JOURNAL OF SOLID STATE CHEMISTRY **47**, 301–306 (1983)

Preparation and Crystal Structure of $Na_2Mn_2S_3$

K. KLEPP, P. BÖTTCHER, AND W. BRONGER

Institut für Anorganische Chemie der RWTH Aachen, Prof.-Pirlet-Strasse 1, 5100 Aachen, Federal Republic of Germany

Received October 14, 1982; in revised form December 3, 1982

$Na_2Mn_2S_3$ was prepared by reacting manganese powder with an excess of anhydrous sodium carbonate and elemental sulfur at 870 K. Extraction of the solidified melt with water and alcohol yielded well developed, bright red crystals. $Na_2Mn_2S_3$ crystallizes with a new monoclinic structure type, space group $C2/c$, $Z = 8$, with $a = 14.942(2)$ Å, $b = 13.276(2)$ Å, $c = 6.851(2)$ Å, and $\beta = 116.50(1)°$. The crystal structure was determined from single crystal diffractometer data and refined to a conventional R value of 0.026 for 1613 observed reflections. The atomic arrangement shows sulfur–manganese–sulfur slabs which are separated from each other by corrugated layers of sodium atoms. A prominent feature of the crystal structure is the formation of short, four-membered zigzag chains built up by MnS_4 tetradedra sharing edges. These chains are further connected by the remaining apices to form an infinite sheet. Short Mn–Mn distances (3.02 and 3.05 Å, respectively) are found within the four membered chains. Susceptibility measurements show antiferromagnetic interactions between the Mn atoms.

Introduction

In the thiomanganates of the heavy alkali metals and barium the manganese atoms are tetrahedrally coordinated by sulfur atoms. The isostructural thiomanganates $Cs_2Mn_3S_4$ and $Rb_2Mn_3S_4$ are built up by infinite $[Mn_3S_4]$ sheets formed by MnS_4 tetrahedra sharing edges, which are separated from each other by layers of alkali-metal atoms. The corresponding ternary chalcogenides of cobalt and zinc are isostructural (*1*, *2*). On the basis of metric relationships of the unit cell a similar structure may also be expected for $K_2Mn_3S_4$ (*3*).

Two barium thiomanganates, Ba_2MnS_3 (*4*) and $BaMnS_2$ (*5*), are known; in both compounds the MnS_4 tetrahedra share corners only. Ba_2MnS_3 contains linear $[MnS_3]$ chains and is isotypic with K_2AgI_3 (*6*); $BaMnS_2$ has a layer structure and is isotypic with $SrZnO_2$ (*7*).

Assuming that the change of connection type for the MnS_4 tetrahedra between the thiomanganates of K and Ba is correlated with the increase of the charge over radius ratio of the corresponding cations, we found it of interest to investigate a thiomanganate of sodium, which has an intermediate e/r ratio.

The preparation of a sodium thiomanganate was carried out by Völker (*8*) as early as 1846. The reported stoichiometry, $Na_2Mn_3S_4$, however, could not be confirmed in the course of the thermoanalytical investigation of the system Na_2S–MnS (*9*), which indicated instead the formation of $Na_2Mn_2S_3$ as the only intermediate phase. The crystal structure of this compound will be presented in this paper.

0022-4596/83 $3.00

Experimental

Preparation. The title compound was prepared by the reaction of sodium carbonate with sulfur and powdered manganese in a stream of purified argon at 870 K. The initial reaction mixture consisted of sodium carbonate (Merck, suprapur), sulfur (Fluka AG, 99.999% nominal purity), and manganese (Alfa Ventron, 99.9% nominal purity) in the molar ratio 2 : 10 : 1. A proper heat treatment was found to be essential in order to obtain a homogeneous product without contamination by MnS. The formation of the binary sulfide could be successfully suppressed by preheating the reaction tube to 570 K before the insertion of the reaction mixture. The temperature was then gradually raised and maintained for 2 hr. The reaction melt was finally allowed to cool very slowly to ambient temperature. The solidified melt was crushed and rapidly extracted with water. The residue was washed with alcohol and dried under vacuum. The product obtained by this preparation consisted of well developed, bright red crystals with columnar shape. Because of its limited stability in a humid atmosphere the compound was handled and stored under purified argon. Color and crystal morphology of the compound correspond with the description given by Völker (*8*) for $Na_2Mn_3S_4$. Since our way of preparation essentially resembles the procedure described by Völker it appears likely that in both cases the same ternary compound was obtained. Chemical analyses (Mn and S) of our reaction product, however, were not compatible with the stoichiometry $Na_2Mn_3S_4$ but yielded values expected for $Na_2Mn_2S_3$. This discrepancy can be explained by the difficulty in obtaining a product without contamination by MnS.

