# Studies of Dioxamide and Dithio-oxamide Metal Complexes. Part 2.* Synthesis and Spectral Characterisation of RNHC(S)C(S)NHR (R = Alkyl or Aryl) Complexes with $SbX_3$ (X = Cl or Br), $BiCl_3$, $SnX_4$ (X = Cl or Br), and $TiCl_4$. Crystal and Molecular Structures† of *NN'*-Di-isopropyldithio-oxamide ($L^3$) and $SbCl_3(L^3)_{1.5}$

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The synthesis and characterisation of a variety of $SbX_3L_{1.5}$ (X = Cl or Br), $BiCl_3L_2$, $SnX_4L$ (X = Cl or Br), and $TiCl_4L$ complexes [where L = RNHC(S)C(S)NHR for R = Me, Et, $Pr^i$, $Bu^n$, cyclo-$C_6H_{11}$, or $CH_2Ph$] is described. In all cases metal–sulphur bonds are formed following *SS'*-bidentate ligand attachment. The potential *N*-donor sites are not involved in co-ordination. The structural characterisation of the uncomplexed ligand $Pr^iNHC(S)C(S)NHPr^i$ ($L^3$) and the antimony(III) complex $SbCl_3(L^3)_{1.5}$ (1) are reported. Crystals of (1) are rhombohedral, space group $R\bar{3}$ with $a = 11.80(1)$ Å, $\alpha = 60.1(1)°$, and $Z = 2$. 1 089 Unique data above background were collected and the structure refined to *R* 0.068. Crystals of $L^3$ are monoclinic, space group $P2_1/c$ with $a = 6.226(7)$, $b = 8.067(11)$, $c = 11.187(12)$ Å, $\beta = 91.0(1)°$, and $Z = 2$. 635 Data above background were measured and the structure refined to *R* 0.077. The structure of (1) is a three-dimensional polymer. The octahedrally co-ordinated Sb atom lies on a three-fold axis and is strongly bound to three chlorine atoms [2.413(2) Å] and also weakly bound to three sulphur atoms from different ligands, which approach their positions *trans* to chlorine [Sb–S 3.197(5) Å] thus giving rise to an octahedral environment. There is no evidence for a stereochemically active lone pair associated with $Sb^{III}$. In the structure of $L^3$ the sulphur atoms are mutually *trans* [C–S 1.680(7) Å] and this orientation is retained on complexation.

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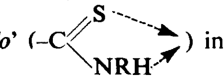
One of the main interests in the co-ordination behaviour of *NN'*-disubstituted dithio-oxamides lies in the particular donor sites involved in metal binding. These can vary from one metal to another according to the hard–soft acid–base classification wherein N is regarded as 'hard' and S as 'soft'. Examples of various *N*/*S*-donor combinations have been cited in the literature, *e.g.*, *cis SS'*-chelation,[1] *trans SS'*-bridging,[2] and *cis NN'*-chelation[3] as supported mainly by spectroscopic evidence. In the particular case of *NS*-co-ordination, not only has *cis NS*-chelation been postulated[4] but also '*endo*' (  ) involvement with either one (chelation) or two (bridging) metal atoms.[5]

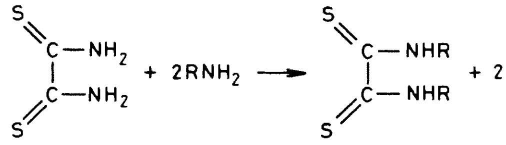
Recently we have described the structural characterisation of *NN'*-diethyldithio-oxamide ($L^2$) and one complex formed with antimony(III) chloride, *viz.* $SbCl_3(L^2)_{1.5}$.[6] Bidentate *SS'*-bridging of the ligand to separate $SbCl_3$ moieties results in a polymeric structure for the complex in which each dithio-oxamide molecule adopts a *trans* conformation. The same *trans* geometry is found for the uncomplexed ligand.

