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Studies of Oxalamide and Dithiooxalamide Metal Complexes.
Part 5.* Synthesis and Crystal Structure Determinations of Tetrabromo(*N*,*N*′-di-tert-butyloxalamide-*OO*′)tin(IV)-tetrahydrofuran (1/1) and Tetrabromo(*N*,*N*′-dimethylsuccinamide-*OO*′)tin(IV)-tetrahydrofuran (1/1)

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Abstract

Structural characterisation of $SnBr_4L^1(thf)$ (**1**) where $L^1 = {}^tBuNH{\cdot}CO{\cdot}CO{\cdot}NHBu^t$ and thf = tetrahydrofuran, and $SnBr_4L^2(thf)$ (**2**) where $L^2 = MeNH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHMe$, by X-ray crystallographic methods shows *OO* bidentate chelate bonding for these mononuclear *cis*-octahedral Sn(IV) complexes. Crystals of **1** are orthorhombic, space group *Pcba* (No. 61) with $Z = 4$. R and R_w were 0.072 and 0.073 respectively for 1401 independent reflections above background.

The six coordinate tin atoms feature Sn–Br 2.524(3), 2.504(3) Å and SN–O 2.180(14) Å. The solvent thf molecule is symmetrically hydrogen bonded to both NH groups of L^1 with O···H–N 178°, O···N 2.85(3) Å. Crystals of **2** are triclinic, space group $P\bar{1}$ with $a = 11.53(1)$, $b = 8.12(1)$, $c = 10.55(1)$ Å and $\alpha = 89.1(1)$, $\beta = 95.1(1)$, $\gamma = 94.5(1)°$ with $Z = 2$. R and R_w were 0.085 and 0.086 respectively for 967 independent reflections above background.

Bond distances for the six coordinate tin atoms are Sn–Br 2.512(4), 2.520(5), 2.542(4), 2.518(4) Å and Sn–O 2.148(20), 2.124(18) Å. Two intermolecular hydrogen bonds are present linking one N–H group of L^2 to a solvent thf molecule O···H–N 176°, O···N 2.69 Å and the other, separately, to a bromine atom of an adjacent molecule Br···H–N 172°, Br···N 3.56 Å. A relative ligand binding order succinamide > oxalamide for Sn(IV) is indicated from a direct comparison of Sn–O bond lengths.

Introduction

Previous studies of oxalamide and dithiooxalamide complexes of Sb(III) have established that ligand binding is consistently ØØ (Ø = O or S) bidentate bridging across separate metal centres with retention of the planar *trans*-configuration which is a hallmark of these particular ligand types [1–3].

The resulting structures are polymeric and feature six-coordinate Sb(III) centres with weak Sb–S or Sb–O bonds. Ligand binding in the form of ØØ bidentate chelation to give discrete mononuclear species demands a change of ligand conformation *trans* → *cis* which, although not realised for Sb(III), has been confirmed for the dithiooxalamide (*SS*′) complexes of Sn(IV) and Bi(III) [4] *viz.*, six coordinate $[SnBr_4(Bu^nNH{\cdot}CS{\cdot}CS{\cdot}NHBu^n)]$ and seven coordinate $[BiCl_3(EtNH{\cdot}CS{\cdot}CS{\cdot}NHEt)_2]$. In both instances the ligands, now in the *cis*-configuration, show severely puckered structures with extensive intermolecular hydrogen bonding. This rather suggests that with a 'suitable' choice of metal ion of the appropriate size/orbitals ~ acceptor characteristics five-membered *cis*-chelate formation should also be feasible for oxalamides. Several examples have been tentatively proposed on the basis of IR spectroscopic evidence [5].

The object of this study has been to confirm such a bonding mode for oxalamides by X-ray data. The choice of metal acceptor was tin(IV) bromide. In addition we have determined the structure of an analogous Sn(IV)–succinamide complex in anticipation that with an increased flexibility and 'bite', as derived from the additional skeletonal $-(CH_2)_2-$ unit, the higher homologue ligand should be even more accommodating towards *OO*-chelate formation.

