N,N'-Disubstituted Dithiomalonamide Complexes of Antimony(III). Crystal and Molecular Structure of $[SbCl_3\{C_2H_5NHC(S)CH_2C(S)NHC_2H_5\}]$ * with Lone-pair Occupation of an Antimony Co-ordination Site

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Direct addition of antimony(III) trichloride to *N,N'*-disubstituted dithiomalonamides, $RHNC(S)CH_2C(S)NHR$ ($R = CH_3$, C_2H_5, i-C_3H_7, n-C_4H_9, or cyclo-C_6H_{11}), gives rise to 1:1 complexes. I.r. and n.m.r. data suggest that the complexes have equivalent structures and the crystal structure of a representative, $[SbCl_3\{C_2H_5NHC(S)CH_2C(S)NHC_2H_5\}]$, has been determined. Crystals are monoclinic, space group $P2_1$, $a = 10.841(8)$, $b = 8.276(9)$, $c = 10.185(11)$ Å, $\beta = 120.9(1)°$, and $Z = 2$. 558 Independent data above background have been refined to $R = 0.099$. The antimony atom is bonded to three chlorine atoms [Sb–Cl 2.344(17), 2.580(14), 2.576(15) Å] and two sulphur atoms of the bidentate thiomalonamide [2.66(1), 2.74(2) Å]. The antimony environment is six-co-ordinate octahedral with the lone pair occupying one site.

Recent work in these laboratories has been concerned with the co-ordination profile of dithio-oxamides, RHNC(S)C(S)NHR (R = alkyl), with selected covalent metal halides.[1–3] Specifically Sb^{III} gives polymeric pseudo-octahedral complexes in which each ligand is bound to two separate metal centres *via* SS-bidentate bridging. The observed distortions are ascribed to crystal packing factors; they are not consistent with deformation of O_h symmetry arising from lone-pair stereochemical activity.

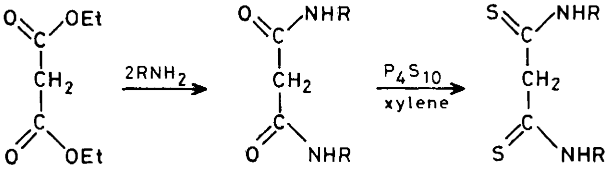
As a natural progression we are investigating the co-ordination behaviour of the corresponding dithiomalonamides, $RHNC(S)CH_2C(S)NHR$, where the introduction of a CH_2 'hinge' to the C_2 backbone not only adds a useful spectroscopic 'flag' but, more importantly, provides a more amenable 'bite' angle and increased skeletal flexibility on the part of the ligand. Several complexes have been reported in the literature but there are no structural data.[4] Hard-soft acid-base[5] considerations give preference of S- rather than N-donor involvement for Sb^{III} with either SS chelation leading to formation of a six-membered SbS_2C_3 ring system or SS bridging across Sb^{III} centres.

From the several *N,N'*-disubstituted dithiomalonamide complexes with Sb^{III} trichloride (1:1) reported here, the crystal and molecular structure of $[SbCl_3\{C_2H_5NHC(S)CH_2C(S)NHC_2H_5\}]$ (1) has been determined as an exemplar. Of particular interest is the stereochemical role played by the lone pair of electrons associated with Sb^{III} in affecting deviations from a regular co-ordination geometry. For (1), where we have a representative AX_3YYE system[6] (A = Sb, X = Cl, Y = S, E = lone pair), there is clear evidence that the non-bonding pair of electrons occupy one site of the octahedral metal environment.

Experimental

All manipulations were conducted under an inert atmosphere most often utilising a dry-nitrogen flushed gloved-box. Solvents (AnalaR) were stored over calcium hydride and/or phosphorus pentoxide and distilled under a nitrogen atmosphere as and when required. Antimony(III) chloride was sublimed *in vacuo* prior to use. I.r. spectra were recorded using a Perkin-Elmer 580B spectrophotometer with samples as Nujol mulls between CsI plates. Mass spectral measurements were carried out using a Kratos MS80 spectrometer (EI 70 eV, source temperature 473 K) using the direct inlet procedure. ^1H N.m.r. spectra were obtained from a Perkin-Elmer R34 (220 MHz) instrument with $CDCl_3$ solutions doped with $SiMe_4$ ($\delta = 0$ p.p.m.) as internal reference. C, H, N, and S analyses were performed by Elemental Micro-Analysis Ltd., Beaworthy, Devon.

