

# Manganoan rockbridgeite $\text{Fe}_{4.32}\text{Mn}_{0.62}\text{Zn}_{0.06}(\text{PO}_4)_3(\text{OH})_5$ : structure analysis and $^{57}\text{Fe}$ Mössbauer spectroscopy

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The structure of the basic iron phosphate rockbridgeite [iron manganese zinc tris(phosphate) pentahydroxide] was reinvestigated with special emphasis on the cation distribution deduced from new X-ray and  $^{57}\text{Fe}$  Mössbauer data. Rockbridgeite is orthorhombic, space group *Cmcm*, and shows three different Fe sites, one with  $2/m$  symmetry, another with *m* symmetry and the third in a general position. One phosphate group has the P atom on a site with *m* symmetry, while the other has the P atom at a site with *mm* symmetry. Two Fe sites are fully occupied by ferric iron, while  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  are situated at a third, principally Fe, site. Structural data, bond-valence sums and polyhedral distortion parameters suggest a new interpretation of the rockbridgeite  $^{57}\text{Fe}$  Mössbauer spectrum.

## Comment

Due to the large number of observed crystal structure types, the (hydrous) basic phosphates of the transition metal cations are regarded as ‘perplexing’ substances within the multitude of minerals (Moore, 1970). Among these substances, several compounds are known with cations in both di- and trivalent valence states. This makes them interesting candidates for possible materials in catalysis and electrode applications. A common structural feature of several basic iron phosphates is a trimer of face-sharing octahedra with  $[\text{M}_3\text{O}_{12}]$ , denoted as the *h*-cluster by Moore (1970). Based on the mode of linkage of these clusters, several different structure types are discerned, among them lipscombite  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3(\text{OH})_2$ , the minerals of the lazulite group  $\text{M}^{2+}\text{M}_2^{3+}(\text{PO}_4)_3(\text{OH})_2$ , burangite  $\text{Na}[\text{Fe}^{2+}\text{Al}_5(\text{PO}_4)_4(\text{OH})_6(\text{H}_2\text{O})_2]$ , dufrenite  $\text{Ca}_{0.5}\text{Fe}^{2+}\text{Fe}_5^{3+}(\text{PO}_4)_4(\text{OH})_6(\text{H}_2\text{O})_2$  and rockbridgeite, ideally  $\text{Fe}^{2+}\text{Fe}_4^{3+}$

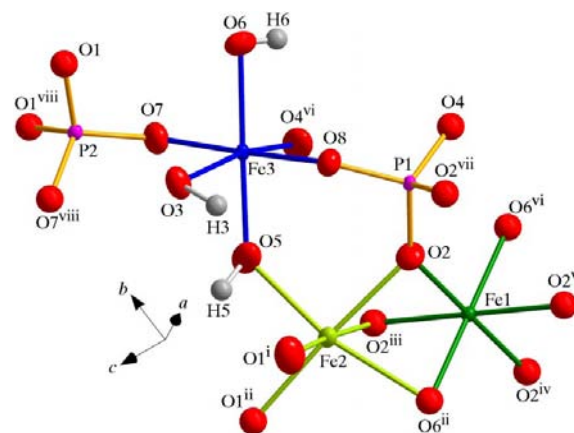
$(\text{PO}_4)_3(\text{OH})_5$  (Huminicki & Hawthorne, 2002). Short inter-atomic *M*···*M* distances are present within an *h*-cluster. These are of special interest with respect to the appearance of electron delocalization between neighbouring  $\text{M}^{2+}$ – $\text{M}^{3+}$  pairs, which occur in infinite structural units such as chains or ribbons (Amthauer & Rossman, 1984).

In nature, the hydrous basic ferric/ferrous iron phosphates often appear as replacements for organic products, or as hydrothermally reworked products of primary lithium–iron–manganese phosphates in pegmatites. Most of them occur as crusts, congregations and masses or as fibrous species. Single crystals are hard to obtain, since the fibres normally consist of several individuals, closely grown together in twisted bundles.

The crystal structures of most of the basic iron phosphates were solved in the late 1960s or early 1970s, while structure refinements or solutions based on modern state-of-the-art X-ray data collection are rare. In the course of a systematic investigation of hydrous ferric/ferrous iron phosphate minerals, we have reinvestigated the rockbridgeite crystal structure by combining single-crystal structure analysis with  $^{57}\text{Fe}$  Mössbauer spectroscopy.

