The OD Structure of Na₂SnS₃. Determination and Refinement of an MDO Structure

By Wanda Mark and Oliver Lindqvist

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg,
P.O.Box, S-402 20 Göteborg 5, Sweden

and Jean-Claude Jumas and Etienne Philippot

Laboratoire de Chimie Minérale C, Université des Sciences et Techniques du Languedoc,
Place Eugène Bataillon, 34060 Montpellier-Cedex, France

Na$_2$SnS$_3$ crystallizes with an OD structure. The family reflexions define a superposition structure, space group $R\bar{3}m$, with $A = B = 3.834$ (2), $C = 19.88$ (1) Å, $Z = 2$. The superposition structure was solved from Patterson and electron-density calculations and refined to an R of 0.046. From this structure it is apparent that Na$_2$SnS$_3$ is of NaCl type, with the tin and sodium atoms distributed over the cation positions. The real structure consists of ordered layers parallel to the *ab* plane. These are composed of two close-packed planes of sulphur atoms between which the sodium and tin atoms occupy $\frac{1}{3}$ and $\frac{2}{3}$ of the octahedral holes, respectively. Between two such planes there are sodium atoms in all the octahedral holes. The disorder arises since each layer can be orientated in three different ways with respect to its predecessor. It is possible to define six structures of maximum degree of order, MDO$_1$–MDO$_6$, corresponding to pronounced maxima on the continuous reciprocal streaks. These can all be described by a hexagonal cell with $a = b = 6.633$ (3), $c = 39.76$ (2) Å, and $Z = 12$. Intensities corresponding to one such MDO structure have been measured, thus making it possible to refine the atomic parameters of the ordered layers ($R = 0.045$ for 314 independent intensities). Both tin and sodium have slightly distorted octahedral coordination. All six Sn–S distances are 2.571 (2) Å, while the Na–S distances range from 2.735 (3) to 2.980 (3) Å.

Introduction

The crystal structure of Na₂SnS₃ has been determined as part of a general investigation of the chemical and structural properties of thiostannate(IV) compounds (Jumas, 1971).

Synthetic work on the BaS–SnS₂, PbS–SnS₂ and Na₂S–SnS₂ systems is in progress, and some structures have been determined. There are different possibilities for the sulphur coordination of tin(IV). Oftedal (1928) showed that tin has octahedral coordination in SnS₂, which is also the case in Sn₂S₃ (Mootz & Puhl, 1967) and PbSnS₃ (Jumas, Ribes, Philippot & Maurin, 1972). SnS₂ has a layer structure, while the latter two compounds have structures related to each other with double chains of SnS₆ octahedra sharing edges. Tetrahedral coordination has been found in Ba₃Sn₂S₇, Na₆Sn₂S₇ (which is isomorphous with Na₆Ge₂S₇) (Jumas, Olivier-Fourcade, Vermot-Gaud-Daniel, Ribes, Philippot & Maurin, 1974), Na₄SnS₄ and Ba₂SnS₄(α), (Jumas, Philippot, Vermot-Gaud-Daniel, Ribes & Maurin, 1974), and Ba₂SnS₄(β) (Susa & Steinfinck, 1971). A recent study of Na₄Sn₃S₈ (Jumas, Philippot & Maurin, 1974), on the other hand, has revealed both four- and fivefold coordinated tin(IV).

Experimental

Crystals of Na₂SnS₃ were prepared by melting a stoichiometric mixture of SnS₂ and Na₂S in an evacuated quartz tube. The melt was maintained at 750 °C for 48 h; crystals formed when the melt was cooled slowly (16 °C h⁻¹) to room temperature (Vermot-Gaud-Daniel & Jumas, 1972).

Preliminary Weissenberg exposures showed that the Na₂SnS₃ modification prepared had an OD structure, since there were intensity streaks along one of the principal reciprocal directions (**c***). More than 20 crystals prepared at different temperatures were mounted, all of which gave continuous streaks along the **c*** direction with more or less pronounced maxima. The intensity distribution on the streaks varied from crystal to crystal, as is to be expected for an OD structure. Photographs obtained from two different crystals are shown in Fig. 1.

Unit cell and data collection

Na₂SnS₃ has a superposition structure, corresponding to the discrete, strong reflexions (family reflexions) visible in Fig. 1. This has $\bar{3}m$ rhombohedral symmetry and the hexagonal unit-cell dimensions are $A = B = 3.83$, $C = 19.87$ Å with $Z = 2$. The use of capital letters is in accordance with the nomenclature given by Dornberger-Schiff (1966), which will be used henceforth. The rhombohedral symmetry of the superposition structure is not readily apparent from Fig. 1, since the rotation axis used when producing these photographs corresponds to $2\mathbf{A} + \mathbf{B}$ (6.64 Å).