Susceptibility measurements. Susceptibility measurements were performed by the Faraday method in the temperature range of 3.8–300 K with field strengths up to 11×10^5 A m^{-1}.

X-ray investigations. Preliminary crystallographic investigations with Weissenberg and precession techniques indicated a monoclinic unit cell. The systematic extinctions for hkl: $h + k \neq 2n$ and $h0l$: $l \neq 2n$ led to $C2/c$ or Cc as possible space groups. A well developed single crystal ($0.06 \times 0.06 \times 0.08$ mm) was sealed into a thin-walled glass capillary and mounted on a computer-controlled single crystal diffractometer (Nonius CAD4, graphite monochromated Mo$K\alpha$ radiation). The lattice constants obtained by least squares refinement of the 2θ values of 25 carefully centered reflections were $a = 14.942(2)$ Å, $b = 13.276(2)$ Å, $c = 6.851(2)$ Å, and $\beta = 116.50(1)°$. Reflection intensities were collected in one quadrant of reciprocal space using the θ–2θ scan mode ($1° \leq \theta \leq 35°$). The possible decomposition of the crystal was monitored by a periodical determination of the intensities of three strong standard reflections. No systematic decrease of these intensities was observed during the course of the data collection. Equivalent reflections were averaged yielding a set of 1613 symmetry independent reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The absorption coefficient was small so the absorption correction was omitted.

Structure Determination

Normalized structure factors were obtained with FAME, assuming the stoichiometry $Na_2Mn_2S_3$ and a cell content of 8 formula units, which gave the best fit between calculated and observed density (2.75 and 2.70 g/cm³, respectively). The statistics of the normalized structure factors indicated the centrosymmetric space group $C2/c$. The signs of 322 reflections with $|E| > 1.4$ were determined with MULTAN. The highest peaks of the corresponding E map were assigned to Mn and S atoms. A refine-

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS ($Å^2 \times 10^2$) FOR $Na_2Mn_2S_3$[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	0.0968(1)	0.9138(1)	0.1173(3)	3.58(7)	1.59(8)	6.80(9)	0.15(4)	1.52(3)	0.36(5)
Na(2)	0	0.7195(2)	$\frac{1}{4}$	1.80(8)	2.3(1)	2.22(9)	0	0.57(3)	0
Na(3)	0	0.4289(2)	$\frac{1}{4}$	1.76(8)	2.2(1)	2.23(8)	0	0.53(3)	0
Mn(1)	0.2109(0)	0.5751(1)	0.2962(1)	1.27(2)	2.21(2)	1.56(2)	0.05(1)	0.37(1)	0.00(1)
Mn(2)	0.1849(0)	0.2627(0)	0.2581(1)	1.39(2)	1.22(2)	1.35(2)	0.09(1)	0.32(1)	0.04(1)
S(1)	0.1448(1)	0.4243(1)	0.0663(1)	1.97(3)	0.98(3)	1.48(3)	−0.02(2)	0.53(1)	0.00(2)
S(2)	0.1369(1)	0.7188(1)	0.0544(1)	1.27(3)	1.32(4)	1.38(3)	−0.02(2)	0.39(1)	0.05(2)
S(3)	0.1138(1)	0.1139(1)	0.0482(2)	1.20(3)	1.19(4)	2.51(4)	−0.03(2)	0.28(1)	−0.08(2)

[a] The anisotropic temperature factor is defined as $\exp\left(-2\pi^2 \sum_{ij}^{3} h_i h_j a_i^* a_j^* U_{ij}\right)$ (estimated standard deviations are given in parentheses).

ment of the partial structure converged to $R = 0.19$. A subsequent Fourier map revealed the positions of the Na atoms. Least squares refinement with isotropic temperature factors and unit weights converged after a few cycles to an R value of 0.05. Refinements with anisotropic temperature factors and weights assigned according to the counting statistics led to a final R of 0.026 ($R_w = 0.022$, $w = 1/\sigma^2(F)$) for 1613 observations and 66 refined variables[1]. A corresponding difference Fourier map was featureless.

