The Structure of Tin(II) Thiocyanate

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The structure of the title compound has been solved with three-dimensional *X*-ray diffraction data and refined to *R* 0.068. The crystals are triclinic, with space group $P\bar{1}$, and $a = 5.665(4)$, $b = 4.924(5)$, $c = 10.242(9)$ Å, $\alpha = 83.13(7)$, $\beta = 79.38(7)$, $\gamma = 93.33(7)°$, and $Z = 2$. Tin is surrounded by nine thiocyanate groups with Sn–N and Sn–S distances ranging from 2.20 to 3.85 and 2.837 to 3.738 Å respectively. The primary co-ordination of Sn involves only a subset of these contacts. Pyramidal co-ordination is achieved with Sn–N contacts of 2.20 and 2.27 Å and an Sn–S contact of 2.837 Å, the Sn lone pair completing a very distorted tetrahedron. Inclusion of two further Sn–S contacts (3.111 and 3.335 Å) gives distorted octahedral co-ordination. The co-ordination of Sn in the thiocyanate is, therefore, entirely analogous to that encountered in the simple orthorhombic tin(II) halides ($PbCl_2$ structure).

IT is apparent from the unit-cell data for tin(II) thiocyanate and the crystal structure of monoclinic lead(II) thiocyanate [1] that the two compounds cannot be isostructural. The crystal structure of tin(II) thiocyanate is of interest not only in extending the available data on the crystal chemistry of Sn^{II} but also for comparison with lead(II) thiocyanate.

EXPERIMENTAL

Crystalline tin(II) thiocyanate was prepared by the metathetical reaction between tin(II) sulphate and sodium thiocyanate, as described by Chamberlain and Moser.[2]

Crystal Data.—$C_2N_2S_2Sn$, $M = 234.85$, Triclinic, white needles, needle axis '*a*', $a = 5.665(4)$, $b = 4.924(5)$, $c = 10.242(9)$ Å, $\alpha = 83.13(7)$, $\beta = 79.38(7)$, $\gamma = 93.33(7)°$, $U = 277.85$ Å^3, $D_m = 2.785$, $Z = 2$, $D_c = 2.806$ g cm^{-3}, space group $P\bar{1}$ (Cu-K_α filtered radiation, single-crystal oscillation, rotation, and Weissenberg photographs about all the three axes). Cell dimensions were refined from *X*-ray powder data obtained with a Philips powder diffractometer scanning at 2° (2θ) min^{-1} with Cu-K_α radiation and silicon as internal standard (spacings >2.0 Å were indexed).

Intensity Data.—Intensities were measured using a Hilger and Watts Y-190 linear diffractometer with Mo-K_α radiation and a zirconia filter. The balanced filter facility of the diffractometer was not employed. Instead, four measurement cycles were made for each reflection. Data were collected for the layers 0—7, *k*, *l*. Only reflections having intensities at least five times the estimated standard deviation were accepted. Equivalent reflections in the zero layer were averaged only if the counts agreed to within 20%: otherwise the higher value was accepted. 1 007 Independent reflections were obtained and converted into structure amplitudes in the usual manner. No corrections were made for absorption.

Computation.—Initial processing of the data was done on an Elliot 803B computer. All the other calculations were carried out on an I.C.L. model 4-50 computer using crystallographic programs written by F. Ahmed for the National Research Council of Canada, and extensively modified by J. S. Knowles and H. F. W. Taylor. The weighting scheme used initially in the refinement was $w^{\frac{1}{2}} = |F_o|/P_1$, if $|F_o| \leqslant P_1$, or $w^{\frac{1}{2}} = P_1/|F_o|$, if $|F_o| > P_1$, where $P_1 = 50$. The weighting scheme used in the later stages of refinement was $w^{\frac{1}{2}} = 1/\{1 + [(F_o - P_2)/P_1]^2\}^{\frac{1}{2}}$ where P_1 and P_2 had the values 18 and 30 respectively. Atomic scattering factors were taken from ref. 3.

Structure Determination.—Negative results were obtained from piezo- and pyro-electric tests; [4] the space group was therefore taken as $P\bar{1}$.

