Crystal and Molecular Structure of the Six-co-ordinate Antimony(III) Complex SbCl$_3$L, where L = *N,N'*-Dimethyloxamide.* Unusual O,O Ligand Binding leading to Four-membered Sb(μ-O)$_2$Sb Ring Formation

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Antimony trichloride reacts with *N,N'*-dimethyloxamide (L) to form SbCl$_3$L. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, with $a = 7.492(8)$, $b = 8.954(11)$, $c = 10.544(10)$ Å, $\alpha = 68.1(1)$, $\beta = 111.0(1)$, and $\gamma = 111.0(1)$°. 1 617 Independent reflections above background were collected on a diffractometer and the structure refined to R 0.065. The unit cell contains two SbCl$_3$ molecules together with two independent oxamide ligands both with an imposed centre of symmetry. The structure is polymeric with the ligands acting as bridges between SbCl$_3$ cores. The antimony atom is strongly bonded to three chlorine atoms [2.400(3), 2.387(3), and 2.350(5) Å] and weakly bonded to three oxygen atoms [2.837(9), 2.722(13), and 2.838(8) Å].

Various metal–oxamide complexes have been reported featuring unsubstituted, *N,N'*-disubstituted, and *N,N,N',N'*-tetrasubstituted ligand species.[1] In the majority of cases bidentate O,O bonding to the metal is favoured, but despite the overwhelming spectroscopic evidence there has been no *X*-ray structural verification of the precise attachments, *e.g.* chelate *versus* bridging. One exception is known, *viz.* the square-planar nickel(II) complex Na$_2$[NiL$_2$]·H$_2$O [H$_2$L = H$_2$NCOCONH(C$_2$H$_4$OH)][2] which incorporates (amide)N,N bidentate chelation following deprotonation at the amine sites.

We report here the crystal structure of the antimony(III) complex with *N,N'*-dimethyloxamide, SbCl$_3$(MeNHCOCONHMe) (**1**), which establishes O,O ligand binding but unusually in the form of two differing modes of bridging attachment.

Results and Discussion

Direct addition of equimolar benzene solutions of SbCl$_3$ and *N,N'*-dimethyloxamide under a strict N$_2$ atmosphere provided the white complex (**1**). Recrystallisation from benzene gave white needle crystals which are noticeably air and moisture sensitive. Characteristic bands in the i.r. spectrum are in accord with O donation,[3,4] *e.g.* ν(CN) 1 540 cm^{-1} representing a high-energy shift (+15 cm^{-1}) and ν(CO) 1 625 cm^{-1} representing a low-energy shift (−35 cm^{-1}) on complexation, but do not give any real indication of the intricacies of ligand binding in the structure. The ν(NH) band at 3 346 cm^{-1} (+46 cm^{-1}) is seemingly insensitive to the weak intermolecular hydrogen bonding NH···X (X = O or Cl) which is present. The two broad and intense ν(Sb–Cl) bands at 296 and 327 cm^{-1} indicate an octahedral antimony(III) geometry. The ^{1}H n.m.r. spectrum shows a close similarity to that of the uncomplexed ligand, which rather suggests facile dissociation, *e.g.* the methyl protons appear as two sharp singlets, δ 2.95 and 2.89 (2.94 and 2.88 for the ligand), and the NH proton appears as a somewhat broader singlet, δ 7.51 (7.52 for the ligand).