Herein we describe the reactions and attendant complex formation of RNHC(S)C(S)NHR [R = Me ($L^1$), Et ($L^2$), $Pr^i$ ($L^3$), $Bu^n$ ($L^4$), cyclo-$C_6H_{11}$ ($L^5$), or $CH_2Ph$ ($L^6$)] with various $Sb^{III}$, $Bi^{III}$, $Sn^{IV}$, and $Ti^{IV}$ halides. The crystal structure of the antimony(III) complex $SbCl_3(L^3)_{1.5}$ (1) and that of the neat ligand $L^3$ are also reported.

## Experimental

Manipulations of materials were carried out either using an all-glass vacuum line or a nitrogen-filled glove-box. Solvents were distilled from $P_2O_5$ or $CaH_2$ under an inert atmosphere prior to use. $SbCl_3$ was resublimed before use and $SbBr_3$ was recrystallised from benzene; the remainder of the covalent halides were used as supplied commercially. Infra-red spectra were recorded on a Perkin-Elmer 580B spectrophotometer with samples as Nujol mulls sandwiched between CsI plates. $^1H$ N.m.r. (220 MHz) spectra were obtained for $CDCl_3$ solutions using a Perkin-Elmer R 34 instrument with $SiMe_4$ as an internal reference. Molecular weight values were determined cryoscopically in benzene under an inert atmosphere. Elemental microanalyses were carried out by Butterworth Laboratories Ltd., and halide was evaluated by the Volhard titration method. Conductivity measurements were performed using a Phillips PR 9500 bridge.

The *NN'*-disubstituted dithio-oxamide ligands were prepared by the modified Wallach reaction as described by Woodburn and Scroog[7] [equation (i)], where R = Me, Et, $Pr^i$, $Bu^n$, cyclo-$C_6H_{11}$, or $CH_2Ph$. Each one of the yellow to deep orange products was recrystallised from methanol.



(i)

*Preparation of the Complexes.*—The metal complexes were

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* Part 1 is ref. 6.

† *Supplementary data available* (No. SUP 23945, 13 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

**Table 1.** Crystal data and refinement details

| | | |
|---|---|---|
| Compound | $SbCl_3(L^3)_{1.5}$ | $L^3$ |
| Formula | $C_{12}H_{24}Cl_3N_3S_3Sb$ | $C_8H_{16}N_2S_2$ |
| *M* | 534.13 | 204 |
| Crystal class | Rhombohedral | Monoclinic |
| Space group | $R\bar{3}$ | $P2_1/c$ |
| Absences | none | $h0l$; $l = 2n + 1$<br>$0k0$; $k = 2n + 1$ |
| *a*/Å | 11.80(1) | 6.226(7) |
| *b*/Å | 11.80(1) | 8.067(11) |
| *c*/Å | 11.80(1) | 11.187(12) |
| α/° | 60.1(1) | (90) |
| β/° | 60.1(1) | 91.0(1) |
| γ/° | 60.1(1) | (90) |
| *U*/Å$^3$ | 1 164.4 | 561.8 |
| *F*(000) | 534 | 220 |
| $D_m$/g cm$^{-3}$ | * | 1.21(2) |
| $D_c$/g cm$^{-3}$ | 1.53 | 1.21 |
| *Z* | 2 | 2 |
| μ/cm$^{-1}$ | 17.96 | 4.16 |
| λ/Å | 0.7107 | 0.7107 |
| Crystal size/mm | 0.5 × 0.7 × 0.35 | 1.8 × 0.5 × 0.25 |
| Rotation axis | (110) | *a* |
| $2\theta_{max.}$/° | 50 | 50 |
| No. of data measured | 3 618 | 1 028 |
| No. of data used in refinement | 1 089 | 635 |
| Criterion for data inclusion | $I > 3\sigma(I)$ | $I > 2\sigma(I)$ |
| *R* | 0.068 | 0.077 |

* Crystal dissolved rapidly in all solvents.

prepared by direct addition of the appropriate ligand in benzene to the metal halide also in benzene.