The structure of the title compound was first described by Moore (1970) using long-exposure Weissenberg photographs and visual intensity data estimations. Some of the isotropic atomic displacement parameters reported take unusual (negative) values and anisotropic refinement of the structure was not performed. Also, the possible space-group symmetry (*Bbmm* or *Bbm2*) has been a matter of debate (Moore, 1970). Finally, the interpretation of the  $^{57}\text{Fe}$  Mössbauer spectrum also deserves some improvements. Amthauer & Rossman (1984) concluded that ‘additional Mössbauer work, combined with diffraction studies, is needed for a complete understanding of the iron distribution in this mineral’.

The crystal structure of the title compound is built up by three different kinds of octahedral sites, Fe1 to Fe3, and two different types of phosphate tetrahedra. A displacement ellipsoid plot, including the atomic nomenclature, is shown in Fig. 1. It is evident that thermal motion, especially that of the



**Figure 1**  
A view of (I), shown with 90% probability displacement ellipsoids. [Symmetry codes: (i)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $-\frac{1}{2} + x, -\frac{1}{2} + y, z$ ; (iii)  $-x, y, z$ ; (iv)  $-x, -y, -z$ ; (v)  $x, -y, -z$ ; (vi)  $-\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; (vii)  $1 - x, y, z$ ; (viii)  $-x, y, \frac{1}{2} - z$ .]

O atoms, appears to be anisotropic, and that an isotropic description as given in Moore (1970) is not sufficient. The basic unit of the octahedral framework is a centrosymmetric *h*-cluster formed by three face-sharing octahedra (a central Fe1 and two Fe2 sites). Each *h*-cluster is connected to adjacent *h*-clusters by shared edges, forming infinite octahedral chains parallel to the *c* axis (Fig. 2). The *h*-cluster is linked by corner-sharing to four Fe3 octahedra. The Fe3 sites themselves form pairs of corner-sharing Fe3 octahedra that are oriented along the *c* direction (Fig. 2). The arrangement of these seven-octahedra clusters is linked together by the phosphate tetrahedra, with the P1O<sub>4</sub> tetrahedra sharing corners with the Fe1, Fe2 and Fe3 octahedra, while the P2O<sub>4</sub> tetrahedron has no common corner with the Fe1 octahedron.

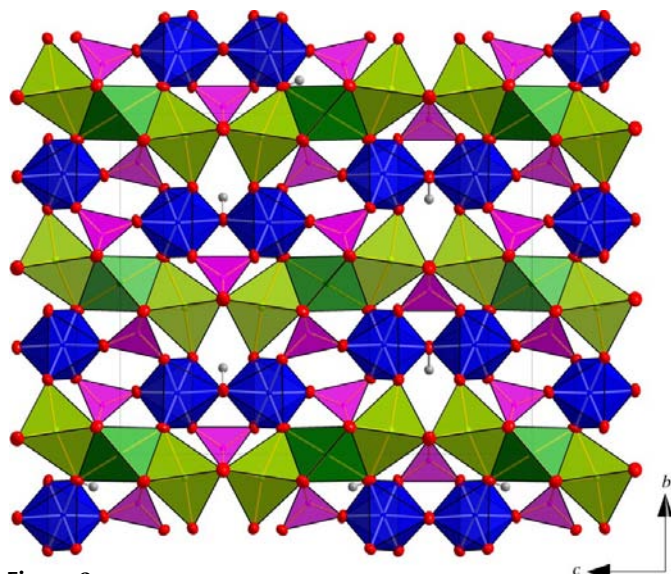
The average Fe–O bond length and the bond-valence sum *S* (Bresle & O’Keeffe, 1991) (Table 1) both imply that the central Fe1 site of the *h*-cluster is occupied by ferric iron only. The average Fe1–O bond length compares well with the Fe<sup>3+</sup>–O bond length found in the lazulite-type mineral barbosolite Fe<sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>, with a mean Fe<sup>3+</sup>–O distance of 2.020 (2) Å (Redhammer *et al.*, 2000). In barbosolite, the Fe<sup>3+</sup> ion also occupies the central octahedron of the *h*-cluster. The distortion of the Fe1 octahedron causes a large angular and edge-length distortion; the bond-length distortion is low (Table 1).

