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CRYSTAL CHEMISTRY OF THE BASIC MANGANESE ARSENATES: III. THE CRYSTAL STRUCTURE OF EVEITE, $Mn_2(OH)(AsO_4)$

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ABSTRACT

Isotypy of eveite, $Mn_2(OH)(AsO_4)$ with andalusite and the olivenite group is confirmed. Refined structural parameters are given; angles for the Mn^{V}-O polyhedron deviate from a regular trigonal pyramid much as in andalusite. Sarkinite, the dimorph of eveite probably has the wagnerite structure, but has not been refined.

INTRODUCTION

Eveite, $Mn_2(OH)(AsO_4)$, *a* 8.57 (1), *b*. 8.77 (1), *c* 6.27 (1) Å, *Pnnm*, Z=4, is a rare mineral from Långban, Sweden, recently described by Moore (1968). He showed that eveite is a member of the olivenite group of minerals which are isostructural with andalusite, $Al_2(O)(SiO_4)$. Thus, half of the Mn^{+2} atoms in eveite are in five-fold coordination which, excepting its dimorph sarkinite, is hitherto undocumented in mineral structures.

To test this conclusion and to obtain further crystallochemical information on the eveite structure, a three-dimensional X-ray diffraction analysis was undertaken.

EXPERIMENTAL

Eveite crystals invariably are warped about the zone [*hk*0] and consist of composites in near-parallel growth. A fragment of 0.0037 mm^3 volume appeared suitable for structure analysis. The crystal was not single, and the data had to be gathered on film using a Weissenberg camera and Zr-filtered Mo radiation. Packets of four films for each level were separated by aluminum foils and the intensities were read visually using a spot scale of fifteen intervals obtained from the crystal. 639 independent intensities representing the *hk*0-*hk*5 levels were obtained thereby and processed to obtain F_{obs} after application of a polyhedral transmission correction for absorption.

SOLUTION OF THE STRUCTURE

The refined structure of andalusite (Burnham and Buerger, 1961) was used as the starting model. Scattering curves for Mn^{+}, As^{3+}, and O^{1-} were obtained from *International Tables for X-ray Crystallography, Vol.*

3 (1962). The R_{hkl} index was 0.30 prior to refinement. Certain reflections were excluded from further refinement: reflections of zero intensity, reflections on the most exposed film for each level which had intensities sufficiently weak that their uncertainities were greater than 50 percent of the adjudged value, and five reflections which were beyond the range of the spot scale. Of the 445 remaining reflections, several cycles of coordinate refinement followed by full-matrix coordinate and isotropic temperature factor refinement led to $R_{hkl}=0.15$. Including all 639 reflections, $R_{hkl}=0.19$. This is a reasonable convergence for film data from a crystal which was not single.

Final atomic and coordinates isotropic temperature factors appear in Table 1 and the F_{obs}-F_{calc} data are given in Table 2.[1]

TABLE 1. EVEITE. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B(Å^2)
Mn^{VI}	0	0	0.2464 (8)	0.98 (8)
Mn^{V}	0.3571 (6)	0.1348 (6)	1/2	1.21 (7)
As	.2417 (3)	.2568 (3)	0	0.33 (4)
O(1)=OH	.3859 (22)	.3722 (22)	1/2	0.46 (28)
O(2)	.4158 (23)	.3574 (23)	0	0.66 (30)
O(3)	.1079 (30)	.3927 (30)	0	1.65 (41)
O(4)	.2204 (17)	.1464 (17)	.2205 (28)	0.91 (23)

DISCUSSION

Aside from minor differences in coordinates, the isotypy of eveite with andalusite and the olivenite group is confirmed. Figure 1 is a spoke diagram of the refined eveite crystal structure. The average distances are Mn^{VI}-O 2.19, Mn^{V}-O 2.12, and As-O 1.69 Å. The O-O′ distances average 3.10 for Mn^{VI}, 3.23 for Mn^{V}, and 2.77 Å for As, with the shortest individual distances representing shared edges. Interatomic distances as well as O-Me-O′ bond angles for the five-coordinated Mn^{V}-O polyhedron are summarized in Table 3. As in andalusite, the angles found for this polyhedron deviate considerably from those representative of a regular trigonal bipyramid.

The andalusite structure type has been discussed in detail by Burnham and Buerger (1961) and only the salient features shall be offered here. The structure consists of infinite Me-O edge-sharing octahedral chains

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[1] For a copy of Table 2, order NAPS Document 00023 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N. Y. 10001; remitting $1.00 for microfiche or $3.00 for photocopies.

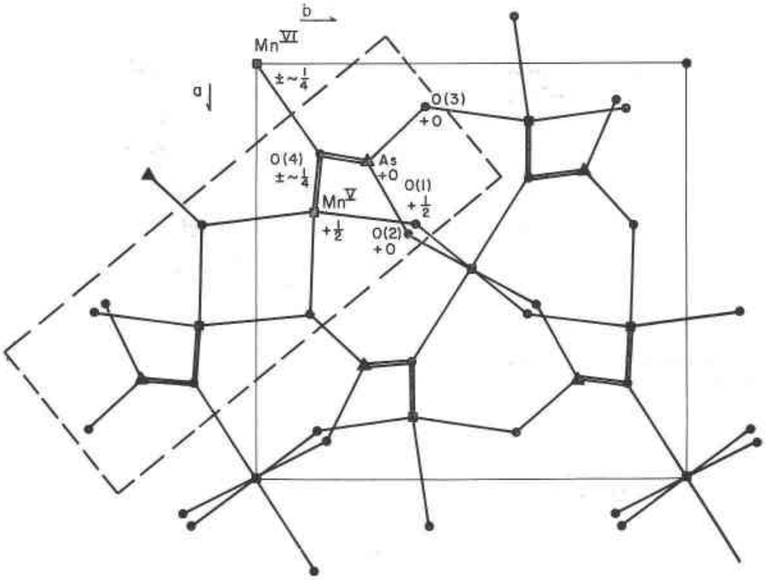

FIG. 1. Spoke diagram of the eveite crystal structure. The tetrahedral and trigonal bipyramidal "ladder" component is dashed in.

