Crystal Structures of Di-μ-hydroxo-bis[aquatrichlorotin(IV)]–1,4-Dioxan (1/3), Di-μ-hydroxo-bis[aquatrichlorotin(IV)]–1,8-Epoxy-*p*-menthane (1/4), Di-μ-hydroxo-bis[aquatribromotin(IV)]–1,8-Epoxy-*p*-menthane (1/4), Di-μ-hydroxo-bis[aquatrichlorotin(IV)]–Water (1/4), and *cis*-Diaquatetrachlorotin(IV)–Water(1/3)

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The structures of five tin(IV) complexes have been determined from film data (Cu radiation). In compounds (1)—(4), $[Sn_2X_6(OH)_2(OH_2)_2].nL$, Lewis-base molecules L are hydrogen-bonded to a hydroxo-bridged dimer which is based on *fac*-octahedral co-ordination. In (1) ($X = Cl$, $nL = 3C_4H_8O_2$) all H atoms of the dimer participate in bonds to 1,4-dioxan, and each dioxan O atom participates in one hydrogen bond. A layer structure results. In (2) ($X = Cl$, $nL = 4C_{10}H_{18}O$) and (3) ($X = Br$, $nL = 4C_{10}H_{18}O$) each ligand of the dimer participates in one hydrogen bond to an oxygen atom of the bulky cyclic ether 1,8-cineole; there is no extended structure. In (4) ($X = Cl$, $nL = 4H_2O$) hydrogen bonding to lattice water links the dimers into chains, which are cross-linked by weak Cl . . . H_2O bonds. In (5), tin tetrachloride pentahydrate, $[SnCl_4(OH_2)_2].3H_2O$, the *cis*-octahedral complexes are also linked into a three-dimensional net *via* H_2O . . . H_2O and Cl . . . H_2O bonds. Crystals of (1) are triclinic, space group *P*1, with $a = 9.033$, $b = 10.455$, $c = 8.942$ Å, $\alpha = 115.34$, $\beta = 115.00$, $\gamma = 91.65°$, $Z = 1$, and $R = 0.071$ for 1 757 reflections; (2): monoclinic, space group $P2_1/c$, with $a = 12.82$, $b = 12.62$, $c = 15.70$ Å, $\beta = 92.4°$, $Z = 2$, and $R = 0.071$ for 1 741 reflections; (3): monoclinic, space group $C2/c$, with $a = 18.73$, $b = 19.67$, $c = 14.37$ Å, $\beta = 81.2°$, $Z = 4$, and $R = 0.083$ for 1 638 reflections; (4): monoclinic, space group $P2_1/n$, with $a = 9.688$, $b = 6.517$, $c = 12.563$ Å, $\beta = 92.97°$, $Z = 2$, and $R = 0.084$ for 892 reflections; (5): monoclinic, space group $C2/c$, with $a = 12.379$, $b = 10.086$, $c = 8.701$ Å, $\beta = 104.13°$, $Z = 4$, and $R = 0.107$ for 757 reflections.

THE present work stems from our earlier studies [1,2] of adducts of the cyclic ether 1,4-dioxan (diox) with hydrated or anhydrous metal salts. We have found that if hot diox is saturated with $SnCl_2{\cdot}2H_2O$ from a sample which has been stored for several weeks after the seal has been broken and which is therefore partly oxidised, then the filtered and cooled solution deposits $SnCl_2{\cdot}$diox and also a tin(IV) compound, (1). We characterised both compounds by *X*-ray structural analysis; our results for $SnCl_2{\cdot}$diox agree with those already published by another group [3] and will not be discussed. Compound (1) proves to be $[Sn_2Cl_6(OH)_2(OH_2)_2]{\cdot}3$diox. It was previously reported by Bokii and Struchkov,[4] who obtained it as the product of the attempted recrystallization of $SnCl_2{\cdot}$diox from dioxan and determined its structure to the rather high residual *R* 0.17. We here give our more accurate results based on a larger data set. We have also prepared analogous adducts of the cyclic ether 1,8-cineole (cin, 1,8-epoxy-*p*-menthane), $[Sn_2X_6(OH)_2(OH_2)_2]{\cdot}4$ cin (2; $X = Cl$ and 3; $X = Br$) from aged samples of $SnX_2{\cdot}2H_2O$ and determined their structures. The dimeric chloro-complex in (1) and (2) is also present in (4), $[Sn_2Cl_6(OH)_2(OH_2)_2]{\cdot}4H_2O$, of which we found one crystal in a sample of $SnCl_4{\cdot}5H_2O$, (5). The structures of (4) and (5) are also discussed below.

