

High-temperature synthesis of $\text{Rb}_2\text{MnP}_2\text{S}_6$ in molten salt medium

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Received 11 May 2001

Accepted 23 October 2001

Online 13 February 2002

Transparent yellow plates of rubidium manganese hexathiodiphosphate, $\text{Rb}_2\text{MnP}_2\text{S}_6$, were synthesized in molten RbBr . The compound is isotypic to other compounds of the type $A_2\text{MP}_2\text{Q}_6$ ($A = \text{K}, \text{Rb}, \text{Cs}$; $M = \text{Mn}, \text{Fe}$; $Q = \text{S}, \text{Se}$). Its structure can be viewed as columns of face-sharing S_6 polyhedra parallel to the a axis, interconnected by Rb^+ . The S_6 polyhedra are centered alternately by Mn (in octahedral coordination) and P_2 units (in trigonal antiprisms). The Mn atom and P_2S_6 group lie on centers of symmetry.

Comment

There are seven known compounds of the type $A_2\text{MP}_2\text{Q}_6$ ($A = \text{K}, \text{Rb}, \text{Cs}$; $M = \text{Mn}, \text{Fe}$; $Q = \text{S}, \text{Se}$), including $\text{K}_2\text{FeP}_2\text{S}_6$

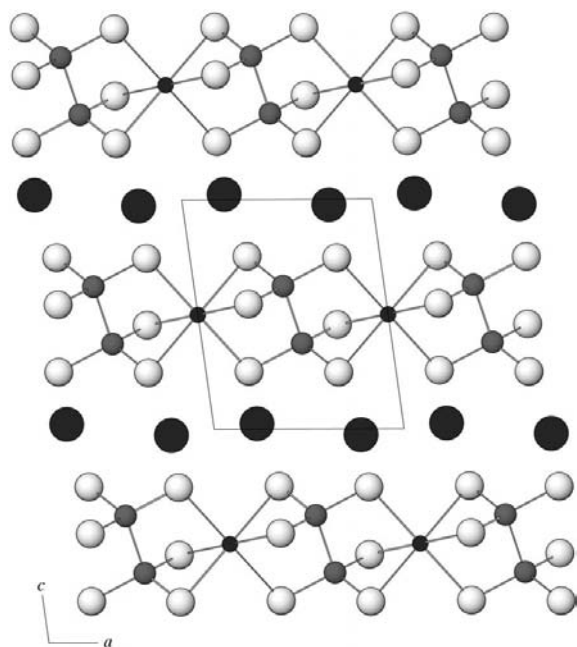


Figure 1

The layered structure of $\text{Rb}_2\text{MnP}_2\text{S}_6$, projected onto the plane of parallel $[\text{MnP}_2\text{S}_6]$ chains, separated by a layer of Rb^+ cations (large black circles). The large light-gray circles represent S, medium gray circles represent P, and small black circles represent Mn atoms.

(Carrillo-Cabrera *et al.*, 1992, 1994) and $\text{K}_2\text{MnP}_2\text{S}_6$ (Menzel *et al.*, 1994); and $\text{K}_2\text{MnP}_2\text{Se}_6$, $\text{Rb}_2\text{MnP}_2\text{Se}_6$, $\text{Cs}_2\text{MnP}_2\text{Se}_6$, $\text{K}_2\text{FeP}_2\text{Se}_6$, and $\text{Cs}_2\text{FeP}_2\text{Se}_6$ (McCarthy & Kanatzidis, 1995). The title compound is typical of this class of compounds. The first two compounds listed above were synthesized from the elements, while the final five were synthesized in a polychalcophosphate flux. We were able to prepare rubidium manganese hexathiodiphosphate using molten rubidium bromide as a flux-growth solvent, similar to the synthesis of $\text{KNb}_2\text{PS}_{10}$ (Do & Yun, 1996), which was performed in a eutectic mixture of LiCl and KCl . As in the other members of this class, the structure is related to that of CdCl_2 (Brec, 1986, and references therein; see Fig. 1).

