Studies of Dioxamide and Dithio-oxamide Metal Complexes. Part 1. Crystal and Molecular Structures of $SbCl_3L_{1.5}$ (L = *NN'*-diethyldithio-oxamide) and Uncomplexed L

By **Michael G. B. Drew,*** Department of Chemistry, The University, Whiteknights, Reading RG6 2AD
Jonathan M. Kisenyi and **Gerald R. Willey,** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Crystals of $SbCl_3L_{1.5}$ are monoclinic, space group *C*2/*c*, with unit cell dimensions *a* = 30.84(1), *b* = 9.37(1), *c* = 13.96(1) Å, β = 107.0(1)°, and *Z* = 8. 1 991 Independent reflections collected on a diffractometer have been refined to *R* 0.055. Crystals of L are monoclinic, space group $P2_1/c$, with *a* = 4.502(7), *b* = 6.024(9), *c* = 16.425(11) Å, β = 91.3(1)°, and *Z* = 2. 495 Independent reflections collected on a diffractometer have been refined to *R* 0.061. The geometry of the ligand is *trans* in both structures. The structure of $SbCl_3L_{1.5}$ is polymeric with each ligand acting as a bidentate bridging group to separate $SbCl_3$ moieties *via SS* donation. The antimony atoms are six-co-ordinate with the three sulphur atoms approaching to the *fac* octahedral positions, Sb–Cl 2.340(3), 2.388(3), 2.381(3); Sb–S 3.212(3), 3.396(3), and 3.165(3) Å.

NUMEROUS dioxamide and dithio-oxamide metal complexes have been reported.[1] Although the choice of donor sites O *versus* S *versus* N varies with the acceptor properties of the particular metal ion, and is often controversial, there is a tacit assumption throughout for a bidentate chelate bonding involvement of the ligand. In the absence of structural data (poor solubility and hydrolytic instability in the majority of cases thwarts single-crystal *X*-ray determinations), inferential confirmation of this point has been derived, in the main, from infrared information.[2] One very recent *X*-ray structure determination[3] is that of $Na_2[NiL'_2]\cdot H_2O$, where $L' = H_2NC(O)C(O)NH(C_2H_4OH)$. Here the square planar Ni^{II} environment involves bidentate σ *NN*-chelation from deprotonated amine centres of two ligand molecules. As part of a current investigation of the molecular structure and metal–ligand binding characteristics of such complexes, the antimony(III) complex $SbCl_3L_{1.5}$ (1) [L = EtNHC(S)C(S)NHEt], was selected for crystallographic study. For comparison we have also determined the structure of the parent ligand L.

EXPERIMENTAL

Ligand (L) and compound (1) were prepared as described previously.[4] For the latter, benzene rather than the original 1,2-dichloroethane was used as solvent. Recrystallisation from benzene gave orange platelets (m.p. 341—342 K). Both crystals were placed in Lindemann tubes along their needle axis, crystalline quality checked, and preliminary cell constants and space groups were obtained from precession photographs. The crystals were then transferred to a Stoe STADI-2 diffractometer equipped with a graphite monochromator. The crystals were adjusted more accurately by *X*-ray counter methods and precise determinations of lattice constants were carried out from the accurate setting angles of a number of axial reflections. Data were taken *via* ω scans of width (2.0 + 0.5 sinμ/tanθ). The scan speed was 0.033° s^{-1} and the background measured at the ends of the ω scan for 20 s. Measurement of standard reflections showed no deterioration. Details of cell constants, data collection, and refinement details are given in Table 1.