(*a*) *Preparation of* $[SnCl_4\{C_6H_{11}NHC(S)C(S)NHC_6H_{11}\}]$; *a typical method. NN′*-Dicyclohexyldithio-oxamide (1.23 g, 4.3 mmol) in benzene (100 cm$^3$) was added dropwise to a stirred solution of $SnCl_4$ (0.5 cm$^3$, 4.3 mmol) in benzene (100 cm$^3$) maintained at 273 K under a nitrogen atmosphere. A purple solution was obtained after several hours of mechanical stirring. Removal of benzene gave the purple *product* which was washed with n-hexane (3 × 40 cm$^3$) and recrystallised from anhydrous nitromethane as purple platelets (yield 1.5 g, 65%) (Found: C, 30.30; H, 5.20; Cl, 26.60; N, 3.30. Calc. for $C_{14}H_{24}Cl_4N_2S_2Sn$: C, 30.85; H, 5.15; Cl, 26.10; N, 4.40%).

(*b*) *Preparation of bismuth*(III) *complexes.* Acetone rather than benzene was found to be more suitable in the preparation of the bismuth(III) complexes, and great care had to be taken to maintain a strict inert atmosphere during reaction. Once reaction was complete, acetone was *slowly* removed until the onset of crystallisation. The resulting crystalline product was collected, pumped dry *in vacuo* at room temperature for several hours and stored in glass ampoules under vacuum. Even with these precautions, decomposition (to a black mass) was evident after several days.

*Structure Determinations.*—Suitable crystals of $SbCl_3(L^3)_{1.5}$ (1) and $L^3$ were selected from recrystallised samples obtained from methanol solutions and placed in Lindemann tubes. Precession photographs established preliminary cell constants and space groups. The crystals were then transferred to a Stoe STADI-2 diffractometer equipped with a graphite monochromator. The crystals were aligned by *X*-ray counter methods and precise determination of lattice constants was carried out from the accurate setting angles of a number of axial reflections. Data were taken *via* ω scans of width (1.5 + 0.5 sinμ/tanθ). The scan speed was 0.033° s$^{-1}$ and the background was 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.

**Table 2.** Atomic co-ordinates (× 10$^5$ for Sb, × 10$^4$ for other atoms) with estimated standard deviations in parentheses for $SbCl_3(L^3)_{1.5}$ (1)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sb(1) | 23 335(7) | 23 335(7) | 23 335(7) |
| S(1) | 5 259(2) | 520(3) | 2 829(2) |
| Cl(1) | 3 685(3) | 1 613(3) | 312(3) |
| C(1) | 5 373(8) | 425(8) | 4 279(9) |
| N(1) | 6 095(8) | 1 019(8) | 4 297(8) |
| C(2) | 6 883(10) | 1 930(10) | 3 072(10) |
| C(3) | 8 371(11) | 1 052(11) | 2 456(11) |
| C(4) | 6 869(14) | 2 988(13) | 3 497(14) |

**Table 3.** Atomic co-ordinates (× 10$^4$) with estimated standard deviations in parentheses for $L^3$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| S(1) | 2 477(3) | 1 825(3) | 365(2) |
| N(1) | 8 600(10) | 1 069(8) | 1 122(5) |
| C(2) | 8 526(12) | 2 412(10) | 2 003(7) |
| C(3) | 6 972(14) | 1 880(14) | 2 996(7) |
| C(1) | 10 175(11) | 742(9) | 400(6) |
| C(4) | 7 873(14) | 4 033(11) | 1 396(8) |

