O12—In1—O11	81.26 (10)	O22—In2—O21	81.08 (9)
O12—In1—O13	77.72 (9)	O22—In2—O23	83.96 (10)
O11—In1—O13	83.13 (10)	O21—In2—O23	77.71 (9)
O12—In1—Cl12	163.54 (7)	O22—In2—Cl23	90.42 (7)
O11—In1—Cl12	93.16 (7)	O21—In2—Cl23	87.34 (7)
O13—In1—Cl12	86.27 (7)	O23—In2—Cl23	164.66 (7)
O12—In1—Cl11	95.81 (7)	O22—In2—Cl22	170.13 (7)
O11—In1—Cl11	88.22 (7)	O21—In2—Cl22	92.55 (6)
O13—In1—Cl11	169.86 (7)	O23—In2—Cl22	87.32 (7)
Cl12—In1—Cl11	99.50 (3)	Cl23—In2—Cl22	96.85 (3)
O12—In1—Cl13	87.82 (7)	O22—In2—Cl21	87.52 (7)
O11—In1—Cl13	168.82 (7)	O21—In2—Cl21	164.26 (7)
O13—In1—Cl13	92.27 (7)	O23—In2—Cl21	90.39 (7)
Cl12—In1—Cl13	96.71 (3)	Cl23—In2—Cl21	103.65 (3)
Cl11—In1—Cl13	95.29 (3)	Cl22—In2—Cl21	97.20 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11*A*···Cl23^{i}	0.785 (18)	2.379 (19)	3.157 (3)	171 (3)
O11—H11*B*···Cl11^{ii}	0.779 (19)	2.67 (3)	3.260 (3)	134 (4)
O12—H12*A*···Cl22	0.786 (19)	2.42 (3)	3.129 (3)	150 (4)
O12—H12*B*···Cl12^{ii}	0.79 (2)	2.43 (2)	3.210 (3)	167 (4)
O13—H13*A*···Cl21^{iii}	0.795 (18)	2.46 (2)	3.208 (2)	158 (3)
O13—H13*B*···Cl11^{iv}	0.781 (18)	2.48 (2)	3.214 (3)	158 (3)
O21—H21*A*···Cl13	0.75 (2)	2.42 (2)	3.149 (3)	164 (5)
O21—H21*B*···Cl21^{v}	0.762 (19)	2.48 (2)	3.220 (2)	164 (5)
O22—H22*A*···Cl13^{vi}	0.750 (19)	2.56 (2)	3.285 (3)	164 (4)
O22—H22*B*···Cl12^{vii}	0.751 (19)	2.56 (2)	3.283 (3)	161 (4)
O23—H23*A*···Cl13^{viii}	0.765 (19)	2.50 (2)	3.242 (3)	165 (4)
O23—H23*B*···Cl22^{v}	0.75 (2)	2.58 (3)	3.236 (3)	147 (4)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $1-x, -y, 1-z$; (vii) $x, y, 1+z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

H atoms were located from electron-density maps and refined using restraints to equalize the O—H distances. They were given isotropic displacement parameters and allowed to refine.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* . Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1325). Services for accessing these data are described at the back of the journal.

References

Abram, S., Maichle-Mössmer, C. & Abram, U. (1997). *Polyhedron*, **16**, 2291–2298.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Atkinson, A. W. & Field, B. O. (1970). *J. Inorg. Nucl. Chem.* **32**, 2601–2606.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Carta, G., Benetollo, F., Sitran, S., Rossetto, G., Braga, F. & Zanella, P. (1995). *Polyhedron*, **14**, 1923–1928.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Karia, R., Willey, G. R. & Drew, M. G. B. (1986). *Acta Cryst.* C**42**, 558–560.

Knop, O., Cameron, T. S., Adhikesavalu, D., Vincent, B. R. & Jenkins, J. A. (1987). *Can. J. Chem.* **65**, 1527–1556.

Malyarick, M. A., Petrosyants, S. P. & Ilyuhin, A. B. (1992). *Polyhedron*, **11**, 1067–1073.

Robinson, W. T., Wilkins, C. J. & Zhang Zeying (1988). *J. Chem. Soc. Dalton Trans.* pp. 2187–2192.

Robinson, W. T., Wilkins, C. J. & Zhang Zeying (1990). *J. Chem. Soc. Dalton Trans.* pp. 219–227.

Self, M. F., McPhail, A. T. & Wells, R. L. (1993). *Polyhedron*, **12**, 455–459.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994*a*). *SMART Software Reference Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*b*). *SHELXTL/PC Reference Manual.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SAINT. Data Integration Software.* Version 4.021. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Streltsova, N. R., Ivanov, M. G., Vashchenko, S. D., Belskii, V. K. & Kalinichenko, I. I. (1991). *Koord. Khim.* **17**, 646–651.