All calculations were performed on a PDP 11/45 computer with programs of the Nonius SDP system (*10*). Atomic scattering factors for neutral atoms and anomalous dispersion coefficients were taken from the "International Tables for X-Ray Crystallography" (*11*). The final positional and thermal parameters are given in Table I.

Discussion

$Na_2Mn_2S_3$ crystallizes with a new structure type, characterized by infinite $[Mn_2S_3]$ sheets running parallel to (100). The sheets are formed by MnS_4 tetrahedra sharing edges and vertices and are separated from each other by corrugated layers of sodium atoms.

The crystal structure of $Na_2Mn_2S_3$ can be traced back to a distorted close packed arrangement of sulfur atoms with hexagonal stacking ABAB, the stacking direction is normal to (100). The sodium and manganese atoms alternatingly occupy the interstices between the sulfur layers. Due to the ordered arrangement of the interstitial atoms a four layer sequence is necessary to obtain identity. For an undistorted structure the cell dimensions should be related to those of a simple h.c.p. unit cell (a', c') by

$$a \sin \beta \triangleq 2c' \quad (1)$$

$$b \triangleq 3a' \quad (2)$$

$$c \triangleq a' \sqrt{3} \quad (3)$$

The deviation of the actual structure from this idealized model is reflected by the fact, that significantly different values for a' are obtained from Eqs. (2) and (3), respectively. Since the axial ratio c'/a' obtained from Eqs. (1) and (3) is close to the ideal value of 1.63, the distortion—as will be dis-

---

[1] Lists of observed and calculated structure factors are available from the authors on request.

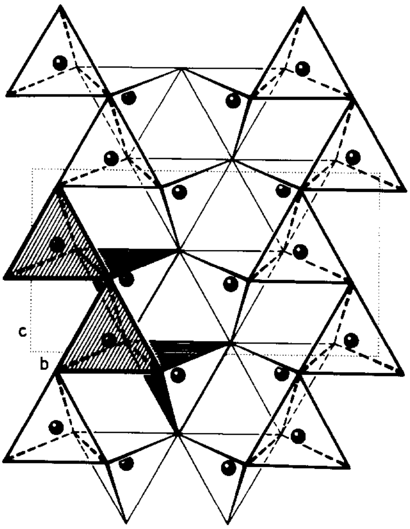

FIG. 1. Projection of the S–Mn–S sheets onto (100). Mn atoms: full circles, S atoms form the apices of the tetrahedra. One four-membered chain of edge-sharing tetrahedra is emphasized by additional shading.

cussed below—predominantly affects the crystallographic *b* axis (see also Fig. 2).

Mn(1) and Mn(2) occupy together two thirds of the tetrahedral voids between two sulfur layers, which leads to the formation of short, four-membered zigzag chains, built up by MnS_4 tetrahedra sharing edges. These chains are connected with each other via the remaining apices, S(1), forming an infinite two-dimensional arrangement (Fig. 1).

The sodium atoms in the alternate interstitial layers are distributed over tetrahedral and octahedral sites. Only one third of the tetrahedral voids, occupied by Na(1), is available, since the other tetrahedra have one face in common with the Mn-centered tetrahedra of the neighboring layers. The remaining sodium atoms, Na(2) and Na(3), occupy two thirds of the octahedral voids. The arrangement of the coordination polyhedra of the sodium atoms is shown in Fig. 2. The occupied octahedra share edges and form ribbons which are connected with each other by zigzag chains of edge-sharing tetrahedra. Each tetrahedron has one face in common with one octahedron (centered by Na(2)). This crowded arrangement of Na^+ ions gives rise to distortions due to cation–cation repulsion, which are in turn responsible for the deviations of the metric relationships with respect to those of the ideal close packed model. The strongest repulsion is to be expected between Na(1) and Na(2) whose coordination polyhedra have one face in common. This leads in fact to a shift of Na(1) parallel to [001] from the center towards one edge of the tetrahedron. The resulting asymmetry of the sulfur environment of Na(1) is reflected by the ele-