Experimental

All manipulations were carried out under an inert atmosphere of dry N_2 gas.

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*Part 4 is ref. 3.

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Preparation of the Complexes

$SnBr_4L^1$ (1) $L^1 = Bu^tNH{\cdot}CO{\cdot}CO{\cdot}NHBu^t$ and $SnBr_4L^2$ (2) $L^2 = MeNH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHMe$ were prepared by direct addition of a solution of the metal halide (1 mol) in the minimum volume of 1,2-dichloromethane to a solution of the corresponding amide ligand (1 mol) in the same solvent.

Typically for **1**. Dropwise addition of $SnBr_4$ (2.7 g, 6.2 mmol) in CH_2Cl_2 (20 cm^3) to a cooled, stirred solution of $Bu^tNH{\cdot}CO{\cdot}CO{\cdot}NHBu^t$ (1.0 g, 5.0 mmol) in CH_2Cl_2 (40 cm^3) under an N_2 atmosphere gave an immediate reaction with the formation of a cloudy white precipitate. After stirring the mixture (2 h) the solvent was removed and recrystallisation of the product from tetrahydrofuran gave colourless needles of **1** as the 1:1 solvate. (Yield 2.96 g, 79%). *Anal.* Found: C, 23.5; H, 4.0; N, 3.6; Br, 44.6. Calc. for $C_{14}H_{28}N_2O_3Br_4Sn$: C, 23.7; H, 4.0; N, 3.9; Br, 45.0%.

Similarly, recrystallisation from tetrahydrofuran gave colourless chunky crystals of **2** as the 1:1 solvate. *Anal.* Found: C, 18.0; H, 3.0; N, 4.6; Br, 48.4. Calc. for $C_{10}H_{20}N_2O_3Br_4Sn$: C, 18.4; H, 3.1; N, 4.3; Br, 48.8%.

Crystal Structure Determinations

The crystals were prepared as described above. Crystal data are given in Table I. The two crystals were set up in turn to rotate about the *a* axis on a Stoe Stadi-2 Diffractometer and data were collected via variable width *w* scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. An empirical absorption correction was applied to both structures but no extinction correction.

TABLE I. Crystal Data for Compounds 1 and 2

Compound	1 $SnBr_4L^1C_4H_8O$	2 $SnBr_4L^2C_4H_8O$
Formula	$SnBr_4O_3C_{14}H_{28}N_2$	$SnBr_4O_3C_{10}H_{20}N_2$
M	710.4	654.6
F(000)	1360	616
Z	4	2
Space group	*Pcba* (No. 61)	*P*1
a (Å)	11.37(1)	11.53(1)
b (Å)	13.55(1)	8.12(1)
c (Å)	18.61(1)	10.55(1)
α (°)	(90)	89.1(1)
β (°)	(90)	95.1(1)
γ (°)	(90)	94.5(1)
U ($Å^3$)	2867.8	980.9
D_m (g cm^{-3})	–	2.20
D_c (g cm^{-3})	1.65	2.21
μ (cm^{-1})	68.1	99.3
No. of data measured	2685	2263
No. used in refinement	1401	967
Criteria for used reflection	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Final *R*	0.072	0.085
R_w	0.073	0.086

Both structures were determined by direct methods which located the tin and bromine atom positions. Fourier methods were then used to locate the remaining positions. All non-hydrogen atoms, except for the solvent molecules in **2** were refined anisotropically. The hydrogen atoms were included in calculated positions and the structures were refined to convergence by full-matrix least squares.

