Unexpected Cyclisation of *NN'*-Diethyldithiomalonamide. Crystal and Molecular Structure of $[EtNHC(S)CHC(S)NHEt]_2[SnCl_6]$ *

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The title compound, $[EtNHC(S)CHC(S)NHEt]_2[SnCl_6]$, was obtained unexpectedly following benzene recrystallisation of the product isolated from the reaction of $SnCl_4$ with *NN'*-diethyldithiomalonamide. The proposed mechanism involves initial 1 : 1 adduct formation with a subsequent chelotropic rearrangement. The compound is triclinic, space group $P\bar{1}$, with $a = 9.047(7)$, $b = 9.429(8)$, $c = 9.935(8)$ Å, $\alpha = 80.4(1)$, $\beta = 63.0(1)$, $\gamma = 65.6(1)°$, and $Z = 1$. 3 260 Independent reflections above background were measured on a diffractometer and the structure refined to R 0.064. The structure consists of independent cations and anions connected by intermolecular hydrogen bonds.

Among the numerous metal complexes of the dithiomalonamides $RNHC(S)CH_2C(S)NHR$, under spectral and structural investigation in our laboratories, that resulting from the 1 : 1 molar addition of $SnCl_4$ to $EtNHC(S)CH_2C(S)NHEt$ has received especial scrutiny. At the outset there was no real reason to suspect the product to be anything other than an octahedral species featuring *cis SS'*-ligand chelation much as described recently for the dithio-oxamide counterpart $[SnBr_4\{Bu^nNHC(S)C(S)NHBu^n\}]$.[1] Suitable crystals for an *X*-ray crystallographic study were ultimately isolated from benzene solutions. However, this product is not the presumed six-co-ordinate neutral adduct but rather the ionic salt $[EtNHC(S)CHC(S)NHEt]_2[SnCl_6]$ (1) featuring the hexachlorostannate(IV) ion.

Tin(IV) halides readily form octahedral hexahalogenometalates of the type $A_2[SnX_6]$ (A = univalent cation, X = halogen) on addition of excess halide.[2] These are commonplace and structural studies utilising both single-crystal *X*-ray diffraction [3] and halogen n.q.r.[4] techniques show conspicuous variations of Sn–X bond lengths within these $[SnX_6]^{2-}$ species; evidently the choice of cation is crucial especially where hydrogen bonding may reasonably be expected.[4d,5]

The structural data of our interesting hexachlorostannate species (1) are presented and discussed along with a plausible reaction sequence to explain its formation.

Experimental

NN'-Diethyldithiomalonamide (0.64 g, 3.3 mmol) in benzene (50 cm^3) was added dropwise to a chilled (273 K) solution of tin(IV) chloride (0.4 cm^3, 3.5 mmol) in benzene (50 cm^3). The resulting pink suspension was stirred for several hours at room temperature after which time the benzene was decanted to leave a pink solid which was washed with hexane (2 × 50 cm^3) and then dried *in vacuo*. Repeated extraction of this pink powder with boiling benzene resulted in a clear yellow solution. Slow evaporation of this saturated solution maintained under a nitrogen atmosphere at room temperature gave yellow needle crystals of (1) suitable for crystallographic study (Found: C, 23.4; H, 3.6; N, 8.1. Calc. for $C_{14}H_{26}Cl_6N_4S_4Sn$: C, 23.7; H, 3.7; N, 7.9%).

Crystal Data.—$C_{14}H_{26}Cl_6N_4S_4Sn$, $M = 709.8$, triclinic, $a = 9.047(7)$, $b = 9.429(8)$, $c = 9.935(8)$ Å, $\alpha = 80.4(1)$, $\beta = 63.0(1)$, $\gamma = 65.6(1)°$, $U = 687.5$ Å^3, $D_m = 1.71$, $Z = 1$, $D_c = 1.71$ g cm^{-3}, $\mu = 18.1$ cm^{-1}, $\lambda = 0.7107$ Å, space group $P\bar{1}$.

The crystal selected for *X*-ray data collection had dimensions 0.3 × 0.3 × 0.3 mm. Intensity data were collected on a Stoe STADI-2 diffractometer using ω scans of width $(1.5 + 0.5 \sin\mu/\tan\theta)$. 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. 3 716 Independent reflections with $2\theta < 50°$ were measured of which 3 260 with $I > 3\sigma(I)$ were used in the subsequent refinement.

