y, $1{\cdot}5-z$) 3·307 (3) and O(33)···O(53) ($-x$, $-0{\cdot}5+y$, $1{\cdot}5-z$) 3·388 (2) Å.

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References

ALLEN, F. H., KENNARD, O., WATSON, D.G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1-S19.

BAILEY, P.D., HOLLINSHEAD, S.P. & DAUTER, Z. (1985). *J. Chem. Soc. Chem. Commun.* p. 1507.

BLESSING, R. H. (1986). *J. Appl. Cryst.* **19**, 412.

BLESSING, R. H. (1987). *Crystallogr. Rev.* **1**, 3–57.

CODDING, P. W. (1983). *Can. J. Chem.* **61**, 529–532.

Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

UNGEMACH, F., SOERENS, D., WEBER, R., DIPIERRO, M., CAMPOS, O., MOKRY, P., COOK, J. M. & SILVERTON, J. V. (1980). *J. Am. Chem. Soc.* **102**, 6976–6984.

VALLELY, D. G. (1983). *ARTIST.* A program for plotting molecular structures and electron density maps. Univ. of York, England.

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Structure of Mn_2SiS_4

BY J. FUHRMANN AND J. PICKARDT*

Institut für Anorganische Chemie der Technischen Universität Berlin, Strasse des 17. *Juni* 135, *D*-1000 *Berlin* 12, *Federal Republic of Germany*

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Abstract. Manganese thiosilicate, $M_r = 266{\cdot}22$, orthorhombic, $Pnma$, $a = 12{\cdot}688\,(2)$, $b = 7{\cdot}429\,(2)$, $c = 5{\cdot}942\,(1)$ Å, $V = 560{\cdot}1\,(2)$ Å^3, $Z = 4$, $D_x = 3{\cdot}157$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 57{\cdot}86$ cm^{-1}, $F(000) = 512$, $T = 298$ K, $R = 0{\cdot}041$, $wR = 0{\cdot}031$ for 1734 unique reflections with $F_o > 4\sigma(F_o)$. Mn_2SiS_4 crystallizes in the olivine structure type. Mn—S bond lengths (octahedral coordination about Mn) are in the range 2·555 (1)–2·646 (1) Å, Si—S bond lengths (tetrahedral coordination about Si) 2·104 (2)–2·144 (1) Å. The mean bond distances in Mn_2SiS_4 agree well with values found in other thiosilicates.

Experimental. Mn_2SiS_4 crystals were grown by chemical transport using I_2 as transporting agent and MnS, Si and S_8 as starting materials. The reaction was carried out in sealed quartz ampoules at 923/873 K for two weeks. A dark-brown, transparent crystal, size 0·14 × 0.10 × 0·18 mm, was used for data collection on a Syntex $P2_1$ diffractometer operated in ω-scan mode (Mo $K\alpha$, graphite monochromator). Lattice constants were obtained from a least-squares fit of 15 reflections in the range $36 < 2\theta < 68°$. Two standard reflections, measured every 50 reflections, showed no significant change during data collection. 1919 reflections in the range $2 < 2\theta < 80°$, $0 \le h \le 22$, $0 \le k \le 13$, $0 \le l \le 9$ were measured and yielded 1734 unique reflections ($R_{\text{int}} = 0{\cdot}078$), of which 1256 were considered as observed [$F_o > 4\sigma(F_o)$]. The data were corrected for Lorentz and polarization effects. A numerical absorption correction (transmission factors 0·5062 to 0·6200) with *SHELX76* (Sheldrick, 1976) was applied. Secondary-extinction effects were taken into account by refinement of an empirical extinction coefficient $X = 7{\cdot}2\,(2) \times 10^{-7}$, $F_o = F_o(1 - XF_o^2/\sin\theta)$. As starting set for the structure refinement, the coordinates of an earlier determination by Hardy, Perez & Serment (1965) were used, but yielded a rather high R value

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* To whom correspondence should be addressed.

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$

	Equipoint	x	y	z	B_{eq}
Mn(1)	4(*a*)	0	0	0	1·08
Mn(2)	4(*c*)	0·22946 (5)	$\frac{1}{4}$	0·51050 (12)	0·98
Si	4(*c*)	0·40964 (9)	$\frac{1}{4}$	0·09316 (19)	0·69
S(1)	4(*c*)	0·40710 (8)	$\frac{1}{4}$	0·73915 (17)	0·75
S(2)	4(*c*)	0·56466 (7)	$\frac{1}{4}$	0·23667 (18)	0·78
S(3)	8(*d*)	0·33299 (5)	0·02463 (8)	0·24595 (12)	0·78

and an unreasonably short Si—S distance (1·80 Å). In the course of our structure determination we found that the Si position was incorrect; the correct atom coordinates were determined by difference syntheses. With these coordinates the structure could be refined to $R = 0{\cdot}041$, $wR = 0{\cdot}031$ [full-matrix least-squares refinement on F, $w = 2{\cdot}19/\sigma^2(F_o)$, anisotropic thermal parameters, 42 parameters]. The extreme values in the final difference synthesis were 2·6, $-1{\cdot}8$ e Å^{-3} near the S atoms, $(\Delta/\sigma)_{max}$ in the final cycle was 0·001. Atomic scattering factors for neutral Si and S atoms were taken from *SHELX76* (Sheldrick, 1976), for Mn^{2+} from Cromer & Mann (1968), anomalous-dispersion coefficients for all atoms from Cromer & Liberman (1970). Geometric calculations were performed with *PLATON* (Spek, 1982). Atomic positions and equivalent isotropic thermal parameters are given in Table 1, bond distances and angles in Table 2.*

