

coordination. The other half, as well as the Sb in nearly all antimony sulfosalts, exhibit five-coordination (square-pyramidal). A fourth and fifth orthogonal bond (and, indeed, a sixth for M(1), which has nearly octahedral coordination) may be found among the more distant neighbors in each metal atom polyhedron, Fig. 1. These bonds, however, are much larger than those usually encountered in  $SbS_5$  groups, and are comparable to van der Waals separations (3.85 Å for As-S, and 4.05 for Sb-S). All S atoms have a polar twofold coordination similar to that found in orpiment and the ring molecules of elemental sulfur (Abrahams, 1955; Donohue, Caron & Goldish, 1961).

Bond angles and lengths are summarized in Table 4. The metal-sulfur bond lengths are, as expected, found to be intermediate between the average bridging As-S (2.31 Å) and Sb-S (2.54 Å) distances found in sulfosalts (Takéuchi & Sadanaga, 1969), and are consistent with the occupancy of the sites, Fig. 2. The shortest bond length observed, M(2)-S(3), involves the metal site which has the highest As content. It is interesting to speculate whether the disorder is a consequence of the crystals having been a synthetic product. Naturally occurring crystals of getchellite, grown over extended periods of time, might well be ordered.

The structure of getchellite consists of sheets equal to  $d_{001}$  in thickness (9.13 Å), which are parallel to (001), the cleavage and twin plane of the structure. Within each layer, the structure is an open and meandering glass-like network. The simplest structural group is a puckered 8-membered ring of symmetry  $\bar{1}$ , parallel to (010). One such ring is shown in Fig. 3(a). These rings are not linked to any neighboring rings in the same (010) plane. Each ring is instead linked to two others above and two below, each related to it by the  $a$  glide [Fig. 3(b)].

The structure of getchellite appears to be unrelated to that of either stibnite or orpiment. While orpiment is also a sheet structure, it consists of 6-membered rings parallel to the plane of the sheets, and linked to form an essentially two-dimensional layer. The 8-membered rings in getchellite are instead normal to the plane of the layers and stacked above one another.

The writers are grateful to Dr B. G. Weissberg, who kindly provided the crystals employed in this study, and to Professor J. Zemann for helpful discussions. This work was supported by Contract AT(30-1)-3773 with the U.S. Atomic Energy Commission.

#### References

- ABRAHAMS, S. C. (1955). *Acta Cryst.* **8**, 661-671.  
 BAYLISS, P. & NOWACKI, W. (1972). *Z. Kristallogr.* **135**, 308-315.  
 BURNHAM, C. W. (1962). *Carnegie Inst. Wash. Year Book*, **61**, 132-135.  
 BURNHAM, C. W. (1966). *Amer. Min.* **51**, 159-167.  
 DONOHUE, J., CARON, A. & GOLDISH, E. (1961). *J. Amer. Chem. Soc.* **83**, 3748-3751.  
 FINGER, L. W. (1969). *Carnegie Inst. Wash. Year Book*, **67**, 216-217.  
 FLEISCHER, E. B., DEWAR, R. B. K. & STONE, A. L. (1967). *Prog. and Abst. Winter Meeting Amer. Cryst. Assoc.*, 20. *International Tables for X-ray Crystallography* (1962). Vol. III, Table 3.3.1. Birmingham: Kynoch Press.  
 MORIMOTO, N. (1954). *Miner. J. Japan*, **1**, 160-169.  
 MULLEN, D. J. E. & NOWACKI, W. (1972). *Z. Kristallogr.* **136**, 48-65.  
 PREWITT, C. T. (1962). Ph.D. Thesis, Dept. of Geology and Geophysics, Mass. Inst. of Tech.  
 ŠČAVNIČAR, S. (1960). *Z. Kristallogr.* **114**, 85-97.  
 TAKÉUCHI, Y. & SADANAGA, R. (1969). *Z. Kristallogr.* **130**, 346-368.  
 WEISSBERG, B. G. (1965). *Amer. Min.* **50**, 1817-1826.