Structure Determination.—In both structures, the Patterson function was utilised to determine the positions of the heaviest atoms. The positions of the remaining atoms were located from Fourier maps and refined by full-matrix least-squares. All atoms except for hydrogen were refined anisotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions at 0.95 Å from the C or N atom to which they were bonded. Their thermal parameters were refined although those of H atoms bonded to the same atom were constrained to be the same. The scattering factors and dispersion corrections were taken from ref. 5. The final difference-Fourier maps showed no important features and in the final cycles of refinement no shift was greater than 0.1σ. Calculations were carried out using SHELX 76[6] at the University of Manchester Computer Centre. The final *R* values were 0.055 for (1) and 0.061 for L. Atomic parameters are given in Tables 2 and 3, bond lengths and angles in Table 4, and torsion angles in Table 5. The

TABLE 1

Crystal data

	(1)	L
Formula	$C_9H_{18}Cl_3N_3S_3Sb$	$C_6H_{12}N_2S_2$
M	492.4	176.2
Crystal class	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
Absences	$h0l,\ l = 2n + 1$ $hkl,\ h + k = 2n + 1$	$h0l,\ l = 2n + 1$ $0k0,\ k = 2n + 1$
a/Å	30.84(1)	4.502(7)
b/Å	9.37(1)	6.024(9)
c/Å	13.96(1)	16.425(11)
β/°	107.0(1)	91.3(1)
U/$Å^3$	3 857.8	445.3
Z	8	2
μ/cm^{-1}	21.6	5.13
D_m/g cm^{-3}	1.70	1.33
D_c/g cm^{-3}	1.70	1.32
λ(Mo-K_α)/Å	0.7107	0.7107
F(000)	1 944	188
Crystal size/ mm	0.5 × 0.5 × 0 55	0.8 × 0.2 × 0.5
Rotation axis	*c*	*a*
$2\theta_{max.}$/°	50	50
No. of data	3 783	750
Criterion for data inclusion	$>2\sigma(I)$	$>3\sigma(I)$
No. of data in refinement	1 991	495
R	0.055	0.061

TABLE 2

Atomic co-ordinates ($\times 10^4$) for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sb	1 109(0)	1 952(1)	−1 853(0)
S(1)	1 411(1)	524(3)	1 938(2)
S(5)	490(1)	−178(3)	−1 012(2)
C(1)	962(3)	618(9)	927(7)
N(2)	630(3)	1 514(9)	813(6)
C(3)	600(5)	2 621(13)	1 558(10)
C(4)	224(5)	3 577(14)	1 098(13)
C(5)	912(3)	−392(9)	49(6)
N(6)	1 222(3)	−1 358(9)	191(6)
C(7)	1 258(5)	−2 456(12)	−540(9)
C(8)	1 687(5)	−3 191(13)	−253(11)
S(11)	2 113(1)	575(3)	−454(2)
C(11)	2 471(3)	1 919(10)	−398(6)
N(12)	2 728(3)	2 094(9)	−993(6)
C(13)	2 767(7)	1 120(15)	−1 769(11)
C(14)	2 619(5)	1 704(14)	−2 750(9)
Cl(2)	462(1)	2 281(3)	−3 214(2)
Cl(3)	1 555(1)	3 579(3)	−2 487(3)
Cl(1)	922(2)	3 728(4)	−821(3)

anisotropic thermal parameters, hydrogen positions, and the observed and calculated structure factor tables for both compound (1) and L are deposited in Supplementary Publication No. SUP 23311 (17 pp.).*

TABLE 3

Atomic co-ordinates ($\times 10^4$) for (L) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	1 067(10)	125(9)	371(3)
S(1)	1 506(4)	2 546(2)	846(1)
N(2)	2 378(9)	−1 719(7)	592(3)
C(3)	2 904(15)	−2 329(10)	2 068(4)
C(4)	4 453(12)	−1 979(10)	1 291(3)