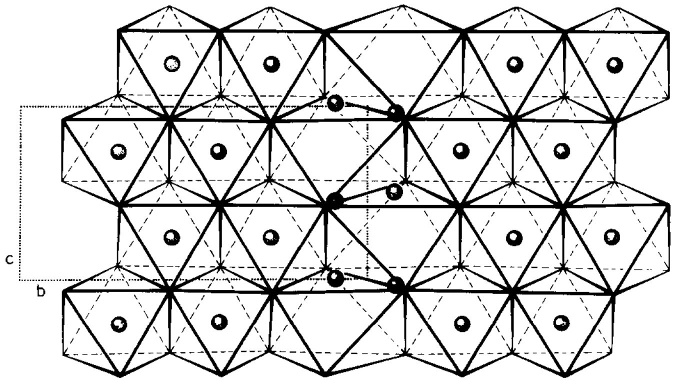

FIG. 2. Connection of the Na-centered sulfur polyhedra. Projection onto (100). Na atoms: dotted circles.

TABLE II

INTERATOMIC DISTANCES (Å) FOR $Na_2Mn_2S_3$ UP TO 4.3 Å[a]

Na(1)–S(3)	2.730(1)	Na(2)–S(2)	2.903(1) (2×)	Mn(1)–S(3)	2.402(1)
–S(2)	2.734(1)	–S(1)	2.972(1) (2×)	–S(2)	2.444(1)
–S(3)	2.853(1)	–S(3)	2.978(1) (2×)	–S(1)	2.457(1)
–S(3)	2.875(1)			–S(1)	2.465(1)
–S(1)	3.487(1)	–Mn(2)	3.350(0) (2×)		
–S(3)	4.032(1)	–Mn(1)	3.580(1) (2×)	–Na(1)	3.416(1)
				–Na(2)	3.580(1)
–Mn(1)	3.416(1)	–Na(1)	3.278(2) (2×)	–Na(3)	3.593(1)
–Mn(2)	3.592(1)	–Na(3)	3.857(2)	–Na(3)	3.663(0)
–Mn(1)	3.757(1)	–Na(3)	3.952(1) (2×)	–Na(1)	3.757(1)
–Mn(1)	4.021(1)				
		Na(3)–S(2)	2.928(1) (2×)	–Mn(2)	3.046(0)
–Na(2)	3.278(2)	–S(1)	2.948(1) (2×)	–Mn(1)	3.964(0) (2×)
–Na(1)	3.471(2)	–S(1)	2.998(1) (2×)	–Mn(2)	3.988(0)
–Na(1)	4.047(2)			–Mn(2)	4.136(1)
–Na(1)	4.120(1) (2×)	–Mn(2)	3.518(1) (2×)	–Mn(2)	4.163(0)
		–Mn(1)	3.593(1) (2×)		
		–Mn(1)	3.663(1) (2×)		
		–Na(2)	3.857(2)		
		–Na(3)	3.911(1) (2×)		
		–Na(2)	3.952(1) (2×)		
Mn(2)–S(3)	2.393(1)	S(1)–Mn(2)	2.446(1)	S(2)–Mn(1)	2.444(1)
–S(1)	2.446(1)	–Mn(1)	2.457(1)	–Mn(2)	2.449(1)
–S(2)	2.449(1)	–Mn(1)	2.465(1)	–Mn(2)	2.455(1)
–S(2)	2.455(1)				
		–Na(3)	2.948(1)	–Na(1)	2.734(1)
–Na(2)	3.350(0)	–Na(2)	2.972(1)	–Na(2)	2.903(1)
–Na(3)	3.518(1)	–Na(3)	2.998(1)	–Na(3)	2.928(1)
–Na(1)	3.592(1)	–Na(1)	3.487(1)		
–Na(1)	4.021(1)			–S(3)	3.764(1)
		–S(2)	3.892(1)	–S(2)	3.862(1)
–Mn(2)	3.022(1)	–S(2)	3.911(1)	–S(1)	3.892(1)
–Mn(1)	3.046(0)	–S(2)	3.944(1)	–S(1)	3.911(1)
–Mn(1)	3.988(1)	–S(1)	3.972(1) (2×)	–S(1)	3.944(1)
–Mn(2)	4.136(1)	–S(3)	4.053(1)	–S(3)	3.999(1)
–Mn(2)	4.163(0)	–S(3)	4.141(1)	–S(3)[b]	4.136(1)
		–S(2)	4.156(1)	–S(1)	4.156(1)
		–S(3)	4.221(1)	–S(3)	4.191(1)
S(3)–Mn(2)	2.399(1)				
–Mn(1)	2.402(1)				
–Na(1)	2.730(1)				
–Na(1)	2.853(1)				
–Na(1)	2.875(1)				
–Na(2)	2.978(1)				
–Na(1)	4.032(1)				
–S(2)	3.764(1)				
–S(3)[b]	3.987(1)				
–S(2)	3.999(1)				
–S(1)	4.053(1)				
–S(2)[b]	4.136(1)				
–S(1)	4.141(1)				
–S(2)	4.191(1)				
–S(1)	4.221(1)				