**Table 4.** Bond lengths (Å) and angles (°)

| | |
|---|---|
| (*a*) For (1) | |
| Sb(1)–Cl(1) | 2.413(2) |
| Sb(1)–S(1) | 3.197(5) |
| S(1)–C(1) | 1.726(9) |
| C(1)–N(1) | 1.359(12) |
| C(1$^{I}$)–C(1) | 1.537(16) |
| N(1)–C(2) | 1.488(12) |
| C(2)–C(3) | 1.533(14) |
| C(2)–C(4) | 1.552(16) |
| S(1)–Sb–Cl(1) | 79.2(18) |
| S(1)–Sb–Cl(1$^{II}$) | 89.6(18) |
| S(1)–Sb–Cl(1$^{III}$) | 171.5(16) |
| S(1)–Sb–S(1$^{I}$) | 98.6(14) |
| Cl(1)–Sb–Cl(1$^{II}$) | 92.5(2) |
| S(1)–C(1)–N(1) | 126.5(6) |
| S(1)–C(1)–C(1$^{I}$) | 119.0(6) |
| N(1)–C(1)–C(1$^{I}$) | 113.9(6) |
| C(1)–N(1)–C(2) | 126.3(8) |
| N(1)–C(2)–C(3) | 110.1(7) |
| N(1)–C(2)–C(4) | 109.8(8) |
| C(3)–C(2)–C(4) | 111.0(9) |
| (*b*) For $L^3$ | |
| S(1)–C(1) | 1.680(7) |
| N(1)–C(2) | 1.466(9) |
| N(1)–C(1) | 1.308(8) |
| C(2)–C(3) | 1.546(10) |
| C(2)–C(4) | 1.526(11) |
| C(1)–C(1$^{IV}$) | 1.508(14) |
| C(2)–N(1)–C(1) | 126.7(6) |
| N(1)–C(2)–C(3) | 107.8(6) |
| N(1)–C(2)–C(4) | 110.2(6) |
| C(3)–C(2)–C(4) | 113.1(7) |
| S(1)–C(1)–N(1) | 124.0(5) |
| S(1)–C(1)–C(1$^{IV}$) | 121.3(5) |
| C(1$^{IV}$)–C(1)–N(1) | 115.0(6) |

Equivalent positions: I $1 - x, -y, 1 - z$; II $y, z, x$; III $z, x, y$; IV $2 - x, -y, -z$.

**Table 5.** Microanalytical and principal i.r. bands (cm$^{-1}$) for the metal complexes of RHNC(S)C(S)NHR [R = Me ($L^1$), Et ($L^2$), Pr$^i$ ($L^3$), Bu$^n$ ($L^4$), cyclo-$C_6H_{11}$ ($L^5$), or $CH_2Ph$ ($L^6$)]