RESULTS AND DISCUSSION

Atomic co-ordinates are given in Tables 1—5, and bond lengths and interbond angles in Tables 6—9. The centrosymmetric dimeric complexes $[Sn_2X_6(OH)_2(OH_2)_2]$ ($X = Cl$ or Br) in compounds (1)—(4) (Figures 1, 2, and 4) contain *fac*-octahedral $SnX_3(OH)_2(OH_2)$ units with the OH^- ligands in common. The solvolysis of a simple tin(IV) compound sometimes affords a dimer $[Sn_2X_6(OR)_2(HOR)_2]$ of this type; examples are $[Sn_2Cl_6(OMe)_2(HOMe)_2]$, (6),[5] $[Sn_2Cl_6(OEt)_2(HOEt)_2]$, (7),[6] and $[Sn_2Et_2Cl_4(OH)_2(OH_2)_2]$, (8).[7] Compound (4) also seems to be a product of hydrolysis, but in the cases of (1)—(3) the dimers result from the oxidation of tin(II). We have noted that the reaction of diox with *aged* $SnCl_2{\cdot}2H_2O$ affords $SnCl_2{\cdot}$diox and (1) in similar amounts whereas if a *fresh* sample of $SnCl_2{\cdot}2H_2O$ is used (even without great care to exclude O_2) the major product is $SnCl_2{\cdot}$diox with only small amounts of (1). This suggests that the dimers may be present in aged samples of $SnCl_2{\cdot}2H_2O$, although we have no direct evidence of this. The lengths of the bridging and terminal Sn–O bonds in (1)—(4), and of the Sn–Cl bonds in (1), (2), and (4), are similar to those in (6), (7), and (8), in which the OR^-

TABLE 1

Atomic co-ordinates ($\times 10^4$) for (1), $[Sn_2Cl_6(OH)_2(OH_2)_2]{\cdot}3C_4H_8O_2$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sn	1 139(2)	−1 230(1)	103(1)
Cl(1)	3 732(6)	469(6)	1 506(8)
Cl(2)	1 523(7)	−3 044(5)	−2 314(6)
Cl(3)	2 207(7)	−2 091(5)	2 317(6)
O(1)	−198(15)	−311(12)	−1 555(13)
O(2)	−1 221(16)	−2 684(13)	−1 046(16)
O(3)	1 906(19)	1 848(15)	5 487(17)
O(4)	2 900(20)	3 057(16)	9 383(17)
O(5)	3 404(16)	4 268(15)	4 603(18)
C(1)	4 926(27)	3 947(24)	5 583(28)
C(2)	6 627(28)	4 195(22)	4 966(28)
C(3)	2 612(36)	1 068(25)	6 513(28)
C(4)	3 810(42)	2 168(34)	8 616(34)
C(5)	2 286(37)	3 912(25)	8 420(29)
C(6)	1 080(35)	2 847(28)	6 407(30)

Table 2

Atomic co-ordinates (× 10^4) for (2), $[Sn_2Cl_6(OH)_2(OH_2)_2]\cdot 4C_{10}H_{18}O$

Atom	*x*	*y*	*z*
Sn(1)	1 021(1)	550(1)	9 559(1)
Cl(1)	166(4)	444(5)	8 205(3)
Cl(2)	1 494(5)	2 336(5)	9 547(4)
Cl(3)	2 568(4)	−160(5)	9 093(4)
O(1)	−376(8)	855(10)	89(7)
O(2)	1 671(10)	469(13)	809(9)
O(10)	8 560(10)	2 733(11)	9 915(8)
O(20)	3 141(10)	1 558(11)	1 499(8)
C(1)	8 346(18)	3 359(21)	677(15)
C(2)	7 189(20)	3 346(22)	755(16)
C(3)	6 576(25)	3 743(28)	9 999(20)
C(4)	7 371(21)	4 094(22)	9 361(17)
C(5)	8 051(22)	5 012(24)	9 771(18)
C(6)	8 737(27)	4 519(35)	555(23)
C(7)	8 960(19)	2 857(22)	1 380(16)
C(8)	8 077(16)	3 134(20)	9 147(13)
C(9)	8 950(20)	3 428(22)	8 575(16)
C(10)	7 444(22)	2 210(24)	8 743(17)
C(11)	2 936(23)	2 236(25)	2 229(18)
C(12)	3 383(26)	1 605(28)	2 996(20)
C(13)	4 597(29)	1 514(30)	2 907(23)
C(14)	4 925(25)	1 830(28)	2 061(21)
C(15)	4 772(41)	2 972(44)	2 100(29)
C(16)	3 642(33)	3 326(35)	2 072(24)
C(17)	1 755(26)	2 353(29)	2 198(20)
C(18)	4 212(19)	1 386(22)	1 732(16)
C(19)	4 347(28)	124(31)	1 268(23)
C(20)	4 420(25)	1 776(25)	499(21)

groups are bridging. In crystals of these last three compounds the complexes are in van der Waals contact and no other species are present. In (1)—(4), however, the OH^- and H_2O ligands are linked through hydrogen bonds to other species, either a cyclic ether, 1,4-dioxan [(1)], 1,8-cineole [(2) and (3)], or water [(4)].