Experimental

Rb_2S_6 powder was prepared by reaction of stoichiometric amounts of rubidium metal (Strem, 99.9+%) and sulfur powder (Aldrich, 99.99%) in liquid ammonia (Fehér, 1975). Crystals of $\text{Rb}_2\text{MnP}_2\text{S}_6$ were synthesized from a mixture of Rb_2S_6 powder (0.1107 g, 0.3044 mmol), MnS powder (Strem, 99.9%; 0.0265 g, 0.3046 mmol) and P_4S_3 powder (Fluka, 98%; 0.3127 g, 1.4209 mmol), with RbBr (GFS, 99.9%; 0.0503 g, 0.3042 mmol) acting as a halide flux-growth solvent. The powders were ground together in an agate mortar inside a nitrogen-filled glove-box, and were then loaded into fused-quartz tubing. The reaction tube was subsequently sealed under vacuum. After heating at 973 K for 5 d, the reaction vessel was allowed to cool to room temperature over a period of 7 d. Transparent yellow plate crystals of $\text{Rb}_2\text{MnP}_2\text{S}_6$ were present throughout the reaction product, which also included MnS crystals, unreacted P_4S_3 powder, and RbBr .

Crystal data

$\text{Rb}_2\text{MnP}_2\text{S}_6$
 $M_r = 480.18$
 Monoclinic, $P2_1/n$
 $a = 6.1570(12) \text{ \AA}$
 $b = 12.308(3) \text{ \AA}$
 $c = 7.5610(15) \text{ \AA}$
 $\beta = 97.74(3)^\circ$
 $V = 567.8(2) \text{ \AA}^3$
 $Z = 2$

$D_x = 2.809 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 6144 reflections
 $\theta = 1.7\text{--}26.1^\circ$
 $\mu = 11.00 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, yellow
 $0.15 \times 0.05 \times 0.05 \text{ mm}$

Data collection

Rigaku APC8 diffractometer
 ω scans
 Absorption correction: multi-scan
 (REQABA; Jacobson, 1999)
 $T_{\min} = 0.258$, $T_{\max} = 0.577$
 5210 measured reflections
 1110 independent reflections

1034 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\max} = 26.1^\circ$
 $h = -7 \rightarrow 7$
 $k = -15 \rightarrow 14$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.137$
 $S = 1.32$
 1110 reflections
 52 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 12.3434P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.06 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.73 \text{ e \AA}^{-3}$

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve

Table 1

Selected geometric parameters (Å, °).

Mn1—S2	2.619 (3)	P1—S1 ⁱ	2.008 (3)
Mn1—S3	2.652 (3)	P1—S2	2.021 (3)
Mn1—S1	2.659 (3)	P1—S3	2.022 (3)
Mn1—P1	2.964 (2)	P1—P1 ⁱ	2.208 (5)
S2—Mn1—S3 ⁱⁱ	102.54 (8)	S1 ⁱ —P1—S2	115.95 (15)
S2—Mn1—S3	77.46 (8)	S1 ⁱ —P1—S3	115.97 (16)
S2—Mn1—S1 ⁱⁱ	89.90 (8)	S2—P1—S3	109.32 (14)
S3—Mn1—S1 ⁱⁱ	90.85 (8)	S1 ⁱ —P1—P1 ⁱ	104.14 (16)
S2—Mn1—S1	90.10 (8)	S2—P1—P1 ⁱ	105.25 (17)
S3—Mn1—S1	89.15 (8)	S3—P1—P1 ⁱ	104.85 (18)

 Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, -y, 1-z$.

structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999).

The authors gratefully acknowledge the continued financial support from the National Science Foundation

(DMR-0077321 and EPS-9977797 for the research and CHE-9808165 for the X-ray diffractometer).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1335). Services for accessing these data are described at the back of the journal.

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