| | Microanalyses (%) Found (calc.) | | | I.r. (Nujol) | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | C | H | N | ν(NH) | Thioamide I ν(CN) | Thioamide IV ν(CS) | ν(MS/MX) | ν(C=O) |
| $L^1$ | | | | 3 179 | 1 540 | 872 | | |
| $SbCl_3(L^1)_{1.5}$ | 23.3 (24.0) | 3.8 (4.0) | 9.0 (9.3) | 3 250, 3 266 | 1 571 | 851 | 330, 287, 264 | |
| $SbBr_3(L^1)_{1.5}$ | 11.7 (12.3) | 1.8 (2.1) | 6.6 (7.2) | 3 222 | 1 563 | 853 | 305, 226 | |
| $BiCl_3(L^1)_2 \cdot Me_2CO$ | 19.1 (19.7) | 3.2 (3.6) | 8.0 (8.4) | 3 190 | 1 570 | 861 | 290, 245 | 1 695 |
| $SnCl_4(L^1)$ | 11.2 (11.8) | 1.4 (1.9) | 6.3 (6.9) | 3 239 | 1 583, 1 570 | 865 | 311 | |
| $SnBr_4(L^1)$ | 8.0 (8.2) | 1.1 (1.4) | 4.2 (4.8) | 3 205 | 1 588, 1 571 | 858 | 220 | |
| $TiCl_4(L^1)$ | 14.1 (14.2) | 1.9 (2.4) | 8.0 (8.3) | 3 255, 3 140 | 1 566, 1 553 | 802 | 400, 371, 340 | |
| $L^2$ | | | | 3 166 | 1 523 | 840 | | |
| $SbCl_3(L^2)_{1.5}$ | 21.4 (22.0) | 3.2 (3.7) | 8.1 (8.5) | 3 210, 3 180 | 1 570, 1 543 | 820 | 325, 301, 262 | |
| $SbBr_3(L^2)_{1.5}$ | 17.0 (17.3) | 2.9 (2.9) | 6.2 (6.7) | 3 200, 3 175 | 1 566, 1 542 | 823 | 325, 208 | |
| $BiCl_3(L^2)_2 \cdot Me_2CO$ | 24.0 (24.8) | 3.8 (4.1) | 7.8 (7.7) | 3 180 | 1 550 | 801, 820 | 240 | 1 695 |
| $SnCl_4(L^2)$ | 16.2 (16.5) | 2.2 (2.8) | 6.1 (6.4) | 3 240, 3 201 | 1 573, 1 558 | 803, 821 | 310 | |
| $SnBr_4(L^2)$ | 11.3 (11.7) | 1.4 (1.9) | 4.0 (4.6) | 3 150 | 1 558 | 800, 821 | 322, 210 | |
| $L^3$ | | | | 3 147 | 1 513 | 890 | | |
| $SbCl_3(L^3)_{1.5}$ (1) | 26.4 (27.0) | 4.0 (4.5) | 7.2 (7.9) | 3 160 | 1 542 | 852 | 351, 314, 290, 241 | |
| $SbBr_3(L^3)_{1.5}$ | 20.1 (21.6) | 3.0 (3.6) | 5.9 (6.3) | 3 163 | 1 528 | 850 | 372, 210 | |
| $BiCl_3(L^3)_2 \cdot Me_2CO$ | 28.8 (29.2) | 4.1 (4.9) | 7.0 (7.2) | 3 160 | 1 540 | 846 | 240 | 1 680 |
| $SnCl_4(L^3)$ | 20.0 (20.7) | 3.6 (3.4) | 5.5 (6.0) | 3 245, 3 178 | 1 550, 1 538 | 844 | 328, 297 | |
| $SnBr_4(L^3)$ | 14.4 (14.9) | 2.5 (2.5) | 4.6 (4.4) | 3 195 | 1 540 | 846 | — | |
| $TiCl_4(L^3)$ | 23.9 (24.4) | 3.6 (4.1) | 6.9 (7.1) | 3 235 | 1 550, 1 535 | 851 | 390, 344 | |
| $L^4$ | | | | 3 180 | 1 520 | 888 | | |
| $SbCl_3(L^4)_{1.5}$ | 30.5 (31.2) | 4.8 (5.2) | 7.1 (7.3) | 3 182 | 1 539 | 849 | 313, 295 | |
| $SbBr_3(L^4)_{1.5}$ | 25.6 (25.4) | 3.7 (4.2) | 5.5 (5.9) | 3 181 | 1 525 | 845 | — | |
| $BiCl_3(L^4)_2 \cdot Me_2CO$ | 33.2 (33.0) | 5.1 (5.5) | 6.3 (6.7) | 3 172 | 1 545 | 825 | 240 | 1 695 |
| $SnCl_4(L^4)$ | 23.4 (24.4) | 3.8 (4.1) | 5.8 (5.7) | 3 230, 3 181 | 1 575, 1 550 | 861 | 346, 307 | |
| $SnBr_4(L^4)$ | 17.3 (17.9) | 2.5 (3.0) | 4.4 (4.2) | 3 170 | 1 564 | 865 | — | |
| $TiCl_4(L^4)$ | 29.0 (28.5) | 4.3 (4.7) | 6.1 (6.6) | 3 258, 3 180 | 1 578 | 868 | 400, 353, 314, 255 | |
| $L^5$ | | | | 3 150 | 1 507 | 872 | | |
| $SbCl_3(L^5)_{1.5}$ | 38.1 (38.5) | 5.2 (5.5) | 6.0 (6.4) | 3 158 | 1 545 | 859, 835 | 349, 328, 287 | |
| $SbBr_3(L^5)_{1.5}$ | 31.1 (32.0) | 4.0 (4.6) | 4.9 (5.3) | 3 159 | 1 530 | 859, 831 | — | |
| $SnCl_4(L^5)$ | 30.3 (30.8) | 5.2 (5.1) | 3.3 (4.4) | 3 160 | 1 545 | 835 | 310, 286, 247 | |
| $SnBr_4(L^5)$ | 22.9 (23.3) | 3.0 (3.3) | 4.0 (3.9) | 3 200 | 1 545, 1 530 | 836 | — | |
| $TiCl_4(L^5)$ | 35.1 (35.5) | 4.7 (5.1) | 5.4 (5.9) | 3 178 | 1 556, 1 540 | 835 | 391, 348, 319 | |
| $L^6$ | | | | 3 170 | 1 519 | 874 | | |
| $SbCl_3(L^6)_{1.5}$ | 42.0 (42.5) | 3.1 (3.5) | 5.9 (6.2) | 3 172 | 1 534 | 859 | 350, 308, 220 | |
| $SbBr_3(L^6)_{1.5}$ | 34.9 (35.5) | 2.7 (3.0) | 5.2 (5.2) | 3 160 | 1 532, 1 520 | 855 | 280, 225 | |
| $BiCl_3(L^6)_2$ | 42.8 (43.2) | 3.0 (3.9) | 5.1 (5.8) | 3 165 | 1 522 | 850 | | 1 680 |
| $SnCl_4(L^6)$ | 33.9 (34.3) | 2.9 (2.9) | 4.6 (5.0) | 3 140 | 1 542 | 847 | 335, 320, 286 | |
| $SnBr_4(L^6)$ | 25.1 (26.0) | 2.3 (2.2) | 3.3 (3.8) | 3 140 | 1 540, 1 520 | 820 | — | |
| $TiCl_4(L^6)$ | 39.4 (39.2) | 3.0 (3.3) | 5.3 (5.7) | 3 170 | 1 545 | 844 | 392, 371, 322 | |