In (1) (Figure 1) each dioxan-oxygen atom acts as a hydrogen acceptor in just one hydrogen bond. The bridging oxygen atoms of the dimer participate in one hydrogen bond apiece [O(1) ··· O(3), 2.786(15) Å], in agreement with their assignment as OH^-, while each of the terminal (water) oxygens participates in two hydrogen bonds [O(2) ··· O(4), 2.652(16) and O(2) ··· O(5), 2.598(15) Å]. There are two independent dioxan molecules (Table 7) with the usual chair conformation; one serves to link the dimers into chains along the *c* axis, while the other (on a centre of symmetry) cross-links the chains into layers along the ($\bar{1}10$) planes. This description of the structure agrees with that given by Bokii and Struchkov.[4] However, we differ from them on points of detail, particularly with regard to hydrogen-bond and Sn–Cl bond lengths; we find the latter are closer to one another and to the bond lengths in (2) and (4) (see Table 6; 2.35—2.37 Å compared with 2.29—2.41 Å in ref. 4).

Table 3

Atomic co-ordinates (× 10^4) for (3), $[Sn_2Br_6(OH)_2(OH_2)_2]\cdot 4C_{10}H_{18}O$

Atom	*x*	*y*	*z*
Sn(1)	1 924(1)	2 087(1)	5 812(1)
Br(2)	884(1)	2 555(2)	6 856(2)
Br(1)	2 822(1)	2 109(2)	6 979(2)
Br(3)	1 670(2)	847(1)	6 019(2)
O(1)	2 285(7)	3 035(6)	5 308(10)
O(2)	1 268(8)	2 088(8)	4 702(11)
O(10)	1 908(8)	4 232(7)	6 150(12)
O(20)	−134(9)	1 995(8)	4 690(12)
C(1)	1 394(12)	4 687(12)	5 806(18)
C(2)	829(16)	4 817(16)	6 516(22)
C(3)	1 079(19)	5 124(21)	7 383(27)
C(4)	1 902(17)	5 196(15)	7 218(23)
C(5)	2 082(21)	5 661(18)	6 317(26)
C(6)	1 835(14)	5 306(13)	5 484(19)
C(7)	1 190(22)	4 345(20)	4 945(30)
C(8)	2 210(15)	4 452(14)	6 949(21)
C(9)	1 972(21)	4 018(20)	7 752(25)
C(10)	2 980(17)	4 511(20)	6 662(25)
C(11)	−593(15)	2 547(14)	4 453(21)
C(12)	−1 217(26)	2 625(24)	5 356(32)
C(13)	−1 591(25)	1 996(25)	5 511(32)
C(14)	−1 328(19)	1 461(17)	4 707(26)
C(15)	−1 358(27)	1 745(30)	3 823(39)
C(16)	−850(25)	2 346(26)	3 639(35)
C(17)	−135(21)	3 169(22)	4 323(32)
C(18)	−518(15)	1 359(14)	4 810(20)
C(19)	−108(23)	863(22)	4 146(33)
C(20)	−378(25)	1 108(26)	5 876(31)

Table 4

Atomic co-ordinates (× 10^4) for (4), $[Sn_2Cl_6(OH)_2(OH_2)_2]\cdot 4H_2O$

Atom	*x*	*y*	*z*
Sn	1 720(1)	365(2)	−13(1)
Cl(1)	2 135(5)	−991(8)	1 733(4)
Cl(2)	2 882(5)	3 524(7)	344(4)
Cl(3)	3 459(5)	−1 551(7)	−766(5)
O(1)	−138(13)	1 730(17)	342(10)
O(2)	1 342(13)	1 508(21)	−1 613(10)
O(3)	−73(20)	4 864(20)	1 833(13)
O(4)	−466(18)	1 235(25)	3 077(12)

Table 5

Atomic co-ordinates (× 10^4) for (5), $[SnCl_4(OH_2)_2]\cdot 3H_2O$

Atom	*x*	*y*	*z*
Sn		2 596(2)	2 500
Cl(1)	1 363(4)	2 795(5)	967(6)
Cl(2)	1 116(4)	1 049(5)	4 272(6)
O(1)	798(11)	4 211(13)	3 822(16)
O(2)	1 422(13)	3 860(15)	7 052(19)
O(3)		1 850(28)	7 500

Table 6

Bond lengths (Å) and bond angles (°) in tin(IV) dimers $[Sn_2X_6(OH)_2(OH_2)_2]$ with estimated standard deviations in parentheses

