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The Crystal and Molecular Structure of Dichloro(thiourea)tin(II)

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Crystals of dichloro(thiourea)tin(II), from tin(II) chloride and thiourea, are monoclinic, space group $P2_1/c$, with a = 5.951(2), b = 13.937(4), c = 8.883(3) Å, β = 111.13(2)°. The structure was solved by Patterson and Fourier techniques, and refined by full-matrix, anisotropic least-squares methods to a final R-value of 0.0348 for 943 independent, non-zero reflections with $I > 3\sigma(I)$. The basic unit of the structure is the $SnCl_2[SC(NH_2)_2]$ unit (Sn–Cl = 2.492(4) and 2.609(4) Å, Sn–S = 2.704(4) Å, valence angles at tin = 88.0(1), 90.6(1), 93.5(1)°). These formula units are tightly bound into chains via chlorine and sulphur bridging, which are, in turn, weakly bound by interchain chlorine bridges into sheets which are reinforced by N–H···Cl hydrogen bonds. Additional N–H···Cl hydrogen bonds connect adjacent sheets forming a three-dimensional network.

Introduction

Although the structures of complexes of tin(II) chloride with oxygen donors such as water [1] and dioxan [2] have been reported, no structural information is available concerning the interaction with sulphur donors. In this paper we report the crystal and molecular structure of the 1:1 complex with thiourea.

Experimental

Synthesis

Tin(II) chloride dihydrate (4.52 g, 0.02 mol) was dissolved in *ca.* 4 cm^3 of cold water to yield a clear, colourless solution. Thiourea (0.76 g, 0.01 mol) was dissolved in the minimum of cold water and the two solutions were mixed and left to stand in the dark for *ca.* one week. Small colourless prismatic crystals were deposited and these were collected in a filter-tube and washed with small quantities of methanol and sodium-dried ether. The crystals were dried *in vacuo* and stored under nitrogen (Found: Cl 27.96, S 12.87, C 5.63, N 10.16, H 1.75%; Calculated for $SnCl_2 \cdot SC(NH_2)_2$: Cl 26.69, S 12.07, C 4.52, N 10.54, H. 1.52%).

Crystal Structure Determination

$CH_4Cl_2N_2SSn$; M = 265.716; Monoclinic; Space group $P2_1/c$; a = 5.951(2), b = 13.937(4), c = 8.883(3) Å, β = 111.13(2)°; U = 687.21 Å^3; D_m = *ca.* 2.5 g cm^{-3}; D_c = 2.568 g cm^{-3}; Z = 4; F(000) = 496; Mo-k$_\alpha$ radiation (λ = 0.71069 Å); (Mo-k$_\alpha$) = 46.79 cm^{-1}. Crystal Dimensions, 0.25 × 0.25 × 0.40 mm^3.

Structure Determination and Refinement

Intensity data were collected in the θ range 0–27.5°, corresponding to the range: $0 < h < 9$; $0 < k < 20$; $-14 < l < 14$.

943 independent, non-zero reflections for which $I > 3\sigma(I)$, were corrected for Lorentz and polarisation effects, but not for absorption (μ = 46.79 cm^{-1}). Atomic positions of non-hydrogen atoms were located by usual Patterson and Fourier techniques. All atomic coordinates were refined by full-matrix anisotropic least-squares methods, converging at a conventional R-value of 0.0348. Atomic scattering factors were obtained from reference 3. All data refinement was carried out using the CRYSTALS suite of programmes [4].

Final values of the fractional atomic coordinates and anisotropic temperature factors are given in Tables I and II respectively. Interatomic distances and angles are quoted in Table III.

Discussion

Preparation and Physical Properties

Dichloro(thiourea)tin(II) has been prepared by the reaction of tin(II) chloride dihydrate and thiourea

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TABLE I. Final Fractional Atomic Coordinates for $SnCl_2 \cdot SC(NH_2)_2$ (estimated standard deviations in parentheses).

Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.07202(8)	0.24500(5)	0.34931(7)
Cl(1)	0.1181(3)	0.1180(2)	0.5742(3)
Cl(2)	0.5198(3)	0.2576(2)	0.4518(3)
S(1)	0.0608(3)	0.1042(2)	0.1374(3)
C(1)	0.319(1)	0.0359(7)	0.225(1)
N(1)	0.324(1)	−0.0350(7)	0.318(1)
N(2)	0.514(1)	0.0546(7)	0.186(1)

in aqueous solution. It is a colourless, crystalline solid, containing no water of crystallisation, which melts at 158–160 °C. It is soluble in common polar solvents and, although stable to atmospheric oxidation and hydrolysis, attempts to recrystallise it from methanol in air result in oxidation, shown by a change of colour to yellow and the appearance of a ^{119m}Sn Mössbauer resonance at about 0.1 mm s^{-1}.