A three-dimensional Patterson synthesis yielded the position of the tin atom, and this was used to determine signs for the observed structure factors; at this stage *R* was 0.36. A three-dimensional electron-density map refined the tin position slightly, and showed the two sulphur atoms in the asymmetric unit clearly, as well as five possible positions for the remaining four light atoms. Four least-squares cycles with isotropic temperature factors, with the positions of the sulphur atoms included in the structure-factor calculation, reduced *R* to 0.187, and the next electron-density map defined the positions of all the atoms unambiguously. Then three further least-squares cycles reduced *R* to 0.141.

At this point the weighting scheme was changed as already indicated. Layer scaling was also applied and an *R* value of 0.133 was obtained. Refinement was continued with anisotropic temperature factors applied to all the atoms and five further cycles achieved the final *R* value of 0.068. In no parameter did the final shift exceed 4×10^{-4}, the parameters of the light atoms being much less well defined than those of the tin and sulphur atoms. A difference map calculated at this stage was featureless. The final parameters are listed in Table 1, and selected bond lengths and angles in Table 2. Observed and calculated structure amplitudes and thermal parameters are available as Supplementary Publication No. SUP 22325 (8 pp.).*

In the following description of the structure, in the Tables and in the diagrams, the two crystallographically distinct thiocyanate groups and their constituent atoms have been labelled (1) and (2) throughout. Tin–thiocyanate distances are measured from tin to the nearer terminal atom, N or S as the case may be.

Description of the Structure.—The seven atoms of the asymmetric unit (one tin atom and two thiocyanate groups) are placed in the general positions of $P\bar{1}$. The structural

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[1] J. A. A. Mokuolu and J. C. Speakman, *Acta Cryst.*, 1975, **B31**, 172.

[2] B. R. Chamberlain and W. Moser, *J. Chem. Soc. (A)*, 1969, 354.

[3] 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1968, vol. 3, pp. 203 and 211.

[4] E. Giebe and A. Scheibe, *Z. Physik*, 1925, **33**, 760; W. A. Wooster and A. J. P. Martin, *Proc. Roy. Soc.*, 1936, **A155**, 150.

features are most readily described by reference to the co-ordination of the tin atoms (Figure 1 and Table 2). The tin atom has nine distinct nearest-neighbour thiocyanate groups at distances ranging from 2.20 to 3.85 Å. Six of these contacts [N(1), S(1″), S(2), S(2″), S(1^{IV}), and N(1^{VI})] lie at the corners of a trigonal prism. Of the three remaining contacts [N(2′), S(1‴), and N(2^{V})], one is found outside each of the prism faces.

TABLE 1

Final parameters (R 0.068) of tin(II) thiocyanate. Estimated standard deviations applicable to the least significant digits of each entry are given in parentheses (calculated as $[(a_{ii}^{-1}\Sigma w\Delta^2/(n - m)]^{\frac{1}{2}}$, where (a_{ii}^{-1}) is the appropriate diagonal element of the inverse normal equations matrix, n is the number of observations, and m the number of variables)

Atom	x	y	z
Sn	0.186 2(2)	0.171 2(3)	0.256 2(1)
S(1)	0.860 2(7)	−0.265 2(9)	0.404 2(4)
S(2)	0.715 9(8)	0.377 3(9)	0.124 5(4)
N(1)	0.413(2)	−0.137(3)	0.348(2)
N(2)	0.775(2)	0.083(3)	−0.093(2)
C(1)	0.597(3)	−0.186(3)	0.371(1)
C(2)	0.747(2)	0.203(3)	−0.001(1)

Tin atoms, and the associated prisms, occur in centrosymmetrically related pairs, sharing thiocyanate (2) groups (Figure 2). Thus S(2) and S(2″) define one edge of the prism surrounding the original tin atom (Sn), and the corresponding N(2) and N(2″) of the same thiocyanate groups are closely associated with two other centrosymmetrically related tin atoms, lying outside their respective prism faces. The thiocyanate groups of both types at the top (triangular face) of one prism also form the base of the next prism along 'a'. In this way the staggered prism pairs form infinite columns parallel to 'a'.

