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CRYSTAL CHEMISTRY OF THE BASIC MANGANESE ARSENATES: IV. MIXED ARSENIC VALENCES IN THE CRYSTAL STRUCTURE OF SYNADELPHITE.

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ABSTRACT

Three-dimensional crystal structure analysis followed by full-matrix parameter refinement elucidated the crystal chemistry of synadelphite. The reliability index, R_{hkl}, converged to 0.089 for 1249 nonequivalent reflections.

Synadelphite is orthorhombic, space group *Pnma*, *a* 10.754(11), *b* 18.865(17), *c* 9.884 (14) Å, with composition $Mn^{2+}{}_9(OH)_9(H_2O)_2(AsO_3)(AsO_4)_2$, $Z=4$. The atomic arrangement is based on "double" hexagonal close-packed oxygen atoms stacked perpendicular to the *c*-axis. Voids appear in the oxygen close-packing so that 88 oxygen atoms, instead of 96 for complete densest packing, occur in the unit cell. The ligands include $(AsO_3)^{3-}$ trigonal pyramids with point symmetry *m*, $(AsO_3)^{3-}$ tetrahedra, $(OH)^-$ ions and H_2O molecules. Synadelphite is the first example of a known structure which contains arsenic in two states of oxidation.

The Mn^{2+} cations occupy octahedral voids. The key to the arrangement is a wedge-shaped cluster of nine edge-sharing Mn-O octahedra in a plane with point symmetry *m*. This cluster, when submitted to the axial glide and inversion operations, generates the three-dimensional edifice through corner- and edge-sharing with symmetry equivalent wedges.

Classical wet chemical analyses consistently have failed to show the presence of mixed valence states of arsenic in synadelphite. This is attributed to hydrolysis of As^{3+} in acid solution to form As^{5+}. Such a mechanism also accounts for consistently lower water contents in chemical analyses in comparison with the crystal structure. Observations on rotation and Weissenberg films and a crystal-chemical examination of the data of Hurlbut (1937) for "plumbosynadelphite" (the red outer shell on Långban synadelphites) indicate that this variety must contain some of the cations in higher oxidation states.

INTRODUCTION

In a series of papers (Moore, 1967a, 1967b, 1968a, 1968b) I have discussed the crystal chemistry of members of the basic manganese arsenate homologous series, $Mn^{2+}{}_n(OH)_{2n-3z}(AsO_4)^{3-}{}_z$. Although this series is restricted in natural occurrences, the compounds are of considerable interest to inorganic chemists and mineralogists who seek underlying principles behind crystal-chemical homology.

Synadelphite, initially accepted as a member of this series on the basis of its crystal chemistry, is confined to low-temperature hydrothermal veins cutting hausmannite ores in dolomitic marbles at several small abandoned orebodies in the province of Värmland, Sweden, in particular Östra Mossgruvan in Nordmarks Odalfält and Långban. It is one of several basic manganese arsenate species orignially described in considerable detail by Sjögren (1884). "Hemafibrite," named by Igelström (1884) and discussed in more detail by Sjögren (1885), was shown by Moore (1967b) to be synonymous with synadelphite. "Allodelphite," named and described as a new Långban species by Quensel and von Eckermann (1930) was shown to be a variety of synadelphite by Hurlbut (1937), who, in a detailed optical investigation on Långban synadelphite, noted anomalous optical features which contradicted the previously accepted orthorhombic symmetry of the mineral. He concluded that the species is triclinic, twinned by reflection on pseudo-orthogonal axial planes. Although his single crystal X-ray studies on both twins and individual yielded essentially identical results which conformed to orthorhombic symmetry, the optical data nevertheless indicated lower symmetry. Adding to the complexity of the problem, Hurlbut noted that the dark crystals from Långban consist of two zones, the interior which is colorless and the surrounding coating which is dark red and contains significant (3.24%) quantities of PbO.

To further our knowledge of this perplexing species and to understand better the basic manganese arsenates in general, I present detailed results concerning the atomic arrangement of synadelphite. These results are of particular interest since the whole problem of formal valence states involving Mn and As in crystals determined by wet chemical methods, consequently the interpretation of their chemical formulae in mineralogical systems, must now be thrown into question. Although synadelphite has been generally accepted as a basic arsenate of divalent manganese principally on the foundation of seven existing analyses of synadelphite, "allodelphite" and "hemafibrite," this crystal structure analysis led to the surprising result that arsenic exists in two states of oxidation and that the correct crystal-chemical formula for the species is

$$Mn_9^{2+}(OH)_9(H_2O)_2(AsO_3)(AsO_4)_2.$$

PRELIMINARY OBSERVATIONS

The garnet-red crystal used in this study was a symmetrical prism parallel to the *a*-axis, nearly rectangular in cross-section and measuring 0.12×0.14×0.18 mm. It was obtained from a specimen labelled Flink unknown 325 (NRMS No. 251554) in the collection of the Swedish Natural History Museum and corresponds to the material used in Hurlbut's study. Preliminary rotation and Weissenberg photographs established extinction criteria compatible with space groups *Pnma* or $Pn2_1a$. In addition, blurred reflections were observed, essentially identical in relation to the sharp reflections, but which indicated an associated isostructural phase with decreased crystal cell parameters. The average intensity of a blurred reflection was about one-fiftieth that of its associated sharp reflection. This observation is entirely compatible with Hurlbut's observation of two color zones in synadelphite but does not support his claim that the predominant distinguishing feature for the thin red outer zone is the presence of lead. Furthermore, his optical data and the chemical analyses for the two zones contradict this claim as well, as we shall see in subsequent discussion.