The Structure of Dichloro(thiourea)tin(II)

Figure 1 shows a diagrammatic representation of the asymmetric unit of (thiourea)tin(II) chloride

TABLE II. Final Anisotropic Thermal Parameters for $SnCl_2 \cdot SC(NH_2)_2$ (estimated standard deviations in parentheses).[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	2.66(2)	3.59(3)	3.71(3)	0.09(3)	1.46(2)	0.24(2)
Cl(1)	3.42(9)	3.6(1)	4.3(1)	0.7(1)	2.19(9)	0.35(7)
Cl(2)	2.62(8)	5.6(1)	5.1(1)	−0.9(1)	1.69(8)	−0.51(9)
S(1)	2.47(8)	3.4(1)	3.4(1)	0.16(9)	1.14(8)	−0.33(7)
C(1)	2.8(3)	3.3(5)	3.6(5)	0.5(4)	1.6(3)	0.0(3)
N(1)	3.8(3)	4.3(5)	5.7(6)	−1.4(4)	2.5(4)	−0.4(3)
N(2)	3.3(3)	5.9(6)	7.4(6)	2.0(4)	3.0(5)	0.6(3)

[a] U_{ij} are of the form: $10^2 \cdot \exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2klU_{23}b^*c^* + 2hlU_{13}a^*c^*)]$.

TABLE III. Interatomic Distances (Å) and Angles (°) in $SnCl_2 \cdot SC(NH_2)_2$ (estimated standard deviations in parentheses).

(a) *Distances*			
Within Asymmetric Unit		*Between Asymmetric Units*	
Sn_1 ——Cl_{11}	2.609(4)	Sn_1- - - - -S_3	3.331(4)
Sn_1 ——Cl_{21}	2.492(3)	Sn_1- - - - -Cl'''_{13}	3.190(4)
Sn_1 ——S_1	2.704(–)	Sn_1· · · · ·Cl'''_{23}	3.861(5)
S_1 ——C_1	1.737(19)	Sn_1· · · · ·Cl'_{21}	3.717(3)
C_1 ——N_{11}	1.280(44)	N_{11}–H–·–Cl''_{22}	3.318(22)
C_1 ——N_{21}	1.343(16)	N_{21}–H–·–Cl_{23}	3.354(5)
		N_{21}–H–·–Cl'''_{22}	3.428(4)
(b) *Angles*			
At Sn_1		*At* Cl_{11}	
Cl_{21} —— Sn_1 —— Cl_{11}	88.0(1)	Sn_1 —— Cl_{11} - - - - Sn_3	99.6(1)
Cl_{21} —— Sn_1 —— S_1	93.5(1)	Sn_1 —— Cl_{11} –·– H–N''_{12}	125.7(7)
Cl_{21} —— Sn_1 - - - - - Cl'''_{13}	82.1(1)	Sn_1 —— Cl_{11} –·– H–N'''_{22}	143.9(1)
Cl_{21} —— Sn_1 · · · · · Cl''''_{23}	141.3(2)	Sn_3 - - - - - Cl_{11} –·– H–N''_{12}	72.0(6)
Cl_{21} —— Sn_1 - - - - - S_3	89.4(1)	Sn_3 - - - - - Cl_{11} –·– H–N'''_{22}	99.0(1)
Cl_{21} —— Sn_1 · · · · · Cl'_{21}	146.2(2)	N''_{12}–H–·–Cl_{11} –·– H–N'''_{22}	88.7(3)

(continued on facing page)