Wells, R. L., Kher, S. S., Baldwin, R. A. & White, P. S. (1994). *Polyhedron*, **13**, 2371–2735.

Whitlow, S. H. & Gabe, E. J. (1975). *Acta Cryst.* B**31**, 2534–2536.

Wignacourt, J.-P., Mairesse, G. & Barbier, P. (1980). *Acta Cryst.* B**36**, 669–671.

Wignacourt, J.-P., Mairesse, G. & Barbier, P. (1982). *Can. J. Chem.* **60**, 1747–1750.

Acta Cryst. (1999). C**55**, 1748-1751

Rb_2MoS_4

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Abstract

The reaction of $(NH_4)_2MoS_4$, AgI, RbI and S in 1,2-ethanediamine under solvothermal conditions yields red crystals of Rb_2MoS_4, dirubidium tetrasulfidomolybdate(2−), as a minor phase and black powdered Ag_2S as the main product. Rb_2MoS_4 crystallizes like Cs_2MoS_4 and $(NH_4)_2MoS_4$ in the β-K_2SO_4 type. The structure contains tetrahedral $[MoS_4]^{2-}$ anions which are connected *via* Rb^+ cations.

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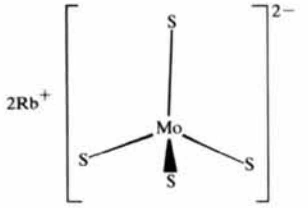
Comment

The structure determination of Rb_2MoS_4, (I), was undertaken within a project on the synthesis of new thiomolybdates under mild solvothermal conditions. The variety in the Mo–S system under solvothermal conditions is shown by the fact that different kinds of anions, ranging from the tetrahedral $[MoS_4]^{2-}$ anion to the more complex $[Mo_3S_{13}]^{2-}$ anion, could be obtained easily. The chemical flexibility of the $[MoS_4]^{2-}$ anion is also demonstrated by the formation of complexes with elements in the Ni, Cu and Zn subgroups (Müller *et al.*, 1971; Callahan & Piliero, 1980), whereas the reaction of $(NH_4)_2MoS_4$ with $NiBr_2$ in 1,2-ethanediamine (en) leads to the tetrathiomolybdate $Ni(en)_3MoS_4$ (Ellermeier *et al.*, 1999).



(I)

The lattice parameters of (I) were first published by Gattow & Franke (1965, 1967), and their values are in good agreement with those based on the present structure determination. Similar to other tetrathiomolybdates, (I) crystallizes in the β-K_2SO_4 type, *e.g.* Cs_2MoS_4 (Raymond *et al.*, 1995) and $(NH_4)_2MoS_4$ (Schaefer *et al.*, 1964).

The packing in (I) is illustrated in Fig. 1. The structure consists of isolated Rb^+ cations and discrete $[MoS_4]^{2-}$ anions. The Mo atom is tetrahedrally coordinated by

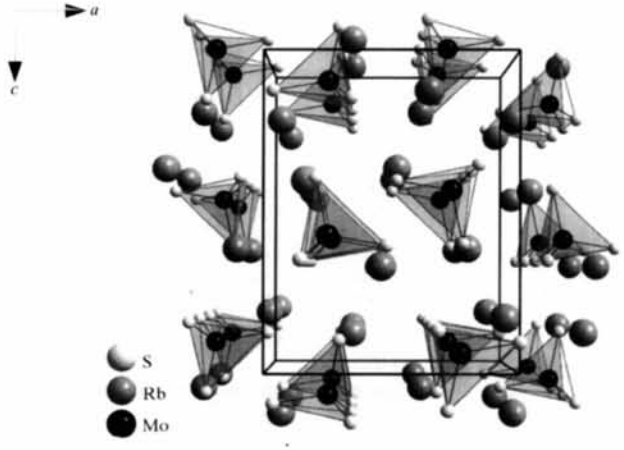


Fig. 1. The packing diagram for (I), viewed along the *b* axis.