Calculations were carried out using SHELX76 [6] and some of our own programs on the Amdahl V7A at the University of Reading. Atomic parameters for

TABLE II. Atomic Coordinates ($\times 10^4$) for 1 (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*
Sn	5000	3444(2)	2500
Br(1)	2855(2)	3579(3)	2163(2)
Br(2)	4549(3)	2334(2)	3540(2)
O(1)	4778(12)	4735(10)	3186(8)
C(2)	4910(18)	5569(15)	2904(10)
N(21)	4871(16)	6381(12)	3265(9)
C(22)	4752(30)	6475(17)	4076(11)
C(23)	5752(24)	5924(26)	4415(12)
C(24)	4695(43)	7530(23)	4206(17)
C(25)	3584(28)	6054(27)	4267(14)
O(50)	5000	1799(17)	7500
C(51)	6020(31)	1161(22)	7510(20)
C(52)	5603(29)	120(30)	7490(27)

TABLE III. Atomic Coordinates ($\times 10^4$) for 2 (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*
Sn	2141(2)	2448(2)	3209(2)
Br(1)	1201(4)	3286(5)	5135(4)
Br(2)	3020(4)	1127(5)	1411(4)
Br(3)	730(3)	3957(4)	1705(4)
Br(4)	3776(3)	4687(4)	3509(4)
O(1)	840(18)	403(27)	3177(21)
C(2)	896(28)	−1138(36)	2986(27)
C(3)	1840(36)	−2025(42)	3653(39)
C(4)	1992(35)	−1468(42)	5064(32)
C(5)	2918(29)	−154(37)	5268(32)
O(6)	3146(16)	877(24)	4415(22)
N(21)	3502(24)	−8(30)	6324(24)
C(22)	4400(30)	1272(44)	6651(32)
N(31)	172(25)	−1861(29)	2208(25)
C(32)	−821(29)	−1174(44)	1482(32)
O(50)	3059(30)	−2439(42)	8035(34)
C(51)	3475(69)	−1973(104)	9367(78)
C(52)	3384(81)	−3836(127)	10020(90)
C(53)	4389(111)	−4309(137)	8763(120)
C(54)	3172(98)	−4387(132)	7970(97)

TABLE IV. Dimensions in the Metal Coordination Spheres: Distances (Å), Angles (°)

In 1	
Sn–Br(1)	2.524(3)
Sn–Br(2)	2.504(3)
Sn–O(1)	2.180(14)
Br(1)–Sn–Br(2)	92.2(1)
Br(1)–Sn–O(1)	88.6(4)
Br(2)–Sn–O(1)	90.3(4)
Br(1)–Sn–Br(1^{a})	171.7(1)
Br(1)–Sn–Br(2^{a})	92.8(1)
Br(1)–Sn–O(1^{a})	84.7(4)
Br(2)–Sn–Br(2^{a})	106.2(1)
Br(2)–Sn–O(1)	90.3(4)
Br(2)–Sn–O(1^{a})	163.4(4)
O(1)–Sn–O(1^{a})	73.3(5)
In 2	
Sn–Br(1)	2.512(4)
Sn–Br(2)	2.520(5)
Sn–Br(3)	2.542(4)
Sn–Br(4)	2.518(4)
Sn–O(1)	2.148(20)
Sn–O(6)	2.124(18)
Br(1)–Sn–Br(2)	170.54(16)
Br(1)–Sn–Br(3)	92.49(16)
Br(2)–Sn–Br(3)	92.92(15)
Br(1)–Sn–Br(4)	93.22(15)
Br(2)–Sn–Br(4)	93.57(16)
Br(3)–Sn–Br(4)	99.18(14)
Br(1)–Sn–O(1)	83.9(6)
Br(2)–Sn–O(1)	88.6(6)
Br(3)–Sn–O(1)	87.7(5)
Br(4)–Sn–O(1)	172.6(5)
Br(1)–Sn–O(6)	88.1(6)
Br(2)–Sn–O(6)	85.4(6)
Br(3)–Sn–O(6)	171.6(5)
Br(4)–Sn–O(6)	89.2(5)
O(1)–Sn–O(6)	84.0(7)

^{a}Symmetry operation $1 - x, y, 0.5 - z$.