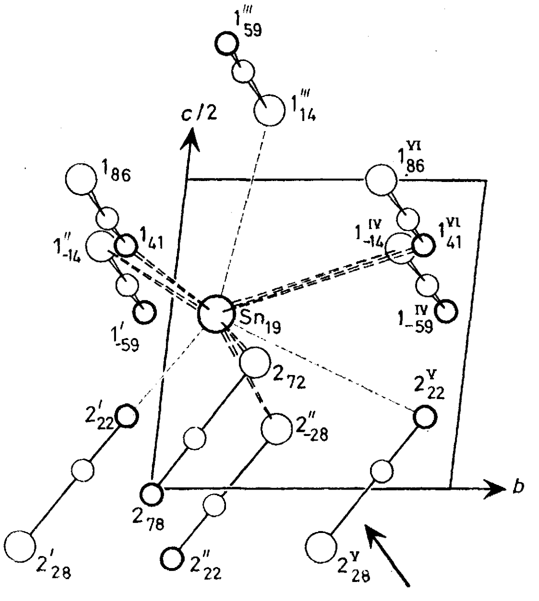

FIGURE 1 Projection down [100] of the structure of tin(II) thiocyanate. The thicker circles are tin (large) and nitrogen (small), the thinner circles are sulphur (large) and carbon (small). Tin, sulphur, and nitrogen atoms are numbered as in Table 1, with superscripts indicating translations of the original atoms as in Table 2, and subscripts indicating fractional co-ordinates (x/a) in units of $a/100$. The arrow represents the direction of view in Figure 2

Thiocyanates (1) are shared between prisms adjacent to one another along 'b'. This link joins the paired prism columns into complex sheets centred on 001 planes. The contacts such as Sn–N(2^{V}) have the same effect. Weak contacts, exemplified by Sn–S(1‴), in turn interconnect adjacent, centrosymmetrically related, 001 sheets.

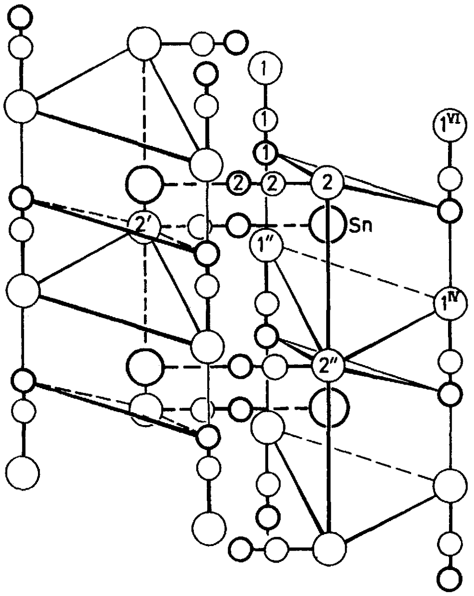

FIGURE 2 An idealized representation of a column of prism pairs in tin(II) thiocyanate. The atom types and numbers follow the same scheme as in Figure 1

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(a) Thiocyanate ions			
S(1)–C(1)	1.65(2)	C(2)–N(2)	1.16(2)
S(2)–C(2)	1.62(2)	S(1)–C(1)–N(1)	178(1)
C(1)–N(1)	1.14(2)	S(2)–C(2)–N(2)	178(1)
(b) Co-ordination of the tin atom			
Sn–N(2′)	2.20(2)	Sn–S(1‴)	3.528(4)
Sn–N(1)	2.27(1)	Sn–S(1^{IV})	3.738(4)
Sn–S(1″)	2.837(4)	Sn–N(2^{V})	3.82(2)
Sn–S(2)	3.111(5)	Sn–N(1^{VI})	3.85(2)
Sn–S(2″)	3.355(5)		
Sn–N(2′)–C(2′)	175(1)	Sn–S(2)–C(2)	98.6(6)
Sn–N(1)–C(1)	148(1)	Sn–S(2″)–C(2″)	98.7(6)
Sn–S(1″)–C(1″)	103.7(5)		
N(2′)–Sn–N(1)	84.0(5)	N(2′)–Sn–S(2)	82.7(4)
N(2′)–Sn–S(1″)	85.6(4)	N(2′)–Sn–S(2″)	82.5(4)
N(1)–Sn–S(1″)	73.5(4)	S(1″)–Sn–S(2)	147.6(1)
N(1)–Sn–S(2)	75.3(4)	S(1″)–Sn–S(2″)	85.7(1)
N(1)–Sn–S(2″)	155.9(4)	S(2)–Sn–S(2″)	122.3(1)

The superscripts indicate the following equivalent positions:

single prime	$1 - x, -y, -z$	IV	$x - 1, 1 + y, z$
double prime	$x - 1, y, z$	V	$1 - x, 1 - y, -z$
triple prime	$1 - x, -y, 1 - z$	VI	$x, 1 + y, z$

