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$Na_2Hg_3S_4$: a thiomercurate with layered anions

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Abstract

Dark red crystals of $Na_2Hg_3S_4$ were obtained by reacting a stoichiometric mixture of Na_2S and HgS at 870 K. $Na_2Hg_3S_4$ is orthorhombic, *oP*36, space group *Pbca* with $a = 7.308(5)$ Å, $b = 14.011(8)$ Å, $c = 8.231(3)$ Å and $Z = 4$. The crystal structure was determined from four-circle diffractometer data and refined to a conventional R of 0.056 for 718 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 43 variables ($R_w = 0.065$).

$Na_2Hg_3S_4$ crystallizes with a new structure type whose outstanding feature is the formation of strongly corrugated anionic layers, ${}^2_\infty-[Hg_3S_4]^{2-}$, running parallel to (010). These layers are based on a network of 16-membered rings formed by alternating mercury and sulphur atoms. Two thirds of the mercury atoms are in a trigonal planar co-ordination by sulphur ($\bar{d}_{Hg-S} = 2.49$ Å) while the remaining atoms are linearly coordinated ($d_{Hg-S} = 2.344$ Å). The Na^+ ions are coordinated by five sulphur atoms in a distorted square pyramidal configuration.

The structure of $Na_2Hg_3S_4$ can formally be derived from a distorted close-packed array of chalcogen atoms (stacking sequence, $(hc)_2$; stacking direction, [010]).

1. Introduction

In contrast to its isoelectronic neighbours, Au(I) with its high preference for linear co-ordination by sulphur and Tl(III), which in sulphides is predominantly tetrahedrally coordinated, the d^{10} ion Hg(II) shows a surprising variability with respect to its co-ordination. This is already evident from the modifications of HgS, cinnabar [1] and metacinnabarite [2] with co-ordination numbers of 2 and 4 respectively.

Until recently, few structural studies on thiomercurates confirmed this peculiarity. Thus, in the K_2S–HgS system, two intermediate compounds with mononuclear anionic groups are formed: $K_6[HgS_4]$ [3] with tetrahedral anions and $K_2[HgS_2]$ [4] with (almost) linear anions. Thiomercurates with higher mercury contents crystallize with unique structures, characterized by the coexistence of different co-ordination geometries of the mercury atoms. In the structure of $BaHgS_2$ [5], isolated $[S–Hg–S]^{2-}$-dumbbells and infinite isotactic chains, ${}^1_\infty[-SHg(S)-]^{2-}$, with a trigonal sulphur co-ordination of mercury are formed. An interesting infinite one-dimensional anion is also found in $K_2Hg_3S_4$ [6]. It is formed by HgS_4 tetrahedra linked together by mercury atoms which attain a linear sulphur co-ordination. In $K_2Hg_6S_7$ [6],

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tetrahedral HgS_4 groups share common edges to form an infinite framework with large channels which are divided into segments by S–Hg–S–Hg–S bridges in which the mercury atoms are almost linearly co-ordinated by sulphur.

Investigations of the Na_2S–HgS system have so far revealed two intermediate compounds: Na_2HgS_2 [4], structurally related to K_2HgS_2; $Na_2Hg_3S_4$, the structure of which, in contrast to $K_2Hg_3S_4$, is characterized by infinite anionic layers, will be presented below.

2. Experimental details

$Na_2Hg_3S_4$ was prepared by the fusion of a powdered mixture of the binary compounds HgS (red modification, Merck, 99.9%) and Na_2S. The latter was obtained by the careful dehydration of recrystallized $Na_2S \cdot 9H_2O$ under vacuum and was demonstrated to be roentgenographically pure. The two components were mixed in the molar ratio 3:1 and sealed in an evacuated silica tube. The sample was heated in steps up to 870 K, annealed at this temperature for several days and finally cooled to ambient temperature with a cooling rate of 2.5 K h^{-1}.