EXPERIMENTAL

6000 reflections were gathered on a PAILRED automated diffractometer using a graphite monochromator and Mo radiation to $2\theta = 80.0°$. These data spanned the 0 to 12 levels with *a* as the rotation axis. The cell parameters in Table 1, in agreement with parameters obtained from omega scans along the axial festoon rows, essentially confirm the previously reported data of Moore (1967b). They were obtained from conventional least squares refinement of the indexed powder data in Table 2. The powder data were obtained from a spherical powder mount with internal silicon ($a = 5.4301$ Å) utilizing a 114.6 mm diameter Buerger camera and Mn filtered Fe radiation. The correct Miller indices were obtained by matching line intensities with the single crystal data. Individual integrated intensities were obtained using a 2.4° half-angle scan, with background counting time on each side of 20 seconds. Since the crystal exhibited *mm* point symmetry parallel to the *a*-axis, reflection pairs of the kind $I(hkl)$, $I(hk\bar{l})$ were essentially identical in intensity.

TABLE 1. SYNADELPHITE CRYSTAL CELL DATA

	1	2	3	4
a (Å)	10.73 (2)	10.65	10.754 (11)	10.62
b (Å)	18.84 (5)	18.70	18.865 (17)	18.42
c (Å)	9.87 (2)	9.91	9.884 (14)	9.74
V (Å^3)	1995	1974	2005 (3)	1905
Space group	*Pnma*	?	*Pnma*	*Pnma*
Formula	$Mn^{2+}_9(OH)_9(H_2O)_2(AsO_3)(AsO_4)_2$			
Z	4			

1. Moore (1967b) on "hemafibrite" crystals from Nordmark, Sweden.
2. Hurlbut (1937) on crystals from Långban, Sweden.
3. This study. Cell parameters obtained from refined powder data in Table 2.
4. Red oxidized shell covering crystal in 3. From blurred reflections on rotation and Weissenberg films. Errors are approximately ±0.04 Å on the cell edges.

These symmetrical reflections were averaged and the data were processed to obtain $|F_{obs}|$. As a consequence of small size and favorable crystal shape, no absorption anisotropy correction was applied. Among the $|F_{obs}|$ data were 1745 "zero" reflections, including the systematic space group absences which confirmed the data obtained in the earlier study of Moore (1967b) based on Långban and Nordmark crystals. 1473 reflections were "nonzero" (above average background) and were the only ones used in the final refinements.

TABLE 2. SYNADELPHITE POWDER DATA[a]

I/I_0	d(obs)	d(calc)	hkl	I/I_0	d(obs)	d(calc)	hkl
7	9.36	9.43	020[b]	3	2.482	2.471	004
10	8.72	8.75	011[b]	2	2.409	2.409	270
2	7.29	7.28	101[b]	4	2.373	2.362	402
5	5.27	5.30	031[b]	3	2.295	2.299	361
3	4.850	4.942	002[b]	3	2.281	2.325	422
3	4.606	4.582	211	1	2.157	2.166	272
1	4.337	4.368	112	7	2.091	2.095	263
1	4.217	4.223	221	4	1.8748	1.8817	532
4	3.942	3.958	141	2	1.8269	1.8272	264
2	3.648	3.654	132	2	1.7898	1.7863	424
2	3.543	3.546	240	3	1.7355	1.7365	463
2	3.526	3.525	051	3	1.6959	1.6991	392
2	3.366	3.370	301	1	1.6212	1.6189	650
2	3.322	3.317	311	7	1.5996	1.5979	265
3	3.245	3.252	142	2	1.5746	1.5721	0·12·0
5	3.080	3.088	250	4	1.5601	1.5571	660
2	2.900	2.918	033	1	1.4384	1.4358	0·13·1
5	2.880	2.889	152	1	1.2947		
3	2.820	2.816	133	1	1.1636		
4	2.772	2.773	322	2	1.1535		
2	2.703	2.714	260				
9	2.636	2.635	332				
2	2.571	2.585	420				

[a] FeKα; silicon standard, $a=5.4301$ Å.

[b] Low angle reflections excluded from cell refinement.

SOLUTION OF THE STRUCTURE

Initially, several structure models were derived, based solely on crystal-chemical arguments. It was noted that $a/2\sqrt{3}\smile b/6\approx 3.1$ Å(O–O′ octahedral edge distance for typical Mn^{2+}–O octahedra), and $c/4\approx 2.4$ Å (*i.e.*, a "double" hexagonal close-packing), which enabled orientation of the octahedra and tetrahedra in combination with symmetry restrictions. Thus, the *b*-axis was chosen parallel to the octahedral edges with the *c*-axis perpendicular to the close-packed layers. In this manner, the orientation of the *a*-axis was determined. Including electrostatic arguments, it was hoped that the correct model could be obtained from first principles. Although these relations subsequently proved correct, the fundamental error lay in the assumption that the cell contents included $Mn_{36}(OH)_{36}(AsO_4)_{12}$, the generally accepted formula for synadelphite. Trial $|F_{obs}|-|F_{calc}|$ tests indicated that all models had to be rejected.

