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**The crystal and molecular structure of 3-nitroperchlorylbenzene: Corrigendum.** By GUS J. PALENIK, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada*, JERRY DONOHUE, *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania*, and K. N. TRUEBLOOD, *Department of Chemistry, University of California, Los Angeles, California, U.S.A.*

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In a paper on the title compound (Palenik, Donohue & Trueblood, 1968) acknowledgement of support of the National Science Foundation was inadvertently omitted.

#### Reference

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**The crystal structure of samsonite,  $2\text{Ag}_2\text{S} \cdot \text{MnS} \cdot \text{Sb}_2\text{S}_3$ .** By J. HRUŠKOVÁ, *Geological Survey, Prague 1, Hradební 9, Czechoslovakia*, and V. SYNEČEK, *Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague 6, Cukrovarnická 10, Czechoslovakia*

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The crystal structure of samsonite,  $2\text{Ag}_2\text{S} \cdot \text{MnS} \cdot \text{Sb}_2\text{S}_3$ , has been determined from three-dimensional X-ray data. The structure is characterized by the presence of  $\text{SbS}_3$  squat pyramids and slightly deformed  $\text{MnS}_6$  octahedra. It can be uniquely described as being built up of  $\text{S-MnSbAg}_2$  tetrahedra which share corner atoms with neighbouring tetrahedra.

According to Bragg's classification (Bragg & Claringbull, 1965) of sulphides, the mineral samsonite belongs to the group of compounds in which the metal atoms are incorporated in structures resembling the compounds of S, As, Sb, and Bi. We have undertaken the crystal-structure investigation of samsonite in an attempt to gain further data on the crystal chemistry of this complex group of minerals.

The first crystallographic data of samsonite were published by Werner & Fraatz (1910) who found the monoclinic symmetry and axial ratio of this mineral. The single-crystal X-ray diffraction investigation of Frondel (1941) led to the following lattice parameters:  $a = 10.31$ ,  $b = 8.07$ ,  $c = 6.62$  Å and the space group  $P2_1/n$ . From density measurements he found two formula units ( $Z = 2$ ) in the unit cell.

Our investigation was carried out on a single crystal of samsonite from a collection of minerals in the National Museum in Prague (Coll. No 591). Small single-crystal fragments of an appropriate shape were used for taking the rotation and zero-layer Weissenberg photographs about three crystallographic axes as well as for taking equi-inclination photographs about the [001] axis. All diffraction photographs were recorded with unfiltered Mo K radiation. Visually estimated intensities of reflexions were corrected for Lorentz and polarization factors and used for calculations of projections of the Patterson function along three crystallographic axes and of the Patterson-Harker sections  $(x, \frac{1}{2}, z)$  and  $(\frac{1}{2}, y, \frac{1}{2})$ . The interpretation of these syntheses led directly to the determination of the positions of the heavy atoms in the unit cell of samsonite. These positions served for the construction of projections of the minimum function along the [001] and [010] axes. The peaks in the latter syntheses were checked by consideration

of the reasonable packing of atoms in the unit cell of samsonite. This procedure enabled us to determine the sulphur atom positions. The first projections of electron density along the [001] and [010] axes were calculated with structure factors whose signs were already reliably determined from the heavy-atom positions. The agreement between the data of minimum and electron density projections was satisfactory. All atoms except Mn lie in general fourfold positions of the space group  $P2_1/n$ . Manganese atoms lie in one of the four twofold positions of this group.