In both structures, the Patterson function was used 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. 8. 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[9] at the University of Manchester Computer

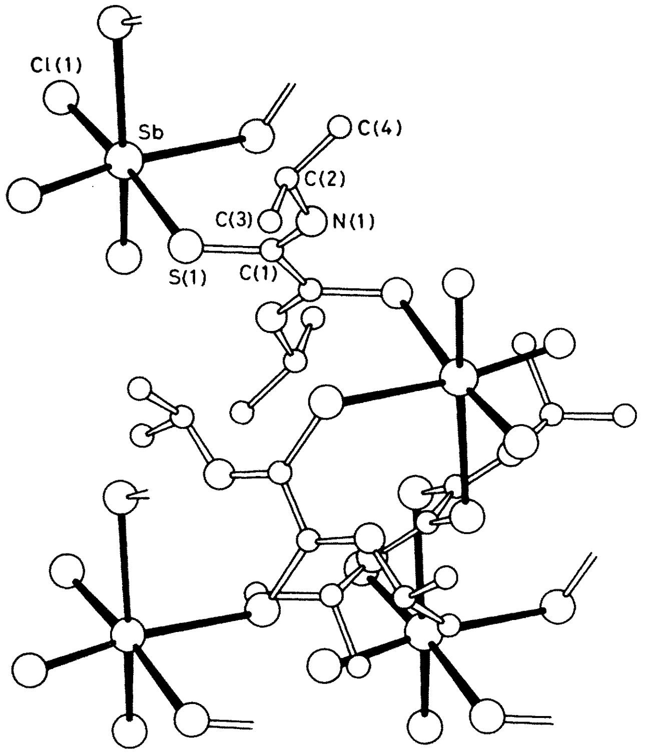

**Figure 1.** The structure of polymeric $SbCl_3(L^3)_{1.5}$ (1; L = *NN'*-di-isopropyldithio-oxamide)

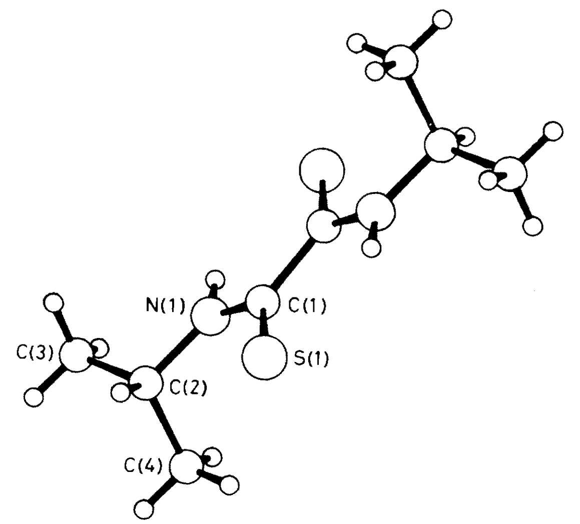

**Figure 2.** The structure of $L^3$, *NN'*-di-isopropyldithio-oxamide

Centre. The final *R* values for (1) and ($L^3$) were 0.068 and 0.077 respectively. Atomic parameters are given in Tables 2 and 3, bond lengths and angles in Table 4.

