Hureaulite, Mn$_{3}^{2+}$ (H$_2$O)$_n$[PO$_4$(OH)$_2$][PO$_4$)$_2$: Its Atomic Arrangement

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Abstract

Hureaulite, Mn$_{3}^{2+}$ (H$_2$O)$_n$[PO$_4$(OH)$_2$][PO$_4$)$_2$, a 17.594(10), b 9.086(5), c 9.404(5), $\beta$ 96.67(8)$^\circ$, Z = 4, space group C2/c, is one of the more persistent low temperature transition metal phosphate hydrates derived from hydrothermal attack of triphylite-lithiophilite. The structure was solved by Patterson and difference synthesis and least-squares refinement converged to $R_{w} = 0.058$ for 3500 reflections.

The structure is based on an octahedral edge-sharing pentamer of point symmetry 2 which has composition Mn$_5$O$_{12}$. It further links at six corners to produce an open octahedral framework of composition Mn$_9$O$_{24}$, where $\vartheta$ = 4 water molecules + 14 oxygens associated with the [PO$_4$]$^2$ tetrahedra. One tetrahedron, [PO$_4$(OH)$_2$], possesses a free hydroxyl group situated in a pocket in the structure. This pocket may spatially accommodate an intermediate-sized cation, extending interest to the series Mn$_{3}^{2+}$ (H$_2$O)$_n$[PO$_4$(OH)$_2$][PO$_4$]$^2$ and may explain the excess of larger cations in some analyses. Me-O averages are Mn(1)-O 2.19, Mn(2)-O 2.16, Mn(3)-O 2.2r, P(1)-O 1.54 and P(2)-O 1.54 Å.

Hureaulite characteristically occurs very late in the secondary phosphate paragenetic sequence. Since nearly all iron is oxidized to the Fe$^{3+}$ state before its crystallization, most natural hureaulites are Mn-rich compounds although extensive (Mn,Fe) solution is known for synthetic material.

Introduction

Hureaulite is one of the more persistent and widespread phases of the aquated first transition series phosphates associated with hydrothermally attacked triphylite-lithiophilite crystals in granite pegmatites. Interest is added to the species as a result of numerous reports on its synthesis and the recent discovery of the isotype sainfeldite, Ca$_5$(H$_2$O)$_4$ [AsO$_4$(OH)$_2$]$_2$ [AsO$_4$]$_2$ (Pierrot, 1964). Sainfeldite crystallized from arsenate-bearing solutions derived from mine waters acting upon arsenides and subsequently reacting with carbonates associated with late stage fissures. The sainfeldite clearly is a post-mine product and formed close to room temperature.

To understand the labyrinthine world of aquated transition metal phosphates, three-dimensional crystal structure analysis is necessary. The underlying goal in these studies is to establish the nature of the polyhedral clustering of the transition metal octahedra and the role of water and hydroxyl groups in these structures. Only in this manner can an unambiguous structural classification evolve and a link be established between the clusters in the crystal and those which existed in the solution from which the crystals grew.

Experimental

A superior single crystal of hureaulite, slightly elongate prismatic in shape, averaging 0.1 mm in thickness and 0.2 mm in length, was selected from a personally collected sample from the White Elephant pegmatite, between Custer and Pringle, South Dakota. The crystal was mounted parallel to the $c$-axis and 4200 reflections were gathered on a Picker automated diffractometer utilizing graphite monochromatized MoK$_\alpha$ radiation ($\lambda = 0.7093$ Å). The very small mosaic spread ($\pm$0.18$^\circ$) and least-squares refinement of 12 reference reflections guaranteed high quality data. Cell parameters resulting from the refinement appear in Table 1. Twenty second background counting times were taken at each side of the reflection, with a scan rate of 1.0$^\circ$/minute and half-angle scans of 1.8$^\circ$. Shells of reflections were gathered to maximum 2$\theta = 75^\circ$.