In contrast with this, the Fe2 site, which occupies the two outer face-sharing octahedra of the *h*-cluster, displays larger individual and average bond lengths. In barbosolite, the analogous mean Fe<sup>2+</sup>–O bond length is 2.112 (2) Å (Redhammer *et al.*, 2000), compared with 2.131 (4) Å in the title compound. This, and a bond-valence sum *S* = 2.17, is only compatible with the assumption that ferrous iron occupies the Fe2 position. Among the three octahedral sites, the Fe2 octahedron has the largest deviation from ideal geometry (Table 1). This may be seen as an indication that Mn<sup>3+</sup> also occupies the Fe2 site and contributes to the large average

polyhedral distortion due to Jahn–Teller distortion. Further evidence comes from <sup>57</sup>Fe Mössbauer spectroscopy. Based on chemical analysis and structure refinement, we propose the composition of the Fe2 site to be approximately Fe<sub>1.32</sub>Mn<sub>0.62</sub>Zn<sub>0.06</sub>. Within the *h*-cluster, the Fe1–Fe2 interatomic distance measured through the common face is 2.806 (2) Å, which is rather short and would allow for electron delocalization according to the criteria of Amthauer & Rossman (1984). However, the Fe2···Fe2 distance across the common edge between two neighbouring *h*-clusters is 3.156 (2) Å and this is probably the factor impeding electron delocalization between pairs of Fe<sup>2+</sup> and Fe<sup>3+</sup>.

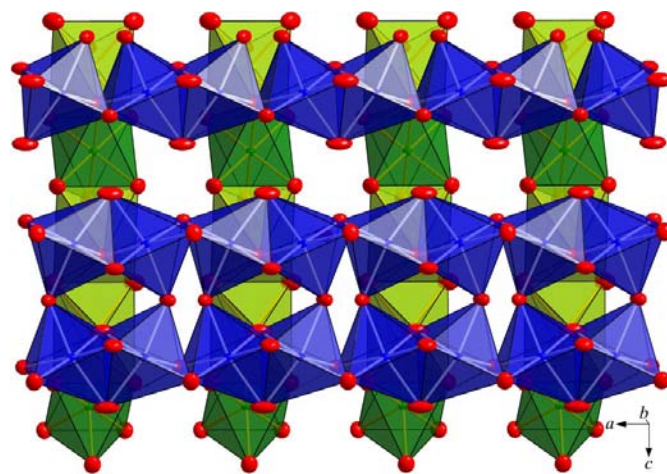
In agreement with Moore (1970), it was found that the Fe3 site (16*h* position) is only half filled. A full occupation of this site would lead to 28 Fe atoms in the unit cell, instead of the 20 demanded by the stoichiometry of the compound. Furthermore, if all of the Fe3 sites were occupied, an infinite double chain consisting of edge-sharing pairs of face-sharing Fe3 octahedra would form (Fig. 3). Within such a chain, a very short interatomic contact between neighbouring Fe3 sites of 2.386 (2) Å would alternate with a somewhat larger one of 2.790 (2) Å. However, such a short Fe–Fe interatomic distance, 2.386 (2) Å, is most improbable. Thus it is assumed that every second Fe3 site is empty, thereby avoiding the formation of the face-sharing double octahedron. As noted by Moore (1970), the O3 site (8*g* position) is also only half filled. This is confirmed by the present structure refinement. Individual and average Fe3–O bond lengths are short (Table 1). This, together with the bond-valence sum *S* = 3.00, allows the conclusion that the Fe3 site – as for the Fe1 site – is occupied by ferric iron exclusively. Compared with the Fe1 site, the Fe3 site appears to be less distorted [lower edge-length distortion (ELD), octahedral angle variance (OAV) and octahedral quadratic elongation (OQE) parameters; Table 1]. This feature is essential for the following interpretation of <sup>57</sup>Fe Mössbauer spectra.

The two different PO<sub>4</sub> tetrahedra appear as regular units with almost identical average bond and edge lengths. In terms



**Figure 2**

A polyhedral representation of (I), viewed along the *a* axis. Displacement ellipsoids are drawn at the 90% probability level.



**Figure 3**

A polyhedral representation of (I), showing the hypothetical infinite octahedral Fe3 double chains. P and H atoms have been omitted for clarity.

of the tetrahedral distortion parameters, the P2 site can be regarded as slightly more regular (Table 1).