	(1) (X = Cl)	(2) (X = Cl)	(4) (X = Cl)	(3) (X = Br)
Sn–X(1)	2.363(6)	2.354(5)	2.379(4)	2.552(3)
Sn–X(2)	2.356(4)	2.335(6)	2.378(4)	2.448(3)
Sn–X(3)	2.371(4)	2.322(5)	2.336(6)	2.496(3)
Sn–O(1)	2.086(11)	2.044(10)	2.077(14)	2.076(12)
Sn–O(1′)	2.056(10)	2.042(10)	2.078(14)	2.028(12)
Sn–O(2)	2.130(12)	2.103(14)	2.158(11)	2.156(16)
Sn ··· Sn	3.358(2)	3.318(3)	3.368(2)	3.346(3)
X(1)–Sn–X(2)	95.6(2)	99.1(2)	95.3(2)	97.7(1)
X(1)–Sn–X(3)	93.5(2)	93.7(2)	94.8(2)	93.8(1)
X(2)–Sn–X(3)	98.4(2)	98.3(2)	101.2(2)	99.9(1)
X(1)–Sn–O(1)	93.1(4)	89.7(3)	93.9(3)	90.1(4)
X(1)–Sn–O(1′)	93.0(4)	91.0(?)	91.7(3)	90.5(?)
X(1)–Sn–O(2)	177.0(4)	172.5(5)	178.4(4)	173.5(4)
X(2)–Sn–O(1)	93.6(3)	93.1(4)	89.8(3)	93.6(3)
X(2)–Sn–O(1′)	163.4(3)	161.5(4)	160.6(4)	160.4(4)
X(2)–Sn–O(2)	87.4(3)	87.8(5)	86.1(4)	87.9(4)
X(3)–Sn–O(1)	165.7(3)	167.4(4)	165.3(3)	165.3(4)
X(3)–Sn–O(1′)	95.3(3)	96.4(?)	97.0(3)	94.9(?)
X(3)–Sn–O(2)	85.9(3)	88.094	84.2(4)	88.5(4)
O(1)–Sn–O(1′)	71.7(5)	71.4(5)	71.7(1.0)	71.7(6)
O(1)–Sn–O(2)	86.9(5)	87.0(5)	86.9(5)	87.2(6)
O(1′)–Sn–O(2)	84.2(5)	81.6(5)	87.3(3)	80.7(4)
Sn–O(1)–Sn′	108.3(5)	108.6(8)	108.3(1.0)	108.3(8)

Primed and unprimed atoms are related by a centre of symmetry.

Several 1,8-cineole adducts of metal halides are known, including $TiCl_4$·2cin,[8] $SnCl_4$·2cin,[8] $SnBr_4$·2cin,[8] and $FeCl_3$·2cin,[9] in which cin probably acts as a ligand, but no structures have been published. Two partly hydrolysed compounds reported[10] as $[Hcin]_2[SnX_3(OH)_3]$ (X = Cl or Br) are probably identical with (2) and (3). In these, the cyclic ether is monofunctional and an extended hydrogen-bond network is not possible (Figure 2).

TABLE 7

Bond lengths (Å) and bond angles (°) for 1,4-dioxan in (1), $[Sn_2Cl_6(OH)_2(OH_2)_2]\cdot 3C_4H_8O_2$

O(3)–C(3)	1.45(2)	C(3)–O(3)–C(6)	108.2(1.6)
O(3)–C(6)	1.47(2)	C(4)–O(4)–C(5)	109.1(1.6)
O(4)–C(4)	1.41(3)	C(1)–O(5)–C(2′)	109.4(1.7)
O(4)–C(5)	1.46(3)	C(2)–C(1)–O(5)	110.0(1.5)
O(5)–C(1)	1.43(2)	C(1)–C(2)–O(5′)	109.5(1.6)
O(5′)–C(1)	1.47(2)	C(4)–C(3)–O(3)	109.9(1.8)
C(1)–C(2)	1.55(3)	C(3)–C(4)–O(4)	109.4(2.2)
C(3)–C(4)	1.55(3)	C(6)–C(5)–O(4)	106.8(1.9)
C(5)–C(6)	1.49(3)	C(5)–C(6)–O(3)	111.8(2.0)

A prime denotes an atom at (1 − x, 1 − y, 1 − z).

TABLE 8

Bond lengths (Å) and selected bond angles (°) for 1,8-epoxy-*p*-menthane (1,8-cineole) molecules in (2) and (3)

	Molecule A		Molecule B	
	(2)	(3)	(2)	(3)
C(1)–C(2)	1.49(3)	1.38(4)	1.62(4)	1.62(4)
C(2)–C(3)	1.48(4)	1.52(4)	1.63(5)	1.42(5)
C(3)–C(4)	1.53(4)	1.53(4)	1.47(3)	1.59(5)
C(4)–C(5)	1.57(4)	1.58(4)	1.52(4)	1.40(4)
C(5)–C(6)	1.61(4)	1.52(4)	1.42(3)	1.51(4)
C(6)–C(1)	1.56(5)	1.51(3)	1.77(5)	1.39(4)
C(1)–C(7)	1.47(3)	1.51(4)	1.46(3)	1.49(4)
C(1)–O(10)	1.47(3)	1.46(3)	1.39(3)	1.46(3)
C(4)–C(8)	1.56(3)	1.60(4)	1.46(3)	1.56(4)
C(8)–O(10)	1.43(2)	1.42(5)	1.43(4)	1.44(3)
C(8)–C(9)	1.51(3)	1.45(4)	1.58(4)	1.49(5)
C(8)–C(10)	1.54(3)	1.44(4)	1.52(4)	1.67(5)
C(1)–O(10)–C(8)	114.1(1.7)	116.9(1.8)	115.0(2.0)	114.7(2.0)
O(10)–C(1)–C(2)	106.3(1.9)	109.7(2.3)	104.3(1.3)	106.3(1.9)
O(10)–C(1)–C(6)	109.4(2.1)	103.9(1.8)	106.6(1.3)	108.4(1.9)
O(10)–C(1)–C(7)	105.5(2.0)	105.6(2.1)	107.7(1.5)	103.1(1.8)
O(10)–C(8)–C(4)	109.3(1.8)	107.4(2.3)	114.5(1.5)	107.9(2.1)
C(8)–C(4)–C(5)	110.2(2.1)	107.9(2.5)	107.2(1.7)	107.3(1.6)
C(8)–C(4)–C(3)	109.0(2.3)	105.7(2.7)	111.3(1.6)	106.0(1.8)