Preparation of Ligands.—The malonamide derivatives (as obtained from the appropriate aminolysis of diethyl malonate) were treated with P_4S_{10} in boiling xylene, equation (1), where



(1)

$R = CH_3$ (dmdtm), C_2H_5 (dedtm), i-C_3H_7 (dpdtm), n-C_4H_9 (dbdtm), or cyclo-C_6H_{11} (dchdtm).

Preparation of Metal Complexes.—The preparation of $[SbCl_3\{C_4H_9NHC(S)CH_2C(S)NHC_4H_9\}]$ is given as a typical example.

A solution of *N,N'*-di-n-butyldithiomalonamide (0.97 g, 3.9 mmol) in benzene (100 cm^3) was added dropwise to a stirred solution of antimony trichloride (0.90 g, 3.9 mmol) in benzene (70 cm^3) maintained at 273 K. The resulting solution was stirred overnight. Solvent was removed slowly until the onset of crystallisation. The orange crystals which deposited over a period of 24 h were collected, washed with n-hexane (2 × 25 cm^3), and pumped *in vacuo* at room temperature for several hours. For storage the crystalline product is best sealed in glass ampoules under a nitrogen atmosphere. Analytical data for this and other products are collected in Table 1.

Structure Determination.—*Crystal data.* $C_7H_{14}Cl_3N_2S_2Sb$, $M = 418.3$, monoclinic, space group $P2_1$, $a = 10.841(8)$, $b =$

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* Trichloro(*NN'*-diethyldithiomalondiamide-*SS'*)antimony(III).

Supplementary data available (No. SUP 56176, 4 pp.): anisotropic thermal parameters, H-atom positions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

8.276(9), c = 10.185(11) Å, β = 120.9(1)°, U = 757.7 Å^3, D_m = 1.55, Z = 2, D_c = 1.55 g cm^{-3}, $F(000)$ = 408, λ = 0.7107 Å, μ(Mo-K_α) = 23.3 cm^{-1}.

Suitable crystals were obtained as described above and placed in Lindemann tubes. Precession photographs established preliminary cell constants and the space group. A crystal was transferred to a Stoe STADI-2 diffractometer and 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. 1 014 Independent reflections were measured with a 2θ maximum of 40°, of which 558 with $I > 2\sigma(I)$ were used in subsequent calculations.

The Patterson function was used to determine the positions of the antimony atoms. In (**1**) the remaining atoms were located from Fourier maps. Hydrogen atoms were included in calculated positions and their thermal parameters refined. Methyl group hydrogen atoms could not be located. Hydrogen atoms on the same carbon atom were given an equivalent thermal parameter. The antimony, chlorine, and sulphur atoms were refined anisotropically; nitrogen, carbon, and hydrogen isotropically. The N–C and C–C bond distances were constrained to be equivalent and the structure refined *via* full-matrix least squares, final R = 0.099 (R' = 0.102). The opposite (and rejected) enantiomorph gave R = 0.104. Scattering factors and values for anomalous dispersion were obtained from ref. 7. 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[8] at the University of Manchester Computer Centre. Final atomic co-ordinates are given in Table 2, bond lengths and angles in Table 3.

Table 1. Analytical data (%) for the complexes*

Complex	C	H	N	Cl
[SbCl$_3$(dmdtm)]	16.7 (15.4)	2.5 (2.6)	7.0 (7.2)	27.4 (27.3)
[SbCl$_3$(dedtm)]	20.2 (20.1)	3.2 (3.3)	7.0 (6.7)	26.2 (25.5)
[SbCl$_3$(dpdtm)]	24.0 (24.2)	3.9 (4.0)	6.2 (6.3)	24.7 (23.9)
[SbCl$_3$(dbdtm)]	26.8 (27.8)	4.5 (4.6)	5.2 (5.9)	21.3 (22.5)
[SbCl$_3$(dchdtm)]	33.7 (34.2)	4.7 (4.9)	4.9 (5.3)	12.0 (12.2)

* Calculated values are given in parentheses.

Discussion

Direct addition of antimony(III) chloride to the appropriate dithiomalonamide leads to orange-red complexes with 1:1 stoicheiometry which are extremely air- and moisture-sensitive (see Table 1). Solubility is limited to the more polar solvents such as acetonitrile, dichloromethane, and acetone.