DISCUSSION

(a) *Thiocyanate Groups*.—The crystallographically distinct thiocyanate groups do not differ significantly in their internal dimensions (Table 2). The bond lengths are within the range of those already known for inorganic thiocyanates.[1,5] Neither thiocyanate group in tin(II) thiocyanate departs significantly from linearity. It is clear that both thiocyanate groups fulfil a bridging function as predicted by the original i.r. data.[2]

The differences between the two thiocyanate groups only become apparent in their co-ordination to tin. In the range of tin–thiocyanate distances considered, thiocyanate (1) has two Sn–N(1) and three Sn–S(1) contacts. No angle Sn–X–C(1) [X = N(1) or S(1)] is $>148°$. Thiocyanate(2), on the other hand, has two Sn–N(2) contacts and two Sn–S(2) contacts. The shortest tin–thiocyanate distance in the whole structure (2.20 Å) is Sn–N(2'). The corresponding angle [Sn–N(2')–C(2')] is 175°.

(*b*) *Co-ordination of Tin.*—The environment of the tin atom in $Sn(NCS)_2$ as described above is strikingly similar to that described by Wyckoff[6] for the lead atom in orthorhombic $PbCl_2$. Therefore it is clear that $Sn(NCS)_2$ although of lower symmetry belongs to the $PbCl_2$ structure type and is closely related in structure to $SnCl_2$[7] and to $SnBr_2$ and SnClI which are being studied in this laboratory. The same tin environment is found in the majority (type 2) site in SnI_2.[8] The Mössbauer spectral parameters have been reported for several ternary tin(II) halides.[9] Of special significance is the presence of little or no quadrupole splitting in the spectra of SnI_2, SnClI, $SnBr_2$, and $SnCl_2$. No quadrupole splitting is observable in the case of tin(II) thiocyanate either. This is strong supporting evidence, not only for the proposed structure but also for its classification with the $PbCl_2$ structure type.

The range of tin–halide distances in the compounds of the $PbCl_2$ structure type renders somewhat arbitrary the selection of an interatomic distance at which the co-ordination of the tin atom may be regarded as complete. In $Sn(NCS)_2$, as in SnI_2 (type 2 sites), there appear to be five significant tin–thiocyanate contacts, all lying to one side of the tin atom. The sterically active lone pair on the tin completes octahedral co-ordination. The first five tin–thiocyanate distances in Table 2 can then be considered to represent partial covalent-bond character to a decreasing extent. The remaining contacts can be regarded as ionic interactions between residual charges on both tin and thiocyanate groups.

(*c*) *Raman Spectroscopy.*—The Raman spectrum of $Sn(NCS)_2$, recorded on a powdered sample with a Cary 83 spectrometer, exhibits bands tentatively assigned as follows: 2 048vs, sharp, C–N stretch; 920vw,br, NCS bend (overtone); 810w, sharp, C–S stretch; 780w, sharp, not assigned; 475s and 455w cm^{-1}, both sharp, NCS bends (fundamentals). The last two bands, below the range of the previous i.r. data, are characteristic of M–NCS bonding.[10] The presence of two bands in this region may reflect the presence of two crystallographically distinct thiocyanate groups. Although the name tin(II) thiocyanate has been retained, the formula has been written $Sn(NCS)_2$ to emphasize the importance of tin–nitrogen bonding. The Raman and *X*-ray results (two Sn–N contacts in the three shortest tin–thiocyanate interactions) support $Sn(NCS)_2$ as the preferred formula.

(*d*) *Comparison with Lead*(II) *Thiocyanate.*—The structure of lead(II) thiocyanate is clearly different from that of tin(II) thiocyanate. Not only is the space group $C_{2/c}$ instead of $P\bar{1}$, but the lead atoms lie on two-fold axes. *X*-Ray powder patterns of the two compounds are completely different. The thiocyanates provide yet another example of corresponding tin(II) and lead(II) compounds differing in structure, with the lead compound having the higher symmetry (*cf.*[8] SnI_2 and PbI_2).

Conclusion.—The structure of tin(II) thiocyanate is clearly of the same type as the orthorhombic structure adopted by the majority of the normal tin(II) halides. The decrease from orthorhombic to triclinic symmetry is necessary to accommodate the linear pseudohalide (thiocyanate) in place of the spherical simple halides.

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