The data were processed by conventional computational procedures to obtain a table of $|F_{o}|$ and $|F_{c}|$. No absorption correction was applied on account of the favorable size and shape of the crystal ($\mu$ = 48.6 cm$^{-1}$); omega-scans about selected reflections revealed that such a correction would be minimal. Remaining were 3500 symmetry independent reflections including the averaged symmetry equivalent data.

Solution of the Structure

The hureaulite heavy atoms were located by three-dimensional Patterson synthesis. Included were three non-equivalent manganese and two non-equivalent phosphorus atoms. Routine inspection of the Pat-
**Refinement**

Refinement of the atomic coordinates and isotropic thermal vibration parameters proceeded without difficulty, using a local version of the ORFLS program for IBM 7094 computers by Busing, Martin and Levy (1962). Scattering curves for Mn, P, and O were obtained from the tabulations of MacGillavry and Rieck (1962). Final full-matrix atomic parameter and isotropic thermal vibration parameter refinement converged to \( R(hkl) = 0.058 \) for all 3500 reflections.

Final atomic coordinate parameters and isotropic thermal vibration parameters are given in Table 2 and a list of \(|F_{\text{obs}}|-|F_{\text{calc}}|\) appears in Table 3.

**Geometry and Topology of the Hureaulite Structure**

Condensation of the octahedral modules. The underlying feature of the rather complicated hureaulite structure is an octahedral edge-sharing pentamer. Such a pentamer belongs to the homologous series \( M_5 \Phi_{5r+2} \) where \( M \) = octahedral core and \( \Phi \) = octahedral vertex of which there are \( r \) cores and \( 4r + 2 \) vertices. This homologous series is identical to the connected tree of edge-sharing hexagons without loops or circuits and, in hureaulite, has the composition \( M_5 \Phi_{22} \). As idealized in Figure 1, the pentamer has point symmetry 2. Individual pentamers are further condensed to symmetry equivalent pentamers via corner sharing through the \( O(5) \) and \( C(10) \) atoms, and Figure 1 reveals that four \( O(5) \) and two \( O(10) \) atoms are associated with each pentamer. This fusion of pentamers results in a very loose and open octahedral framework of formal composition \( M_5 \Phi_{18} \), where

\[
R(hkl) = \frac{\sum|F_{\text{obs}}| - |F_{\text{calc}}|}{\sum|F_{\text{obs}}|} = 0.41.
\]

All ten oxygen atoms were located by subsequent difference synthesis.

**Table 1. Hureaulite. Crystal Cell Contents**

| \( a \) (\( \AA \)) | 17.594(10) |
| \( b \) (\( \AA \)) | 9.086 (5) |
| \( c \) (\( \AA \)) | 9.404 (5) |
| \( \beta \) | 96.67 (8)° |
| Space group | \( \text{C}22_1/\text{C} \) |
| formula | \( (\text{Mn}_0.74 \text{Fe}_{0.26})_5 \text{H}_4 \text{O}_{24} [\text{PO}_4(\text{OH})]_2 [\text{PO}_4]_2 \) |
| Specific gravity | 3.17 |
| Density (calc.) \( \text{gm/cm}^3 \) | 3.24 |

1 Sample from White Elephant pegmatite, Custer, South Dakota. Octahedral cations determined from ARL electron probe analysis. The specific gravity was obtained with a Beman microbalance.

2 To obtain a copy of Table 3, order NAPS Document Number 2024 from Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N.Y. 10017. Please remit in advance $1.50 for microfiche or $5.00 for photocopies. Please check the latest issue of this journal for the current address and prices.
$\theta_{ls} = 4O_H + 14O_P$, $O_H$ being water molecules and $O_P$ oxygen atoms associated with the $(PO_4)^{3-}$ tetrahedra. All water molecules in hureaulite are bonded to the transition metals, so behave as ligand groups. Since there are no "zeolitic" water molecules in the structure, the formula should be written $Mn_5^2+(H_2O)_4[PO_3(OH)]_4[PO_4]_b$. One oxygen atom associated with the $P(1)$ atom is not bonded to any transition metal and remains an $(OH)^{-}$ group in an open pocket in the structure and participates in hydrogen bonding. Thus, hureaulite is an acid crystal. Of the oxygen atoms associated with $P(1)$, $O(3)$ and $O(4)$ bond to two, $O(1)$ to one, and $O(2)$ to no transition metals. For $P(2)$, $O(5)$, $O(7)$, and $O(8)$ bond to two and $O(6)$ to one transition metal. Figure 2 reveals the rather elegant structure down the $z^*$ direction.