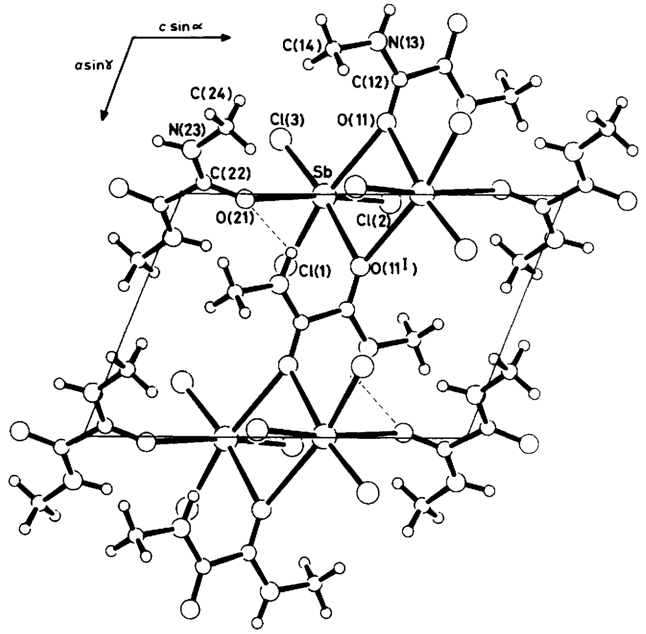

Figure. The unit cell of complex (**1**) in the *b* projection. Hydrogen bonds are shown as dotted lines

Crystal Structure.—The structure of complex (**1**) is polymeric. The unit cell is shown in the Figure together with the atomic numbering scheme. It contains two SbCl$_3$ molecules together with two independent oxamide ligands both with a crystallographically imposed centre of symmetry. The antimony atom is strongly bonded to three chlorine atoms [Sb–Cl(1) 2.400(3), Sb–Cl(2) 2.387(3), and Sb–Cl(3) 2.350(5) Å] with Cl–Sb–Cl angles all greater than 90° at 91.6(1), 96.1(2), and 95.5(2)°. In addition the antimony atom is weakly bonded to three oxygen atoms.

This SbCl$_3$ core is found in a number of structures with similar geometries. In these, as in complex (**1**), the SbCl$_3$ dimensions are relatively unchanged from those of pure

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^4) for complex (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sb	60(1)	1 675(1)	3 197(1)
Cl(2)	316(7)	3 530(5)	4 432(4)
Cl(1)	2 925(7)	3 456(5)	2 373(4)
Cl(3)	−2 252(11)	2 705(8)	1 138(6)
O(11)	−2 965(12)	−161(11)	4 628(10)
C(12)	−4 712(16)	−407(14)	4 603(13)
N(13)	−6 275(15)	−1 410(14)	3 951(13)
C(14)	−5 997(26)	−2 299(24)	3 140(23)
O(21)	209(15)	−252(11)	1 779(9)
C(22)	−432(17)	−579(14)	624(11)
N(23)	−1 803(17)	−1 937(12)	392(10)
C(24)	−2 748(25)	−3 177(17)	1 415(16)

Table 2. Molecular dimensions (distances in Å, angles in °) in complex (**1**)

Sb–Cl(2)	2.387(3)	Sb–O(11)	2.837(9)
Sb–Cl(1)	2.400(3)	Sb–O(21)	2.722(13)
Sb–Cl(3)	2.350(5)	Sb–O(11$^{\rm I}$)	2.838(8)
Cl(2)–Sb–Cl(1)	91.63(13)	Cl(2)–Sb–O(11$^{\rm I}$)	93.91(26)
Cl(2)–Sb–Cl(3)	96.12(20)	Cl(3)–Sb–O(11)	90.99(24)
Cl(1)–Sb–Cl(3)	95.49(22)	Cl(3)–Sb–O(21)	86.46(29)
Cl(1)–Sb–O(11)	168.74(24)	Cl(3)–Sb–O(11$^{\rm I}$)	169.55(34)
Cl(1)–Sb–O(21)	82.02(24)	O(21)–Sb–O(11)	107.62(30)
Cl(1)–Sb–O(11$^{\rm I}$)	81.27(20)	O(11)–Sb–O(11$^{\rm I}$)	93.88(25)
Cl(2)–Sb–O(11)	78.50(25)	O(21)–Sb–O(11$^{\rm I}$)	83.26(31)
Cl(2)–Sb–O(21)	173.37(24)		

Symmetry element: I $-x$, $-y$, $1 - z$.

crystalline SbCl$_3$,[5] where the corresponding bond lengths are 2.340(2) and 2.368(1) Å (× 2) and bond angles are 90.98(5) and 95.70(5)° (× 2). In (**1**) and in SbCl$_3$, the smallest Cl–Sb–Cl angle is opposite the shortest bond.