For solution of the structure, Patterson techniques were ruled out since the large number of heavy atoms in the asymmetric unit in combination with a likely dense-packed system would lead to great difficulty with the interpretation of the vector sets.

Consequently, recourse was made to MAGIC, an efficient and well-proven fully computerized version of the symbolic addition procedure (Dewar, 1968). Apprehensions about direct methods applied to close-packed systems, given a complete set of data, are well-known to the author from previous experience and have been discussed in print (Moore, 1968c). The essential problem with direct methods applied to close-packed structures is the high geometrical correlation among atomic positions in the crystal cell and the subsequent breakdown of the statistical arguments which assume a "random atom" asymmetric unit. However, even though the solution proved to be based on principles of densest packing, randomness still exists since the phase determining atoms in synadelphite are clearly the heavy atoms, *i.e.* Mn and As. These atoms occupy only a fraction of the available octahedral and tetrahedral voids. The solution is straightforward if one assumption is made: that atoms in octahedral coordination in the asymmetric unit prefer to cluster as edge-sharing groups, populating one of the two permissible symmetry-independent octahedral levels normal to the *c*-axis (the axis normal to the close-packed layers). This assumption is not without basis, since nearly all known close-packed structures with Mn^{2+} atoms partially populating octahedral sites are based on edge-sharing octahedral clusters. Indeed, the resulting *E*-map resolved octahedrally coordinated atoms into two symmetry independent levels within the cell asymmetric unit, since statistically (discounting polyhedral distortions) either choice is as likely. Both levels exhibited the same kind of octahedral cluster, but the normalized electron density at one level was attenuated relative to the other. This is attributed to the distortions away from ideal closest packing in the crystal and consequent influence on the phases of the high angle reflections used in sign determination. Only those solutions for the level with higher normalized electron density were chosen and ascribed to the Mn atoms.

Likewise, for the As atoms, those positions on the E-map which were electrostatically compatible with the octahedral model were chosen. Five Mn atoms and two As atoms in the asymmetric unit were applied to least-squares coordinate refinement using a local version of the full matrix program of Busing, Martin and Levy (1962). Refinement converged to $R = \|F_{\text{obs}}| - |F_{\text{calc}}\| / |F_{\text{calc}}| = 0.19$ for metals only, where three-dimensional difference synthesis of the phases thus obtained revealed all twelve oxygen atoms in the asymmetric unit.

REFINEMENT

A Wilson plot, optionally built into the MAGIC program, revealed a centrosymmetric structure and the space group *Pnma* was selected. Centrosymmetry is also assured on the basis of persistent morphological point symmetry $2/m$ with respect to the crystallographic b-axis in combination with the systematic space group absences.

All atomic free parameters in the asymmetric unit were refined according to full-matrix least-squares procedures mentioned above, including isotropic thermal vibration in the final stages, until R_{hkl} converged to 0.089 for the 1249 reflections whose $|F_{\mathrm{obs}}|$ were three times above mean background error, and 0.102 for all 1473 non-zero reflections. Scattering curves for Mn^{1+}, As^{3+} and O^{-} were obtained from MacGillavry and Rieck (1962). All final isotropic thermal vibration parameters closely corresponded to values expected for their ionic species. The atomic coordinates and isotropic thermal vibration parameters are listed in Table 3 and the $|F_{\mathrm{obs}}| - F_{\mathrm{calc}}$ data appear in Table 4.[1]

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[1] To obtain a copy of Table 4, order NAPS Document #00178 from National Auxiliary Publications Service of ASIS, c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies payable to CCMIC-NAPS.

TABLE 3. SYNADELPHITE: CELL MULTIPLICITY, ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS[1]

	M	x	y	z	B(Å^2)
Mn(1)	4	0.2941 (5)	0.7500	0.3868 (5)	0.88 (7)
Mn(2)	8	.5613 (4)	.6635 (2)	.3729 (4)	.85 (5)
Mn(3)	8	.8269 (4)	.5863 (2)	.3614 (4)	.82 (5)
Mn(4)	8	.0887 (4)	.5039 (2)	.3627 (4)	.93 (5)
Mn(5)	8	.3564 (3)	.4225 (2)	.3575 (4)	1.05 (5)
As(1)	4	.9672 (3)	.7500	.3618 (3)	.12 (4)
As(2)	8	.3225 (2)	.5811 (1)	.5654 (2)	.12 (3)
O(1)	4	.1151 (23)	.7500	.2854 (23)	.99 (32)
O(2) = OH$^-$	4	.4748 (27)	.7500	.4832 (26)	1.33 (38)
O(3)	8	.2401 (18)	.6535 (9)	.5163 (18)	1.33 (28)
O(4)	8	.4018 (17)	.6818 (9)	.2373 (18)	1.32 (26)
O(5)	8	.4714 (16)	.5867 (8)	.5176 (15)	1.10 (22)
O(6) = OH$^-$	8	.6630 (15)	.5927 (8)	.2420 (15)	.72 (20)
O(7) = OH$^-$	8	.7158 (16)	.6491 (8)	.4997 (17)	.97 (24)
O(8)	8	.7417 (18)	.4940 (9)	.4987 (17)	.88 (24)
O(9) = OH$^-$	8	.9293 (17)	.5115 (8)	.2381 (16)	.77 (23)
O(10) = OH$^-$	8	.9757 (16)	.5726 (8)	.4980 (17)	1.11 (22)
O(11)	8	.1838 (16)	.4225 (8)	.2349 (15)	.83 (21)
O(12) = $\mathrm{H_2O}$	8	.4170 (19)	.3306 (10)	.2232 (18)	2.00 (29)

[1] (Estimated standard errors in parentheses)

Throughout this study, it was not necessary to consider possible lower symmetry for synadelphite. The anomalous optical properties of Hurlbut (1937) cannot be explained solely on structural grounds and the averaging nature of X-ray diffraction analysis does not permit examination of more subtle phenomena such as valence transfer. Likewise, refinement based on a triclinic cell would have little meaning because of the high parameter correlations among the atomic positions.