Between each row of discrete reflexions and the next there are two streaks of continuously varying intensity. The streaks have well defined maxima with different
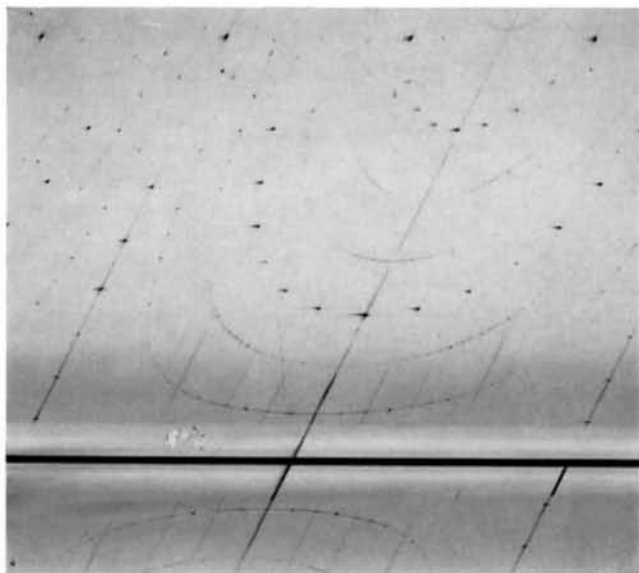
(a)
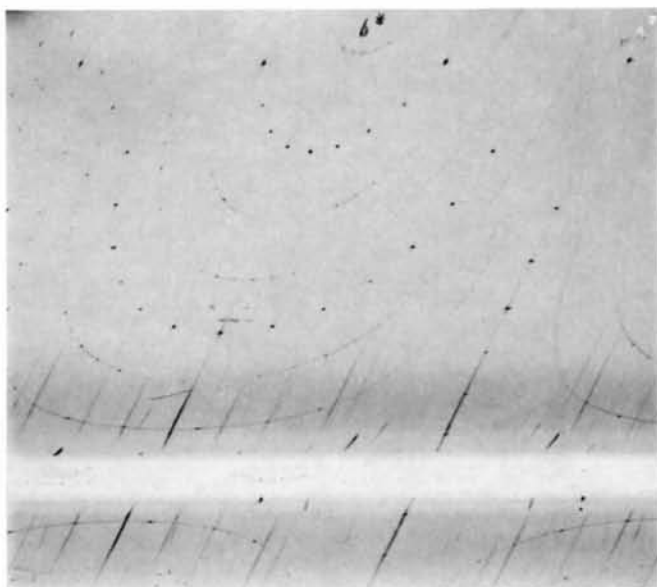
(b)

Fig. 1. Weissenberg photographs ($0k\zeta$) obtained from two different Na_2SnS_3 crystals. The (b) photograph was obtained from the crystal investigated.

relative intensities for different crystals. The smallest distance between two such maxima in reciprocal space was found to be 0·0252 Å^{-1}, whereas the corresponding distance for the superstructure reflexions in the same direction was 0·151 Å^{-1}. All the possible intensity maxima which are visible in Fig. 1(a) can be described in terms of a hexagonal lattice with the cell dimensions $a = b = 6·64$, $c = 39·8$ Å with $Z = 12$.

Accurate cell dimensions for Na_2SnS_3 have been given by Vermot-Gaud-Daniel & Jumas (1972). The cell dimensions of the superposition and the real structures (Table 1) were obtained by transforming these values, which were based on a monoclinic cell.

The crystal which was used for the data collection was mounted along the $a (= 6·64$ Å) axis in the true structures. The dimensions of the crystal are given in Table 2. Only one third of the possible weak maxima $(h - k \neq 3n)$ were present (cf. Fig. 1(b) and Fig. 2) corresponding to $2k + l = 3n$.

The data were collected with a Philips PAILRED diffractometer and Mo $K\alpha$ radiation (graphite monochromator). The moving-crystal–fixed-detector tech-

Table 2. *Boundary planes of the crystal and their distances from an internal origin*

Crystal volume: $0·31 \times 10^{-2}$ mm^3.

h k l	d (mm)
$\bar{1}$ 0 0	0·106
1 $\bar{2}$ 0	0·088
1 0 0	0·133
0 1 0	0·062
$\bar{2}$ 1 0	0·124
0 0 1	0·044
0 0 $\bar{1}$	0·044

nique (ω scan) was used. The scan speed was 2·5° min^{-1} and the background was measured for 40 s at both ends of the scan interval. One quarter of the reflexion sphere was explored out to $\sin \theta/\lambda \sim 0·7$. The reflexions corresponding to the superposition structure were collected first, and the weak maxima appearing on the intensity streaks were measured subsequently.

The reflexions of the superposition structure, *i.e.* the family reflexions, were obtained with the usual accuracy in this way, but the evaluation of the weak

Table 1. *Some crystallographic data for* Na_2SnS_3

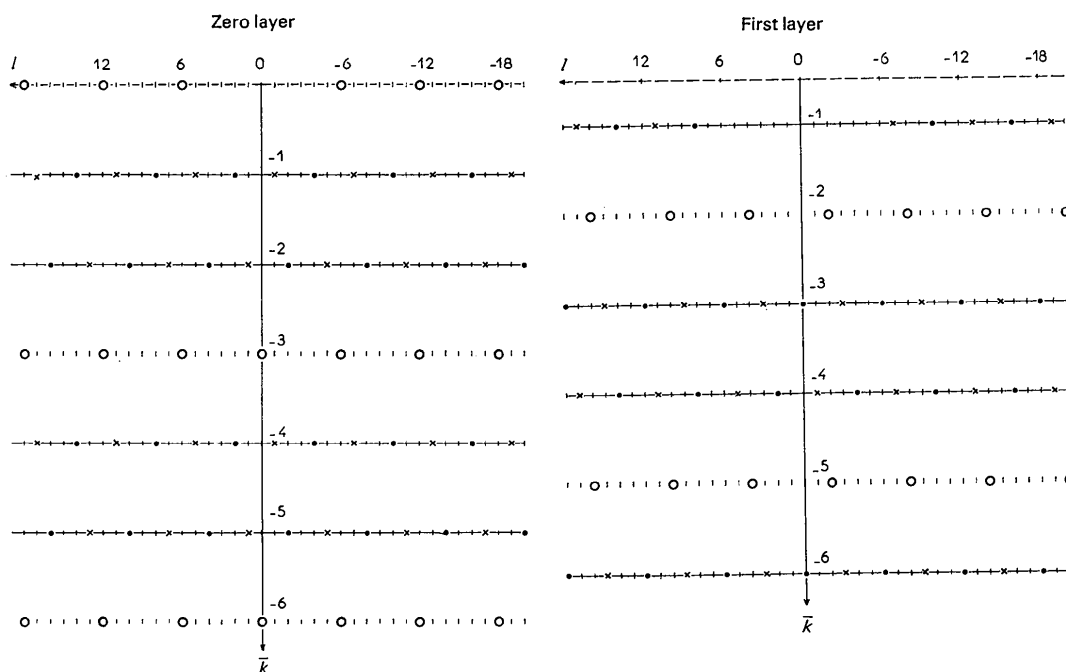|	Symmetry	a (Å)	c (Å)	V (Å^3)	Z
Superposition structure	hex.	3·834 (2)	19·876 (9)	253·0	2
Real structures	hex.	6·640 (3)	39·75 (2)	1517·8	12
Formula weight	$M = 260·8$				
Density	$\varrho_o = 3·39$ g cm^{-3}, $\varrho_c = 3·43$ g cm^{-3}				
Crystal habit	Black plates				
Absorption coefficient	μ(Mo $K\alpha) = 62·6$ cm^{-1} (*International Tables for X-ray Crystallography*, 1962)				