The Patterson function indicated the presence of a heavy atom at the origin. 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. Scattering factors and dispersion corrections were taken from ref. 6. Calculations were carried out using SHELX 76 [7] at the University of Manchester Computer Centre. The final R value was 0.064 (R' 0.068). Atomic parameters are given in Table 1, bond lengths and angles in Table 2.

Discussion

The observed pink to yellow colour change following recrystallisation from benzene provided the first indication of the structural reorganisation of the Sn^{IV} complex. In the i.r. spectrum of (1), ligand modifications included a shift to higher energy of ν(NH) (3 180 ⟶ 3 280 cm^{-1}), increased multiplicity of the thioamide I ν(CN) band based at 1 545 cm^{-1}, and a low-energy shift of 85 cm^{-1} of the thioamide IV ν(CS) band reflecting a marked change in the C=S bond order. A new intense band at 514 cm^{-1} is assigned to a ν(S–S) vibrational mode.[8] The presence of two ν(SnCl) stretching bands at 310 and 280 cm^{-1} suggests some localised variations in metal-halogen bond lengths within the basic octahedral $[SnCl_6]^{2-}$ species.

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* Bis[3,5-bis(ethylamino)-1,2-dithiolylium]hexachlorostannate(2−).

Supplementary data available (No. SUP 23954, 17 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

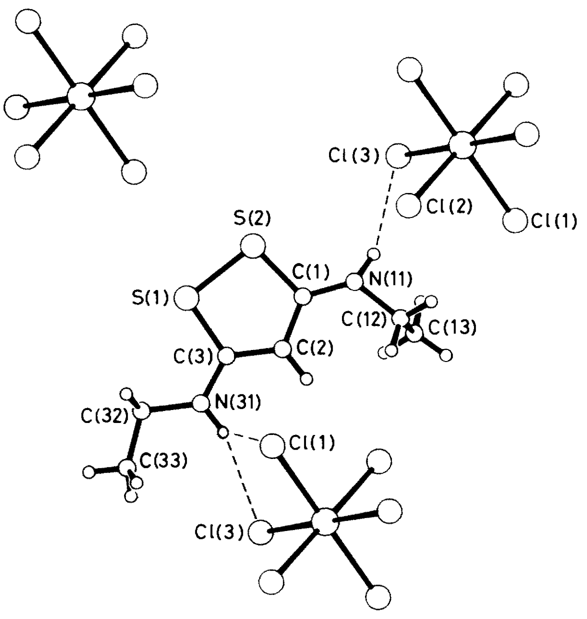


Figure. The environment of one $[\mathrm{EtNHC(S)CHC(S)NHEt}]^+$ cation showing the intermolecular hydrogen bonds

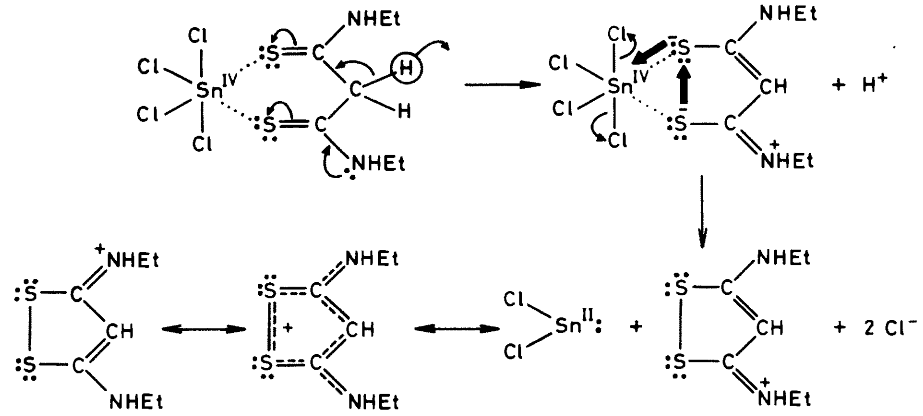
The proposed mechanism involves initial 1 : 1 adduct formation with a subsequent chelotropic rearrangement (see Scheme). The fate of the H^+ and Sn^{II} species is unknown. The ^1H n.m.r. spectrum of (1) {δ_H [220 MHz, solvent $(CD_3)_2CO$, standard $SiMe_4$]: 1.28 (t, 6 H, $2CH_3$), 3.62 (m, 4 H, $2CH_2$), 7.35 (s, 1 H, CH), and 9.90 p.p.m. (br, s, 2 H, 2NH)} shows only one major and significant change compared with that of neat ligand, *i.e.* the appearance of the methine (=CH−) singlet (δ 7.35) at the expense of the original methylene ($-CH_2-$) singlet (δ 6.03).