1 and 2 are given in Tables II and III respectively; dimensions of the coordination spheres are given in Table IV. See also 'Supplementary Material'.

Results and Discussion

The title compounds are readily obtained following addition (1:1 molar ratio) of tin(IV) bromide and the appropriate ligand in dichloromethane solution. Recrystallisation from tetrahydrofuran solutions provided crystals suitable for X-ray studies. Both are unstable to air moisture hydrolysis and must be handled under an inert atmosphere. Neither compound shows a clean melting point but each can be sublimed at temperatures in excess of 200 °C. The IR spectroscopic evidence is consistent with bonding through the O atoms [7] *i.e.*, low energy shifts for ν(C=O), 1 −20 cm^{-1}, 2 −11 cm^{-1} and high energy shifts for ν(C–N), 1 +19 cm^{-1}, 2 +25 cm^{-1}. The appearance of a complex band profile in the ν(NH) region, as distinct from the sharp doublet characteristic of uncomplexed ligand, suggests an appreciable involvement of NH sites in hydrogen bonding for both 1 and 2 (see structural discussion). Only one intense band attributable to ν(Sn–Br) is observed in the far IR region *viz.* 1 242 cm^{-1}, 2 251 cm^{-1}; the remainder – a *cis*-octahedral geometry requires four such bands – are expected below 200 cm^{-1} which is outside the range of the instrument used.

Discussion of the Crystal Structures

The two structures 1 and 2 are shown in Figs. 1 and 2 together with the respective atomic numbering scheme. Both molecules co-crystallise with 1 molecule of tetrahydrofuran (thf) and form strong hydrogen bonds of the form N–H···O.

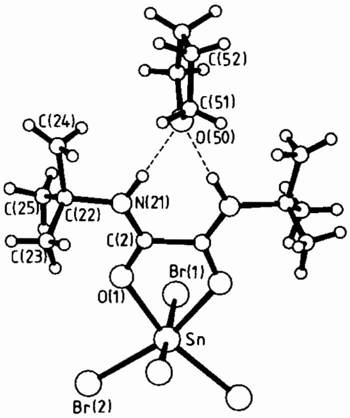

Fig. 1. The structure of $SnBr_4L^1 \cdot thf$ with hydrogen bonds shown as dotted lines.

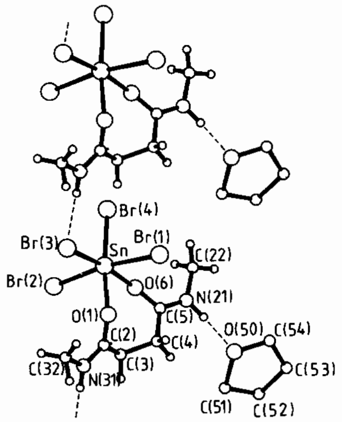

Fig. 2. The structure of $SnBr_4L^2 \cdot thf$ with hydrogen bonds shown as dotted lines.

In **1** both the $SnBr_4L^1$ and the solvent thf molecules have crystallographically imposed C_2 symmetry. The tin atom is six-coordinate with a distorted octahedral environment. Bond lengths are Sn–Br(1) 2.524(3), Sn–Br(2) 2.504(3), Sn–O(1) 2.180(14) Å. The largest distortion from octahedral geometry occurs in the O(1)–Sn–O(1*) angle at 73.3(5)°, a value caused by the constraints of the five-membered ring. The five-membered ring is planar within 0.035 Å. N(21) and C(22) are respectively 0.11 and 0.25 Å from the plane.