Description of the Structure

Topology. The atomic arrangement for synadelphite is one of the more unusual of Nature's inorganic architectural masterpieces. The underlying motif, singled out in Figure 1, includes all Mn atoms in the asymmetric unit and their equivalents which are related by the reflection operation. This motif consists of a "wedge" of nine edge-sharing octahedra with point symmetry *m* which, when isolated, has formal composition Mn_9O_{37}. This wedge, when submitted to the axial glide operation, leads to the next level of octahedral populations similarly disposed and linked to the former by corner-sharing. Each wedge contains a trigonal

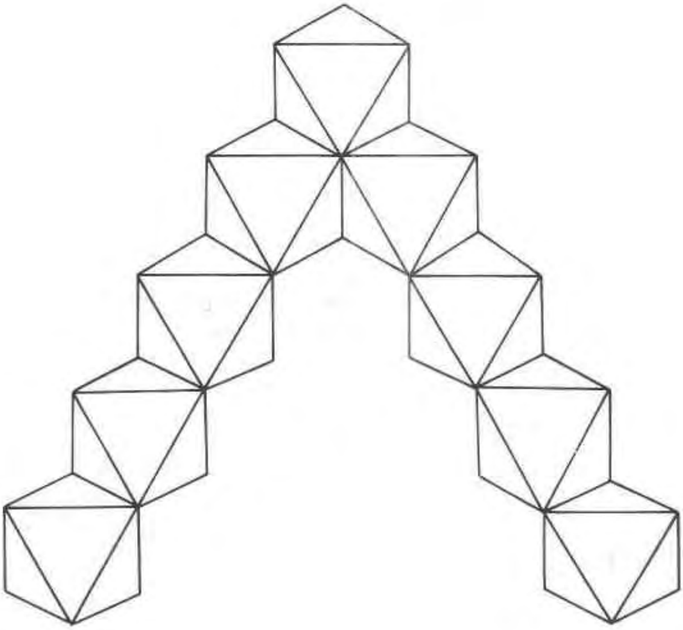

FIG. 1. The idealized wedge of nine Mn–O octahedra which is the principal motif of the synadelphite atomic arrangement. This wedge has composition Mn_9O_{37} and possesses point symmetry *m*.

triplet of Mn–O octahedra, that is, octahedra each of which shares two edges with the two remaining planar octahedra. Above this triplet and sharing three edges with it occurs an $(As^{3+}O_3)^{3-}$ trigonal pyramid with point symmetry m, a previously unexpected feature in the structure. The remaining As atoms, coordinated to form $(As^{5+}O_4)^{3-}$ tetrahedra, span the equivalent octahedral wedges at the same level by corner-sharing. The entire complex thus produced is depicted in Figure 2. The remaining half of the unit cell is obtained by inversion of this complex through the cell center. The inversion operation results in further edge- and corner-sharing with the complex. These extra shared edges are depicted as bold lines in Figure 2.

Octahedral populations occur at the levels $z\backsim\frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$ and oxygen atoms occur in a "double" hexagonal close-packed array (. . . ch . . .) at levels $z\backsim 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$. The structure involves missing oxygen atoms at two nonequivalent special positions with Hole (1)$\backsim$0.50, $\frac{3}{4}$,$\backsim$0.00 and Hole (2)$\backsim$0.31, $\frac{3}{4}$, $\backsim -0.25$. Thus, in the actual synadelphite crystal, there are 88 oxygen atoms in the unit cell, instead of 96 required for totally occupied densest-packed sites. The $(OH)^-$ anions are each bonded to three Mn^{2+} ions, and one H_2O molecule occurs in the asymmetric unit bonded to one Mn^{2+} ion. The oxygen atoms identified with the As^{3+} trigonal pyramid are also associated with three Mn^{2+} ions and are electrostatically neutral. Oxygen atoms associated with the $(AsO_4)^{3-}$ tetrahedra are associated with one, two or three Mn^{2+} atoms, exhibiting the rare instance of oversaturation of O(8) with $3Mn^{2+}+As^{5+}$. Cation electrostatic valence balances about each of the nonequivalent oxygens are presented in Table 5.