Microscopic investigation of the crushed ingot revealed the major component to be a dark red crystalline phase, the composition of which was shown to be $Na_2Hg_3S_4$ in the course of the structure refinement. The compound is sensitive to moisture and, hence, was handled under inert conditions.

3. Structure determination

Preliminary roentgenographic investigations were performed with rotating crystal and Weissenberg methods (Cu Kα). They revealed an orthorhombic cell. From the systematically extinct reflections ($0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$ and $hk0$: $h \neq 2n$) the space group was uniquely determined to be *Pbca* (No. 61).

For the structure determination, a rather small irregularly shaped crystal with the approximate dimensions $0.06 \times 0.06 \times 0.05$ mm^3 was chosen and sealed at random orientation into a thin walled glass capillary. Intensity data were collected on a computer-controlled four-circle diffractometer (Enraf-Nonius CAD4) using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The reflections were measured over one octant of the reflection sphere up to $2\theta = 52°$ applying background–peak-background (BPB) scans (ω–2θ scan mode; scan width, $0.8° + 0.35° \tan \theta$; maximum scan time, 180 s). The stability of the crystal was monitored by the periodic determination of three intensity control reflections. No significant changes were registered during the time of data collection.

Precise lattice constants were obtained by least-squares refinement of the angular positions of 24 high-angle reflections centred at four different settings. The lattice constants, together with other relevant crystallographic data, are given in Table 1.

TABLE 1

Crystallographic data for $Na_2Hg_3S_4$

Pearson symbol	*oP*36	
a (Å)		7.308(5)
b (Å)		14.011(8)
c (Å)		8.231(3)
Space group	*Pbca* (No. 61)	
Z		4
V (Å^3)		842.7
d (g cm^{-3})		6.12
Relative formula mass (RFM)		776.0
Absorption coefficient ($\mu_{Mo\ K\alpha}$) (cm^{-1})		554.8
Crystal dimensions (mm^3)		0.05×0.06×0.06
Structure refinement		
Unique reflections		819
$F_o^2 > 3\sigma(F_o^2)$		718
Refined variables		43
$R = \Sigma\lvert F_o\rvert - \lvert F_c\rvert/\Sigma\lvert F_o\rvert$		0.056
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$		0.065
$w = [\sigma(I)^2 + (0.002F_o^2)^2]^{-1/2}$		
Residual electron density (e Å^{-3})		3.3

The crystal structure was solved by direct methods (MULTAN-82 [7]). An *E*-map calculated from a phase set of 185 normalized structure factors ($E_{min} > 1.2$, 3770 triplet relationships) revealed the positions of the mercury atoms. The remaining atoms were located from subsequent difference Fourier syntheses. Isotropic refinement of the complete structure converged at $R = 0.099$. The refinement with anisotropic temperature factors led to a final residual of 0.056 ($R_w = 0.065$ for 718 observations and 43 refined parameters). A subsequent difference Fourier map was featureless.

The atomic scattering factors for the neutral atoms and anomalous dispersion corrections were taken from the *International Tables* for *X-Ray Crystallography* [8]. The absorption effects were accounted for approximately by a spherical absorption correction ($\mu R = 1.5$). All the calculations were performed on a DEC-MicroVAX 3520 computer using programs of the Enraf–Nonius crystallographic software package [9]. The atomic co-ordinates and equivalent isotropic thermal parameters are given in Table 2. Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited under C.S.D. No. 55721 with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., W-7514 Eggenstein-Leopoldshafen 2, FRG.

4. Discussion

The interatomic distances and bond angles for $Na_2Hg_3S_4$ are given in Table 3. Figure 1 shows a projection of the unit cell along the shortest axis.