Fig. 2. The reciprocal lattice zones $0k\zeta$ and $1k\zeta$ for the Na_2SnS_3 crystal investigated. Maxima appearing on the intensity streaks are denoted by dots ($l = 2n$) and crosses ($l = 2n + 1$). Superposition reflexions are denoted by open circles.

maxima on the diffuse streaks involved appreciable errors. The streaks were crossed at different angles by the ω scan motion for different reflexions. Thus both the integrated intensity within the scan interval and the background measurements contain different proportions of the continuously varying intensity streaks (cf. Fig. 3). However, the information desired for quantitative determination of elements of an OD structure of this type consists of the measurement of the intensity at reciprocal points, defined by a given MDO structure, along the intensity streaks. In this case, it was therefore considered more appropriate to estimate the peak intensity (I_p) of the weak maxima. This was done by reading the heights of the reflexions as plotted during the data collection (cf. Fig. 3). The retardation of the plotting pen is slightly dependent on the peak height, and therefore a correction term, empirically found to be dependent on I_p^2, was applied. The background was considered as varying only with $\sin \theta/\lambda$, and the peak intensity was corrected as $I_{corr} = I_p + k_{ret} \cdot I_p^2 - k_{back} \cdot (\sin \theta/\lambda)^{-1}$. With the scale used in the peak measurements (cf. Fig. 3), k_{ret} was obtained as 0·0002 from measurements of the ratio $I_{integrated}/I_{peak}$ for another crystal, and the value k_{back} was chosen as 3·0, giving a reasonable estimate of the background radiation.

All data were corrected for absorption effects by the Gaussian integration method with data specified in Table 2. The transmission factors varied from 0·41 to 0·56.

The numbers of reflexions measured for the superposition structure and the real structure were 220 and 774, respectively. Of the latter, 616 reflexions with $[I_p - k_{back} \cdot (\sin \theta/\lambda)^{-1}] > 0·9$ were defined as significant.

Structure determination

The superposition structure

The family reflexions were used to calculate a Patterson synthesis. From this and subsequent electron-density calculations it was possible to find the atomic sites in the superposition structure.

Table 3. Atomic parameters of the superposition structure with cell parameters: $A = B = 3·83$, $C = 19·88$ Å

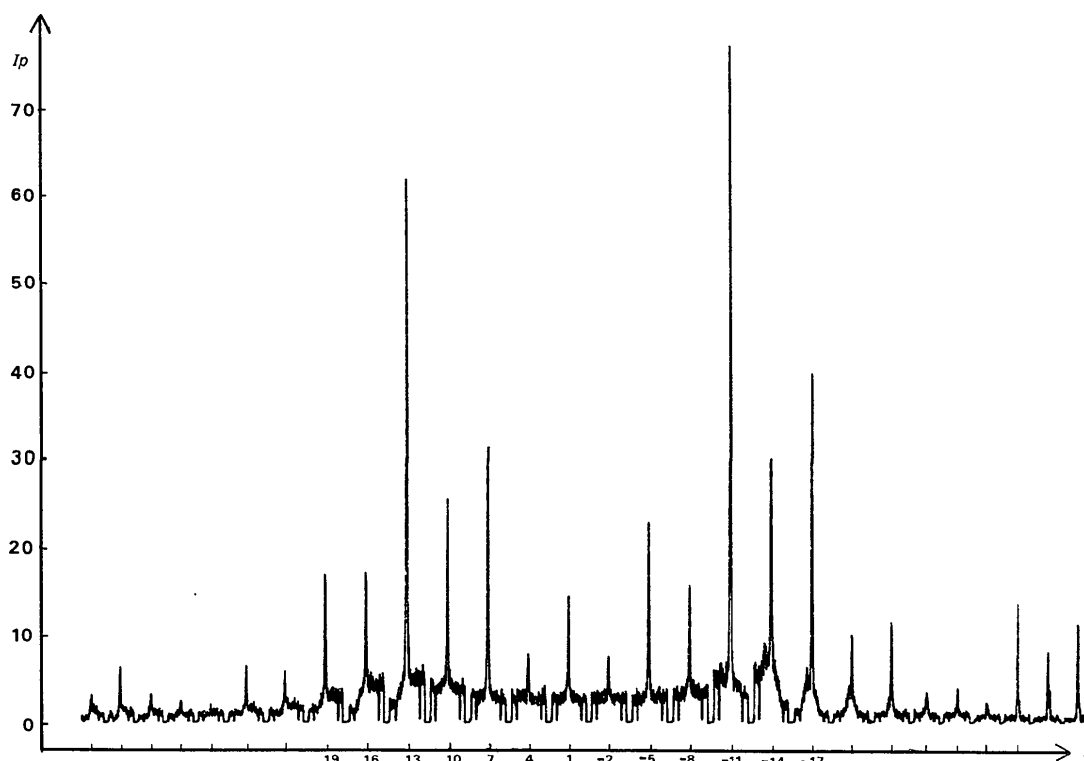|			Occupation number	x/A	y/B	z/C	B
Sn	in	3(a)	$\frac{2}{3}$	0	0	0	0·66 (2)
Na₁	in	3(a)	$\frac{1}{3}$	0	0	0	0·4 (3)
Na₂	in	3(b)	1	0	0	$\frac{1}{2}$	1·3 (1)
S	in	18(h)	1	0·6915 (9)	−0·6915	0·0730 (2)	1·2 (1)