## Discussion

Direct equimolar addition of the appropriate *NN'*-disubstituted dithio-oxamide (L) and covalent metal halide leads to complex formation of the following types: $MX_3L_{1.5}$ (M = Sb; X = Cl or Br), $BiCl_3L_2$, and $MX_4L$ (M = Sn or Ti; X = Cl or Br). All complexes are listed in Table 5. The stoicheiometries are invariant with conditions of mixing and quantities of reactants. Although several attempts were made, no $As^{III}$ complexes could be isolated to complete the As, Sb, and Bi 'trio' of Group 5B metals. Interestingly, the *NNN'N'*-tetrasubstituted counterparts $R_2NC(S)C(S)NR_2$ (R = Me or Et) have been reported to form adducts with $AsCl_3$.[10] As a general rule, $Sb^{III}$ and $Bi^{III}$ complexes show a greater thermal and hydrolytic stability than their $As^{III}$ counterparts.

Principal i.r. bands are listed in Table 5. Assignments are based on those used by Desseyn and Herman.[1b,c,11] For the $M^{III}$ complexes the shift to lower frequency of the composite thioamide IV band [$\approx$870 $cm^{-1}$ and with high ν(CS) contribution] and the shift to higher frequency of the thioamide I band [$\approx$1 520 $cm^{-1}$ and with a major ν(CN) contribution] confirm a donor role for the S atoms. The shift to higher frequency of the thioamide I band is invariably accompanied by a slight shift to higher frequency of the ν(NH) band (*ca.* 3 150—3 180 $cm^{-1}$) which, in turn, implies neither N→metal co-ordination nor intermolecular hydrogen bonding. The ν(CN) band ($\approx$1 520 $cm^{-1}$) shifts to lower frequency with increasing substitution at the nitrogen centres. A band at *ca.* 1 695 $cm^{-1}$ [ν(CO)] common to all the $Bi^{III}$ complexes is consistent with the inclusion of a molecule of acetone in the crystal lattice.[12]

The $M^{IV}$ complexes show similar shifts in the thioamide I ν(CN) and thioamide IV ν(CS) bands consistent with sulphur co-ordination to metal but both sets now show multiplet character. Such splitting has been noted previously and used as the basis for a *cis SN*-chelate bonding involvement. The structural resolution of $[SnBr_4\{Bu^nNHC(S)C(S)NHBu^n\}]$[12] rules this out (and, incidently, cautions over-indulgent use of i.r. data alone for such bonding assignments) and we favour an explanation based on local lattice imperfections. Within the 400—200 $cm^{-1}$ region, although there can be no clear delineation between metal-halogen and metal-sulphur vibrational modes, general assignments are made as follows: ν(SbCl) 320—350, ν(SbBr) 210—230, ν(TiCl) 270—390, ν(SnCl) 290—350, ν(SnBr) 190—340, ν(SbS) 280—300, and ν(BiS) 240—260 $cm^{-1}$. For the $M^{IV}$ complexes, the presence of multiple ν(MCl) bands tends to favour a *cis* octahedral metal geometry.