TABLE 2

Positional and equivalent isotropic thermal parameters for $Na_2Hg_3S_4$

Atom	x	y	z	B (Å^2)
Na(1)	0.568(2)	0.6076(9)	0.381(1)	1.7(2)
Hg(1)	0.7285(2)	0.30704(9)	0.2226(2)	1.82(2)
Hg(2)	0.500	0.500	0.000	1.34(3)
S(1)	0.262(1)	0.4816(5)	0.3388(8)	1.1(1)
S(2)	0.487(1)	0.7287(5)	0.0999(8)	1.1(1)

Estimated standard deviations are given in parentheses.

TABLE 3

Interatomic distances (up to 4 Å) and bond angles for $Na_2Hg_3S_4$

Bond	Distance (Å)	Bond	Distance (Å)	Angle (deg)
Na–S(1)	2.869(5)	S(1)–Hg(1)–S(2)		105.00(7)
Na–S(1)	2.902(4)	S(1)–Hg(1)–S(2)		129.04(7)
Na–S(1)	2.895(5)	S(1)–Hg(1)–S(2)		125.03(9)
Na–S(2)	2.926(4)			
Na–S(2)	2.976(4)	Hg(2)–S(1)	2.344(2) (2×)	
Na–S(2)	3.500(5)	Hg(2)–S(1)	3.294(2) (2×)	
Na–Na	3.732(8)	Hg(2)–S(2)	3.306(2) (2×)	
Na–Hg(1)	3.419(4)			
Na–Hg(1)	3.635(4)	S(1)–Hg(2)–S(1)		180.00
Na–Hg(1)	3.397(4)			
Na–Hg(2)	3.511(4)	S(1)–S(1)	3.934(2) (2×)	
Na–Hg(2)	3.632(4)			
Hg(1)–S(2)	2.410(2)	Hg(1)–S(1)–Hg(2)		98.09(8)
Hg(1)–S(1)	2.508(2)	Hg(1)–S(2)–Hg(1)		95.49(7)
Hg(1)–S(2)	2.560(2)			
Hg(1)–S(2)	3.124(2)			
Hg(1)–S(2)	3.770(2)			
Hg(1)–Hg(1)	3.6810(1) (2×)			
Hg(1)–Hg(2)	3.6656(4)			

Estimated standard deviations are given in parentheses.

The outstanding feature of the crystal structure is the formation of infinite, strongly corrugated, anionic layers $^{2}_{\infty}-[Hg_3S_4]^{2-}$ oriented parallel to (010) (Fig. 2). These layers are based on an open network which is composed of 16-membered rings formed by mercury and sulphur atoms in an alternating sequence. With respect to their central plane formed by the Hg(2) and S(1) atoms, these rings are in a chair-like conformation. The nodes of the network are occupied by the Hg(1) atoms which are common to three rings. Hg(1)–S(2) bonds (approximately equatorial to the central plane) join the rings in the [100] direction while the rather axial Hg(1)–S(1) bonds connect them along [001]. The resulting fishbone-like arrangement of the rings is shown in greater detail in Fig. 3.