DISCUSSION

Antimony(III) chloride and *NN*′-diethyldithio-oxamide (L) give the bright orange complex $SbCl_3L_{1.5}$ (1) under strict anhydrous conditions regardless of the ligand : metal ratio and of the conditions of mixing. The structure is polymeric (Figure 1) with $SbCl_3$ units connected by ligand molecules which are bidentate bridging to separate Sb atoms. In the unit cell each antimony assumes a distorted octahedral environment of three chlorine and three sulphur atoms. The Sb–Cl bond distances 2.340(3), 2.388(3), and 2.381(3) Å are virtually unchanged from those of pure crystalline $SbCl_3$;[7] Cl–Sb–Cl angles lie in the range 92.4(1)—95.8(2)°. Three sulphur atoms approach to the metal octahedral positions for a *fac* isomer with Sb–S distances 3.212(3), 3.396(3), and 3.165(3) Å reflecting very weak Sb $\cdots$ S interactions. This loose association persists only in the solid state; in solution there is dissociation to free ligand as indicated by spectral data (i.r. and ^1H n.m.r.). For comparison, complexes with cyclic thioethers, *e.g.* $SbCl_3\cdot(S_2C_4H_8)$ (ref. 8) ($S_2C_4H_8$ = 1,4-dithian) Sb–S 3.135, 3.065 Å, $SbCl_3\cdot(S_3C_3H_6)$ (ref. 9) ($S_3C_3H_6$ = 1,3,5-trithian) Sb–S average 3.258 Å, and $SbCl_3\cdot(S_2C_5H_{10})$ (ref. 10) ($S_2C_5H_{10}$ = 1,4-dithiacycloheptane) Sb–S 3.13, 3.23, and 3.40 Å, are also referred to as 'weak' in respect

TABLE 4

Bond lengths (Å) and angles (°) in (1) and (L)

Metal co-ordination sphere in (1)

Sb–Cl(2)	2.340(3)
Sb–Cl(3)	2.388(3)
Sb–Cl(1)	2.381(3)
Sb–S(5)	3.212(3)
Sb–S(11)	3.396(3)
Sb–S(1^{I})	3.165(3)
Cl(2)–Sb–Cl(3)	93.50(13)
Cl(2)–Sb–Cl(1)	95.79(17)
Cl(3)–Sb–Cl(1)	92.41(12)
Cl(2)–Sb–S(1^{I})	88.73(10)
Cl(1)–Sb–S(5)	86.46(14)
Cl(3)–Sb–S(5)	178.59(10)
Cl(2)–Sb–S(5)	85.51(10)
S(5)–Sb–S(11)	95.34(07)
S(5)–Sb–S(1^{I})	92.20(07)
Cl(2)–Sb–S(11)	159.27(10)
Cl(3)–Sb–S(11)	85.92(10)
S(11)–Sb–Cl(1)	104.99(12)
S(11)–Sb–S(1^{I})	70.54(07)
Cl(1)–Sb–S(1^{I})	175.22(11)
Cl(3)–Sb–S(1^{I})	88.82(10)

Ligand dimensions in (1)

S(1)–C(1)	1.668(9)
S(5)–C(5)	1.673(9)
C(1)–N(2)	1.289(11)
C(1)–C(5)	1.523(13)
N(2)–C(3)	1.493(14)
C(3)–C(4)	1.470(17)
C(5)–N(6)	1.293(11)
N(6)–C(7)	1.462(13)
C(7)–C(8)	1.464(17)
S(11)–C(11)	1.660(10)
C(11)–N(12)	1.323(11)
C(11)–C(11^{II})	1.529(13)
N(12)–C(13)	1.428(15)
C(13)–C(14)	1.426(19)
Sb–S(1)–C(1)	100.8(4)
Sb–S(5)–C(5)	90.4(3)
Sb–S(11)–C(11)	102.8(3)
S(1)–C(1)–C(5)	120.6(6)
N(2)–C(1)–C(5)	114.4(7)
C(1)–N(2)–C(3)	124.6(8)
N(2)–C(3)–C(4)	109.4(11)
S(5)–C(5)–C(1)	120.4(6)
S(5)–C(5)–N(6)	124.7(6)
C(1)–C(5)–N(6)	114.9(7)
C(5)–N(6)–C(7)	125.1(8)
N(6)–C(7)–C(8)	112.6(9)
S(11)–C(11)–N(12)	125.6(7)
C(11)–N(12)–C(13)	125.1(10)
N(12)–C(13)–C(14)	113.3(11)
S(11)–C(11)–C(11^{II})	120.5(7)
C(11^{II})–C(11)–N(12)	114.1(8)

Ligand dimensions in L

S(1)–C(1)	1.664(5)
C(1)–N(2)	1.305(6)
C(1)–C(1^{III})	1.542(6)
N(2)–C(3)	1.472(6)
C(3)–C(4)	1.483(8)
S(1)–C(1)–C(1^{III})	121.4(3)
N(2)–C(1)–C(1^{III})	114.0(4)
C(1)–N(2)–C(3)	125.6(4)
N(2)–C(3)–C(4)	112 6(4)