Approximate coordinates of atoms are listed in Table 1. Although these coordinates require further refinement they enable us to describe the general features of the crystal structure of samsonite. Fig. 1 shows the electron-density projection and its interpretation in terms of the atomic positions in one unit-cell of samsonite. The presence of two atomic polyhedra – the squat pyramids,  $\text{SbS}_3$ , and slightly deformed octahedra,  $\text{MnS}_6$ , – is the most characteristic feature of the crystal structure of samsonite. Although the small difference in the scattering powers of Sb and Ag does not permit the reliable distinction between these two kinds of atoms from diffraction data only, the appearance of the pyramidal  $\text{SbS}_3$  group indirectly indicates the correct fourfold positions occupied by the Sb atoms. The  $\text{SbS}_3$  group is a squat pyramid, with an Sb atom at the vertex and three sulphur atoms at an average distance of 2.4 Å at the basal corners; this can be compared with the corresponding Sb-S distance in proustite, equal to 2.44 Å (Harker, 1936). The sulphur atoms forming the triangular base of one  $\text{SbS}_3$  pyramid lie in three different fourfold positions; their average separation is 3.6 Å.

The manganese atoms are situated in one of four twofold positions of the centres of symmetry within the octa-

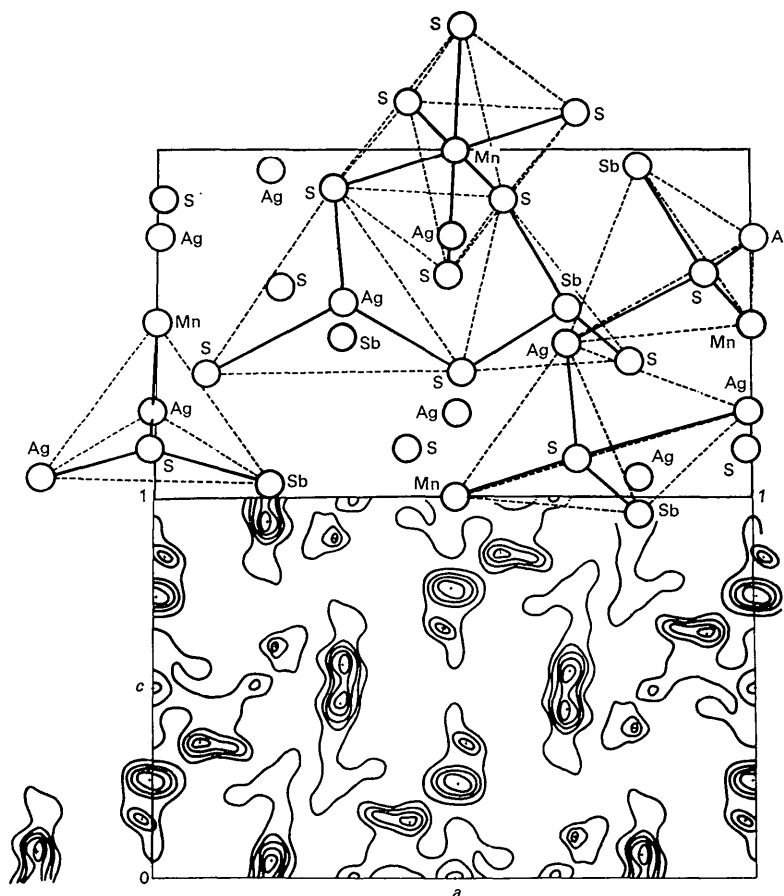


Fig. 1. Electron density projection of one unit-cell of samsonite along the [010] axis. The schematical drawing shows both the conventional polyhedra of cations surrounded by anions and the polyhedra of anions surrounded by cations. The latter are shown for all three crystallographically different sulphur atoms.

Table 1. *Positional parameters of atoms, in fractional coordinates*

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0.000	0.000	0.500
Sb	0.185	0.163	0.037
Ag(1)	0.300	0.242	0.571
Ag(2)	0.505	0.040	0.750
S(1)	0.083	0.250	0.352
S(2)	0.980	0.150	0.840
S(3)	0.767	0.067	0.392

hedral groups of sulphur atoms. The sulphur atoms in the  $\text{SbS}_3$  pyramid belong to three different  $\text{MnS}_6$  octahedra. The  $\text{MnS}_6$  octahedra are thus built from three pairs of crystallographically different sulphur atoms surrounding the Mn atom at the centre of symmetry. The average Mn-S distance of 2.5 Å in the somewhat distorted  $\text{MnS}_6$  octahedra can be compared with the corresponding distance of 2.6 Å in alabandite (Wyckoff, 1921). The average S-S distance within one  $\text{MnS}_6$  octahedron is equal to 3.5 Å. The three-dimensional network formed by  $\text{SbS}_3$  groups sharing sulphur atoms with three different  $\text{MnS}_6$  groups is stabilized by Ag-S links.