The Mössbauer spectrum of rockbridgeite, collected at 298 K, consists of four more or less well separated resonance absorption lines arising from overlapping contributions of both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . As in the study of Amthauer & Rossman (1984), the spectrum was fitted with four doublets (solid lines in Fig. 4), two for  $\text{Fe}^{3+}$  [low values for isomer shift (IS) and quadrupole splitting (QS); Table 2] and two for  $\text{Fe}^{2+}$  (high values for IS and QS, respectively). A weak shoulder and some residual resonance absorption contributions gave evidence for an additional doublet, low in relative intensity and having  $^{57}\text{Fe}$  Mössbauer parameters typical for ferric iron (Fig. 4). Tentatively, the  $\text{Fe}^{3+}$  doublet with the smallest quadrupole splitting and the highest relative area ratio was assigned to the less distorted Fe3 site, and that with the intermediate QS and relative area ratio to the Fe1 site, which shows larger polyhedral distortion (Table 1). The assignment is based on the fact that, for ferric iron, a positive correlation holds true between quadrupole splitting and octahedral distortion. Furthermore, the relative area fraction of the two main  $\text{Fe}^{3+}$  components is almost 2:1, which correlates very well with the 2:1 ratio of Fe3:Fe1 sites in the title compound.

Assuming 4.32 Fe atoms per formula unit (a.p.f.u.) in rockbridgeite (from chemical analysis), and taking into account the relative area fractions for  $\text{Fe}^{3+}$  on Fe1 and Fe3 as obtained from Mössbauer spectroscopy, the Fe1 site is filled with 0.98 (3)  $\text{Fe}^{3+}$  a.p.f.u., while the Fe3 site is filled with 2.00 (3)  $\text{Fe}^{3+}$  a.p.f.u. These data correspond almost ideally to the theoretical values and are consistent with the crystal structure analysis. The third  $\text{Fe}^{3+}$  doublet is assigned to the Fe2 site and corresponds to 0.13 (4)  $\text{Fe}^{3+}$  a.p.f.u. The somewhat larger isomer shift value found for  $\text{Fe}^{3+}$  on the Fe2 site is in good accord with the distinctly larger average Fe2–O bond length. The problem now arises that the two remaining  $\text{Fe}^{2+}$ -

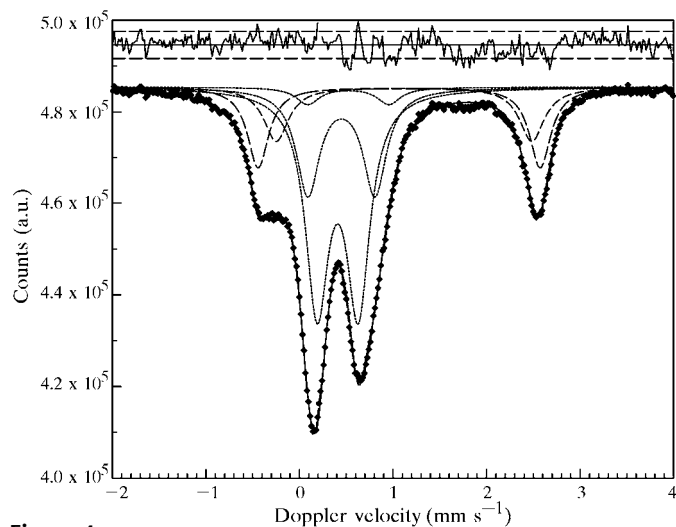
doublets have to be ascribed to one crystallographic site, namely to Fe2. However, it is well known that the quadrupole splitting of  $\text{Fe}^{2+}$  is sensitive to even small changes within the local geometric/electronic nearest (*e.g.* oxygen) and next nearest neighbour (*e.g.* neighbouring cations) environment. As the Fe2 octahedron shares a common edge with a neighbouring Fe2 site, and the Fe2 site shows a mixed occupation with  $\text{Fe}^{2+}$  and mainly Mn, the two different  $\text{Fe}^{2+}$  quadrupole splitting values are ascribed to next-nearest neighbour (NNN) effects arising from  $\text{Fe}^{2+}$ – $\text{Fe}^{2+}$  and  $\text{Fe}^{2+}$ –Mn clusters for the edge-sharing doublet of Fe2 sites. The relative area ratios of these two different  $\text{Fe}^{2+}$  components correlate well with the probability of having the two NNN configurations, namely approximately 50:50% from chemical composition and 56:44% from Mössbauer spectroscopy for the  $\text{Fe}^{2+}$ – $\text{Fe}^{2+}$  and  $\text{Fe}^{2+}$ –Mn $^{2+}$  clusters, respectively.