TABLE III. *(continued)*

Cl_{11} —— Sn_1 —— S_1	90.6(1)
Cl_{11} —— Sn_1 ---- $Cl_{13}^{'''}$	168.1(1)
Cl_{11} —— Sn_1 .... $Cl_{23}^{'''}$	120.9(1)
Cl_{11} —— Sn_1 ---- S_3	82.3(1)
Cl_{11} —— Sn_1 .... $Cl_{21}^{'}$	72.7(1)
S_1 —— Sn_1 ---- $Cl_{13}^{'''}$	83.7(1)
S_1 —— Sn_1 .... $Cl_{23}^{''''}$	63.7(1)
S_1 —— Sn_1 ---- S_3	172.2(1)
S_1 —— Sn_1 .... Cl_{21}	113.7(1)
$Cl_{13}^{'''}$ ----- Sn_1 .... $Cl_{23}^{''''}$	65.5(1)
$Cl_{13}^{'''}$ ----- Sn_1 ---- S_3	104.0(1)
$Cl_{13}^{'''}$ ----- Sn_1 .... $Cl_{21}^{'}$	119.1(1)
$Cl_{23}^{''''}$ ..... Sn_1 ---- S_3	117.5(1)
$Cl_{23}^{''''}$ ..... Sn_1 .... $Cl_{21}^{'}$	71.8(1)
S_3 ----- Sn_1 .... $Cl_{21}^{'}$	61.2(1)
At N_{11}	
C_1 —— N_{11}–H–·–Cl_{22}	128.4(19)
At C_1	
S_1 —— C_1 —— N_{11}	121.3(6)
S_1 —— C_1 —— N_{21}	119.0(6)
N_{11} —— C_1 —— N_{21}	119.6(7)
At Cl_{21}	
Sn_1 —— Cl_{21} –·–H–N_{23}	91.9(1)
Sn_1 —— Cl_{21} .... $Sn_1^{'}$	146.2(2)
Sn_1 —— Cl_{21} .... $Sn_3^{'}$	141.2(2)
N_{23}–H–·–Cl_{21} .... $Sn_1^{'}$	113.4(1)
N_{23}–H–·–Cl_{21} .... $Sn_3^{'}$	68.6(1)
$Sn_1^{'}$ ..... Cl_{21} .... $Sn_3^{'}$	71.8(1)
At N_{21}	
C_1 —— N_{21}–H –·– Cl_{23}	120.9(8)
C_1 —— N_{21}–H –·– $Cl_{22}^{'}$	97.0(8)
$Cl_{22}^{'}$—— H–N_{21}–H–·–Cl_{23}	141.7(1)
At S_1	
Sn_1 —— S_1 —— C_1	106.9(7)
Sn_1 —— S_1 ----- $Sn_3^{''''}$	94.3(1)
C_1 —— S_1 ----- Sn_3	115.4(6)

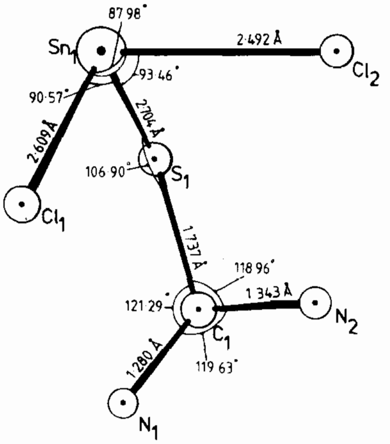

Fig. 1. Diagrammatic view of the asymmetric unit of $SnCl_2 \cdot SC(NH_2)_2$.

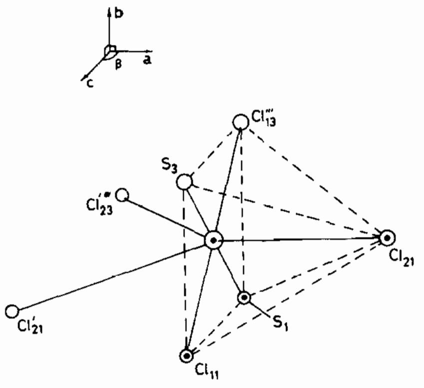

Fig. 2. Diagrammatic view of the first coordination sphere of tin in $SnCl_2 \cdot SC(NH_2)_2$.

with the atoms labelled in a simple manner, and showing the principal structural dimensions. However, as will be seen later, due to the complexity of the intermolecular bonding in this material, a more comprehensive system of labelling, together with a bond-type coding is used in the discussion and in the associated tables and figures.

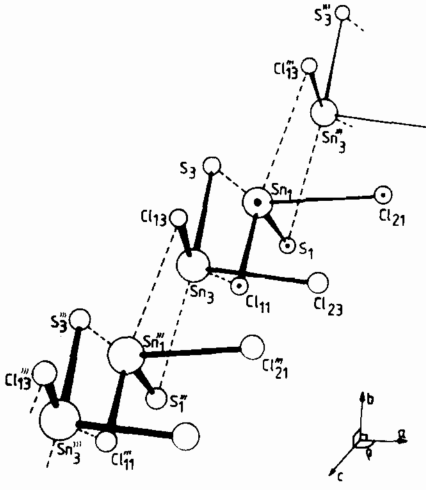

Fig. 3. Diagrammatic view of the primary polymeric bonding in the *c* direction in $SnCl_2 \cdot SC(NH_2)_2$.