Molecule A has atoms C(n); molecule B has atoms C(10 + n).

Crystals of both compounds contain two independent cineole molecules. Although the space groups differ, the asymmetric units are very similar. We have four independent determinations of the structure of 1,8-cineole in the presence of the heavy tin and halogen atoms. These reveal no surprises. All bond lengths and angles are typical (Table 8). The presence of the shorter C–O bonds among the rigid framework of C–C bonds causes the angle at oxygen to be significantly larger than the tetrahedral angle (mean 115.2°). The numbering scheme for all the cineole molecules is shown in the diagram. Cineole A is hydrogen-bonded to the oxygen atom of the μ-OH ligand, O(1) [O · · · O: 2.742(18) for (1); 2.691(20) Å for (2)]. The ether-oxygen atom, O(10), lies 0.61 Å [for (2)] and 0.22 Å [for (3)] from the Sn, Sn′, O(1), O(1′) plane. The normal to this plane makes an

TABLE 9

Bond lengths (Å) and bond angles (°) for (5), $[SnCl_4(OH_2)_2]\cdot 3H_2O$

Sn–Cl(1)	2.401(4)	Sn–Cl(2)	2.383(5)
Sn–O(1)	2.098(14)		
Cl(1)–Sn–Cl(2)	92.3(3)	Cl(1)–Sn–O(1)	86.5(3)
Cl(1)–Sn–Cl(1′)	170.4(4)	Cl(2)–Sn–O(1)	91.9(4)
Cl(1)–Sn–Cl(2′)	94.0(3)	Cl(1)–Sn–O(1′)	86.0(4)
Cl(2)–Sn–Cl(2′)	98.2(3)	Cl(2)–Sn–O(1′)	169.7(6)
O(1)–Sn–O(1′)	78.1(8)		

A prime denotes an atom at (−x, y, $\frac{1}{2}$ − z).

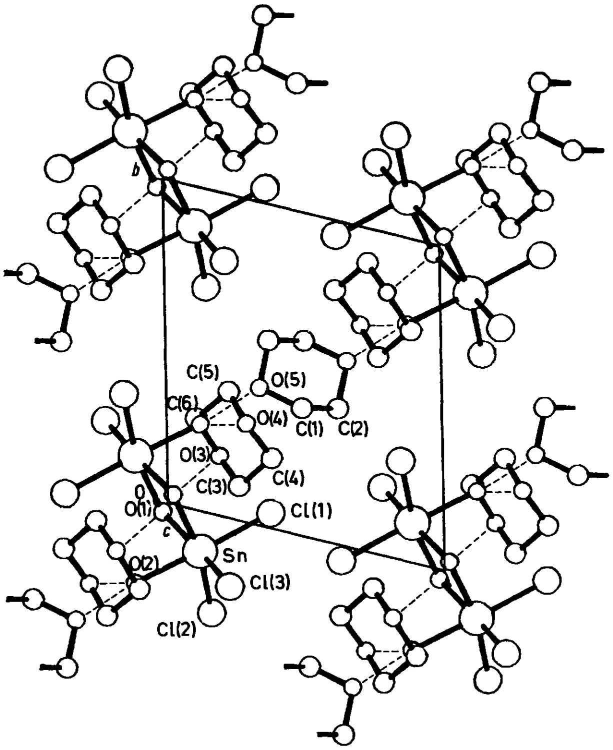


FIGURE 1 Unit cell of (1), $[Sn_2Cl_6(OH)_2(OH_2)_2]\cdot 3C_4H_8O_2$; c-axis projection

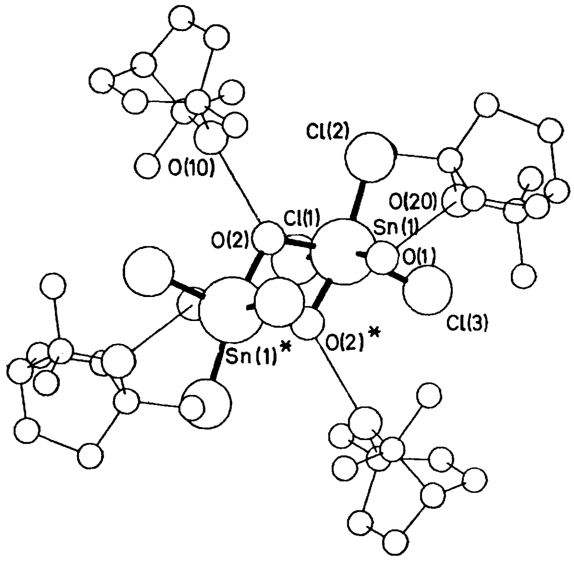
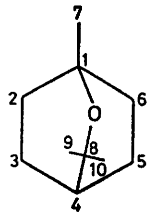