*Acta Cryst.* (1973). **B29**, 2541

## The Crystal Structure of Hureaulite, $Mn_5(HOPO_3)_2(PO_4)_2(H_2O)_4$

BY S. MENCHETTI AND C. SABELLI

*Centro di Studio per la Mineralogia e la Geochimica dei Sedimenti, Istituto di Mineralogia dell'Università di Firenze, Italy*

(Received 16 April 1973; accepted 12 June 1973)

Hureaulite is monoclinic  $C2/c$  with  $Z=4$  and cell dimensions  $a=17.66$  (2),  $b=9.123$  (2),  $c=9.498$  (2) Å and  $\beta=96.58$  (2)°. Three-dimensional data were collected with a Weissenberg camera (Cu  $K\alpha$  radiation). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares analysis to an  $R$  index of 0.053 for 1116 observed reflexions. The structure consists of  $PO_4$  and  $HOPO_3$  tetrahedra, linked together by a hydrogen bond, and by groups of five edge-shared Mn octahedra. The hydrogen atom positions were determined from a difference synthesis. On the basis of the structure determination and according to the chemical analysis, the crystal-chemical formula for the specimen studied is  $(Mn_{4.34}, Fe_{0.55}, Mg_{0.07}, Ca_{0.04})(HOPO_3)_2(PO_4)_2(H_2O)_4$ .

#### Introduction

Hureaulite was first described by Alluaud (1826). The main physical and chemical properties are given in

*Dana's System of Mineralogy* (Palache, Berman & Frondel, 1951). The structure determination of hureaulite was undertaken in order to define the crystal-chemical formula and the structural role played by the

Table 1. *Chemical analyses of hureaulite*

	1	2	3	4	5	6	7
Li <sub>2</sub> O						2.1	—
CaO				2.02	1.33	not > 0.7	0.34
MgO				0.26	0.40	not > 1.7	0.36
FeO	4.56	7.86	11.10	10.57	11.34	6.0	5.48
MnO	42.29	41.67	32.85	36.01	36.16	37.0	42.75
P <sub>2</sub> O <sub>5</sub>	38.36	38.00	38.00	38.83	38.91	43.0	n.d.
H <sub>2</sub> O	12.20	11.98	18.00	12.42	12.37	n.d.	n.d.
Insol.	2.70	0.38					

References: 1. Branchville, Connecticut. Average of two (Wells, 1890).\* 2. La Vilate, France (Damour, 1858).\* 3. Huréaux, France (Dufrenoy, 1829).\* 4. Baldaufite, Hagendorf, Germany (Strunz, 1954). 5. Wenzelite, Hagendorf, Germany (Strunz, 1954). 6. Black Hills (Fischer, 1964). 7. Hagendorf, Germany (new).

\* In Palache, Berman & Frondel (1951).

hydrogen atoms. According to the results of the present work, the crystal-chemical formula of this mineral should be written  $Mn_5(HOPO_3)_2(PO_4)_2(H_2O)_4$  with the ligand waters specified in parentheses as suggested by Moore (1965).

### Experimental

The crystals used in this work came from Hagendorf, Bavaria, Germany. According to *Dana's System of Mineralogy*, Fe substitutes for Mn up to at least Fe:Mn = 1:3. In wenzelite and in baldaufite, both identical with hureaulite, there are also small amounts of calcium and magnesium (Strunz, 1954); a lithian hureaulite is known also (Fisher, 1964). In order to achieve the best results in the structure determination, a partial chemical analysis of the Hagendorf sample was performed by means of the atomic absorption technique.\* The results for Mn, Fe, Ca, Mg and Li are given in Table 1; no allowance was made for P<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O determinations, both considered unnecessary for the present work. The cation atomic ratios are Mn:Fe:Mg:Ca = 4.34:0.55:0.07:0.04 (cation sum = 5). On the basis of the above ratios the atomic scattering factors, the absorption coefficient, the anomalous dispersion factor and the calculated density were computed.