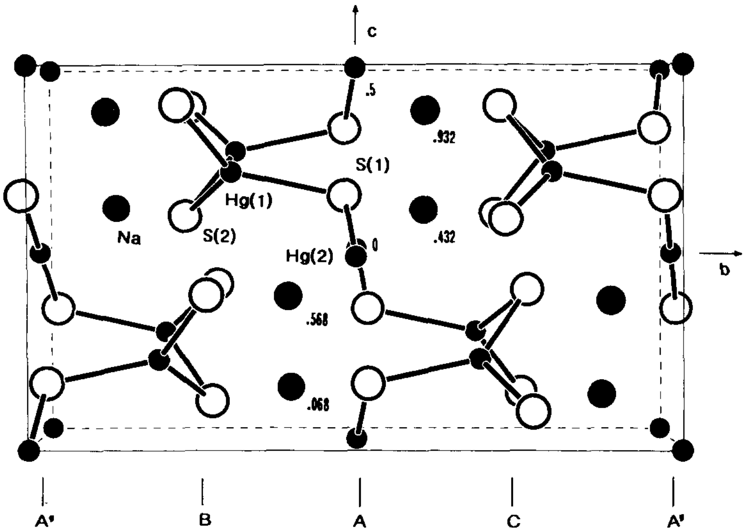

Fig. 1. Projection of the unit cell of $Na_2Hg_3S_4$ along [100]. Hg(1) and S(1) are at $x \approx 0.25$ and $x \approx 0.75$. S(2) is at $x \approx 0$ and $x \approx 0.5$. The other heights are given in the figure. The capital letters at the bottom of the figure correspond to the different stacking positions of the layers formed by the S(1) and S(2) atoms respectively (see also Fig. 4).

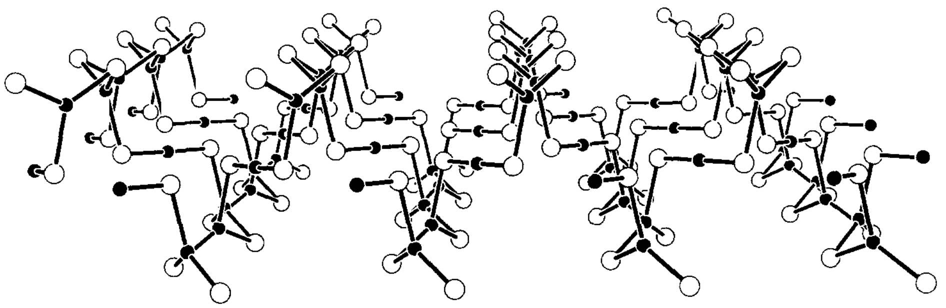

Fig. 2. Perspective view of the layered $^{2}_{\infty}-[Hg_3S_4]^{2-}$ anion. Open circles: sulphur, full circles: mercury.

A structural feature of $Na_2Hg_3S_4$ common to other mercury-rich thiomercurates is the appearance of mercury atoms with different co-ordination numbers. Thus, Hg(1) is irregularly co-ordinated by three sulphur atoms in an almost planar configuration (sum of S–Hg(1)–S angles, 359.1°), while Hg(2) is in a strictly linear co-ordination by sulphur. Hg(1)–S bond distances are in the range 2.410 Å and 2.560 Å. The average value ($\bar{d}_{Hg(1)-S} = 2.49$ Å) is comparable to the mean bond length of the trigonally co-ordinated mercury atom in $BaHgS_2$ [5] (2.51 Å). The Hg–S bond length of the linearly co-ordinated Hg(2) atoms is 2.344 Å, slightly shorter than that in the red modification of HgS (2.364 Å [1]). A comparable bond length (2.345 Å) is found for the linearly co-ordinated mercury atom in $K_2Hg_6S_7$ [6], while the

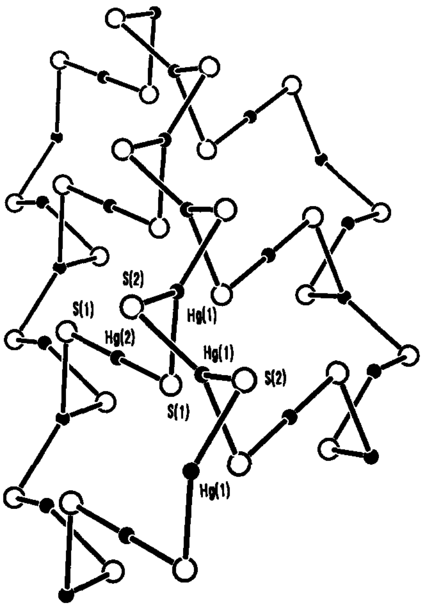

Fig. 3. Detail of the $^2_\infty-[Hg_3S_4]^{2-}$ layer. The 16-membered rings of alternating mercury and sulphur atoms, which are the basic building units of the layers, and their connection through the Hg(1) atoms should be noted (five rings are shown).