Fig. 3. Intensity peaks from the reciprocal row $0\bar{2}l$ as recorded during the data collection.

From the relative numbers of different atoms in the hexagonal super-cell, the distribution of the atoms in the positions of space group $R\bar{3}m$ could be eval-
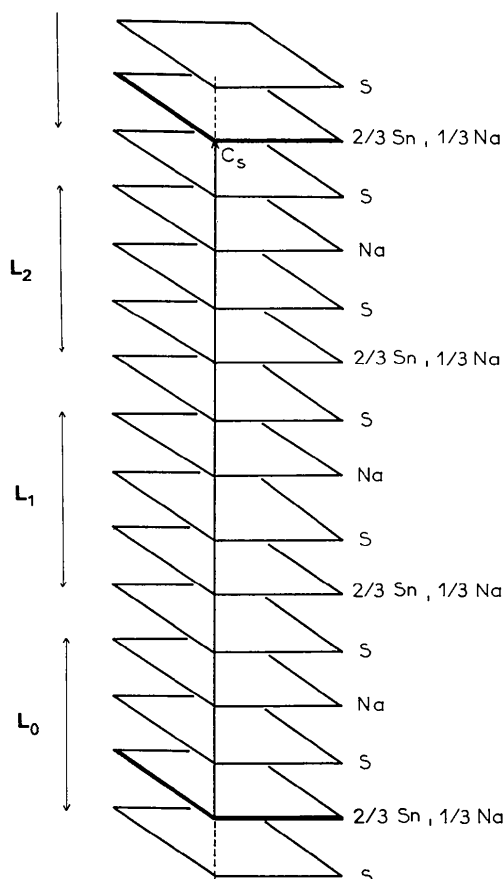

Fig. 4. Schematic description of the atomic layers in one unit cell of the superposition structure.
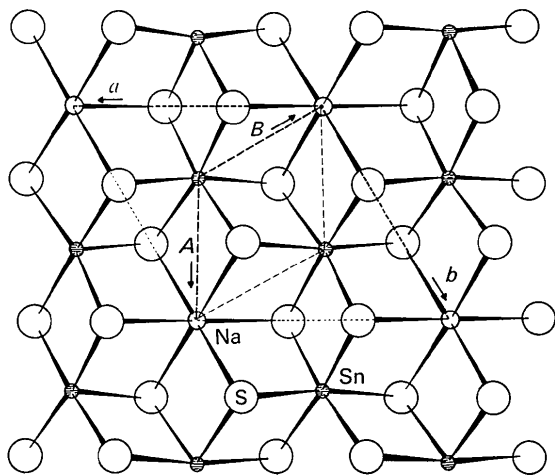

Fig. 5. The (Sn, Na) layer at $z=0$ surrounded by (S) layers. The relationship between the dimensions of the superposition and the true ab cell is indicated.

uated. Two thirds of the atomic sites, 3(a), are occupied by tin, while the remaining third contain sodium. This was verified by the isotropic atomic temperature factors obtained during subsequent least-squares refinement.

The final R for the superposition structure was 0·046, based on 115 independent reflexions. The scattering factors for Na$^+$, S and Sn given by Doyle & Turner (1968) were used, and the observations were weighted according to the formula $w=(a+F_o+cF_o^2+dF_o^3)^{-1}$, suggested by Cruickshank (1970). The tin and sulphur contributions were corrected for the real part of the anomalous dispersion (Cromer, 1965). The final atomic parameters are given in Table 3.

The atoms are arranged in planes, which are outlined schematically in Fig. 4. The structure can be described as an approximate cubic close-packed arrangement of sulphur atoms with tin and sodium atoms situated in the octahedral holes. The fact that the sodium atoms are larger than the tin atoms causes a dependence between the distribution of the atoms in the (Sn, Na) planes and the packing of the sulphur atoms. Hence, the tin and sodium atoms ought to be arranged in a regular rather than in a statistical way. That this is the case is verified by the OD nature of the structure.

The OD structure

To evaluate the true structures the complete intensity distribution, $I=I_{hk\zeta}$, has to be taken into consideration. The reciprocal coordinates of the streaks are $hk\zeta$, where one unit in the ζ direction corresponds to $c_o=C/3$. The distance $c_o(=6·63$ Å$)$ is the separation between two adjacent (Sn, Na) planes.