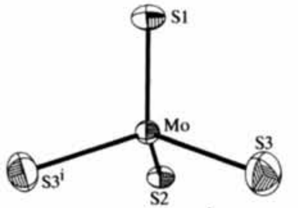
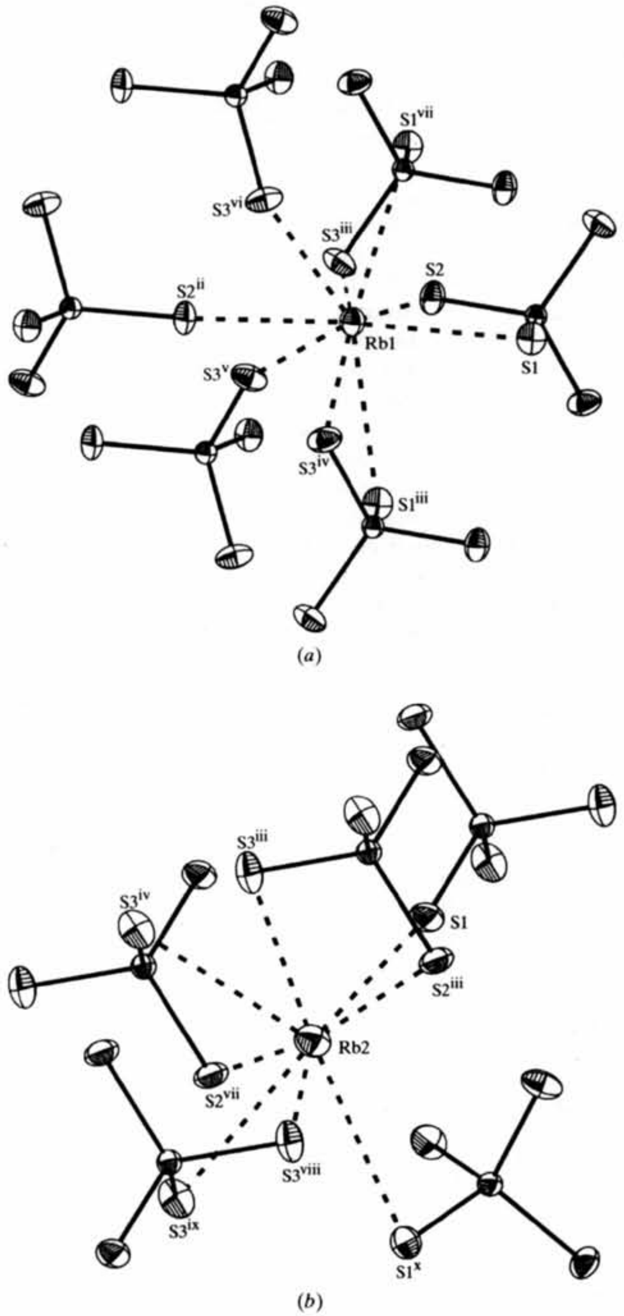


Fig. 2. The crystal structure of the $[MoS_4]^{2-}$ anion, showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level. The symmetry code is as in Table 2.



(*a*)

(*b*)

Fig. 3. The coordination spheres of (*a*) the Rb1 cation and (*b*) the Rb2 cation, showing the atom-labelling schemes and displacement ellipsoids drawn at the 50% probability level. The symmetry codes are as in Table 2.

S atoms (Fig. 2), with Mo—S distances of 2.178 (1), 2.181 (2) and 2.192 (2) Å, and corresponding S—Mo—S angles ranging from 108.18 (6) to 111.31 (6)°. The bond lengths and angles are in good agreement with those found in other compounds containing the $[MoS_4]^{2-}$ anion.

Two crystallographically independent Rb^+ cations are present in the asymmetric unit (Fig. 3) and both are coordinated by S atoms within irregular polyhedra. All atoms, except S3, lie on mirror planes. Rb1 (Fig. 3*a*) is bound to six symmetry-related $[MoS_4]^{2-}$ tetrahedra *via* nine S atoms, whereas Rb2 (Fig. 3*b*) is surrounded by five symmetry-related $[MoS_4]^{2-}$ anions *via* eight S atoms. The Rb1—S distances range from 3.297 (2) to 3.602 (1) Å [average 3.454 (2) Å]. Rb2 exhibits seven Rb2—S distances between 3.450 (2) and 3.618 (2) Å, and one long distance of 3.802 (2) Å. The mean Rb2—S distance [3.602 (2) Å] is significantly longer than the average Rb1—S distance. Additionally, there are two more S atoms around Rb2 at a distance of 3.948 (1) Å, which are not shown in Fig. 3(*b*).

Recently, we demonstrated that under solvothermal conditions the $[Mo_3S_{13}]^{2-}$ anion could be obtained easily in an aqueous ammonia solution (Bensch & Schur, 1997). Apparently, the reaction in 1,2-ethanediamine leads to less complex Mo–S anions, such as the tetrahedral $[MoS_4]^{2-}$ anion described here. Further studies are in progress in order to obtain more information about the influence of the chemical and geometrical properties of the solvent on product formation under solvothermal conditions.