Hg–S bonds in the isolated linear thioanions of Na_2HgS_2 and K_2HgS_2 [4] are significantly shorter (2.31 Å).

The two crystallographically independent sulphur atoms are co-ordinated to only two mercury atoms with comparable Hg–S–Hg bond angles of 95.5° and 98.1° respectively. The Na^+ ions which occupy the voids between the anionic layers have five close sulphur neighbours ($d_{Na-S} = 2.87–2.98$ Å) forming a distorted square pyramid which is completed to an octahedron by a further sulphur atom at a distinctly larger distance of 3.500 Å.

Although the atomic arrangement of $Na_2Hg_3S_4$ appears to be rather extraordinary, it may still be related to well-known packing principles. Essentially, the crystal structure is based on a close-packed arrangement of sulphur atoms. S(1) and S(2) atoms are arranged in distorted close-packed layers running parallel to (010). In the stacking direction [010] the layers formed by S(2) are at two different stacking positions, designated B and C respectively (Figs. 1 and 4), while the stacking positions of the S(1) layers (A and A′) are practically coincident in that direction. The stacking is A′BACA′ and, hence, may be represented by the Jagodzinski symbol $(hc)_2$. The relation to close packing is also apparent from the metric relationships. Thus, the axis ratio a:b:c which calculates as 0.89:1.70:1, is in satisfactory agreement with the values obtained from the model of ideal sphere packing ($0.87:1.63:1 = \surd 3:4\surd 2/\surd 3:2$).

The arrangement of the metal atoms can be derived from the occupation of interstitial voids in the chalcogen packing. For sodium and Hg(1) this is

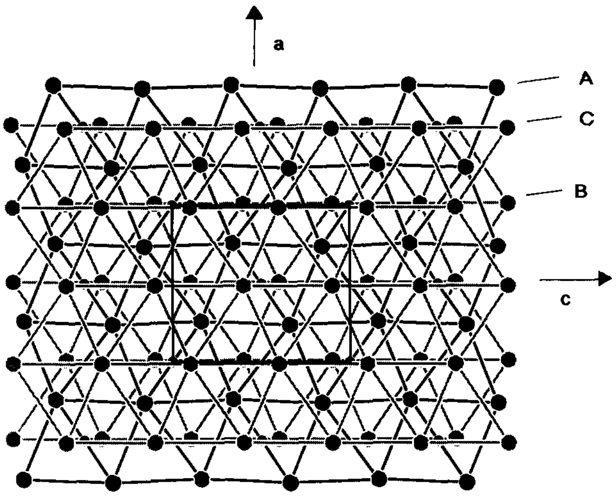

Fig. 4. Distorted close-packed layers of sulphur atoms as seen in the projection along [010]. The layers B and C are formed by S(2), the central layer A is formed by S(1). The designation of the layers corresponds to that in Fig. 1. It should be noted that in layer A, a part of the S–S edges is centred by Hg(2) (represented by small full circles).

apparent from their co-ordination. Sodium atoms occupy half of the octahedral voids in an off-centred position. Sharing edges only, the occupied octahedra form a three-dimensional framework. Hg(1) atoms occupy half of the tetrahedral voids originating from the *h* stacking step of the chalcogen layers. However, they are shifted from the centres of the tetrahedra to one of the faces, attaining a trigonal planar co-ordination. With a distance of 3.124 Å, the fourth sulphur neighbour is clearly outside the primary co-ordination sphere of Hg(1). In a similar way, the positions of the Hg(2) atoms may be related to the tetrahedral sites created by the *c* stacking step of the close-packed layers. However, (in order to attain linear co-ordination) the mercury atoms are now shifted from the centres of these sites to the edges shared by two tetrahedra, thus becoming incorporated into the close-packed layers formed by the S(1) atoms (Fig. 4).

Acknowledgments

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