The present doublet assignment is somewhat different from that of Amthauer & Rossman (1984). Those authors also ascribed the  $\text{Fe}^{3+}$  doublet with smaller QS to the Fe1 site, and the  $\text{Fe}^{2+}$  doublet with the larger QS to the Fe2 site. However, the remaining two doublets were assigned by them to the Fe3 site, giving rise to some apparent deviation of the area ratio (Fe1 – Fe2)/Fe3 from the ideal value of 1.5. As we have strong evidence from structure analysis that the Fe1 and the Fe3 sites are occupied by ferric iron only, and as the iron cationic distribution extracted from our Mössbauer data almost perfectly fits the ideal values, we believe that the present doublet assignment is correct. Thus, the present  $^{57}\text{Fe}$  Mössbauer data and structure analysis yield a consistent and complete understanding of the cationic distribution in the title compound. One remaining point of question is the valence state of Mn, which cannot be fixed with the methods available to us. On the basis of structure formula calculations, we propose Mn to be in the trivalent state.

The room-temperature  $^{57}\text{Fe}$  Mössbauer spectrum of the title compound did not show any evidence for electron delocalization between  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  pairs within the infinite chains of edge-sharing *h*-clusters. Obviously the distance between neighbouring *h*-clusters is too large to facilitate fast thermally induced electron hopping in rockbridgeite. This finding is in agreement with Amthauer & Rossman (1984).

## Experimental

The sample of rockbridgeite was a natural specimen originating from Hagendorf pegmatite (Bavaria, Germany). In its natural form it appears as a coarse polycrystalline dark-green–black material with some very tiny free-standing crystals appearing in small veins. A specimen of rockbridgeite of dimensions  $3 \times 3 \times 2$  cm was selected by hand from the minerals collection of the Division of Mineralogy and Materials Science, University of Salzburg (collection No. VIII/14155). From this, some very small prismatic crystals could be separated from a small vein and these were prepared for single-crystal X-ray diffraction. The chemical composition of the sample was determined by electron microprobe analyses, yielding the following weight percentages of oxides: FeO 47.9 (3)%, MnO 6.49 (13)%,  $\text{P}_2\text{O}_5$  32.48 (15)%, ZnO 0.70 (14)%, CaO 0.46 (9)% and  $\text{Na}_2\text{O}$  0.28 (11)%. Calculation of the crystal chemical formula was done on the basis of 17 O atoms and the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio as determined by  $^{57}\text{Fe}$  Mössbauer



**Figure 4**  
 $^{57}\text{Fe}$  Mössbauer spectrum of (I), recorded at 298 (2) K and refined with five subcomponents. Dots represent experimental data, dashed lines the  $\text{Fe}^{2+}$  components and dotted lines the  $\text{Fe}^{3+}$  components. The solid line through the experimental points is the calculated sum spectrum. A difference plot is given at the top.

spectroscopy, assuming a water content of 6.8 wt% as given in Moore (1970). Assuming all the Mn to be in the divalent state yields a chemical formula of  $\text{Ca}_{0.06}\text{Na}_{0.06}\text{Zn}_{0.06}\text{Mn}_{0.62}\text{Fe}_{1.24}\text{Fe}_{3.20}^{3+}(\text{P}_{3.08}\text{O}_{12})(\text{OH})_5$ . The formula is balanced in charge but shows an overestimation of the P content and gives a surplus of 0.24 metal cations for the octahedral sites. Under the assumption that all the Mn atoms are in a trivalent state, the structural formula is  $\text{Ca}_{0.05}\text{Na}_{0.06}\text{Zn}_{0.06}\text{Mn}_{0.61}\text{Fe}_{1.22}\text{Fe}_{3.14}^{3+}(\text{P}_{3.01}\text{O}_{12})(\text{OH})_5$ . This formula is also balanced in charge but gives an almost ideal P content with a lower surplus of metal cations (0.13 atoms per formula unit). This value corresponds quite well to the total amount of  $(\text{Ca}+\text{Na}) = 0.11$ . Thus, we conclude that Ca+Na do not occupy octahedral sites but reside in interstices. The sample studied here corresponds to an Mn-rich rockbridgeite (or iron-rich frondelite), in contrast with the Mn-free sample studied by Moore (1970).