The Ag(1) atom resembles the Sb atom in its sulphur environment, with the somewhat larger Ag(1)-S distance

of 2.6 Å as compared with 2.4 Å in the  $\text{SbS}_3$  pyramid. The sulphur atoms in the  $\text{AgS}_3$  group are again in three different fourfold positions. There is a still longer Ag-S(3) bond, equal to 2.9 Å, to a deformed tetrahedron of sulphur atoms which completes the Ag(1) environment. The average Ag-S distance is thus 2.8 Å. The Ag(2) atoms make only two bonds with the S(1)-S(2) atoms belonging to different  $\text{MnS}_6$  and  $\text{SbS}_3$  groups, with a Ag(2)-S distance of 2.55 Å, and are thus more typical of this group of sulphides in their bonding. The polyhedra of cations surrounded by sulphur atoms are shown in the upper part of Fig. 1. The bonds between the central atoms and the sulphur atoms are indicated by solid lines and the edges of the polyhedra are shown by broken lines.

The detailed examination of the sulphur environment revealed an interesting characteristic of the structure of samsonite. Each of the three crystallographically different sulphur atoms is surrounded by one Mn, one Sb, and two Ag atoms resembling a deformed tetrahedron around each sulphur atom. The overall mean distance of nearest neighbours from the central sulphur atom, averaged over all three kinds of S-MnSbAg<sub>2</sub> group, is 2.5 Å. The same average distance of sulphur atom nearest-neighbours among themselves is 4.1 Å. The structure of samsonite can be thus uniquely described as being built up of S-MnSbAg<sub>2</sub> tetra-

hedra which share corner atoms with neighbouring tetrahedra. The tetrahedra formed by cations surrounding the anions are shown in projection along the [010] direction in Fig. 1. Three of these tetrahedra, corresponding to crystallographically different central sulphur atoms, are drawn in this figure. The sulphur atom links to their nearest cations are shown by solid lines and edges of the tetrahedra are marked by broken lines.

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**On the unit-cell dimensions and space group of L-tyrosine and L-tryptophane.** By B. KHAWAS and G. S. R. KRISHNA MURTI, *Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi-12, India*

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The Debye-Scherrer patterns of L-tyrosine,  $\alpha$ -amino- $\beta$ -(*p*-hydroxyphenyl)propionic acid, and L-tryptophane,  $\alpha$ -amino-3-indolepropionic acid, have been analysed. L-Tyrosine, crystallized from aqueous solution, is orthorhombic, space group *Pnam*, with eight molecules per unit cell of dimensions  $a=13.89$ ,  $b=21.08$  and  $c=5.84_2$  Å. L-Tryptophane, crystallized from aqueous solution, is also orthorhombic, space group *Pmmm*, with eight molecules per unit cell of dimensions  $a=16.81$ ,  $b=17.90$  and  $c=6.90_4$  Å.

For the interpretation of X-ray diffraction photographs of animal materials like silk, keratin, proteins, etc. it is necessary to have a knowledge of the crystal structure of pure aminoacids. Bernal (1931) reported on the unit-cell dimensions of fifteen aminoacids; recently the dimorphism of DL-aspartic acid (Krishna Murti, Natarajan & Deb, 1965) and the unit-cell dimensions and the space group of DL-tryptophane and DL- $\beta$ -phenylalanine (Khawas & Krishna Murti, 1968) have been determined. The data on the crystal structure of L-tyrosine and L-tryptophane has not been reported so far.