In the true hexagonal cell $(a=b=6·64$ Å, $c=39·8$ Å$)$ the ab plane is three times the AB plane of the superposition cell. Accordingly, there are 2Sn and 1Na in one (Sn, Na) plane. The relationship between the superposition and the true ab planes, indicated in Fig. 5, requires that the positions of the atoms in the first (Sn, Na) plane are: 1Na in 0,0,0 and 2Sn in $\frac{1}{3},\frac{2}{3},0$; $\frac{2}{3},\frac{1}{3},0$, assuming hexagonal plane symmetry. These atoms together with adjacent (S) planes and one (Na) plane above were considered to constitute one layer, called L_0, cf. Fig. 4. All possible structures may be composed of such ordered layers, which are stacked upon each other in a disordered way in the c direction. Taking the superposition structure and the differences in the Na–S and Sn–S distances into account, the highest possible plane symmetry of an ordered layer is $P111(\bar{3})mmm$. To conform to this symmetry the (Na) planes have to be considered as belonging to two neighbouring layers. The symmetry elements are illustrated in Fig. 6.

There are three possible ways in which the ordered layers may be stacked perpendicular to the ab plane, so that the sulphur atoms retain their approximate cubic close packing. With respect to the cell parameters $a=b=6·64$ Å and $c_o=6·63$ Å as defined above for the real structures, the possible translations for a layer

relative to the preceding layer are $(a/3 + c_o)$, $(b/3 + c_o)$ or $(-a/3 - b/3 + c_o)$, according to the threefold symmetry of the superposition structure.

Repetition of each of the three different translations throughout the structure gives rise to structures of maximum degree of order, so-called MDO structures. These are denoted MDO_1, MDO_2 and MDO_3. If every other pair of layers is related by one kind of translation and the pairs in between by another, thus combining the translations two by two, three more MDO structures arise, i.e. MDO_4, MDO_5 and MDO_6. To facilitate a comparison between the six structures these can all be related to the hexagonal cell $a = b = 6.64$ Å, $c = 39.8$ Å, although the c axes of the MDO_1–MDO_3 structures are $c/2$. The translations within MDO_1–MDO_6 are outlined in Fig. 7 in which the origins of the layers L_0–L_6 are denoted by a circle together with a figure 0–6, respectively. In Table 4 the extinctions for each of the proposed real structures are given.

Fig. 6. Symmetry elements in layers L_0 and the three alternative layers L_1. The z coordinates of the layers (A) are 0 and $\frac{1}{6}$, respectively.

Table 4. *Extinction rules for the different structures* MDO_1–MDO_6

MDO_1	$2h + l \neq 6n$
MDO_2	$2k + l \neq 6n$
MDO_3	$2i + l \neq 6n$
MDO_4	$-k + l = 3n$
MDO_5	$-h + l = 3n$
MDO_6	$2i + l = 3n$

The pronounced maxima on the diffuse streaks which can be seen in Fig. 1(a) are thus related to one or two of the MDO structures given above, whereas the family reflexions occurring for $h - k = 3n$, $2h + l = 6n$ receive contributions from the MDO structures as well as from any arbitrary stacking of the layers. The diffraction patterns for the different MDO structures were also verified by the relative intensities for different crystals.

A comparison of Fig. 1(b) and Fig. 8 indicates that the crystal used for data collection, has mainly an MDO_4 structure. There may also be a slight contribution from the MDO_2 structure to every other weak maximum, but this was not taken into account during the first stages of the investigation.

Refinement of an MDO structure

The data collected along the streaks at the reciprocal points hkl for which $-k + l = 3n$ were used separately in the preliminary refinement of the MDO_4 structure. The atomic arrangement of the layers could be deduced from the superposition structure and electron-density calculations. The results indicate that the symmetry is $P111(\bar{3})mmm$ for the layers, with all atoms occupying special positions.

After a few cycles of refinement R had converged to about 13 %. However, it was noticed that the observed structure factors with $l = 2n$ always had too small F_c values. When the data set was separated into two parts, with $l = 2n$ and $l = 2n + 1$, respectively, R dropped
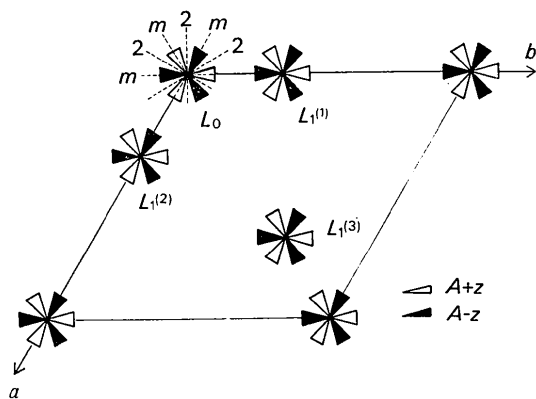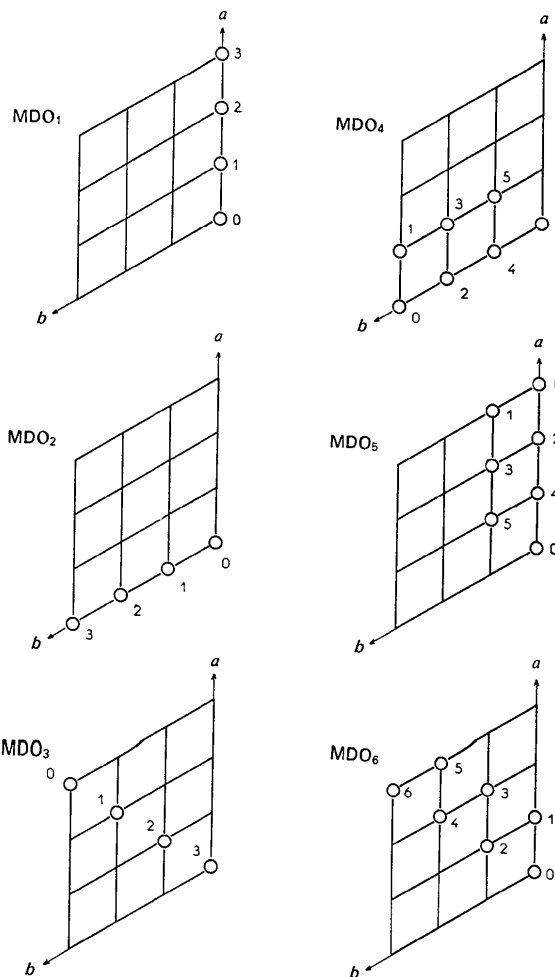