Crystal data

$\text{Fe}_{4.32}\text{Mn}_{0.62}\text{Zn}_{0.06}(\text{PO}_4)_3(\text{OH})_5$  Mo  $K\alpha$  radiation  
 $M_r = 649.19$  Cell parameters from 9128 reflections  
 Orthorhombic,  $Cmcm$   $\theta = 2.4\text{--}27.5^\circ$   
 $a = 5.1761$  (4) Å  $\mu = 6.27$  mm<sup>-1</sup>  
 $b = 13.9774$  (11) Å  $T = 298$  (2) K  
 $c = 16.8689$  (14) Å Prism, dark green  
 $V = 1220.44$  (17) Å<sup>3</sup>  $Z = 4$   $0.11 \times 0.06 \times 0.04$  mm  
 $D_x = 3.533$  Mg m<sup>-3</sup>

Data collection

Bruker SMART APEX CCD area-detector diffractometer 801 independent reflections  
 $\omega$  and  $\varphi$  scans 767 reflections with  $I > 2\sigma(I)$   
 Absorption correction: numerical  $R_{\text{int}} = 0.044$   
 via equivalents ( $X\text{-SHAPE}$  and  $X\text{-RED}$ ; Stoe & Cie, 1996)  $\theta_{\text{max}} = 27.5^\circ$   
 $T_{\text{min}} = 0.65$ ,  $T_{\text{max}} = 0.79$   $h = -6 \rightarrow 6$   
 9119 measured reflections  $k = -18 \rightarrow 18$   
 $l = -21 \rightarrow 21$

Table 1

Selected structural and polyhedral distortion parameters for (I) at 298 (2) K.

Octahedral sites	Fe1	Fe2	Fe3
<Fe—O> (Å)	2.019 (4)	2.131 (4)	2.017 (4)
<O—O> (Å)	2.851 (4)	3.000 (4)	2.853 (4)
$S^\dagger$ (v.u.)	3.00	2.17	3.00
Volume (Å <sup>3</sup> )	10.766 (3)	12.378 (3)	10.801 (3)
BLD‡ (%)	1.46	1.68	2.12
ELD§ (%)	5.80	7.18	4.11
OAV¶ (°)	48.19	103.63	31.26
OQE††	1.0132	1.0281	1.0096
Tetrahedral sites	P1	P2	
<P—O> (Å)	1.534 (3)	1.538 (3)	
<O—O> (Å)	2.504 (3)	2.511 (3)	
$S^\dagger$ (v.u.)	5.01	4.95	
Volume (Å <sup>3</sup> )	1.850 (3)	1.866 (3)	
BLD‡ (%)	0.77	0.19	
ELD§ (%)	0.60	0.50	
TAV‡‡ (°)	4.53	1.07	
TQE§§	1.0011	1.0003	

† Bond-valence sum  $S$  (Brese & O’Keeffe, 1991). ‡ Bond-length distortion (BLD) =  $(100/m)\sum_{i=1}^n [|(X-O)_i - \langle X-O \rangle| / \langle X-O \rangle]$ , with  $n$  = number of bonds,  $(X-O)_i$  = central cation–oxygen bond length and  $\langle X-O \rangle$  = average cation–oxygen bond length (Renner & Lehmann, 1986). § Edge-length distortion (ELD) =  $(100/m)\sum_{i=1}^n [|(O-O)_i - \langle O-O \rangle| / \langle O-O \rangle]$ , with  $n$  = number of edges,  $(O-O)_i$  = polyhedron edge length and  $\langle O-O \rangle$  = average polyhedron edge length (Renner & Lehmann, 1986). ¶ Octahedral angle variance (OAV) =  $\sum_{i=1}^6 (\theta_i - 90) / 11$  (Robinson *et al.*, 1971). †† Octahedral quadratic elongation (OQE) =  $\sum_{i=1}^6 (l_i/l_o)^2 / 6$ , with  $l_o$  = centre-to-vertex distances for a regular octahedron whose volume is equal to that of the undistorted octahedron with bond length  $l_o$  (Robinson *et al.*, 1971). ‡‡ Tetrahedral angle variance (TAV) =  $\sum_{i=1}^4 (\theta_i - 109.47) / 5$  (Robinson *et al.*, 1971). §§ Tetrahedral quadratic elongation (TQE) =  $\sum_{i=1}^4 (l_i/l_o)^2 / 4$  (Robinson *et al.*, 1971).