Discussion of the Structure.—The structure of the salt (1) consists of discrete centrosymmetric $[SnCl_6]^{2-}$ anions and $[\mathrm{EtNHC(S)CHC(S)NHEt}]^+$ cations in the ratio 1 : 2. The ions are connected *via* N−H ··· Cl hydrogen bonds which are illustrated in the Figure. The atom N(11) is involved in a single strong hydrogen bond [*viz.* N(11) ··· Cl(3) 3.33 Å $(1-x, 1-y, -z)$, N(11)−H ··· Cl(3) 165°]. However the arrangement around N(31) is more complicated; N(31) forms a hydrogen bond with Cl(3), *viz.* N(31) ··· Cl(3) 3.54 Å $(-x, 1-y, 1-z)$, N(31)−H ··· Cl(3) 153°; it also has a short contact with Cl(1) of the same anion [N(31) ··· Cl(1) 3.46 Å, N(31)−H ··· Cl(1) 105°]. Although N(31) is closer to Cl(1) than Cl(3), the hydrogen atom is closer to Cl(1). It seems likely therefore that N(31) probably forms two weak hydrogen bonds to two chlorines from a $[SnCl_6]^{2-}$ anion. This hydrogen-bond formation has been previously recognised in, and is a significant feature of, the structures of dithio-oxamide and dithiomalonamide metal complexes. Thus in both $BiCl_3(L^1)_2$ and $SnBr_4L^2$ where L^1 and L^2 are dithio-oxamides, all the —NH groups are involved in hydrogen bonding,[1] as indeed occurs also in $SbCl_3L^3$ where L^3 is *NN'*-diethyldithiomalonamide.[9]

In the present structure, the three Sn−Cl bond lengths are different: Sn−Cl(1) 2.422(1), Sn−Cl(2) 2.405(1), and Sn−Cl(3) 2.467(1) Å. It is significant that the longest Sn−Cl bond involves the chlorine atom Cl(3) that forms the strongest hydrogen bond. Indeed all three bond lengths are consistent with the premise that the formation of hydrogen bonds lengthens the Sn−Cl bond.[5a]

The five-membered 1,2-dithiolylium ring in the cation is planar within experimental error. Of the non-hydrogen atoms only C(12) at 0.05 Å and C(13) at 1.49 Å deviate significantly from this ring plane.

A search of the Cambridge Data Centre files showed that only two structures had been previously determined which include the cationic S_2C_3 ring and two nitrogen substituents: 3,5-bis(acetamido)-1,2-dithiolylium bromide[10] (2), in which S−S is 2.075(2) Å, and 3,5-bis(amino)-1,2-dithiolylium iodide[11] (3), in which S−S is 2.08(2) Å. In (1) the S(1)−S(2) distance is 2.063(3) Å and the remaining dimensions of the five-membered ring are similar within experimental error to those found in the other two cations of (2) and (3). The S−S distances in these three similar structures are longer than expected. Of 21 crystal structures[12] with S−S bonds present, the actual bond length of a disulphide unit varies between 1.999 and 2.098 Å. A correlation was found between the S−S bond lengths and the X−C−S−S (X = C or N) torsion angle. When X−C−S−S lies between −20 and 20°, the average S−S bond length is 2.03 Å (15 structures) while if it lies between 70 and 90° the distance is 2.08 Å (six structures). In (1) the torsion angles are close to 0° and therefore the S−S distance is expected to be *ca.* 2.03 Å. Indeed, it is interesting that the structures of the 3- and 4-phenyl-1,2-dithiolylium ions[13,14] show S−S distances of



Scheme.