The phosphate tetrahedra further knit the octahedral pentamers together by bridging to symmetry equivalent pentamers generated by the $c$-axial glide operation and the inversion centers at $1/4$, $3/4$, 0; etc. But no $\cdots$ O-P-O-M $\cdots$ bonds cross the $a$-axis at $x = 0$, $1/2$; this promotes the good {100} cleavage observed for hureaulite.

The acid pocket. The $O(2) = (OH)^{-}$ groups point into an open pocket in the structure whose center is on the 2-fold rotor at $1/2$, $y$, $3/4$; etc., where $y \sim 0$. Two geometrically plausible hydrogen bonds can be described, as revealed in Figure 3. The bonds $O(9)-H \cdots O(6)^{\cdots} 2.703$ Å and $O(2)-H \cdots O(9)^{\cdots} 2.714$ Å occur within the pocket. But $O(2)$ does not appear to receive any bonds, since the second nearest distance is $O(9)-H \cdots O(2)^{\cdots} 3.330$ Å. Accordingly, $O(2)$ is interpreted as an acid portion of the structure, with the $P(1)$ tetrahedral group written as $[PO_3(OH)]^{3-}$.

A curious and potentially important feature of the acid pocket is its spatial properties. From our Fourier syntheses, we concluded that the site is empty, at least in the crystal we studied. In addition, a probe analysis showed only Fe and Mn were present as large cations and these totalled to 4.96 in the formula unit. Defining its approximate center as the empty position $X$ in Figure 2, there exist six bonds occurring pairwise to $O(2)$, $O(6)$ and $O(9)$ with a polyhedral shape resembling a distorted octahedron. These $X-O$ distances include $X-O(9)$ 1.56, $X-O(2)$ 2.55 and $X-O(6)$ 2.71 Å. $O(9)$ is a terminal water molecule, bonded to Mn(2), the terminus pointing into the pocket. Allowing some flexural freedom for $O(9)$ and some "sliding" of $X$ along the two-fold rotor, it is not difficult to conceive partial to complete replacement of $X$ by intermediate-sized cations, such as Li$^+$, Na$^+$, Ca$^{2+}$, etc., neutralizing the acid character of the crystal. This argument is advanced further to explain two analyses where an excess of larger cations is reported.

![Fig. 1. Idealizations of the octahedral pentamer in hureaulite. a. Down the $z^*$-direction, showing the 2-fold rotor and the six points of corner-fusion to other symmetry equivalent pentamers. b. Down the $y^*$ direction showing the 2-fold rotor. Unshaded octahedra are all above (or all below) the plane of the ruled octahedron.](image)

![Fig. 2. The hureaulite structure down the $z^*$-direction. Remaining symmetry equivalent polyhedra in the cell are generated by the $c$-glide operation. Points of fusion of the pentamers are drawn as black dots. The MnO$_6$ octahedra are stippled and the $(PO_4)^{3-}$ tetrahedra appear as P-O spokes. The X-O bonds are dashed in.](image)

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Hydrogen bonds. The O(9) and O(10) water molecules are donors of hydrogen bonds. Probable contributions by O(10) are O(10)-H···O(7)' 2.78 and O(10)-H···O(1) 2.65 Å with an angle O(7)′- O(10)-O(1) 117.9°. O(9) is more difficult to assess. The geometrically most compatible configuration is O(9)-H···O(6)'' 2.70 and O(9)-H··· O(1)'' 3.50 Å with an angle O(6)''-O(9)-O(1)'' 92.6°. It may be argued that O(2) receives as well as donates a bond from O(9), but the angle O(6)''- O(9)-O(2) 140.3° is way out of range, even for a distorted tetrahedral angle.