There are a number of structures of SbCl$_3$ adducts in which this SbCl$_3$ unit is augmented by a number of weak bonds to ligand atoms.* These feature S-donor ligands, *e.g.* in SbCl$_3$L$_{1.5}$[6] (L = *N*,*N'*-di-isopropyldithio-oxamide) the unique Sb–Cl bond lengths are 2.413(2) Å with Sb–S 3.197(5) Å and in SbCl$_3$L$_{1.5}$[7] (L = *N*,*N'*-diethyldithio-oxamide) the Sb–Cl bond lengths range from 2.340(3) to 2.388(3) Å with Sb–S 3.165(3)—3.396(3) Å. In both these molecules, and in a series of cyclic thioether adducts listed in ref. 7, each of the three sulphur atoms is *trans* to a chlorine atom.

The same arrangement is found in the present structure with the three oxygen atoms approaching the metal in octahedral positions to form the *fac* isomer. Thus the Sb atom is bonded to O(11) at 2.837(9), O(21) at 2.722(13), and O(11$^{\rm I}$) at 2.838(8) Å. This means that O(11) is bridging two antimony atoms and it is noticeable that the Sb–O(11) distances are *ca.* 0.10 Å longer than the Sb–O(21) bond. The Sb–O(11)–Sb$^{\rm I}$ angle is only 86.2(3)° but this is an indication of the weakness of the Sb–O(11) bonds. The Sb ··· Sb distance is 3.874 Å. This centrosymmetric Sb(μ-O)$_2$Sb bridging leads to a polymeric chain between the ligands and SbCl$_3$ units as shown in the Figure. The lone pair associated with Sb$^{\rm III}$ appears to exert no stereochemical influence.

This is a unique structure, not only because of the mode of bridging of the ligands which leads to the formation of polymeric chains, but also because such Sb–O linkages are comparatively rare. A search of the Cambridge Data Centre files has revealed only four structures in which an antimony atom is strongly bonded to three chlorine atoms and weakly to at least one oxygen atom; these examples exhibit varying co-ordination numbers and geometries. Thus in 1,4-diacetylbenzeneantimony trichloride[8] there are two Sb–O distances of 2.67 and 2.81 Å together with an Sb–Cl distance of 3.21 Å, making up the octahedron; in 1,3,5-triacetylbenzene–trichloroantimony (1/2)[9] there are two antimony atoms in the asymmetric unit of which one is six-co-ordinate with three extra oxygen atoms (3.023, 3.040, and 2.695 Å) and one is four-co-ordinate with an extra oxygen at 2.879 Å. In terephthaldehydeantimony trichloride[10] the metal is five-co-ordinate being bonded to two extra oxygens at 2.93 and 2.93 Å. Finally in tris(2-hydroxyethyl)ammonium trichloroantimony(III) chloride[11] the metal is five-co-ordinate being bonded to an additional oxygen at 2.74 Å and an additional chlorine at 2.90 Å.

For the uncomplexed ligand, structural data[11] confirm a planar *trans* configuration with a crystallographic centre of symmetry. There are strong intermolecular hydrogen bonds between N–H and C=O in adjacent molecules. The dimensions are C–C 1.548, C=O 1.226, and N–C 1.327 and 1.454 Å. There are no significant changes from these dimensions in complex (**1**). Both ligands in (**1**) are also planar within experimental error.

Significantly there are no strong intermolecular hydrogen bonds in the unit cell, primarily because the carbonyl groups are bonded to antimony and are no longer available to form strong hydrogen bonds to N–H groups. Thus the carbonyl oxygen of one ligand O(11) is bonded to Sb and Sb$^{\rm I}$ while in the other ligand O(21) is bonded only to one antimony atom leaving a lone pair available for secondary bonding. A weak interaction O(21) ··· H(13$^{\rm II}$)–N(13$^{\rm II}$) (II 1 + *x*,*y*,*z*) where O ··· H 2.48, O ··· N 3.02 Å, and O ··· H–N 116° is indeed formed but this is much less significant than that in the free ligand where the corresponding dimensions are 1.98, 2.84 Å, and 149°. The weakness of the interaction is presumably due to the steric constraints of the polymer.