Experimental

$(NH_4)_2MoS_4$ (0.50 mmol), AgI, RbI and S (in a 1:2:2:3 molar ratio) were reacted in 1,2-ethanediamine (3 ml) in Teflon-lined steel autoclaves at 393 K for 7 d. The product was filtered off and after washing with ethanol, a black powder, which was identified by X-ray powder diffraction as Ag_2S (~90%), and red crystals of the title compound (~10%) were obtained.

Crystal data

Rb_2MoS_4
$M_r = 395.12$
Orthorhombic
Pnma
$a = 9.6596 (18)$ Å
$b = 7.0354 (12)$ Å
$c = 12.436 (2)$ Å
$V = 845.2 (3)$ Å^3
$Z = 4$
$D_x = 3.105$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 15–25°$
$\mu = 13.881$ mm^{-1}
$T = 293 (2)$ K
Polyhedron
0.15 × 0.10 × 0.03 mm
Red

Data collection

Stoe AEDII four-circle diffractometer
ω/θ scan
Absorption correction: analytical (*XP* in *SHELXTL/PC*; Bruker, 1997)
$T_{min} = 0.068$, $T_{max} = 0.285$
2581 measured reflections
1328 independent reflections

1044 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 30.02°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 17$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.066$
$S = 0.998$
1328 reflections
41 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.690$ e Å^{-3}
$\Delta\rho_{min} = -1.211$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0030 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo	0.74700 (4)	3/4	0.42447 (3)	0.01850 (11)
S1	0.52351 (13)	3/4	0.39408 (11)	0.0314 (3)
S2	0.79156 (15)	3/4	0.59642 (10)	0.0321 (3)
S3	0.84077 (10)	0.49924 (12)	0.35203 (9)	0.0355 (2)
Rb1	0.46273 (5)	3/4	0.66734 (4)	0.02789 (13)
Rb2	0.15706 (6)	3/4	0.39354 (5)	0.03637 (15)

Table 2. *Selected geometric parameters (Å, °)*

Mo—S3^{i}	2.1782 (9)	Rb1—S1^{iii}	3.6021 (7)
Mo—S3	2.1782 (9)	Rb2—S1	3.540 (2)
Mo—S2	2.1813 (14)	Rb2—S2^{vii}	3.5547 (6)
Mo—S1	2.1917 (14)	Rb2—S2^{iii}	3.5547 (6)
Rb1—S2	3.297 (2)	Rb2—S3^{viii}	3.5656 (12)
Rb1—S2^{ii}	3.3711 (15)	Rb2—S3^{ix}	3.5656 (12)
Rb1—S3^{iii}	3.4246 (12)	Rb2—S3^{iv}	3.6176 (14)
Rb1—S3^{iv}	3.4246 (12)	Rb2—S3^{iii}	3.6176 (14)
Rb1—S1	3.449 (2)	Rb2—S1^{x}	3.802 (2)
Rb1—S3^{v}	3.4573 (11)	Rb2—S3^{xi}	3.9482 (13)
Rb1—S3^{vi}	3.4573 (11)	Rb2—S3^{x}	3.9482 (13)
Rb1—S1^{vii}	3.6021 (7)		
S3^{i}—Mo—S3	108.18 (6)	S3—Mo—S1	109.77 (3)
S3—Mo—S2	108.87 (4)	S2—Mo—S1	111.31 (6)

Symmetry codes: (i) $x, \frac{3}{2}-y, z$; (ii) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, \frac{1}{2}+y, 1-z$; (v) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vi) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (vii) $1-x, 2-y, 1-z$; (viii) $x-1, y, z$; (ix) $x-1, \frac{3}{2}-y, z$; (x) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (xi) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}-z$.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *DIAMOND* (Brandenburg, 1999). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1304). Services for accessing these data are described at the back of the journal.

References

Bensch, W. & Schur, M. (1997). *Z. Kristallogr.* **212**, 303–304.

Brandenburg, K. (1999). *DIAMOND. Visual Crystal Information System.* Version 2.1a. Bonn, Germany.

Bruker (1997). *SHELXTL/PC. Program Package for the Solution, Refinement and Graphical Presentation of Crystal Structures.* Bruker AXS Inc., Madison, Wisconsin, USA.

Callahan, K. P. & Piliero, P. A. (1980). *Inorg. Chem.* **19**, 2619–2626.

Ellermeier, J., Näther, C. & Bensch, W. (1999). *Acta Cryst.* C**55**, 501–503.

Gattow, G. & Franke, A. (1965). *Naturwissenschaften*, **52**, 493.

Gattow, G. & Franke, A. (1967). *Z. Anorg. Allg. Chem.* **352**, 11–23.