It appears that the most likely acceptors of hydrogen bonds would be O(1) and O(6), further substantiated by the electrostatic valence balance calculations in Table 4 and the polyhedral interatomic distances in Table 5. Disregarding the contributions by hydrogen bonds, both O(1) and O(6) are severely undersaturated with respect to coordinating cations, with Δ2 = −0.42. But the Me-O(1) and Me-O(6) distances are not among the shortest for their polyhedra, so their degree of undersaturation is probably relieved by the hydrogen bond contributions.

Polyhedral distances. The Me-O averages are Mn(1)-O 2.19, Mn(2)-O 2.16, Mn(3)-O 2.21, P(1)-O 1.54 and P(2)-O 1.54 Å, which compare favorably with the Mn-O 2.22 and P-O 1.57 Å averages based on the tables of Shannon and Prewitt (1969) and the numerous recently refined manganese phosphate structures. In addition, Table 5 reveals that shared octahedral edges are among the shortest individual polyhedral distances, about 10 percent shorter than the polyhedral edge averages.
with ratios of 1.25 and 1.50 respectively. This peculiar series is possible because the acid pocket in the structure at 1/2, ~0, 1/4 of equipoint rank number 4 is dimensionally suitable for intermediate-sized cations like Na⁺, Li⁺, Ca²⁺, etc. Thus, Volborth suggested the composition Ca₂Mn₂(PO₄)₄·4H₂O for his compound which is, in effect, a neutral salt. To confirm the existence of a neutral salt for hureaulite, a most careful analysis of cations and water content or a difference synthesis on the structure of Volborth's material would be necessary.

Paragenetically, hureaulites are either products of hydrothermal attack on primary phosphates, particularly the triphylite-lithiophilite series, or the reaction products of Mn-rich phosphatic solutions during the late hydrothermal stage which were independent of the existence of some parent phase. Of interest is the synthesis of hureaulite-type compounds by Klements et al. (1970). By hydrolysis of metal chloride and sodium dihydrogen phosphate solutions at intermediate pH, they were able to synthesize mixed crystals of Mn²⁺, Fe²⁺ (Co²⁺, Zn²⁺, Cd²⁺, and Cu²⁺) hureaulites. Solid solution of Fe²⁺ in Mn²⁺ appears limited with maximum reported 35 percent replacement, which is the upper limit reported in the analysis of hureaulite from Hureaux. But most natural hureaulites occur in assemblages where the mineral is clearly contemporary to or postdates the appearance of the basic ferric phosphates such as strengite, rockbridgeite, etc., and are consequently low in Fe²⁺ content compared with the triphylite parent phase. Where lithiophilite is the parent phase, hureaulite forms directly as druses upon the parent without the appearance of the ferric compounds.

Table 5. Hureaulite: Polychedral Interatomic Distances

<table>
<thead>
<tr>
<th>Mn(1) octahedron</th>
<th>Mn(2) octahedron</th>
<th>Mn(3) octahedron</th>
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<tr>
<td>H2O(+) 3.20</td>
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<td>H2O(+) 3.20</td>
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<tr>
<td>H2O(+) 3.05</td>
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<td>H2O(+) 3.00</td>
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Table 6. Hureaulite: Analyses with Excess Large Cations

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<tr>
<th>Na₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>H₂O(*)</th>
<th>H₂O(+)</th>
<th>P</th>
<th>Cations (F=16)</th>
<th>Cations in cell</th>
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</thead>
<tbody>
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<td>0.0</td>
<td>1.0</td>
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<td>0.0</td>
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The primed superscripts refer to the following transformations performed on the parameters in Table 2: 1/2 -1/2 -1/2, 0, 1/4, 1/4, 1/4. Estimated standard errors: 0.003 H₂O(+) for Fe₂O₃ < 0.75.

*Oxide shared edges.