Fig. 7. Diagrams showing the origin translations along the c axis between successive layers which give rise to the six structures MDO_1–MDO_6. The origin of each layer is denoted by a circle.

to 0·082 (*l* odd) and 0·102 (*l* even). It was found that the F_o/F_c ratio was 14% lower for the odd reflexions than it was for the even ones. This indicated that the crystal investigated had, besides the MDO$_4$ structure, a proportion of MDO$_2$ arrangement corresponding to about 13% of that of MDO$_4$.

The sodium atoms in the (Na) planes are octahedrally surrounded by sulphur atoms. If the sodium atoms occupy special positions of the plane symmetry $P111(\bar{3})mmm$ the six Na–S distances would differ considerably in length. To achieve a more plausible structure model further refinement was performed assuming the atoms to be positioned in a less symmetric arrangement. It was shown that the best fit for the data was obtained for the (S) and (Sn,Na) planes retaining the high symmetry, with the only symmetry element for

Fig. 8. Reciprocal points $0kl$ corresponding to the six structures MDO$_1$–MDO$_6$.

the (Na) planes being a mirror plane. This arrangement made R drop to 0·066 for the odd reflexions (328) and 0·080 for the even reflexions (288). This feature can be expressed as follows: The building units of the structure have to be regarded as two different layers instead of one layer as suggested earlier. The (Sn,Na) plane and the (S) planes above and below together form one layer, called L_0 etc. The other kind of layer, called L_o' etc. consists of the plane of sodium atoms between the other layers and hence the layer sequence of the structure will be: $L_0, L_o', L_1, L_1', L_2$ and so forth.

The plane symmetry of layers L_n is $P111(\bar{3})mmm$ and the atomic arrangement of this kind of layer is shown in Fig. 5 for layer L_0. The general equivalent positions for the MDO$_4$ arrangement are (*cf.* Fig. 6):

$$\{L_0\} = [x,y,z; \bar{y},x-y,z; y-x,\bar{x},z; \bar{x},\bar{y},\bar{z}; y,y-x,\bar{z};$$
$$x-y,x,\bar{z}; y,x,z; \bar{x},y-x,z; x-y,\bar{y},z;$$
$$\bar{y},\bar{x},\bar{z}; x,x-y,\bar{z}; y-x,y,\bar{z}]$$
$$\{L_1\} = (\tfrac{1}{3},0,\tfrac{1}{6}) + \{L_0\}$$
$$\{L_{2n}\} = (0,-n/3,n/3) + \{L_0\}$$
$$\{L_{2n+1}\} = (0,-n/3,n/3) + \{L_1\} \,.$$

The sodium layers L_n' have either the symmetry $P111(1)m11$, $P111(1)1m1$ or $P111(1)11m$ depending on the translations between the surrounding L_n layers. Table 5 gives the plane symmetries of layers L_n' when layers L_n are transformed in different ways to layers L_{n+1}. The three possible layers L_n' are related to each other by a 120° rotation as are also the three different layers L_{n+1}.

In the MDO$_4$ structure the translation between the layers is alternately I and III (*cf.* Table 5), while the layers in the MDO$_2$ structure all are translated by II. As a consequence, in MDO$_4$ every other L' layer has the symmetry $P111(1)m11$ and the rest $P111(1)11m$. In MDO$_2$ all L' layers have the symmetry $P111(1)1m1$.

Table 5. *Plane symmetries of layers* L_n' *[(Na) planes] with respect to the translations between surrounding* L_n *layers*

General equivalent positions are given for layer L_o'.

No.	Translation $L_n \to L_{n+1}$	Plane symmetry of layers L_n'	General equivalent positions of layers L_o'
I	$a/3 + c_0$	$P111(1)m11$	$\{L_o'\} = [x,y,z; x-y,\bar{y},z]$
II	$b/3 + c_0$	$P111(1)1m1$	$\{L_o'\} = [x,y,z; \bar{x},y-x,z]$
III	$-a/3 - b/3 + c_0$	$P111(1)11m$	$\{L_o'\} = [x,y,z; y,x,z]$

Table 6. *Atomic coordinates and isotropic thermal parameters for the layers* L_0, L_0' *and* L_1', *respectively, in* MDO$_4$

The standard deviations are given in parentheses. The fractional coordinates correspond to the hexagonal cell
$a = b = 6·64$, $c = 39·76$ Å.

Layer	Plane symmetry	Atom	x	y	z	B
L_0	$P111(\bar{3})mmm$	Sn	$\tfrac{2}{3}$	$\tfrac{1}{3}$	0	0·64 (3)
		Na$_1$	0	0	0	2·5 (6)
		S	0·3641 (5)	0	0·03662 (6)	0·91 (4)
L_0'	$P111(1)m11$	Na$_2$	$\tfrac{2}{3}$	0	$\tfrac{1}{12}$	1·36 (11)
		Na$_3$	$\tfrac{1}{3}-y^*$	$\tfrac{1}{3}-2y^*$	$\tfrac{1}{12}$	1·36 (11)
L_1'	$P111(1)11m$	Na$_2$	$\tfrac{2}{3}$	$\tfrac{1}{3}$	$\tfrac{3}{12}$	1·36 (11)
		Na$_3$	y^*	$-y^*$	$\tfrac{3}{12}$	1·36 (11)

* Where $y = 0·0081$ (4).