Roman numeral superscripts refer to the following symmetry elements: I *x*, −*y*, 0.5 + *z*; II 0.5 − *x*, 0.5 − *y*, −*z*; III −*x*, −*y*, −*z*, relative to the *x*, *y*, *z* sets given in Tables 2 and 3.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

of their Sb–S bond lengths and their instability other than in the solid state. Like (1) these all feature bridging attachment of ligand.

Consideration of the bond angles shows a definite distortion from a regular octahedron as might be expected given the varied bond lengths. The atom S(11) is at a significantly further distance [3.396(3) Å] from the metal centre than the other two sulphur atoms [Sb–S(mean) 3.186 Å]. We will therefore define an equatorial plane with atoms Sb, S(5), S(1^{I}), Cl(3), and Cl(1) which is almost planar (maximum deviation 0.08, mean deviation 0.05 Å). In this plane the interligand angles S–Sb–S 92.2 and Cl–Sb–Cl 92.4° are greater than those for Cl–Sb–S 86.5, 88.8°. The angles involving S(11) are far more distorted from 90° being 85.9, 95.3, 70.5, and 105.0°. Thus S(11) is significantly tilted out of the axial position towards S(1^{I}) and away from Cl(1). This could suggest that the lone pair is operative between Cl(1) and S(11) but this seems unlikely as it does not fit any obvious mode of deformation from O_h symmetry observed when the lone pair is sterically active.* A similar situation wherein two of the three immediate S atom neighbours are evidently preferentially bonded has been noted by Schmidt *et al.*[10] for $SbCl_3\cdot(S_2C_5H_{10})$. Their rationale that Sb^{III} can achieve an enhanced bonding situation *via* a co-ordination increase from five † to six to form linked distorted octahedra at the expense of stereochemical involvement of the lone pair of electrons seems equally applicable in the present instance. Because of steric interactions between ligands and the general bulkiness of L, significant crowding of the Sb^{III} environment might reasonably be expected were the ligand more closely attached. As it is there are no significant intermolecular contacts between the ligands and the $SbCl_3$ unit.

TABLE 5

Torsion angles (°)

Compound (1)	
S(1)–C(1)–N(2)–C(3)	1.0
S(1)–C(1)–C(5)–S(5)	−173.3
S(1)–C(1)–C(5)–N(6)	4.8
N(2)–C(1)–C(5)–N(6)	−174.7
N(2)–C(1)–C(5)–S(5)	7.2
S(5)–C(5)–N(6)–C(7)	−1.2
C(1)–N(2)–C(3)–C(4)	170.1
C(5)–N(6)–C(7)–C(8)	167.8
S(11^{II})–C(11^{II})–C(11)–S(11)	180.0
S(11)–C(11)–N(12)–C(13)	−3.7
C(11)–N(12)–C(13)–C(14)	117.0
Ligand L	
S(1)–C(1)–N(2)–C(3)	1.8
S(1)–C(1)–C(1^{III})–S(1^{III})	180.0
C(1)–N(2)–C(3)–C(4)	83.7

For definition of Roman numeral supercripts see Table 4.

As is apparent in Figure 1, there are two polymeric chains of $(SbCl_3L)_n$ which are connected by an additional ligand over centres of symmetry. It is probably significant that this additional ligand is more weakly bound to the antimony atom than the other two although we cannot find any non-bonded contacts to account directly for this increased value.

It is interesting that the Sb–S–C angles are 100.8(4), 90.4(3) and 102.8(3)°, roughly what one might expect if the Sb–S bonds were far shorter. This supports our view that the Sb–S interactions do indeed represent bonding albeit of a very weak nature.