Fletcher and Palermo No. 1 pegmatites, N. Groton, New Hampshire, and from a pegmatite at Coosa Co., Alabama (P.B. Leavens, pers. comm.).

Of considerable interest are the analyses by Volborth (1954) on hureaulite from Viitaniemi, Eräjärvi, central Finland, and the analysis reported by Fisher (1964) on the lithian hureaulite from the Black Hills. Both analyses suffer faults: Volborth's material was contaminated with minor morinite (but he reports only a trace of Al₂O₃) and the water determination was by difference, and Fisher's analyses are crude. Table 6 presents these analyses and computations of cations based on 16 tetrahedra (= P + Be) in the former and the crystal cell in the latter analysis. The ratios Σ large cations: ΣT cations are 1.46 and 1.47 respectively, and extend our interest to the series

\[ \text{M}_5^2+(\text{H}_2\text{O})_4\text{[PO}_4\text{(OH)}_4\text{[PO}_4\text{]_2} \]

and \[ X^2+M_5^2+(\text{H}_2\text{O})_4\text{[PO}_4\text{(OH)}_4\text{[PO}_4\text{]_2} \]

Table 5. Hureaulite: Polychedral Interatomic Distances

| Polychedral Interatomic Distances
<table>
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<tbody>
<tr>
<td>H₂O(+) 3.20</td>
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<tr>
<td>H₂O(+) 3.05</td>
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</tbody>
</table>

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<table>
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<tr>
<th>Weight percent Cations (F=16)</th>
<th>Weight percent Cations in cell</th>
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<tbody>
<tr>
<td>Na₂O 0.0</td>
<td>2.92</td>
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<tr>
<td>MgO 0.0</td>
<td>8.58</td>
</tr>
<tr>
<td>CaO 0.0</td>
<td>38.85</td>
</tr>
<tr>
<td>FeO 0.0</td>
<td>1.44</td>
</tr>
<tr>
<td>MnO 0.0</td>
<td>1.35</td>
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<tr>
<td>P₂O₅ 0.0</td>
<td>36.35</td>
</tr>
<tr>
<td>H₂O(*) 0.0</td>
<td>10.00</td>
</tr>
<tr>
<td>H₂O(+) 0.0</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Fisher (1954), computed using his R, = 17.64, b, = 9.13, c, = 9.49, which is dimensionally suitable for intermediate-sized cations like Na⁺, Li⁺, Ca²⁺, etc. Thus, Volborth suggested the composition Ca₂Mn₂(PO₄)₄·4H₂O for his compound which is, in effect, a neutral salt. To confirm the existence of a neutral salt for hureaulite, a most careful analysis of cations and water content or a difference synthesis on the structure of Volborth's material would be necessary.
This is the paragenesis typical for Branchville, Connecticut, and Custer Mountain, South Dakota, pegmatites. Strunz (1954) observed that hureaulite from Hagendorf Süd has an Fe:Mn ratio of 1:3 whereas that of the parent triphylite was nearly 3:1. Consistent with the synthetic studies on hureaulite, the species evidently appears at the final stages after oxidation of iron to the ferric state and after precipitation of such species as rockbridgeite, leucophosphate and strengite. For the hureaulite in this study (Table 1), the Fe:Mn ratio is based on electron probe analysis and the White Elephant parent phase was unquestionably an iron-rich triphylite. It is concluded, as it was by Strunz, that the manganese content of the solution is enriched as the ferric iron is removed by precipitation at higher temperature. What ferrous iron remains enters into solution at the final stage in the predominantly manganese-rich hureaulite and is limited to a Fe:Mn ~ 1:3 ratio as observed in the synthetic studies.

Acknowledgments

Dr. Jo Ann Molin-Case assisted in the collection of three-dimensional intensity data and Mr. G. R. Zechmann performed the electron probe analysis for the large cations. We appreciate the continued interest of Mr. W. L. Roberts and Dr. D. H. Garske, whose extensive experience and guidance in Black Hills pegmatite localities have provided us with exceptional specimens.

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References


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