FIGURE 2 The centrosymmetric complex in (2), $[Sn_2Cl_6(OH)_2(OH_2)_2]\cdot 4C_{10}H_{18}O$. The complex in (3) is very similar

angle of 77.4° [for (2)] and 80.4° [for (3)] with the normal to the plane C(7), C(1), O(10), C(8), C(4). The vector O(1)–O(10) is close to both planes (Figure 3). Cineole B is hydrogen-bonded to the water ligand through O(2) [O ··· O: 2.539(18) for (1); 2.635(20) Å for (2)]. It is placed so that C(11), C(12), and C(16) are close to the plane X(2), Sn, O(2), X(1), O(1′) (X = Cl or Br). The torsion angle X(2)–Sn–O(20)–C(11) is −28.3° in (2) and −28.2° in (3). The torsion angle Sn–O(2)–O(20)–C(11) is 115.7° in (2) and 109.3° in (3). The hydrogen bond lies close to the plane C(17), C(11), O(20), C(18), C(14) (compare cineole A) and presumably uses the combined lone pairs of the ether-oxygen atom. The isotropic thermal parameters for the carbon and oxygen atoms show cineole molecules A and B pivoting about the hydrogen bonds, with large values of U for the carbon atoms remote from these bonds. In both (2) and (3) the thermal parameters for molecule A are smaller than those for molecule B. Molecule A occupies a more constrained site, with, in (3), six Br ··· H contacts in the range 3.05—3.20 Å (assuming calculated hydrogen positions) compared with two such contacts for molecule B.



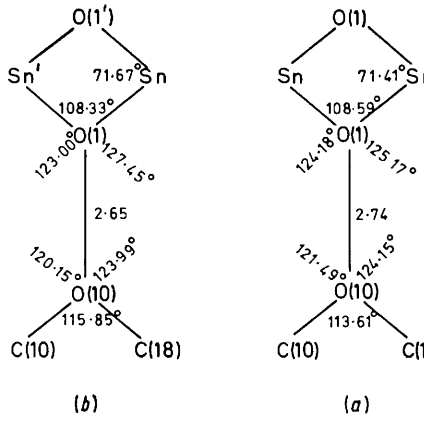


FIGURE 3 The hydrogen bond connecting cineole molecule A to the μ-hydroxo-group in (2) (*a*) and (3) (*b*)

In compound (4) (Figure 4) the dimers are hydrogen bonded to molecules of lattice water, O(3) and O(4). Chains ensue along the b axis. As in (1), the μ-OH ligands participate in one hydrogen bond apiece [from O(1)] and the water ligands, in two [from O(2)]. The hydrogen-bond lengths are: O(1) ··· O(3), 2.77(2); O(2) ··· O(3), 2.67(2); O(2) ··· O(4), 2.67(2); and O(3) ··· O(4), 2.87(2) Å. The lattice waters also apparently participate in long hydrogen bonds to ligand chlorine atoms [O(3) ··· Cl(1) and O(4) ··· Cl(2), both 3.34(2) Å]; as a result, the dimers are linked into a three-dimensional network.

Tin(IV) chloride pentahydrate, first reported in 1789,[11] proves to be $[SnCl_4(OH_2)_2]\cdot3H_2O$. The *cis*-octahedral complex lies on a crystal diad axis (Figure 5). A similar complex is believed to be present in $SnCl_4\cdot2H_2O\cdot2$diox from its isomorphism with the analogous bromo-compound of known structure.[1] The Sn–Cl bond lengths and the interbond angles lie within the ranges observed for other *cis*-$[SnCl_4L_2]$ complexes.[12] The mean Sn–Cl bond length (Table 9) is 2.392 Å; the hydrolysis of $[SnCl_4(OH_2)_2]$ to $[Sn_2Cl_6(OH)_2(OH_2)_2]$ reduces the mean Sn–Cl bond length to 2.355 Å (*cf.* Table 6). The mean Sn–Br bond lengths in $[SnBr_4(OH_2)_2]$ (2.532 Å)[1] and $[Sn_2Br_6(OH)_2(OH_2)_2]$ (3; 2.499 Å) are related similarly. In (5), each $[SnCl_4(OH_2)_2]$ complex is linked, through sequences of hydrogen bonds involving lattice water, to the units related to it by the c translation [O(1) ··· O(2), 2.75(2); O(2) ··· (3), 2.78(2) Å] and by a c glide operation