The i.r. data are given in Table 4. The observed high-energy shift (+32 cm^{-1} on average) of the ν(CN) absorption (*ca.* 1 540 cm^{-1}) accompanied by the low-energy shift (−90 cm^{-1} on average) of the ν(CS) band (*ca.* 870 cm^{-1}) are in accord with *S* donation.[4,9]

The ν(NH) and π(NH) vibrations remain essentially unchanged. In the ν(SbCl) stretching region we find two broad and intense bands at *ca.* 320 and 250 cm^{-1} [which, doubtless, have ν(SbS) components],[9c] suggestive of octahedral Sb^{III} species.

The ^{1}H n.m.r. data of the complexes simply reinforce the non-co-ordination of NH sites and are without controversy. Typically, (**1**) shows δ_H (220 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.58 (2 H, s, 2NH), 4.09 (2 H, s, $-CH_2-$), 3.65 (4 H, m, 2 $-CH_2-CH_3$), 1.22 (6 H, t, 2 $-CH_2-CH_3$). Uncomplexed ligand shows δ_H 9.52 (2 H, s, 2NH), 4.01 (2 H, s, $-CH_2-$), 3.62 (4 H, m, 2 $-CH_2-CH_3$), 1.20 (6 H, t, 2 $-CH_2-CH_3$). Clearly the backbone CH$_2$ retains its identity and there can be no question of pseudo-aromaticity around the six-membered SbS$_2$C$_3$ chelate ring incipient with proton loss.

The structure of (**1**) is shown in the Figure together with the atom numbering scheme. The antimony atom is bonded to three chlorine atoms and two sulphurs of the chelated bidentate dithiomalonamide. The environment of the antimony atom is six-co-ordinate with the lone pair occupying one site. An AB$_5$E type geometry (A = metal, B = ligand, E = lone pair) is well established for Sb^{III} compounds, as for example in [NH$_4$]$_2$-[SbCl$_5$][10] and K$_2$[SbCl$_5$].[11] In such octahedral compounds, the bond lengths *cis* to the lone pair (observed in the range 2.5—2.8 Å) are lengthened relative to the bond length *trans* to the

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sb(1)	1 723(3)	2 500	3(4)	C(3)	2 028(44)	6 091(56)	−1 463(45)
Cl(1)	3 620(17)	980(23)	23(15)	N(1)	3 926(54)	7 762(87)	2 397(51)
Cl(2)	−155(19)	542(22)	−2 059(16)	N(2)	1 785(66)	7 665(115)	−2 360(69)
Cl(3)	1 927(18)	636(21)	2 128(16)	C(11)	5 683(54)	7 267(66)	3 721(50)
S(4)	4 000(16)	4 285(16)	2 022(15)	C(12)	5 931(57)	8 960(66)	4 508(54)
S(5)	2 093(19)	4 352(21)	−2 005(15)	C(21)	1 678(84)	7 579(123)	−3 916(79)
C(1)	3 387(37)	6 259(44)	1 338(39)	C(22)	1 748(65)	8 946(90)	−4 683(65)
C(2)	1 866(44)	6 381(55)	30(46)				

Table 3. Bond lengths (Å) and angles (°)

Sb(1)–Cl(1)	2.344(17)	Sb(1)–S(5)	2.738(17)	C(1)–N(1)	1.55(7)	N(2)–C(21)	1.53(9)
Sb(1)–Cl(2)	2.580(14)	S(4)–C(1)	1.76(4)	C(2)–C(3)	1.63(9)	C(11)–C(12)	1.57(5)
Sb(1)–Cl(3)	2.576(15)	S(5)–C(3)	1.56(5)	C(3)–N(2)	1.53(10)	C(21)–C(22)	1.40(6)
Sb(1)–S(4)	2.658(11)	C(1)–C(2)	1.46(8)	N(1)–C(11)	1.68(6)		

Cl(1)–Sb(1)–Cl(2)	87.6(6)	Cl(3)–Sb(1)–S(5)	168.6(5)	S(5)–C(3)–C(2)	121(5)
Cl(1)–Sb(1)–Cl(3)	88.2(6)	S(4)–Sb(1)–S(5)	81.4(5)	S(5)–C(3)–N(2)	127(4)
Cl(2)–Sb(1)–Cl(3)	90.4(5)	Sb(1)–S(4)–C(1)	102.1(10)	C(2)–C(3)–N(2)	111(6)
Cl(1)–Sb(1)–S(4)	82.6(5)	Sb(1)–S(5)–C(3)	101.8(19)	C(1)–N(1)–C(11)	103(4)
Cl(2)–Sb(1)–S(4)	169.9(6)	S(4)–C(1)–C(2)	115(5)	C(3)–N(2)–C(21)	119(8)
Cl(3)–Sb(1)–S(4)	91.7(5)	S(4)–C(1)–N(1)	123(3)	N(1)–C(11)–C(12)	91(4)
Cl(1)–Sb(1)–S(5)	82.0(6)	C(2)–C(1)–N(1)	115(6)	N(2)–C(21)–C(22)	123(8)
Cl(2)–Sb(1)–S(5)	94.9(5)	C(1)–C(2)–C(3)	105(6)		