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

Atom	*x*	*y*	*z*
Sn(1)	0(0)	0(0)	0(0)
Cl(1)	−1 008(2)	1 692(2)	2 089(1)
Cl(2)	2 831(2)	303(2)	−1 187(2)
Cl(3)	−1 297(2)	2 294(2)	−1 304(2)
S(1)	6 943(3)	3 747(2)	5 566(2)
S(2)	8 365(3)	4 974(2)	3 984(2)
C(1)	7 234(7)	6 684(7)	5 098(6)
C(2)	5 908(7)	6 628(6)	6 523(6)
C(3)	5 635(7)	5 251(5)	6 920(6)
N(11)	7 688(8)	7 882(7)	4 509(6)
C(12)	6 959(9)	9 348(7)	5 313(8)
C(13)	7 940(12)	9 255(9)	6 252(11)
N(31)	4 425(7)	5 014(5)	8 237(6)
C(32)	4 115(11)	3 569(8)	8 649(9)
C(33)	2 674(20)	3 698(12)	10 162(11)

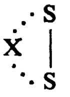
Table 2. Dimensions; bond lengths (Å) and angles (°)

Sn(1)–Cl(1)	2.422(1)
Sn(1)–Cl(2)	2.405(1)
Sn(1)–Cl(3)	2.467(1)
S(1)–S(2)	2.063(3)
S(1)–C(3)	1.738(5)
S(2)–C(1)	1.754(6)
C(1)–C(2)	1.390(7)
C(1)–N(11)	1.316(8)
C(2)–C(3)	1.382(7)
C(3)–N(31)	1.329(7)
N(11)–C(12)	1.455(9)
C(12)–C(13)	1.525(11)
N(31)–C(32)	1.459(7)
C(32)–C(33)	1.458(11)
Cl(1)–Sn(1)–Cl(2)	90.59(5)
Cl(1)–Sn(1)–Cl(3)	89.26(5)
Cl(2)–Sn(1)–Cl(3)	90.72(6)
S(2)–S(1)–C(3)	94.63(20)
S(1)–S(2)–C(1)	95.49(20)
S(2)–C(1)–C(2)	115.3(4)
S(2)–C(1)–N(11)	117.9(4)
C(2)–C(1)–N(11)	126.8(5)
C(1)–C(2)–C(3)	117.6(4)
S(1)–C(3)–C(2)	117.0(4)
S(1)–C(3)–N(31)	118.3(3)
C(2)–C(3)–N(31)	124.8(4)
C(1)–N(11)–C(12)	124.7(5)
N(11)–C(12)–C(13)	111.5(5)
C(3)–N(31)–C(32)	124.8(5)
N(31)–C(32)–C(33)	111.2(5)

2.028(10) and 1.998(10) Å consistent with the data from ref. 12. Later work with other 4-phenyl-1,2-dithiolylium halides [15,16] also gave S–S bond distances of *ca.* 2.02 Å.

The 1,2-dithiolylium cation has an aromatic sextet which on delocalisation around the S_2C_3 ring should lead to a shortening of the S–S bond as a result of a π component; calculations indicate a probable bond length of *ca.* 2.00 Å.[17] As pointed out by Hordvik,[10,11] the observed lengthening of S–S in (2) and (3) to an approximate single bond length (2.08 Å) can be viewed as a direct result of the nitrogen substituents at the 3- and 5-positions. These give rise to multiple C–NH_2 (3) and C–$NHCOCH_3$ (2) bonding interactions at the expense of the π bonding in the sulphur–sulphur linkage.

The same rationale can be used here for (1) where we have NHEt group substituents at the 3- and 5-positions (see Scheme). The observed N–C distances, 1.329(7) and 1.316(8) Å, imply an appreciable π-bond component.

In the 1,2-dithiolylium halides, it was found [18] that the sulphur atoms have close interactions (*ca.* 3.5 Å) with the halide anions in both linear X ··· S–S ··· X and triangular  arrangements. In the present structure (see Figure) there is an SSCl 'triangular' interaction in evidence, the S ··· Cl distances being rather long at 3.55 and 3.60 Å [S(1) ··· Cl(1) and S(2) ··· Cl(1) (1 + *x*,*y*,*z*)] respectively and these could represent just van der Waals contacts. However the Cl(1) atom is only *ca.* 1.0 Å from the ring plane.

Acknowledgements

We thank the S.E.R.C. for funds for the diffractometer and A. W. Johans for his help with the crystallographic investigations. J. M. K. thanks the E.E.C. for a research grant.

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Received 23rd November 1983; Paper 3/2082