.7 (1)	Cl(22)—Sn(2)—Cl(23)	93.3 (1)
Cl(22)—Sn(2)—O(231)	90.2 (1)	Cl(22)—Sn(2)—O(232)	95.7 (1)
Cl(22)—Sn(2)—O(12)	175.6 (1)	Cl(23)—Sn(2)—O(231)	96.6 (1)
Cl(23)—Sn(2)—O(232)	166.8 (1)	Cl(23)—Sn(2)—O(12)	84.6 (1)
O(12)—Sn(2)—O(232)	86.3 (2)	O(12)—Sn(2)—O(232)	85.7 (2)
O(231)—Sn(2)—O(232)	73.7 (2)	Sn(2)—O(232)—Sn(3)	106.7 (2)
Cl(31)—Sn(3)—Cl(32)	95.5 (1)	Cl(31)—Sn(3)—Cl(33)	94.0 (1)
Cl(31)—Sn(3)—O(231)	93.2 (1)	Cl(31)—Sn(3)—O(232)	91.9 (1)
Cl(31)—Sn(3)—O(13)	175.2 (1)	Cl(32)—Sn(3)—Cl(33)	99.8 (1)
Cl(32)—Sn(3)—O(231)	92.1 (1)	Cl(32)—Sn(3)—O(232)	163.4 (1)
Cl(32)—Sn(3)—O(13)	89.3 (1)	Cl(33)—Sn(3)—O(231)	165.5 (1)
Cl(33)—Sn(3)—O(232)	94.5 (1)	Cl(33)—Sn(3)—O(13)	84.3 (1)
O(13)—Sn(3)—O(231)	87.5 (2)	O(13)—Sn(3)—O(232)	83.8 (2)
O(231)—Sn(3)—O(232)	72.6 (2)	Sn(1)—O(12)—Sn(2)	140.3 (2)
Sn(3)—O(231)—C(1)	125.5 (4)	O(231)—C(1)—C(2)	110.8 (6)
O(12)Sn(1)O(13)/O(12)Sn(2)Sn(3)O(13)			13.7 (1)
C(1)—O(231)/Sn(2)O(231)Sn(3)			16.4 (3)

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