[a] Estimated standard deviations are given in parentheses.

[b] S–S contacts between different $[Mn_2S_3]$ sheets.

vated value of U_{33} (Table I). The distance, $d_{\mathrm{Na(1)-Na(2)}} = 3.28$ Å, still remains the shortest homonuclear contact between $\mathrm{Na^+}$ ions within the structure. The geometry of the Na-centered tetrahedron is further affected by the repulsion between the Na(1) atoms which causes a stretching of the tetrahedron in the direction of the crystallographic *b* axis. As a consequence of this the ratio $b/c = 1.94$ is larger than $\sqrt{3}$ expected from the unit cell relationships above.

The occupation of both tetrahedral and octahedral voids by Na leads to a clear separation between the $[\mathrm{Mn_2S_3}]$ sheets. Thus only two of the S–S distances up to 4.3 Å represent contacts between different sheets (Table II).

The outstanding feature of the crystal structure is certainly the formation of the four-membered chains of $\mathrm{MnS_4}$ tetrahedra. Edge sharing of the tetrahedra gives rise to short Mn–Mn contacts within the chains (3.022 and 3.046 Å, respectively). The closest interchain Mn–Mn distance is 3.96 Å. Susceptibility measurements show a nearly temperature independent paramagnetism which decreases slightly from 2670×10^{-6} $\mathrm{cm^3\ mole^{-1}}$ at 297 K to 2480×10^{-6} $\mathrm{cm^3\ mole^{-1}}$ at 7 K. This indicates antiferromagnetic coupling between the Mn atoms. A neutron diffraction study on the spin structure is in preparation.

Acknowledgments

The authors express their thanks to Mrs. Eyck for performing the magnetic measurements. Moreover, we thank the Landesamt für Forschung des Landes NRW and the Fonds der Chemischen Industrie for supporting this work.

References

1. W. Bronger, *Angew. Chem.* **93,** 12 (1981).
2. W. Bronger and U. Hendriks, *Rev. Chim. Minér.* **17,** 555 (1980).
3. W. Bronger, *Angew. Chem.* **78,** 113 (1966).
4. I. E. Grey and H. Steinfink, *Inorg. Chem.* **10,** 691 (1971).
5. D. Schmitz and W. Bronger, *Z. Anorg. Allg. Chem.* **402,** 225 (1973).
6. C. Brink and H. A. Kroese, *Acta Crystallogr.* **5,** 433 (1952).
7. H. G. von Schnering and R. Hoppe, *Z. Anorg. Allg. Chem.* **312,** 87 (1961).
8. A. Völker, *Liebigs Ann. Chem.* **59,** 35 (1846).
9. K. Geissler and E. J. Kohlmeyer, *Z. Anorg. Allg. Chem.* **297,** 189 (1958).
10. B. A. Frenz, "Computing in Crystallography" (R. Schenk, R. Olthof-Hazekamp, H. v. Koningsveld and G. C. Bassi, Eds.), p. 64, Delft Univ. Press, Delft (1978).
11. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England (1974).