Müller, A., Ahlborn, E. & Heinsen, H.-H. (1971). *Z. Anorg. Allg. Chem.* **386**, 102–106.

Raymond, C. C., Dorhout, P. K. & Miller, S. M. (1995). *Z. Kristallogr.* **210**, 775.

Schaefer, H., Schaefer, G. & Weiss, A. (1964). *Z. Naturforsch. Teil B*, **19**, 76.

Sheldrick, G. M. (1997*a*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Version 7.09X/DOS. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.

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Manganese-rich natural Franklinite

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Abstract

A natural Franklinite has been characterized by X-ray diffraction techniques. The structure was refined in the space group $Fd\bar{3}m$. The almost normal spinel structure was confirmed. All the Zn^{2+} ions are located on tetrahedral sites. The best cation distribution was determined to be $(Zn_{0.65(1)}Mn_{0.35(1)})[Fe_2]O_4$, zinc manganese diiron tetraoxide.

Comment

AB_2O_4 spinels are some of the most studied substances in the solid-state sciences because of their magnetic, optical, dielectric and other properties (Banerjee, 1991; Cornell & Schwertmann, 1996). There are two basic types of spinel structure: if the tetrahedral *T* site is occupied by the divalent cation and the octahedral *M* site is occupied by the trivalent cation, the structure is called normal, and if the *T* site is occupied by the trivalent cation and the *M* site is occupied by a random arrangement of divalent and trivalent cations, the structure is called inverse spinel (Verwey *et al.*, 1947). An intermediate cation distribution may be represented as $(A_{1-i}B_i)[B_{2-i}A_i]O_4$ (the ( ) and [ ] sets of parentheses refer to *T* and *M* sites, respectively), where *i* is the so-called degree of inversion, which ranges from 0.0 (normal structure) to 1.0 (inverse structure) (Hill *et al.*, 1979). Spinels can also form a series of substitutional solid solutions in which the cation introduced normally replaces a cation of the same charge and similar size. The structure of Franklinite, $ZnMnO_4$, has been determined by X-ray powder diffraction methods (O'Neill, 1992). The structure of some natural Mn-rich spinels have been reported by Lucchesi *et al.* (1997), including the Mn-substituted Franklinite $Zn_{0.34}Mn_{0.30}Mg_{0.02}Al_{0.064}Ti_{0.025}Fe_{2.26}O_4$. This work is part of a project aimed at studying the cation distribution in natural ferrites.

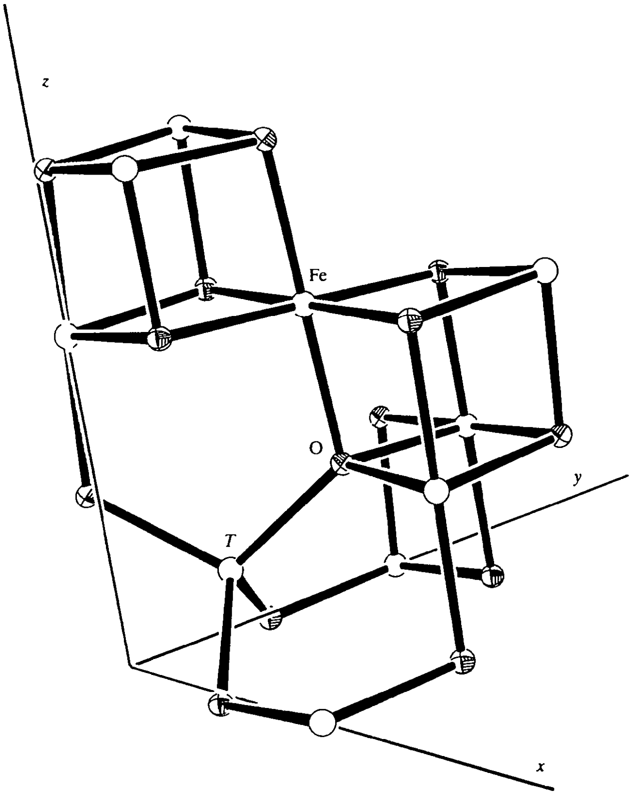

Fig. 1. *ORTEP*III (Burnett & Johnson, 1996) drawing of the structure of Franklinite, showing the atom designation (origin at the inversion center $\bar{3}m$). The Zn^{2+} and Mn^{2+} tetrahedral cations are represented together by the *T* label. $0 < x < \frac{1}{2}$, $0 < y < \frac{1}{2}$ and $0 < z < \frac{3}{4}$ is shown. Ellipsoids are drawn at the 50% probability level.

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