The conformations of the two ligands are very similar in that they are both *trans* with S–C–C–S torsion angles of −173.3(1) and 180°. Also the S–C–N–C angles are *ca.* 0, being −1.2 and −3.7°. This brings the hydrogen on N adjacent to the other sulphur atom in the ligand (as is apparent from Figure 1) but the geometry is probably not suitable for a hydrogen bond, despite S · · · N, S · · · H distances of 2.9 and 2.4 Å, as the angles C–S · · · H and N–H · · · S are 71.1 and 115.7° respectively. The only difference in conformation between the two ligands involves the position of the last carbon atom C(4). Torsion angles C(5)–N(6)–C(7)–C(8) and C(11)–N(12)–C(13)–C(14) are 167.8 and 117.0° respectively.

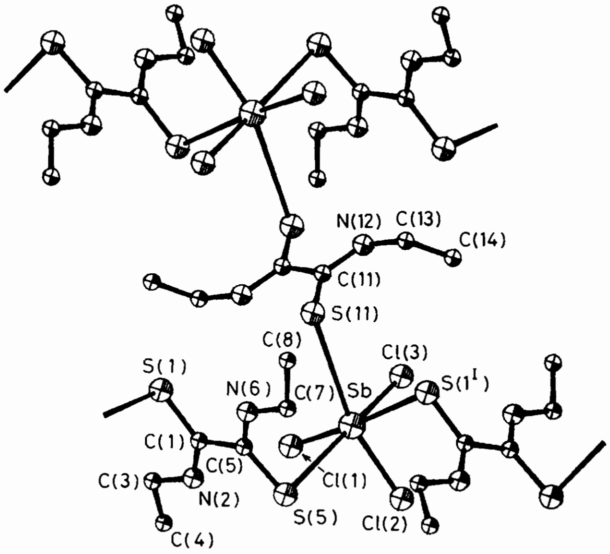

FIGURE 1 Molecular structure of $SbCl_3L_{1.5}$ (1) showing the atomic numbering

Turning to the ligand L, a crystal structure determination shows two centrosymmetric ligands in the unit cell so again the *trans* conformation is found (Figure 2). Also

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* A trigonal distortion (C_{3v}) with the lone pair located in the face defined by Cl(1), S(5), S(11) and assuming full stereochemical activity would constitute a seven-co-ordinate system of the v.s.e.p.r. (valence shell electron pair repulsion) model. See R. J. Gillespie, 'Molecular Geometry,' van Nostrand–Reinhold, New York, 1972.

† Examples of formal five-co-ordinate Sb^{III} species involving a distorted square pyramidal configuration with a stereochemically active lone pair occupying the sixth position include $SbCl_3\cdot 2(O{=}AsPh_3)$ (I. Lindqvist, 'Inorganic Adduct Molecules of Oxo-compounds,' Academic Press Inc., New York, 1963), $SbCl_3\cdot 2(CH_3)_2SO$ (R. P. Oertel, *Spectrochim. Acta, Sect. A*, **1970**, **26**, 659), $SbCl_3\cdot 2L$ (L = 2-pyrrolidinone) (S. T. Yuan and S. K. Madan, *Inorg. Chim. Acta*, 1972, **6**, 463), $SbCl_3\cdot 2L'$ (L′ = substituted 1,2-dithiole-3-thiones) (F. Petillon and J. E. Guerchais, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1863; here the ligands assume *trans* rather than *cis* positions in the basal plane), and $SbCl_3\cdot 2(O{=}PPh_3)$ (L. Golic and S. Milicev, *Acta Crystallogr., Sect. B*, **1978**, **34**, 3379).

the S(1)–C(1)–N(2)–C(3) torsion angle is close to zero at 1.8°. This time however the C(1)–N(2)–C(3)–C(4) torsion angle is 83.7°. Such a wide variation in position of C(4) is not unexpected and can be ascribed to packing effects. There is only one $N \cdots S$ intermolecular contact that could represent a hydrogen bond, namely $S(1) \cdots N(3)$ of 3.50 Å $(1 + x, y, z)$ with a $S \cdots H$ distance of 2.85 Å, but this does seem rather long. There are no other intramolecular distances of note less than the sum of van der Waals radii.