Interatomic Distances. Me–O and O–O′ interatomic distances are given in Table 6 and polyhedral distortions and site labelling in the asymmetric unit appear in Figure 3. Of particular interest is the presence of arsenic in two states of oxidation. The evidence, both on topological and crystal-chemical grounds, appears to be indisputable. The As(1) atom with point symmetry m coordinates as a nearly ideal trigonal pyramid to three oxygen atoms and has 1 As(1)–O(1) 1.76, 2 As(1)–O(4) 1.76 Å distances. The average, 1.76 Å, is considerably above the average observed for As^{5+}–O tetrahedral distances; abundant data for the latter yield distances averaging in the range 1.65 to 1.68 Å. Unfortunately, comparable examples of reliable As^{3+}–O distances are practically unknown, the only example occurring in asbecasite, $Ca_3Ti(As_3SiBeO_{10})_2$, recently investigated by Cannillo, Giuseppetti, and Tadini (1969). In this structure, the average As^{3+}–O distance is 1.797 Å, but the nature of the bonding results in one severely oversaturated oxygen atom in the

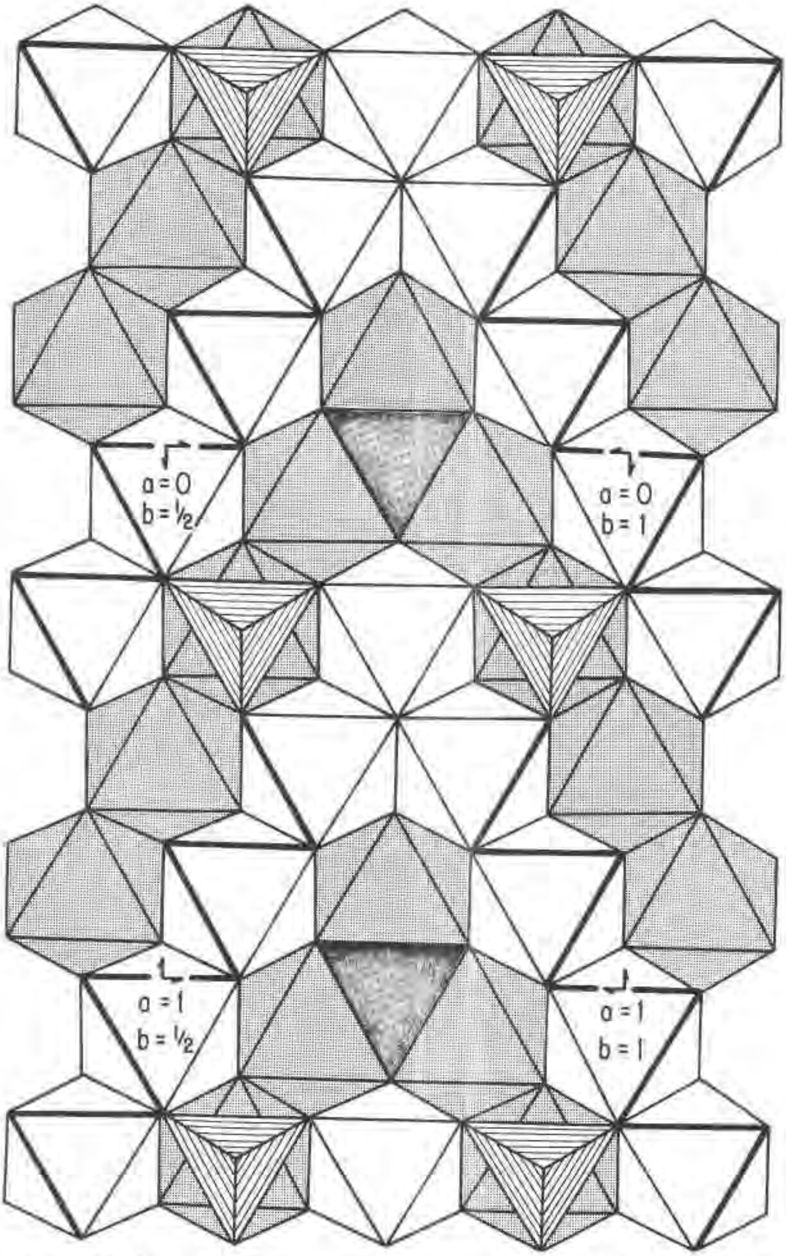

FIG. 2. The idealized synadelphite atomic arrangement obtained by adding the As-O polyhedra and performing the axial glide operation on Fig. 1. Stippled octahedra are at $z\sim 1/8$, unstippled octahedra at $z\sim 3/8$. The As^{3+}–O trigonal pyramids appear as solid triangles and the As^{5+}–O tetrahedra are ruled. Edges shared by the octahedra at $z\sim 3/8$ with those generated by the inversion operation are drawn bold.