The atomic labelling will be of two forms depending on whether or not the atom-type is unique in the asymmetric unit. The two forms are, for example:

Cl_{ab} and Sn_b,

where 'a' refers to the number as used in Fig. 1, and serves to differentiate atoms of the same type in the same asymmetric unit, and where 'b' refers to the asymmetric unit within the unit cell to which the atom belongs. Thus 'b' values range from 1 to 4, where 1 refers to the asymmetric unit for which atomic coordinates are given in Tables I, II and III represent the transformations according to –x, –y, –z, x, ½ – y, ½ + z and –x, ½ + y, ½ – z respectively. Singly primed atoms are as unprimed atoms with the same subscript(s) but translated by one cell unit in the +*a* direction. Double and triple primes refer to similar translations in the +*b* and +*c* directions respectively.

The bond codings:

Solid	(———)	Intraasymmetric unit bonds
Broken	(---------)	Coordination in the *c* direction
Dotted	(.........)	Coordination in the *a* direction
Dot/Dash	(–·–·–H—)	Hydrogen-bonding, chiefly in the *b* direction,

are used consistently in the diagrams and tables. Thin, broken lines in Fig. 6 show continuation of hydrogen bonds between unit cells.

Diagrams showing how the structure of the unit cell is built-up from the asymmetric unit are shown in Figs. 3 to 6. Each successive diagram shows the different types of bonding which prevail in different planes of the structure.

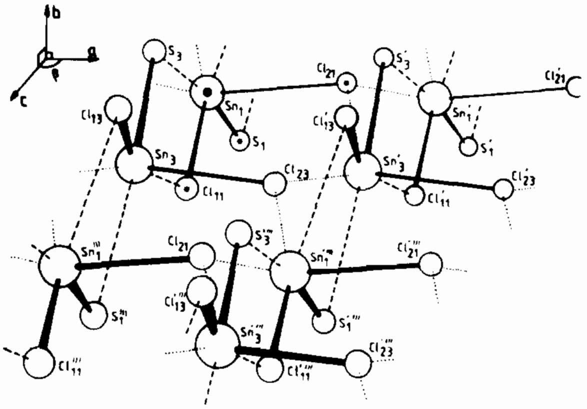

Fig. 4. Diagrammatic view of the secondary polymeric bonding in the *a* direction in $SnCl_2 \cdot SC(NH_2)_2$.

Figure 3 shows the assembly of five formula units to form part of an infinite linear polymer chain parallel to the *c* direction. (The carbon and nitrogen atoms have been omitted for clarity). It can be seen that, because of the non-equivalence of the chlorine atoms, in the solid state, alternate $[Sn_1Cl_{11}Cl_{21}S_1]$ pyramids are configurationally enantiomorphic; there being equal numbers of each enantiomer in the crystal. Clearly, in solution, the chlorine atoms might well become equivalent, by exchange, destroying the asymmetry.

The individual pyramids are joined, with bond vectors $Sn_1–Cl_{21}$ approximately parallel, in an alternating up and down arrangement, by means of sulphur and chlorine bridges, in such a way that the bridging atoms are always *trans* to atoms of their own kind. Atoms of type Cl_2 play no part in the polymeric bonding in this direction.

Figure 4 shows how these linear polymer chains repeat in the *a* direction to form an infinite sheet structure. Because the β-angle of the unit cell is not 90°, the $Sn_1–Cl_{21}$ bond projects mid-way between atoms Sn_1' and Sn_3' allowing Cl_{21} to be coordinated to both these latter tin atoms in a symmetrical manner, binding the polymer chains into a slightly puckered sheet in the *a c* plane. (The $Sn_1–Sn_3–Sn_1'''$ angle is 176.41(6)° but they all have equal *x*/*a* coordinates).