Table 2. *Bond distances* (Å) *and angles* (°)

Si tetrahedra

Si—S(1^{vi})	2·104 (2)	S(1^{vi})—Si—S(3), S(3^{ii})*	114·7 (1)
Si—S(2)	2·144 (1)	S(1^{vi})—Si—S(2)	114·3 (1)
Si—S(3), S(3^{ii})*	2·139 (1)	S(3)—Si—S(3^{ii})	103·1 (1)
		S(2)—Si—S(3), S(3^{ii})*	104·4 (1)

Mn(1) octahedra

Mn(1^{iv})—S(1), S(1^{v})*	2·619 (1)	Mn(1^{iv})—S(3^{ii}), S(3^{iv})*	2·608 (1)
Mn(1^{iv})—S(2), S(2^{iv})*	2·563 (1)		

S(1), S(1^{v})—Mn(1^{iv})—S(2), S(2^{iv})*	87·8 (1)
S(1), S(1^{v})—Mn(1^{iv})—S(2^{iv}), S(2)*	92.2 (1)
S(1), S(1^{v})—Mn(1^{iv})—S(3^{ii}), S(3^{iv})*	84·2 (1)
S(1), S(1^{v})—Mn(1^{iv})—S(3^{iv}), S(3^{ii})*	95·8 (1)
S(2), S(2^{iv})—Mn(1^{iv})—S(3^{ii}), S(3^{iv})*	81·7 (1)
S(2), S(2^{iv})—Mn(1^{iv})—S(3^{iv}), S(3^{ii})*	98·3 (1)

Mn(2) octahedra

Mn(2)—S(2^{i})	2·555 (1)	Mn(2)—S(1)	2·632 (1)
Mn(2)—S(3^{iii}), S(3^{iv})*	2·598 (1)	Mn(2)—S(3), S(3^{ii})*	2·646 (1)

S(2^{i})—Mn(2)—S(3), S(3^{ii})*	93·7 (1)
S(2^{i})—Mn(2)—S(3^{iii}), S(3^{iv})*	93.4 (1)
S(3^{iii})—Mn(2)—S(3^{iv})	103·5 (1)
S(3^{iii}), S(3^{iv})—Mn(2)—S(1)*	89·0 (1)
S(3), S(3^{ii})—Mn(2)—S(3^{iii}), S(3^{iv})*	88·5 (1)
S(1)—Mn(2)—S(3), S(3^{ii})*	83·2 (1)
S(3)—Mn(2)—S(3^{ii})	78·5 (1)
S(2^{i})—Mn(2)—S(1)	176·0 (1)
S(3), S(3^{ii})—Mn(2)—S(3^{iv}), S(3^{iii})*	165·6 (1)

Symmetry code: (i) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $x, \frac{1}{2}-y, z$; (iii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (v) $1-x, \frac{1}{2}+y, 1-z$; (vi) $x, y, z-1$.

*Two equivalent distances or angles.

Related literature. The compound Mn$_2$SiS$_4$ was described as of the olivine type by Rocktäschel, Ritter & Weiss (1964). The crystal structure of Mn$_2$SiS$_4$ was first determined by Hardy, Perez & Serment (1965), but yielded an incorrect Si position. The mean bond distances in Mn$_2$SiS$_4$ from our work agree well with those found in many other thiosilicates, *e.g.* in Fe$_2$SiS$_4$, which also has the olivine structure, the mean Si—S bond length is 2·131 Å (Vincent, Bertaut, Baur & Shannon, 1975). The distortions of the polyhedra in Mn$_2$SiS$_4$ [Si tetrahedron almost regular, Mn(1) octahedron less distorted than Mn(2) octahedron] are comparable with those in Fe$_2$SiS$_4$ and many other olivine-type compounds.

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References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Hardy, A., Perez, G. & Serment, J. (1965). *Bull. Soc. Chim. Fr.* pp. 2638–2640.

Rocktäschel, G., Ritter, W. & Weiss, A. (1964). *Z. Naturforsch. Teil B*, **19**, 958.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Vincent, H., Bertaut, E. F., Baur, W. H. & Shannon, R. D. (1975). *Acta Cryst.* **B32**, 1749–1755.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52056 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.