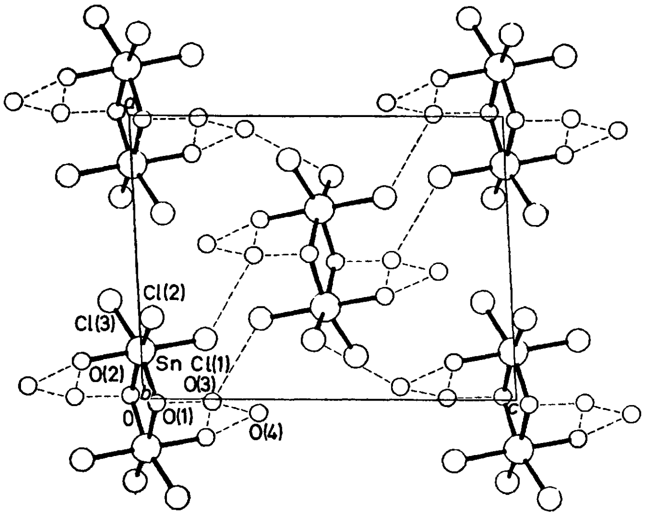


FIGURE 4 Unit cell of (4), $[Sn_2Cl_6(OH)_2(OH_2)_2]\cdot4H_2O$; b-axis projection

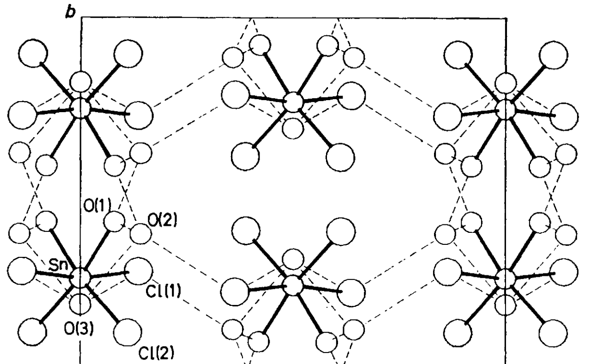


FIGURE 5 Unit cell of (5), $[SnCl_4(OH_2)_2]\cdot3H_2O$; c-axis projection

[O(1) ··· O(2), 2.71(2) Å]. Weak hydrogen bonds O(3) ··· Cl(1) [3.22(2) Å] and O(2) ··· Cl(1) [3.31(2) Å] reinforce the *c*-axis chains and link the complexes across the ($\frac{1}{4}$,$\frac{1}{4}$,0) inversion centres. A three-dimensional network results.

EXPERIMENTAL

A suspension of an aged commercial sample of $SnCl_2$·$2H_2O$ in 1,4-dioxan (90 °C) was stirred for 1 h and filtered. The filtrate deposited (1), *di-μ-hydroxo-bis*[*aquatrichlorotin*(IV)]–1,4-*dioxan* (1/3), as colourless plates (easily distinguished from prisms of $SnCl_2$·diox) during several days at 5 °C. *Di-μ-hydroxo-bis*[*aquatrichlorotin*(IV)]–1,8-*epoxy*-p-*menthane* (1/4), (2), and *di-μ-hydroxo-bis*[*aquatribromotin*(IV)]–1,8-*epoxy*-p-*menthane* (1/4), (3), were prepared similarly [(3), from $SnBr_2$·$2H_2O$]; crystals of these compounds were deposited in good yield at room temperature. A freshly opened commercial sample of $SnCl_4$·$5H_2O$ [cis-*diaquatetrachlorotin*(IV) *trihydrate*, (5)] was dissected under paraffin oil; most of the roughly equi-dimensional fragments so obtained were split or otherwise unsatisfactory but two fragments were eventually found from which an adequate set was obtained. During this procedure the unique crystal of *di-μ-hydroxo-bis*[*aquatrichlorotin*(IV)]–*water* (1/4), (4), was found. All crystals were at once sealed into thin-walled glass capillaries.

Crystal Data.—(1). $[Sn_2Cl_6(OH)_2(OH_2)_2]$·$3C_4H_8O_2$, $C_{12}H_{30}Cl_6O_{10}Sn_2$, $M = 784.2$, Triclinic, $a = 9.033(10)$, $b = 10.455(10)$, $c = 8.942(10)$ Å, $\alpha = 115.34(7)$, $\beta = 115.00(7)$, $\gamma = 91.65(7)°$, $U = 668.7$ Å^3, $D_c = 1.95$ g cm^{-3}, $Z = 1$, $F(000) = 384$, space group $P\bar{1}$; Cu-K_α radiation ($\lambda = 1.541\,8$ Å), μ(Cu-K_α) = 202 cm^{-1}.

(2). $[Sn_2Cl_6(OH)_2(OH_2)_2]$·$4C_{10}H_{18}O$, $C_{40}H_{78}Cl_6O_8Sn_2$, $M = 1\,136.1$, Monoclinic, $a = 12.82(2)$, $b = 12.62(2)$, $c = 15.70(1)$ Å, $\beta = 92.4(1)°$, $U = 2\,537.9$ Å^3, $D_c = 1.49$ g cm^{-3}, $Z = 2$, $F(000) = 1\,168$, space group $P2_1/c$; Cu-K_α radiation, μ(Cu-K_α) = 108 cm^{-1}.