The ^{119m}Sn Isomer Shift of the compound is fairly high (3.711(5) mm s^{-1}), indicating that the tin lone pair is located in an orbital of fairly high 5s character and this is substantiated by the quite regular angular disposition of the ligands about the central metal atom (Fig. 2). The base of the idealised pyramid illustrated is in fact planar (the sum of its internal angles is 360.0(4)°). The three bonds to the atom in the same formula unit, Cl_{11}, Cl_{21} and S_1 are the shortest (2.609(4), 2.492(3) and 2.704(4) Å, respectively) followed by these bonds to the primary bridging atoms, Cl_{13}''' and S_3 (3.190(0) and 3.33(4)

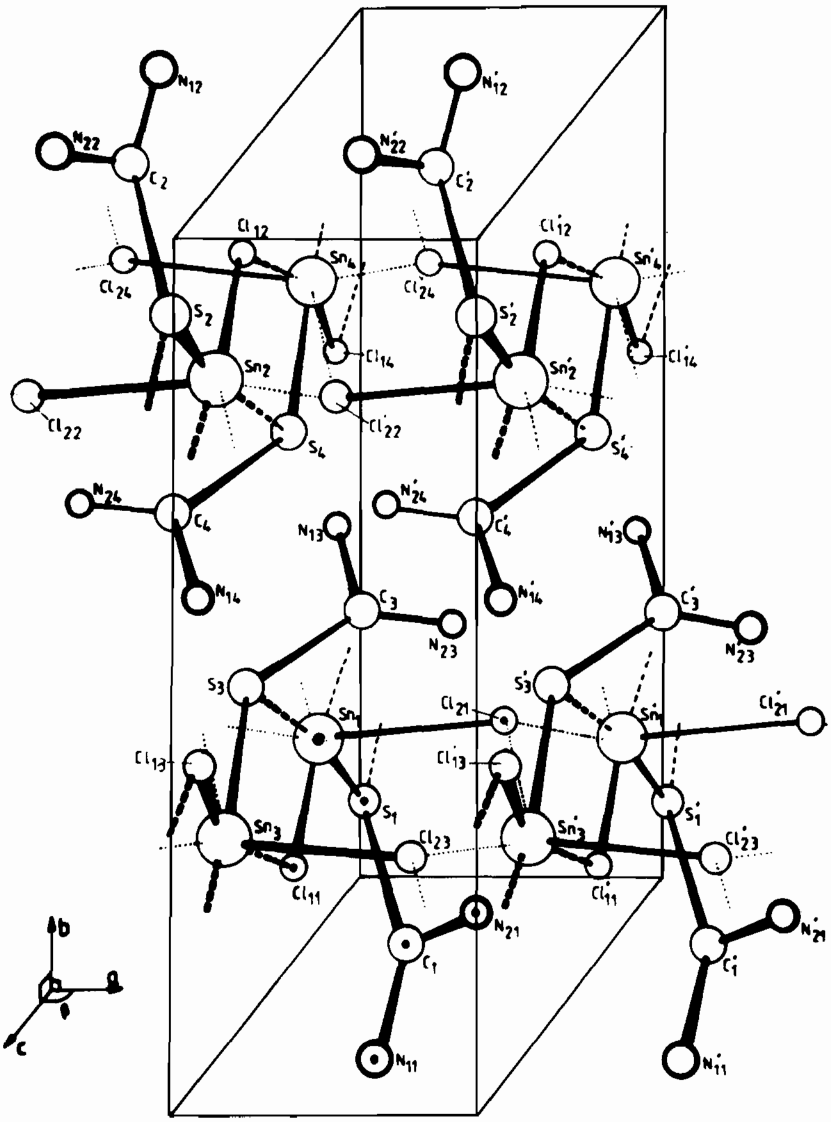

Fig. 5. Diagrammatic view of the stacked sheet structure of $SnCl_2 \cdot SC(NH_2)_2$.

Å respectively). The two remaining, secondary, bridging interactions to atoms Cl_{23}''' and Cl_{21}' (3.86(5) and 3.717(3) Å respectively) are longer but less than the sum of the tin and chlorine van der Waals radii at 4.0 Å (415). Any stereochemical activity of the lone-pair is clearly directed approximately diametrically away from atom Cl_{21}.

Similar observations of lone-pair activity and symmetry in a seven-coordinate tin(II) compound has been made by Auel, Lüth and Amma in (C_6H_6)-$Sn(AlCl_4)_2 \cdot C_6H_6$ [5, 6] whose Isomer Shift is approximately 3.6 mm s^{-1} relative to $CaSnO_4$. The tin–chlorine distances are more closely than in (thiourea)tin(II) chloride but their mean value is of the same order (Range 2.766(7) to 3.291(7) Å). This reflects the higher degree of symmetry prevailing in this compound.