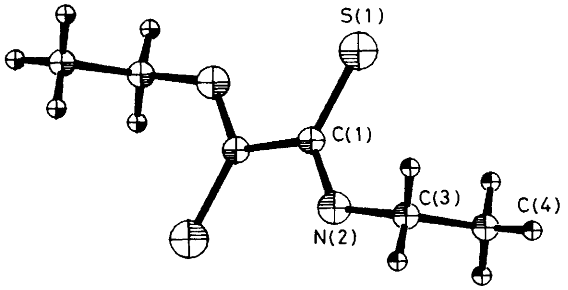

FIGURE 2 Molecular structure of the ligand L

Other ligands such as oxamide,[11] succinamide,[12] dithio-oxamide,[13] *NN'*-bis(trimethylsilyl)dithio-oxamide,[14] and *NN*-dimethyldithio-oxamide [15] similarly exhibit a *trans* geometry. What is interesting is that whereas $H_2NC(O)C(O)NH(C_2H_4OH)$ (L'), which is also *trans* in the uncomplexed form, shows a change of conformation in the nickel complex $Na_2[NiL'_2]\cdot H_2O$ (bidentate chelation of the two *cis* ligand molecules leads to a square planar Ni^{II} atom [3]), there is no such *trans–cis* rearrangement for L in the present instance on complexation with $SbCl_3$. Presumably with such a weak set of Sb–S bonds and the ' unfavourable ' size of Sb^{III}, chelate stabilisation effects in terms of five-membered ring formation are minimal, and there is a marginal preference for bridging. Molecular models suggest that with a suitable choice of metal ion acceptor, bidentate chelation is a possibility and efforts in this direction are being continued.

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REFERENCES

[1] See, for example, G. Peyronel, G. C. Pellacani, and A. Pignedoli, *Inorg. Chim. Acta*, 1971, **5**, 627; G. Peyronel, A. C. Fabretti, and G. C. Pellacani, *J. Inorg. Nucl. Chem.*, 1973, **35**, 973; A. J. Aarts, H. O. Desseyn, and M. A. Herman, *Inorg. Chim. Acta*, 1978, **29**, L197; H. O. Desseyn, W. Van Riel, L. Van Heverbeke, and A. Geominne, *Transition Met. Chem.*, 1980, **5**, 88 and refs. therein.

[2] See, for example, A. C. Fabretti, G. C. Pellacani, and G. Peyronel, *J. Inorg. Nucl. Chem.*, 1971, **33**, 4247; G. Peyronel, A. C. Fabretti, and G. C. Pellacani, *Spectrochim. Acta, Part A*, 1974, **30**, 1723; S. R. Wade and G. R. Willey, *Inorg. Chim. Acta*, 1980, **43**, 73 and refs. therein.

[3] W. Van Riel, H. O. Desseyn, W. Van de Mieroop, and A. T. H. Lenstra, *Transition Met. Chem.*, 1980, **5**, 330.

[4] S. O. Wandiga, L. S. Jenkins, and G. R. Willey, *J. Inorg. Nucl. Chem.*, 1979, **41**, 941.

[5] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[6] G. M. Sheldrick, SHELX 76 Program for crystal structure determination, University of Cambridge, 1976.

[7] R. Hulme, D. Mullen, and J. C. Scruton, *Acta Crystallogr., Sect. A*, 1969, **25**, S171.

[8] G. Kiel and R. Engler, *Chem. Ber.*, 1974, **107**, 3444.

[9] W. Lindemann, R. Wögerbauer, and P. Berger, *Z. Anorg. Allg. Chem.*, 1977, **437**, 155.

[10] M. Schmidt, R. Bender, and Ch. Burschka, *Z. Anorg. Allg. Chem.*, 1979, **454**, 160.

[11] E. M. Ayerst and J. R. C. Dukes, *Acta Crystallogr.*, 1954, **7**, 588.

[12] D. D. Davies and R. A. Pasternak, *Acta Crystallogr.*, 1956, **9**, 334.

[13] P. J. Wheatley, *J. Chem. Soc.*, 1965, 396.

[14] D. Rinne and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1978, **443**, 185.

[15] A. Christensen, H. J. Geise, and B. S. Van der Veken, *Bull. Chem. Soc. Belg.*, 1975, **84**, 1173.