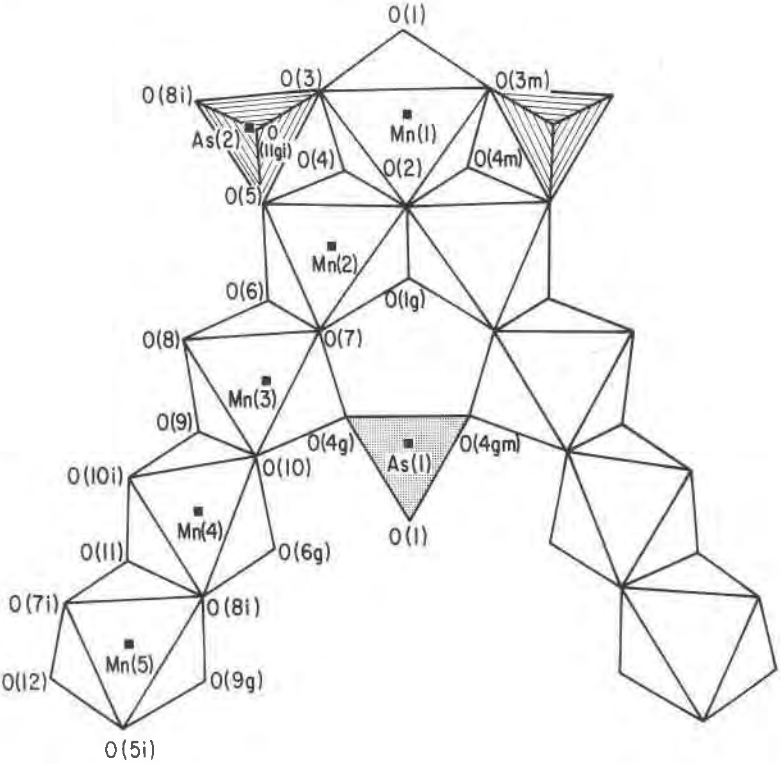

FIG. 3. Labelling of the synadelphite atomic positions in Tables 3 and 6. This polyhedral diagram features the asymmetric unit and its mirror equivalent. Actual polyhedral distortions are shown.

trigonal pyramid. The O–O′ distances associated with As^{3+} in synadelphite average 2.61 Å, considerably shorter than O–O′ distances associated with As^{5+}–O tetrahedra which usually average 2.75 to 2.80 Å. The As^{5+}–O average in synadelphite is 1.69 Å, with O–O′ averaging 2.75 Å. Electrostatic arguments account for one seemingly peculiar effect: all metal distances associated with O(8) are the longest distances for their polyhedra. This is because O(8) is the only oversaturated anion in the structure (Table 5).

The edges shared by the octahedra also conform to simple electrostatic arguments. As seen in Table 6, O–O′ edges which are shared are the shortest edges for their polyhedra. The only exception—O(8)—does not obey this relationship because of its severe cation over-saturation. Thus, interatomic distances in this complex crystal structure conform to simple electrostatic arguments in every detail, adding further confidence to the crystal-chemical interpretation.

TABLE 5. SYNADELPHITE: ELECTROSTATIC VALENCE BALANCES (Σ)

Anion	Coordinating cations		Σ
$O(1)=O^{2-}$	Mn(1) + Mn(2) + Mn(2) + As(1)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}+\frac{3}{3}$	2.00
$O(2)=OH^-$	Mn(1) + Mn(2) + Mn(2)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}$	1.00
$O(3)=O^{2-}$	Mn(1) + As(2)	$\frac{2}{6}+\frac{5}{4}$	1.58
$O(4)=O^{2-}$	Mn(1) + Mn(2) + Mn(3) + As(1)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}+\frac{3}{3}$	2.00
$O(5)=O^{2-}$	Mn(2) + Mn(5) + As(2)	$\frac{2}{6}+\frac{2}{6}+\frac{5}{4}$	1.92
$O(6)=OH^-$	Mn(2) + Mn(3) + Mn(4)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}$	1.00
$O(7)=OH^-$	Mn(2) + Mn(3) + Mn(5)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}$	1.00
$O(8)=O^{2-}$	Mn(3) + Mn(4) + Mn(5) + As(2)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}+\frac{5}{4}$	2.25
$O(9)=OH^-$	Mn(3) + Mn(4) + Mn(5)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}$	1.00
$O(10)=OH^-$	Mn(3) + Mn(4) + Mn(4)	$\frac{2}{6}+\frac{2}{6}+\frac{2}{6}$	1.00
$O(11)=O^{2-}$	Mn(4) + Mn(5) + As(2)	$\frac{2}{6}+\frac{2}{6}+\frac{5}{4}$	1.92
$O(12)=H_2O$	Mn(5)	$\frac{2}{6}$	0.33

Crystal chemistry. Synadelphite has the composition $Mn^{2+}_9(OH)_9(H_2O)_2 \cdot (AsO_3)(AsO_4)_2$, and is the first example of a known structure displaying arsenic in two oxidation states. The occurrence of As^{3+} above the Mn–O trigonal triplet is quite unusual on grounds of strict electrostatic reasoning. Therefore, it is tempting to state that the entire cluster—the three Mn–O octahedra in a plane and the capping As^{3+}–O pyramid—will be a key structural feature in other possible basic manganese arsenite-arsenates, such as dixenite, armangite, hematolite and mcgovernite.

Why hasn't the As^{3+} state been detected in any of the seven reported analyses for the species? There is strong evidence that synadelphite—like allactite, native lead and pyrochroite with which it often occurs—has formed under strongly alkaline conditions (Boström, 1965). Disso-

TABLE 6. SYNADELPHITE, POLYHEDRAL INTERATOMIC DISTANCES[a]

Mn(1)	
1 Mn(1)—O(2)	2.16Å
1 Mn(1)—O(1)	2.17
2 Mn(1)—O(4)	2.27
2 Mn(1)—O(3)	2.30
average	2.24Å
1 O(4)—O(4m)	2.57[b]
2 O(2)—O(4)	2.86[c]
2 O(2)—O(3)	3.12
2 O(1)—O(3)	3.21
2 O(3)—O(4)	3.30
2 O(1)—O(4)	3.37
1 O(3)—O(3m)	3.64
	3.16