Table 4. Principal i.r. bands (cm^{-1}) of ligands and metal complexes

Compound	ν(NH)	Thioamide I ν(CN)	Thioamide IV ν(CS)	Thioamide V π(NH)	ν(MCl/MS)
dedtm	3 186, 3 057	1 540	875	722	
dpdtm	3 194, 3 060	1 542	874	719	
dbdtm	3 191, 3 040	1 536	890	732	
dchdtm	3 518, 3 282, 3 230, 3 050	1 541	895	746	
[SbCl$_3$(dmdtm)]	3 206, 3 109	1 584	785	722	315, 250
[SbCl$_3$(dedtm)]	3 180, 3 060	1 572	803	717	320, 276, 240
[SbCl$_3$(dpdtm)]	3 188, 3 044	1 577	790	721	318, 279
[SbCl$_3$(dbdtm)]	3 264, 3 200, 3 068	1 565	782	730	323, 275, 231
[SbCl$_3$(dchdtm)]	3 260, 3 078	1 561	790	758	321, 288

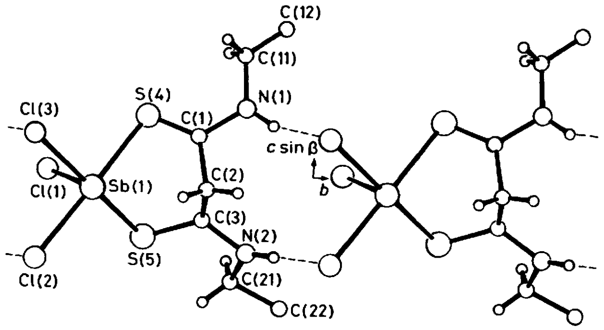

Figure. The structure of (**1**) (*a* projection) showing the intramolecular hydrogen bonds which form a chain between molecules along the *b* axis. Hydrogen atoms on the methyl carbons C(12) and C(22) were not located

lone pair (observed 2.35—2.39 Å). The same pattern is observed in (**1**), *i.e.* Sb–Cl(1) 2.344(17) Å (*trans* to the lone pair) is much shorter than Sb–Cl(2) [2.580(14) Å] and Sb–Cl(3) [2.576(15) Å] which are mutually *cis* to the lone pair.

The Sb–S distances, at 2.66(1) and 2.74(2) Å, are considerably shorter than values found in a whole range of SbCl$_3$ adducts with other sulphur-donor ligands including dithio-oxamides,[1—3] where Sb–S values are *ca.* 3.2 Å. For the latter the dithio-oxamide ligand forms a bridge between adjacent antimony atoms and the lone pair is inactive. It is possible that the ligand bite in dithio-oxamides is too small for chelate formation. The bite in dithiomalonamides is larger and more flexible.

From our observations it would appear that the stereoactivity of the lone pair is concomitant with formation of a six-membered chelate ring and strong Sb–S bonds. Where the ligand is unidentate, and therefore weakly bonded, the lone pair is not active.

In (**1**) the antimony atom is distorted from the equatorial plane by 0.20 Å towards the lone pair; angles subtended at the metal involving Cl(1) with *cis* atoms are for Cl(2) 87.6(6), Cl(3) 88.2(6), S(4) 82.6(5), and S(5) 82.0(6)°.

The molecules in the unit cell are connected in the *y* direction by intramolecular hydrogen bonds N(1)–H(1)···Cl(3) and N(2)–H(2)···Cl(2) (see Figure). Dimensions are N(1)···Cl(3) 3.09, NH(1)···Cl(3) 2.14 Å; N(1)–H(1)···Cl(3) 173°; N(2)···Cl(2) 3.25, NH(2)···Cl(2) 2.41 Å; N(2)–H(2)···Cl(2) 147°. Similar NH···halogen contacts were also found in the dithio-oxamide structures.[1—3]

The present structure is to our knowledge the first example of an antimony(III) complex with a *cis*-chelating ligand resulting in a square-pyramidal complex.

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