The intramolecular (N)H ··· O distances in the ligand across the centre of symmetry are quite short at *ca.* 2.31 and 2.33 Å in (**1**) but we do not consider this to represent any interaction.

This structure suggests that oxamides can be directly compared with thio-oxamides in terms of a *trans*-configuration preference both in the free state and in complexes with antimony(III) halides. As we have shown previously,[6,7] S,S bidentate bridging to separate pseudo-octahedral antimony(III) centres to give polymeric structures with retention of ligand *trans* planarity appears to be the norm for dithio-oxamides. Presumably the rigid bite of a cisoid-bidentate dithio-oxamide (oxamide) cannot be reconciled with the relative sizes of the sulphur (oxygen) and antimony atoms in terms of effective five-membered chelate formation. By the same token, dithiomalonamides, where the additional CH$_2$ group in the carbon skeleton allows a larger and more flexible bite, do give S,S bidentate chelate formation, *e.g.* six-co-ordinate SbCl$_3$[EtNHC(S)CH$_2$C(S)NHEt][12] in which the lone pair occupies one of the octahedral sites.

Experimental

A nitrogen-filled glove-box was used for handling all materials. Benzene was distilled from CaH$_2$ under an inert atmosphere prior to use. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer with samples as Nujol mulls placed between CsI plates. Proton (^{1}H) n.m.r. spectra were obtained (220 MHz, Perkin-Elmer R34) for CDCl$_3$ solutions doped with SiMe$_4$ as internal reference.

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* Indeed there are such interactions in SbCl$_3$ itself. Apart from the three Sb–Cl bonds already mentioned, there are Sb ··· Cl interactions of 3.457 (× 2), 3.609, and 3.736 Å (× 2).

Preparation of $SbCl_3(MeNHCOCONHMe)]$ (**1**).—Antimony trichloride (3.72 g, 16.3 mmol) in benzene (20 cm^3) was added dropwise to an ice-cold, stirred solution of *N*,*N'*-dimethyloxamide (2.08 g, 17.9 mmol) in benzene (30 cm^3). The resulting solution was warmed at 50 °C for several hours when a white solid deposited. This product was collected by filtration (5.09 g, 80.9%) and purified by vacuum sublimation. Recrystallisation from benzene gave white needles, m.p. 135—136 °C (Found: C, 13.9; H, 2.4; N, 8.2. Calc. for $C_4H_8Cl_3N_2O_2Sb$: C, 14.0; H, 2.3; N, 8.1%).

Crystallography.—Crystal data. $C_4H_8Cl_3N_2O_2Sb$, $M = 344.23$, triclinic, $a = 7.492(8)$, $b = 8.954(11)$, $c = 10.544(10)$ Å, $\alpha = 68.1(1)$, $\beta = 111.0(1)$, $\gamma = 111.0(1)°$, $U = 591.9$ $Å^3$, $F(000) = 328$, $Z = 2$, $D_c = 1.92$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu = 30.0$ cm^{-1}, space group $P\bar{1}$ from the successful structure determination.

The crystal was set up to rotate about the *a* axis on a Stoe Stadi-2 diffractometer and data were collected *via* variable-width ω scan. Background counts were for 20 s and a scan rate of 0.033° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 1 997 Independent data with a $2\theta_{max.} = 50°$ were collected of which 1 617 with $I > 3\sigma(I)$ were used in subsequent calculations. An empirical absorption correction was applied but no extinction correction. The structure of complex (**1**) was determined from Patterson and Fourier calculations.

The hydrogen atoms were included in calculated positions although the methyl groups were refined as rigid groups. In the full-matrix refinement, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The refinements were carried out using full-matrix least squares with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. The final *R* value was 0.065 ($R' = 0.067$). Calculations were carried out using SHELX 76[13] and our own programs on the Amdahl V7A at the University of Reading. Positional parameters are given in Table 1 and bond lengths in the co-ordination sphere in Table 2.

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