Table 2

<sup>57</sup>Fe Mössbauer hyperfine parameters for (I) at 298 (2) K.

IS† (mm s <sup>-1</sup> )	QS‡ (mm s <sup>-1</sup> )	Γ§ (mm s <sup>-1</sup> )	Area (%)	Site
0.408 (2)	0.439 (4)	0.149 (3)	46.2 (4)	Fe <sup>3+</sup> Fe3
0.449 (3)	0.715 (9)	0.151 (3)	22.7 (4)	Fe <sup>3+</sup> Fe1
0.523 (5)	0.867 (9)	0.151 (4)	3.1 (6)	Fe <sup>3+</sup> Fe2
1.066 (4)	3.014 (12)	0.137 (4)	15.7 (5)	Fe <sup>2+</sup> Fe2
1.118 (5)	2.732 (9)	0.164 (7)	12.3 (4)	Fe <sup>2+</sup> Fe2

† IS = isomer shift relative to  $\alpha\text{-Fe}$ . ‡ QS = quadrupole splitting. §  $\Gamma$  = line width expressed as half width at half maximum.

Refinement

Refinement on  $F^2$   $w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 14.5365P]$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$  where  $P = (F_o^2 + 2F_c^2)/3$   
 $wR(F^2) = 0.078$   $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $S = 1.39$   $\Delta\rho_{\text{max}} = 0.89$  e Å<sup>-3</sup>  
 801 reflections  $\Delta\rho_{\text{min}} = -0.81$  e Å<sup>-3</sup>  
 85 parameters  
 All H-atom parameters refined

The analysis of systematic extinction criteria and  $E$  statistics confirms  $Cmcm$  space-group symmetry. Structure solution using direct methods and subsequent structure refinement yields a model which is similar to that provided by Moore (1970) using the non-standard setting  $Bbmm$ , which is the  $bca$  setting of space group  $Cmcm$ . Atomic nomenclature follows that proposed by Moore (1970) and fractional atomic coordinates can be directly transformed to those of this study. During refinement, it was assumed that the Fe3 and O3 sites were both only half filled. Both sites are disordered in the same manner.

Bond-valence calculations (Brese & O’Keeffe, 1991) show atoms O3, O5 and O6 to be distinctly underbonded ( $S = 0.96, 1.46$  and  $1.56$  v.u., respectively). Thus, it is tentatively proposed that H atoms are bonded to these O atoms. In fact, two H atoms, which could be located easily in the difference Fourier maps, are bonded to O3 and O6. The only refineable difference peak with a reasonable distance to O5 was located at approximately (0.0, 0.195, 0.225), giving rise to a very short interatomic contact of  $\sim 0.85$  Å between neighbouring H atoms. Furthermore, it makes impossibly short contacts to a congener of O5 (1.7 Å) and with the metal site Fe2 (2.13 Å). Therefore, this H5 position cannot be correct and H5 remains ‘not located’. Because of the problems with H-atom location, three further crystals of the compound were investigated, yielding structural data identical to those reported here to within one standard uncertainty (including positions for atoms H3 and H6). The only possible site for atom H5 was found to be located at the position noted above, which has to be ruled out, however, for the reasons given. It is assumed that atom H5 might be disordered in some way.

It should also be noted that the highest difference peak of  $\sim 0.9\text{--}1.0$  e Å<sup>-3</sup> in all four crystals investigated here could not be ascribed to H atoms but was found consistently at a position of approximately (0, 0.072, 0.109). This is  $\sim 0.8$  Å away from the Fe2 position. It is concluded that this position, containing the Jahn–Teller ion Mn<sup>3+</sup> and Zn<sup>2+</sup> with its tendency for fourfold coordination, displays a slight positional disorder. This could be the reason for the significant diffuse scattering, which is observed along the  $c$  direction in the diffraction images. Additionally, it is the  $c$  direction in which the infinite chains of edge-sharing  $h$ -clusters run. Measurements at 100 K neither remove the diffuse scattering nor facilitate location of atom H5. The location of a reasonable position for Na and Ca was not possible from the diffraction data.

Data collection: *SMART-Plus* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Version 1.70.00; Farrugia 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1177). Services for accessing these data are described at the back of the journal.

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