In **2** the $SnBr_4L^2$ molecule is in a general position in the unit cell. Again the tin atom is six-coordinate with a distorted octahedral environment. Bond lengths are Sn–Br 2.512(4), 2.520(5), 2.542(4), 2.518(4) and Sn–O(1) 2.148(20), Sn–O(6) 2.124(18) Å. Here the O(1)–Sn–O(6) chelating angle is 84.0(7)°, a full 10° greater than the value in **1** and indicative of the less constrained 7-membered ring compared to the 5-membered ring in **1**. The 7-membered ring is puckered with torsion angles of 47.3° for Sn–O(1)–C(2)–C(3), 43.3° for O(1)–C(2)–C(3)–C(4) and then successively −95.8, 31.3, 51.3, −37.1° respectively around the ring.

From a simple comparison of Sn–O bond lengths – those in **2** are shorter than those in **1** – it would appear that the succinamide ligand binds more effectively to Sn(IV) than the oxalamide but this may well be the result of the steric strain imposed by the 5-membered ring in the structure of the latter. A search of the files of the Cambridge Data Centre showed that Sn(IV)–O distances usually fall in the range 2.08–2.22 Å but known compounds were not sufficiently similar to **1** and **2** to decide the reason(s) for the variations in bond lengths.

In both molecules, the dimensions of the ligands are as expected with C–O bond lengths increasing and C–N bond lengths decreasing on complexation. Thus the former at 1.26(2) Å in **1** and 1.28(3), 1.25(3) Å in **2** are slightly longer *cf.* 1.236 Å (oxalamide) [8], 1.227 Å (*N,N'*-dimethyloxalamide) [9], 1.238 Å (succinamide) [10], and the latter at 1.29(2) Å in **1** and 1.24(3) 1.25(3) Å in **2** are shorter *cf.* 1.31 to 1.33 Å than the corresponding values for free ligands. The ligand interbond angles remain *ca.* 120° as expected.

In both molecules the thf solvent molecule is linked to an N–H group(s) by hydrogen bonding rather than directly bound to the metal. Indeed this type of hydrogen bond appears to be a feature of these oxalamide and related complexes. Thus in all the structures included in refs. 1–4 every N–H bond is linked by hydrogen bonding to an available electronegative atom e.g. solvent oxygen, ligand oxygen or sulphur, or halogen attached to metal acceptor. The hydrogen bonds in each structure are shown in Figs. 1 and 2. In **1** the two N(21)–H groups in the $SnBr_4L^1$ molecule form hydrogen bonds to the oxygen atom O(50) of the tetrahydrofuran molecule. The dimensions of this hydrogen bond O(50)···H–N(21) are O···H–N 178°, O···H 1.90, O···N 2.85(3) Å. The N(21)···O(50)···N(21*) angle is surprisingly only 60.2(7)° rather than the expected tetrahedral angle. This distortion is presumably a result of packing the two molecules around the two-fold axis. The hydrogen bonding pattern in **2** is somewhat different. Whereas one of the amine groups N(21)–H is again linked directly to the solvent oxygen atom O(50) with dimensions N–H···O 176°, H···O 1.75 Å, N···O 2.69 Å, the other N(31)–H forms a bond with a bromine atom Br(3) of an adjacent molecule with dimensions Br···H–N 172°, Br···H 2.67 Å, Br···N 3.56 Å. This interaction with halogen, although much weaker than that with the solvent group, has a pronounced effect on Br(3): not only is there marked distortion from 90° of those angles around the tin atom involving Br(3) e.g., Br(3)–Sn–Br(4) 99.2(1)°, but the Sn–Br(3) bond length is significantly longer than the other Sn–Br distances. This distinction apart, the Sn–Br bonds in both **1** and **2** are as expected within the region 2.5–2.6 Å e.g., *cis*-$SnBr_4L_2{}^3$ where $L^3 = (EtNH)_2C{=}O$ shows Sn–Br 2.56(1), 2.56(1), 2.59(2), 2.55(1) Å [11].

Supplementary Material

Remaining dimensions, thermal parameters, hydrogen positions and structure factor tables are available from the authors on request.

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