The parameters of the MDO$_4$ structure accordingly give an incorrect fit of the weak intensities with l even, since these reflexions have an intensity contribution from the MDO$_2$ structure. The refinement was therefore continued without the structure factors with l even.

Mean values of the F_o equivalent for symmetry reasons were calculated. The final refinement, based on 115 family reflexions and 199 weak reflexions, gave an R of 0·045. A total of 9 parameters were refined and the structure factors were calculated in the same manner as for the superposition structure.

The ratio of the scale factors for the family and the weak reflexions corresponds to 72% of MDO$_4$ arrangement in the crystal used in the investigation.

The final atomic parameters are given separately for the layers L_0, L_o' and L_1' in Table 6 together with their standard deviations. The corresponding observed and calculated structure factors for MDO$_4$ are listed in Table 7.

Table 7. *Observed and calculated structure factors for* MDO$_4$ *arrangement with the exception of* F_{nkl} *with* $l = 2n$

Unobserved structure factors are denoted by an asterisk.

All computations were performed on an IBM 360/65 computer, with the program library of the Department of Inorganic Chemistry, Göteborg. *DATAP*1 (data reduction) and *BLOCK* (least-squares block-diagonal approximation) have been written by O. Lindgren, Göteborg; *DATAP*2 (absorption correction) was originally written by Coppens, Leiserowitz & Rabinovich (1965); *DRF* (Fourier) and *DISTAN* by A. Zalkin, Berkeley, California; *LINUS* (full-matrix least-squares) is the Busing, Martin & Levy (1962) least-

squares program, modified for refinement of extinction parameters (Coppens & Hamilton, 1970).

Discussion

The structure of Na$_2$SnS$_3$ has approximately cubic close-packed sulphur atoms. The octahedral holes are occupied either by tin or by sodium atoms, and the structure therefore has an arrangement similar to that of NaCl (*cf.* Fig. 9). The most important distances and angles are given in Table 8. The distribution of the tin and sodium atoms over the cation sites is not regular, but depends on the OD character of the crystal under investigation. The structure portion shown in Fig. 9 is drawn in accordance with the MDO$_4$ arrangement (*cf.* Table 6).

Fig. 9. Schematic drawing showing the NaCl structure character of Na$_2$SnS$_3$.

Fig. 10. Phases with known structures in the Na$_2$S–SnS$_2$ system. The Sn–S coordination numbers are indicated.

Table 8. *Interatomic distances and unique angles in the MDO$_4$ structure with standard deviations in parentheses*

Sn—S	6 × 2·571 (2) Å	Na(3)–S	2 × 2·795 (4) Å
Na(1)–S	6 × 2·822 (3)	Na(3)–S'	2 × 2·915 (3)
Na(2)–S	2 × 2·735 (3)	Na(3)–S''	2 × 2·980 (3)
Na(2)–S'	4 × 2·973 (2)		
		S–Na(1)–S	95·79 (7)°
S–Sn–S	83·56 (7)°		180·00
	91·08 (7)		
	94·81 (10)	S–Na(3)–S	78·82 (8)°
	172·10 (9)		79·95 (7)
			90·53 (9)
S–Na(2)–S	90·47 (8)°		94·32 (13)
	100·12 (5)		95·97 (10)
	180·00		98·09 (11)
			169·6 (6)
			174·3 (4)

The compounds in the Na$_2$S–SnS$_2$ system with known structures are plotted in Fig. 10. Those with a molar ratio Na$_2$S/SnS$_2$ > 1 all show a tetrahedral Sn(IV)–S coordination, while tin is octahedrally coordinated in SnS$_2$ (Oftedal, 1928) and in Na$_2$SnS$_3$. The SnS$_2$ structure is of CdI$_2$ (C6) layer type, i.e. the sulphur atoms are hexagonally close-packed. The layers, L_n,
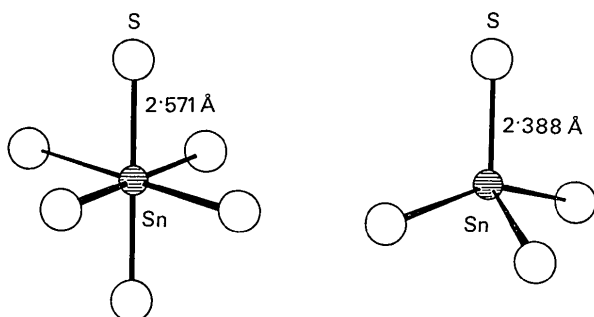
Fig. 11. The octahedral and tetrahedral coordination of Na$_2$SnS$_3$ and Na$_4$SnS$_4$, respectively.
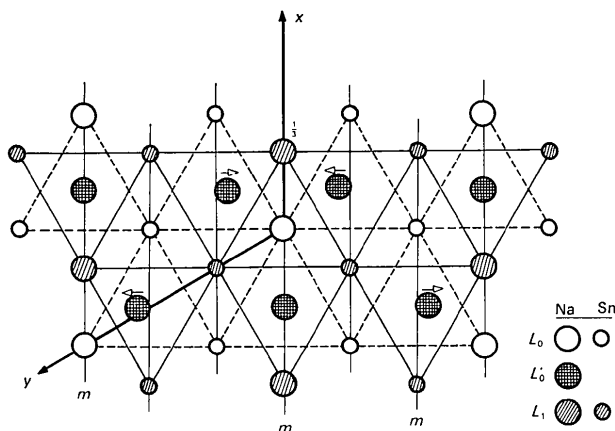
Fig. 12. The deviation of Na(3) from the $P111(\bar{3})mmm$ plane symmetry.

found in Na$_2$SnS$_3$ (cf. Fig. 5) are of the same kind as in SnS$_2$, but with one third of the tin atoms replaced by sodium atoms, corresponding to the formula [NaSn$_2$S$_6$]$_n^{3n-}$. The octahedral holes between such layers are occupied by sodium atoms.