Figure 5 shows that the upper sheet in the unit cell is related to the lower sheet described above, by a two-fold screw transformation along *c*, followed by a half-cell translation along *b*. The carbon and nitrogen atoms have been replaced, in this diagram, to reveal the alternating layers of Sn, S, Cl and C, N, H repeating indefinitely in the *b* direction. Fig. 5 also shows the complete labelling system for the unit cell and its unit *a* translation (single primes).

Figure 6 shows that these alternating layers are joined by hydrogen bonds from nitrogen to chlorine. Atomic labelling has been omitted for clarity but is

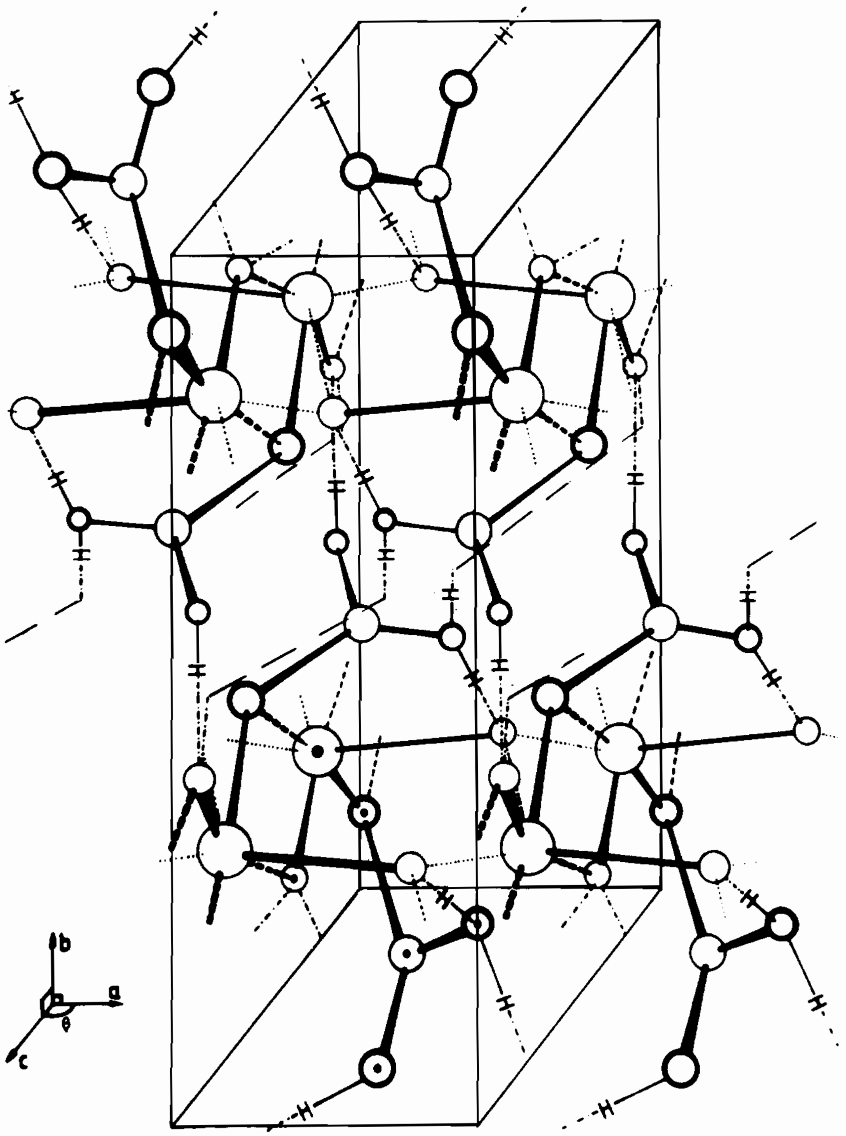

Fig. 6. Diagrammatic view of the structure of $SnCl_2 \cdot SC \cdot (NH_2)_2$ showing the inter-sheet hydrogen bonding.

identical to that in Fig. 5. Table III reveals that the nitrogen–chlorine distances fall in the range 3.316(7)–3.428(4) which, according to Bindi [7] and Falk *et al.* [8] is indicative of bent N–H···Cl bonding. The two nitrogen atoms can be seen to be non-equivalent, inasmuch as N_2 participates in two hydrogen bonds whereas N_1 is only involved in one hydrogen bond.

In conclusion, the structure is seen to be composed of individual formula units quite tightly bound into chains by chlorine and sulphur bridging. The chains are weakly bound by inter-chain chlorine bridges into sheets which are reinforced by N–H··· Cl hydrogen bonds. Further hydrogen bonds, of the same type, then join the sheets into a three-dimensional structure.

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