running parallel to the *c*-axis. Me-O trigonal bipyramids alternating with tetrahedra form ladders with the edge-sharing trigonal bipyramids as rungs. The ladders run parallel to the *c*-axis and link to the octahedral chains by corner-sharing to form a three-dimensional structure with strong chain character.

Relationship with Sarkinite. Sarkinite is the dimorph of eveite and structure cell data suggest that it belongs to the wagnerite, $Mg_2(F)(PO_4)$, structure type. Though the crystal structure of sarkinite has not been refined, the highly complicated wagnerite structure type is now known [Coda, Giuseppetti, and Tadini 1967)] and its structure sheds light on the nature of the eveite-sarkinite dimorphism.

The wagnerite structure includes 32 unique atoms in the asymmetric unit. The structure is very complex and is difficult to compare with the andalusite type. The general stoichiometry of polyhedra is $Mg^{VI}Mg^{V}(F)(P^{IV}O_4)$, identical with the andalusite type. However, the arrangement of polyhedra is quite different since the octahedral chains and the trigonal bipyramidal and tetrahedral ladders are not intact; the polyhedra are arranged to form a more evenly distributed three-dimensional structure with no chain character. Table 4 clearly shows that the topology of the two structures is quite different; though the magnitudes and the sum of

TABLE 3. EVEITE. INTERATOMIC DISTANCES AND TRIGONAL BIPYRAMIDAL ANGLES

Mn^{VI}–O

2 Mn^{VI}–O(1)	2.14
2 Mn^{VI}–O(2)	2.15
2 Mn^{VI}–O(4)	2.29
average	2.19 Å

O–O′ distances

1[a] O(1)–O(1′)	2.97	2 O(2)–O(4′)	3.29
1[a] O(2)–O(2′)	2.89	2 O(1)–O(4)	3.19
2 O(2)–O(1)	3.15	2 O(1)–O(4′)	2.92
2 O(2)–O(4)	3.14	average	3.10 Å

Mn^{V}–O

1 Mn^{V}–O(1)	2.10
1 Mn^{V}–O(3′)	2.14
1 Mn^{V}–O(3)	2.16
2 Mn^{V}–O(4)	2.11
average	2.12 Å

O–O′ distances

1[a] O(3)–O(3′)	2.64	2 O(4)–O(1)	3.00
1 O(4)–O(4′)	3.50	2 O(4)–O(3)	3.77
1 O(3)–O(1)	3.00	2 O(4)–O(3′)	3.19
		average	3.23 Å

O–Mn^{V}–O angles

1 O(1)–Mn^{V}–O(3′)	163.4°	2 O(1)–Mn^{V}–O(4)	91.0
2 O(4)–Mn^{V}–O(3)	123.9	1 O(1)–Mn^{V}–O(3)	86.6
1 O(4)–Mn^{V}–O(4′)	112.4	1 O(3)′–Mn^{V}–O(3)	75.4
2 O(3′)–Mn^{V}–O(4)	97.2		

As

As–O

1 As–O(2)	1.73
1 As–O(3)	1.65
2 As–O(4)	1.70
average	1.69 Å

O–O′ distances

1 O(4)–O(4′)	2.76	2 O(4)–O(3)	2.74
1 O(3)–O(2)	2.66	2 O(4)–O(2)	2.85
		average	2.77 Å

[a] Shared edges.

Estimated standard errors: Mn, As-O ±0.03 Å; O-O′ ±0.05 Å.

TABLE 4. EVEITE. ELECTROSTATIC VALENCE BOND STRENGTHS

		ξ
OH=O(1)	$Mn^{VI}+Mn^{VI\prime}+Mn^{V}$	1.07
O(2)	$Mn^{VI}+Mn^{VI\prime}+As$	1.92
O(3)	$Mn^{V}+Mn^{V\prime}+Aa$	2.05
O(4)	$Mn^{VI}+Mn^{V\prime}+As$	1.98

For a 20 oxygen aliquot:

Eveite	Sarkinite	ξ
4	4	1.07
4	7	1.92
4	7	2.05
8	2	1.98

the nonequivalent electrostatic valence bond strengths are the same, their relative frequency in an aliquot volume within the two structures is different.

Further insight is obtained by the packing index, *volume of cell/Σ anions in cell*. For sarkinite, this is 20.8 Å^3/anion and eveite 23.6 Å^3/anion. Thus, eveite is the low pressure dimorph of the eveite-sarkinite pair.

Finally, it is interesting to note the contrast in colors between eveite and sarkinite. Eveite is apple-green whereas sarkinite is flesh-red. Since the color is a crude indicator of the crystal field stabilization energy for transition metal complexes, it can be concluded that eveite has a greater crystal field stabilization energy than sarkinite. Detailed analysis of the crystal field spectra for the two structure types would be a very difficult problem since sarkinite has a large number of nonequivalent atoms in the asymmetric unit.

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