Mn(5)	
1 Mn(5)—O(9g)	2.08
1 Mn(5)—O(7i)	2.10
1 Mn(5)—O(11)	2.21
1 Mn(5)—O(5i)	2.22
1 Mn(5)—O(12)	2.28
1 Mn(5)—O(8i)	2.37
	2.21
1 O(5i)—O(7i)	2.88[c]
1 O(7i)—O(8i)	2.94[c]
1 O(8i)—O(9g)	2.99
1 O(11)—O(12)	3.05
1 O(5i)—O(9g)	3.05
1 O(12)—O(7i)	3.11
1 O(11)—O(9g)	3.13
1 O(11)—O(7i)	3.14
1 O(11)—O(8i)	3.17[c]
1 O(12)—O(5i)	3.23
1 O(5i)—O(8i)	3.39
1 O(12)—O(9g)	3.43
	3.13

Mn(2)	
1 Mn(2)—O(7)	2.10
1 Mn(2)—O(6)	2.15
1 Mn(2)—O(2)	2.17
1 Mn(2)—O(4)	2.20
1 Mn(2)—O(5)	2.25
1 Mn(2)—O(1g)	2.33
	2.20
1 O(4)—O(1g)	2.63[b]
1 O(6)—O(7)	2.81[c]
1 O(2)—O(4)	2.86[c]
1 O(5)—O(7)	2.88[c]
1 O(6)—O(1g)	3.02
1 O(2)—O(1g)	3.05[c]
1 O(2)—O(5)	3.10
1 O(2)—O(7)	3.21
1 O(4)—O(6)	3.27
1 O(4)—O(5)	3.38
1 O(5)—O(6)	3.41
1 O(7)—O(1g)	3.56
	3.10

Mn(3)	
1 Mn(3)—O(10)	2.11
1 Mn(3)—O(6)	2.12
1 Mn(3)—O(9)	2.16
1 Mn(3)—O(7)	2.16
1 Mn(3)—O(4g)	2.20
1 Mn(3)—O(8)	2.39
	2.19
1 O(6)—O(7)	2.81[c]
1 O(9)—O(10)	2.86[c]
1 O(8)—O(10)	2.92[c]
1 O(7)—O(8)	2.94[c]
1 O(6)—O(4g)	3.07
1 O(7)—O(4g)	3.14
1 O(7)—O(10)	3.14
1 O(10)—O(4g)	3.20
1 O(9)—O(4g)	3.23
1 O(6)—O(9)	3.24
1 O(6)—O(8)	3.25
1 O(8)—O(9)	3.28
	3.09

As(1)	
1 As(1)—O(1)	1.76
2 As(1)—O(4g)	1.76
	1.76
1 O(4g)—O(4gm)	2.57[b]
2 O(1)—O(4g)	2.63[b]
	2.61

Mn(4)	
1 Mn(4)—O(10i)	2.11
1 Mn(4)—O(9)	2.11
1 Mn(4)—O(6g)	2.12
1 Mn(4)—O(10)	2.22
1 Mn(4)—O(11)	2.23
1 Mn(4)—O(8i)	2.28
	2.18
1 O(10)—O(10i)	2.79[c]
1 O(9)—O(10)	2.86[c]
1 O(8i)—O(10i)	2.92[c]
1 O(9)—O(6g)	2.94
1 O(8i)—O(6g)	3.08
1 O(10)—O(6g)	3.13
1 O(11)—O(10i)	3.14
1 O(11)—O(8i)	3.17[c]
1 O(9)—O(11)	3.21
1 O(9)—O(10i)	3.22
1 O(11)—O(6g)	3.22
1 O(10)—O(8i)	3.28
	3.08

As(2)	
1 As(2)—O(5)	1.67
1 As(2)—O(11gi)	1.68
1 As(2)—O(3)	1.70
1 As(2)—O(8i)	1.70
	1.69
1 O(3)—O(11gi)	2.72
1 O(5)—O(11gi)	2.72
1 O(8i)—O(11gi)	2.74
1 O(5)—O(8i)	2.75
1 O(3)—O(5)	2.78
1 O(3)—O(8i)	2.79
	2.75

[a] m = reflection operation, i = inversion operation, g = axial glide operation performed on coordinates in Table 3.

[b] Shared edges between As(1) trigonal pyramid and Mn octahedra.

[c] Shared edges between Mn octahedra.

(Errors: Me—O ± 0.02, O—O′ ± 0.03 Å, except Me—O(1), O(2) ± 0.03 and O(1), O(2)—O(1)′, O(2)′ ± 0.04 Å).

lution in strongly acidic solution, an early step in most wet chemical analyses of arsenates, may lead to rapid formation of As^{5+} by hydrolysis, through a reaction of the form $(As^{3+}O_3)^{3-} + H_2O \rightarrow (As^{5+}O_4)^{3-} + H_2\uparrow$. I have recognized a similar reaction mechanism, $2[Fe^{2+}(H_2O)]^{2+} \rightarrow 2[Fe^{3+}(OH)^-]^{2+} + H_2\uparrow$ for continuous oxidation of Fe^{2+}, without structural damage, in certain iron orthophosphate hydrate crystals.