The compounds could not be obtained as good single crystals by the ordinary methods of crystallization so information regarding the structure of these compounds had to be obtained from powder patterns alone; these were taken on a Philips 11.48 cm camera with Cu  $K\alpha$  radiation.

The spacings of the reflexions were calculated from measurements of the distances between arcs of symmetrical pairs in the powder patterns to an accuracy of 0.1 mm. The patterns could not be indexed in terms of a unit cell of cubic, tetragonal or hexagonal symmetry. The patterns were then analysed by a modification (Krishna Murti *et al.*, 1965) of Lipson's (1949) method.

#### L-Tyrosine

Pure L-tyrosine, obtained from the British Drug Houses Ltd., England, was crystallized from its aqueous solution, by evaporation at room temperature, in clusters of very fine needle-shaped crystals. The fibre pattern, about the fibre axis (Fig. 1), of such a bundle of crystals was also taken.

The values of the constants *A*, *B* and *C* from the analysis are found to be 0.00518, 0.00225 and 0.0293 respectively, where  $A=1/a^2$ ,  $B=1/b^2$  and  $C=1/c^2$ . There is good agreement between the observed and calculated  $Q(1/d_{hkl}^2)$  values as shown in Table 1.

Table 1. *Data on the powder pattern of L-tyrosine*

Intensity*	Spacing observed	$Q(1/d_{hkl}^2)$		Indices
		Observed	Calculated	
<i>m</i>	6.583 Å	0.0231	0.0229	210
<i>vw</i>	6.237	0.0257	0.0254	130

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Table 1 (cont.)

Intensity*	Spacing observed	$Q(1/d_{hkl}^2)$		Indices
		Observed	Calculated	
<i>s</i> (broad)	5.829 Å	0.0294	0.0297	220
<i>w</i>	5.624	0.0316	0.0315	011
<i>w</i>	5.294	0.0357	0.0360	040
			0.0367	111
<i>vs</i>	4.955	0.0407	0.0409	230
			0.0412	140
<i>m</i>	4.493	0.0495	0.0495	031
			0.0500	201
<i>vs</i>	4.376	0.0522	0.0522	211
<i>vw</i>	4.231	0.0559	0.0556	320
			0.0567	240
<i>m</i> (broad)	4.124	0.0588	0.0590	221
<i>s</i>	3.619	0.0764	0.0769	250
<i>s</i>	3.485	0.0823	0.0826	340
			0.0829	400
<i>s</i>	3.421	0.0854	0.0849	321
			0.0855	051
			0.0860	241
<i>s</i>	3.296	0.0921	0.0919	420
<i>s</i> (broad)	3.132	0.1019	0.1017	260
			0.1028	350
<i>m</i>	2.974	0.1131	0.1122	401
<i>w</i>	2.880	0.1206	0.1212	421
<i>vw</i>	2.822	0.1256	0.1262	022
<i>m</i>	2.754	0.1318	0.1310	261
			0.1314	351
			0.1321	122
<i>m</i>	2.679	0.1393	0.1385	520
			0.1391	450
			0.1401	212
<i>m</i>	2.614	0.1463	0.1469	222
<i>vw</i>	2.561	0.1525	0.1532	042
<i>vw</i>	2.519	0.1576	0.1569	361
			0.1581	232
			0.1584	142
<i>w</i>	2.475	0.1632	0.1639	460
<i>w</i>	2.404	0.1730	0.1728	322
			0.1732	242
<i>vwv</i>	2.336	0.1833	0.1841	332
<i>m</i>	2.279	0.1925	0.1932	461
<i>vw</i>	2.232	0.2007	0.2001	402
<i>vw</i>	2.183	0.2098	0.2091	422
			0.2105	560
<i>s</i>	2.149	0.2165	0.2158	601
			0.2167	191