(3). $[Sn_2Br_6(OH)_2(OH_2)_2]$·$4C_{10}H_{18}O$, $C_{40}H_{78}Br_6O_8Sn_2$, $M = 1\,402.9$, Monoclinic, $a = 18.73(2)$, $b = 19.67(2)$, $c = 14.37(2)$ Å, $\beta = 81.2(1)°$, $U = 5\,231.9$ Å^3, $D_c = 1.78$ g cm^{-3}, $Z = 4$, $F(000) = 2\,768$, space group $C2/c$; Cu-K_α radiation, μ(Cu-K_α) = 128 cm^{-1}.

(4). $[Sn_2Cl_6(OH)_2(OH_2)_2]$·$4H_2O$, $H_{14}Cl_6O_8Sn_2$, $M = 592.2$, Monoclinic, $a = 9.688(8)$, $b = 6.517(8)$, $c = 12.563(18)$ Å, $\beta = 92.97(16)°$, $U = 792.1$ Å^3, $D_c = 2.48$ g cm^{-3}, $Z = 2$, $F(000) = 560$, space group $P2_1/n$; Cu-K_α radiation; μ(Cu-K_α) = 337 cm^{-1}.

(5). $[SnCl_4(OH_2)_2]$·$3H_2O$, $H_{10}Cl_4O_5Sn$, $M = 350.6$, Monoclinic, $a = 12.379(12)$, $b = 10.086(10)$, $c = 8.701(9)$ Å, $\beta = 104.13(10)°$, $U = 1\,053.3$ Å^3, $D_c = 2.21$ g cm^{-3}, $Z = 4$, $F(000) = 672$, space group $C2/c$; Cu-K_α radiation; μ(Cu-K_α) = 278 cm^{-1}. Cell dimensions were measured from NaCl-calibrated Weissenberg photographs, and were refined following the microdensitometer scan. The crystal axes of (1) have been chosen to coincide with the axes defined by Bokii and Struchkov,[4] although there are some discrepancies (they reported $a = 8.85$, $b = 10.30$, $c = 8.95$ Å, $\alpha = 112.7$, $\beta = 111.6$, and $\gamma = 95.8°$).

Data Collection.—All intensity data were collected on film. Multi-film equi-inclination Weissenberg photographs were scanned by use of a microdensitometer (S.R.C. Service, Daresbury Laboratory). The reciprocal lattice levels recorded were: levels 0—5 about [111], 0—6 about [$\bar{1}$10], and *hk*0—5 for (1); levels 0—1 about [0$\bar{1}$1] and *h*0—10*l* for (2); levels 0—2 about [$\bar{1}$01] and *hk*0—11 for (3); levels 0—8*kl* and *hk*0—4 for (4). Compound (5) was originally thought to be triclinic, and levels 0—8 about [1$\bar{1}$2] and 0—2 about [0$\bar{1}$1] were recorded before the diad axis was revealed by tilting the second crystal; levels *h*0—3*l* were also recorded. The number of independent reflections above background were: 1 757 for (1); 1 741 for (2); 1 638 for (3); 892 for (4); and 757 for (5). For each compound, the data reduction was repeated with correction for absorption after the composition of the crystal had become apparent. The SHELX 76 program system [13] was used in all calculations.

Structure Determination and Refinement.—The tin atoms in (1), (4), and (5) were located from Patterson syntheses, and the SnX_3 (X = Cl or Br) groups in the asymmetric units of (2) and (3) were located by use of the TANG direct-methods routine incorporated in SHELX. The structures were expanded by Fourier syntheses and were refined by full-matrix least squares. Difference syntheses not surprisingly gave no clear indications of hydrogen-atom positions. The dioxan–hydrogen atoms of (1) and the cineole–hydrogen atoms of (3) were included at calculated positions in the last cycles of refinement, but otherwise the hydrogen atoms were ignored. Tin and halogen atoms were allowed to refine with anisotropic thermal parameters; the lighter atoms were allowed anisotropic parameters in the cases of (1) and (4) only. Refinement converged at the following conventional R values: 0.071 for (1) (136 parameters, unit weights); 0.071 for (2) (134 parameters, unit weights); 0.083 for (3) (160 parameters, unit weights); 0.084 for (4) [73 parameters, $w = 1/(1 + 0.017F^2)$, $R' = 0.084$]; 0.107 for (5) [34 parameters, $w = 1/(1 + 0.020F^2)$, $R' = 0.109$]. The final difference maps showed no anomalies; the strongest peaks were in each case close to the tin atom (up to 2 e Å^{-3}) The refinement of (1) and (5) in the alternative non-centrosymmetric space groups did not lower the residual significantly and moreover resulted in improbable discrepancies between chemically-equivalent bond lengths. Observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 22728 (44 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

[9/1150 *Received*, 20*th July*, 1979]

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