TABLE 7. SYNADELPHITE CHEMICAL ANALYSES[a]

	1 Weight percent	k	2 Weight percent	k	3 Weight percent
SiO_2	0.63	0.0013	1.45	0.0030	—
As_2O_5	26.18	.0442	26.89	.0454	21.20
As_2O_3	—	—	—	—	9.12
Fe_2O_3	0.48	.0015	0.86	.0026	—
Al_2O_3	—	—	1.41	.0027	—
MnO	52.27	.0998	53.10	.1014	58.89
CaO	1.25	.0028	1.55	.0035	—
MgO	5.89	.0118	4.62	.0092	—
PbO	3.24	.0044	—	—	—
K_2O	0.70	.0013	0.79	.0015	—
Na_2O	0.59	.0011	0.62	.0011	—
H_2O	8.74	.0309	8.52	.0302	10.79
	99.97	0.1991	99.81	0.2006	100.00

[a] Specific refractive energies (k) computed from Larsen and Berman (1934).

1. Gonyer analysis in Hurlbut (1937). Red outer shell of crystals (="plumbo-synadelphite"). Using $\rho=3.79$ in Hurlbut, $\langle n\rangle$ calc.$=1.755$. $\langle n\rangle$ obs$=$ 1.870 averaging the refractive indices of Hurlbut.

2. Gonyer analysis in Hurlbut (1937). Colorless interior of crystals (=synadelphite). Using $\rho=3.57$ in Hurlbut, $\langle n\rangle$ calc.$=1.718$. $\langle n\rangle$ obs$=1.754$ averaging the refractive indices of Hurlbut.

3. For $Mn^{2+}_9(OH)_9(H_2O)_2(AsO_3)(AsO_4)_2$. The computed density for this formula is $\rho=3.59$ gm/cm^3, in good agreement with Hurlbut's observed density on the colorless interiors. The slightly higher computed density for the ideal formula probably reflects the presence of some magnesium in the natural material.

Since synadelphite on structural grounds has mixed valence states of arsenic, not detected in the chemical analyses, the accepted compositions of many other as yet unknown arsenite and arsenate structures must be thrown into question.

It now remains to explain the peculiar zoning and contradictory chemical and optical properties observed for synadelphites. Moore (1967b) has already stated that synadelphites with anomalously high indices of refraction are probably oxidized varieties. This is substantiated by the data in Table 1. The blurred reflections on rotation and Weissenberg photographs yield a substantially smaller cell than that of synadelphite. The cell volume difference in this study is about -5 percent. This does not support Gonyer's analysis in Hurlbut (1937) for "plumbosynadelphite", which should theoretically have a slightly larger cell volume. Table 7 presents Gonyer's analyses of synadelphite and its "plumbosynadelphite" coating as published in Hurlbut. Gladstone-Dale calculations based on these two analyses using the specific refractive energies of Larsen and Berman (1934) and the specific gravities of Hurlbut further substantiate the conclusion that the analysis for "plumbosynadelphite" must be incorrect and that some of the cations must be in higher oxidation states. It is concluded that the high density and mean indices of refraction of "plumbosynadelphite" and the dark red color of synadelphites are in fact contributed to a large degree by partially oxidized isostructural material. Since the crystal structure is based on close-packed oxygen atoms, it is difficult to imagine how a large cation like Pb^{2+}, even in small amounts, can be incorporated into the structure. More likely is the presence of a thin film of some other phase, such as PbO, contributing to the presence of PbO in the red outer shell and in part to the higher density of this material. Indeed, the deep ruby-red crystals from Nordmark also yield single-crystal photographs showing weak blurred reflections at higher Bragg angles.

There are no symmetry restrictions placed on the manganese atoms which would militate against tetragonal Jahn-Teller distortion resulting from the presence of the Mn^{3+} cation in oxidized material. In fact, the non-uniform cell contraction for the blurred reflections in Table 1 suggests that Jahn-Teller distortion occurs in the outer dark red zone of the crystal and that oxidation involves $Mn^{2+} \rightarrow Mn^{3+}$. Oxidation of As^{3+} is unlikely since three-coordinated As^{5+} would be highly unstable, unless oxygen atoms are being added to the voids in the close-packed system.

It must also be concluded that existing wet chemical analyses for most mixed-valence arsenic compounds, arsenites in particular, are not necessarily correct as they are presently interpreted. The ideal weight percentage of water for synadelphite in Table 7 is 10.79 percent, but existing analyses consistently show lower water content, around 8.7 percent. It is believed that a water determination involving Penfield tube methods without a catalytic hydrogen combustion system will lead to low results in water content, arising from the reaction $2(OH)^- + 2As^{3+} \rightarrow 2(As^{5+}O)^{3+} + H_2\uparrow$. Indeed, computing water content assuming $As^{3+} \rightarrow As^{5+} - 2H^+$ leads to 9.1 percent water, close to the values reported in the literature for synadelphite.

CONCLUDING REMARKS

The crystal structure of synadelphite opens up a new avenue of research inasmuch as the basic arsenites of manganese must also be considered. It is clear that the "homologous series" of basic manganese arsenates must be extended to include the arsenites as well. More interesting is the prevalence of dense-packed oxygen atoms among the basic manganese arsenate structures investigated so far and, with eventual solution of the atomic arrangements of arsenoclasite, armangite and dixenite now in progress, it is hoped that a unifying principle will evolve.

Most important, however, is the sobering fact that Nature is still one step ahead of us insofar as underlying crystal-chemical principles are concerned, and that synadelphite is yet another example where carefully performed classical wet chemical analyses had to be called into question.

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