Proton n.m.r. data are inconclusive. There is very little difference in chemical shift values for the N(H)R groups on metal complexation: *e.g.* $L^1$, δ(NH) 10.47 (singlet, 2 H), δ(Me) 3.30 (doublet, 6 H); $SbBr_3(L^1)_{1.5}$, δ(NH) 10.39 (singlet, 2 H), δ(Me) 3.27 (doublet, 6 H); $TiCl_4(L^1)$, δ(NH) 10.38 (singlet, 2 H), δ(Me) 3.30 (doublet, 6 H) (for $CDCl_3$ solutions w.r.t. $SiMe_4$). With S donation this is, perhaps, to be expected but we cannot rule out some slight ionisation in solution as evidenced by conductivity measurements in acetonitrile, *e.g.* for $SbBr_3(L^1)_{1.5}$ $\Lambda = 22.4\ \Omega^{-1}\ cm^2\ mol^{-1}$ and for $NEt_4Cl$ $\Lambda = 103.7\ \Omega^{-1}\ cm^2\ mol^{-1}$.

*Discussion of the Structures.*—The structures of polymeric $SbCl_3(L^3)_{1.5}$ (1) and monomeric $L^3$ are shown in Figures 1 and 2 respectively. In (1) the metal atom has crystallographically-imposed three-fold symmetry. The unique Sb–Cl and Sb–S distances are 2.413(2) and 3.197(5) Å respectively. The Sb–Cl bond lengths are slightly longer than the values of 2.340(3), 2.388(3), and 2.381(3) Å found in $SbCl_3(L^2)_{1.5}$ (2; $L^2$ = *NN'*-diethyldithio-oxamide).[6] These shorter values are virtually unchanged from those of pure crystalline $SbCl_3$.[13]

The three Cl–Sb–Cl angles in (1) are all 92.5(2)°. Three sulphur atoms approach the metal octahedral positions to form a *fac* isomer. The distance 3.197(5) Å reflects very weak Sb ··· S interactions. A number of similar adducts of $SbCl_3$ with cyclic thioethers show equivalent Sb ··· S distances

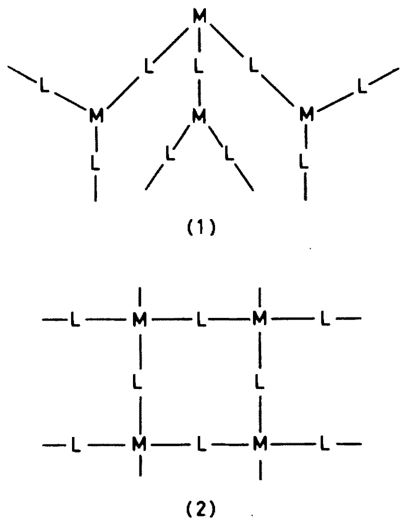

**Figure 3.** The polymeric nature of SbCl$_3$(L$^3$)$_{1.5}$ (1) and SbCl$_3$(L$^2$)$_{1.5}$ (2). M represents the metal, L the S–C–C–S linkage of the ligand

(listed in Part 1, ref. 6). In (1), as in (2),[6] there is no indication that the lone pair is stereochemically active.

The polymeric nature of (1) is unique for this type of SbCl$_3$ adduct. The antimony atom is bonded to three sulphurs from three different ligands. Each ligand has a crystallographically-imposed centre of symmetry and each symmetry-related sulphur atom is then bonded to a different SbCl$_3$ moiety. This is shown in Figure 3. The resulting polymer is three-dimensional. The structure is in sharp contrast to that found in SbCl$_3$(L$^2$)$_{1.5}$ (2) [6] where two polymeric chains are connected by an additional ligand over centres of symmetry. The polymeric nature of complexes (1) and (2) is shown in Figure 3.

In (1) the Sb–S–C angles are 117.1(5)° which are rather larger than those found in (2) [100.8(4), 90.4(3), and 102.8(3)°], but still roughly what would be expected if the Sb–S bonds were far shorter. We suspect that these variations are due to the steric requirements of the polymer chains and do not indicate any difference in the bonding. The ligand has the expected *trans* conformation in both structures. Indeed in L$^3$, as in (1), the centrosymmetric symmetry is crystallographically imposed. In L$^3$ there are two centrosymmetric ligands in the unit cell (Figure 2). The equivalent conformation was found for *NN'*-diethyldithio-oxamide (L$^2$).[6] In L$^2$ there was one N $\cdots$ S intramolecular contact of 3.50 Å which could be indicative of a N–H $\cdots$ S hydrogen bond; in L$^3$ there is no such short contact.

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