Although Na$_2$SnS$_3$ has an OD structure, the refinement of the MDO$_4$ arrangement has supplied accurate information concerning the octahedral sulphur coordination of both tin(IV) and the sodium ions. All six Sn–S distances have the same length due to symmetry, while some of the S–Sn–S angles deviate by more than 5° from the ideal value of 90° (cf. Table 8). The length of the octahedral Sn(IV)–S bond in Na$_2$SnS$_3$ of 2·571(2) Å agrees well with the corresponding values found in the two isomorphous compounds Sn$_2$S$_3$ (Mootz & Puhl, 1967) and PbSnS$_3$ (Jumas, Ribes, Philippot & Maurin, 1972), i.e. 2·497(2)–2·611(2) Å and 2·469–2·599 Å, respectively. The octahedral Sn(IV)–S bond is about 0·1–0·2 Å longer than those found for tetrahedral coordination (cf. Fig. 11). In Na$_4$SnS$_4$, for example, the tetrahedral bond was found to be 2·388(4) Å (Jumas, Vermot-Gaud-Daniel & Philippot, 1973).

The octahedral configuration seems to be preferred when the composition allows all cations to be placed in octahedral sites, as in SnS$_2$ and Na$_2$SnS$_3$. Other examples are the two isomorphous compounds Sn$_2$S$_3$ and PbSnS$_3$, which are structurally related to SnS$_2$ (Mootz & Puhl, 1967).

The fact that the tin atom is small compared to the sulphur atom suggests that the tetrahedral Sn(IV)–S coordination is more stable than the octahedral. However, since the coordination polyhedron may be either tetrahedral, trigonal bipyramidal or octahedral it is reasonable to assume that the covalent Sn(IV)–S bonds are dependent on to the stoichiometric and structural features. This view is also supported by the fact that structures with tetrahedral Sn(IV)–S coordination are better described in terms of SnS$_4^{4-}$ ions than Sn^{4+} ions in tetrahedral holes. The presence of SnS$_4^{4-}$ ions in Na$_4$SnS$_4$ (Jumas, Vermot-Gaud-Daniel & Philippot, 1973) results in a considerable deviation from a close-packed arrangement of the sulphur atoms.

There are three independent sodium ions in the structure. Na(1), which belongs to the [NaSn$_2$S$_6$]$_n^{3n-}$ layer, has a nearly regular octahedral coordination (cf. Table 8), with all Na–S distances equal to 2·822(3) Å. This is in excellent agreement with the value of 2·826 Å reported in International Tables for X-ray Crystallography (1962).

Every sulphur atom is shared between two tin and one sodium atom in an (Sn, Na) plane and three sodium atoms in an (Na) plane. Due to the covalent character of the Sn–S bonds the close-packing of the sulphur atoms is distorted. This affects the sulphur coordination of both Na(2) and Na(3) in the (Na) planes in such a way that two Na–S distances are significantly shorter than the remaining four (cf. Table 8). The average Na–S bond distance for the interlayer sodium

ions is 2·895 Å, and the slight elongation compared with Na(1) is probably due to strains caused by the strong Sn-S bonds. The only deviation of the Na(2) and Na(3) arrangement from the L_n symmetry $P111(\bar{3})mmm$ is that Na(3) has been shifted by a distance of 0·058(3) Å. This effect, which is evident from the results of the refinement, has its chemical explanation in the fact that Na(3) has the two neighbouring Na atoms in *cis* position, while they are in *trans* position for Na(2) (Fig. 12).

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Structure Cristalline et Moléculaire du Diméthyl-5,11 6H-Pyrido[4,3-b]carbazole (Ellipticine)

PAR C. COURSEILLE, B. BUSETTA ET M. HOSPITAL

Laboratoire de Cristallographie et Physique Cristalline associé au CNRS,
Université de Bordeaux I, 351 cours de la Libération, 33405-Talence, France

The structure of ellipticin (5,11-dimethyl-6H-pyrido[4,3-b]carbazole), a new antitumoral molecule, was solved by direct methods. The crystal belongs to the monoclinic system, space group $P2_1/c$ ($Z=4$) with cell parameters $a=5\cdot105$, $b=15\cdot588$, $c=16\cdot161$ Å and $\beta=97\cdot03°$. The main feature of crystal packing appears to be different from that observed for some other dye molecules.

Introduction

L'ellipticine est une molécule dérivée d'un composé naturel extrait de '*l'ochrosia elliptica*' qui est dotée d'une activité antitumorale et antileucémique. La formule chimique et la numération de ses atomes sont présentées sur la Fig. 1. Cette molécule semble avoir la propriété de se fixer sur l'ADN par intercalation comme les différents produits antimalariques et anti-

trypanosomiques que nous avons déjà étudiés: chloroquine (Courseille, Busetta & Hospital, 1973*a*), sulfate de chloroquine (Leger & Bideau, 1972) chlorhydrate de quinacrine (Courseille, Busetta & Hospital, 1973*b*), bromhydrate d'éthidium (Hospital & Busetta, 1969), bromhydrate de dimidium (Courseille, Busetta & Hospital, 1972).

Il est intéressant d'étudier l'ellipticine pour sa conformation mais aussi pour savoir quel est le mode