The unit-cell dimensions and standard errors of hureaulite were obtained from Ag-calibrated basal Weissenberg photographs, taken with the crystals rotating about [001] and [110] using Cu K $\alpha$  radiation, and refined by the least-squares method applied to 60 high-angle reflexions. The values thus obtained (see Table 2) are in good agreement with those given by Fisher (1964). The space groups *C2/c* or *Cc*, found by this author from the systematic absences, were confirmed on examination of Weissenberg pictures *hk0*, *hk1* and *hk2*. The space group *C2/c* was chosen on the basis of the morphological data (Palache, Berman & Frondel, 1951); the refinement of the structure gave no evidence in favour of the acentric space group. The density was measured by immersion in a mixture of methylene iodide and bromoform.

\* Analyst: Dr A. Bencini of this Institute.

Table 2. *Crystallographic data*

Chemical formula (Mn<sub>4.34</sub>, Fe<sub>0.55</sub>, Mg<sub>0.07</sub>, Ca<sub>0.04</sub>)  
(HOPO<sub>3</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>.  
Monoclinic, space group *C2/c*,  
 $a = 17.66 \pm 0.02$ ,  $b = 9.123 \pm 0.002$ ,  $c = 9.498 \pm 0.002$  Å,  
 $\beta = 96.58^\circ \pm 0.02^\circ$   $V = 1520.1$  Å<sup>3</sup>,  
 $D_m = 3.177$  g cm<sup>-3</sup>  $Z = 4$   $D_x = 3.173$  g cm<sup>-3</sup>.  
Absorption coefficient for X-ray (Cu K $\alpha$ ):  $\mu = 374.8$  cm<sup>-1</sup>.

For intensity-data collection a well-formed pink crystal was ground to a spherical shape (radius 0.013 cm). Layers *hk0* to *hk7* were recorded with the equi-inclination Weissenberg method and multiple-film exposures. 1246 independent reflexions were collected, 130 of which were too weak to be measured. The intensities of the integrated spots were photometrically evaluated; Lorentz-polarization and absorption corrections ( $\mu/\rho$  values from Cromer & Liberman, 1970) were applied together with a correction for the  $\alpha_1$ - $\alpha_2$  splitting. A secondary extinction correction was applied to the calculated structure factors towards the end of the refinement (extinction coefficient  $8 \cdot 10^{-7}$ ). The atomic

Table 3. *Fractional atomic coordinates with e.s.d.'s*

	x	y	z
Mn(1)	0.0	0.89728 (21)	0.25
Mn(2)	0.18202 (8)	0.41135 (15)	0.31546 (18)
Mn(3)	0.17442 (8)	0.02769 (15)	0.36543 (18)
P(1)	0.0829 (1)	0.1790 (2)	0.0898 (3)
P(2)	0.3392 (1)	0.2392 (2)	0.3720 (3)
O(1)	0.0119 (3)	0.2843 (7)	0.0819 (8)
O(2)	0.0771 (3)	0.0668 (6)	0.2063 (8)
O(3)	0.1543 (3)	0.2706 (6)	0.1343 (7)
O(4)	0.4156 (3)	0.3919 (6)	0.0559 (7)
O(5)	0.1640 (3)	0.2359 (7)	0.4683 (8)
O(6)	0.2985 (3)	0.0968 (6)	0.3271 (7)
O(7)	0.2982 (3)	0.3651 (6)	0.2892 (7)
O(8)	0.4236 (3)	0.2345 (6)	0.3423 (7)
W(1)	0.2597 (3)	0.0808 (6)	0.0293 (7)
W(2)	0.4220 (4)	0.0118 (7)	0.1508 (8)
H(1)	0.475	0.225	0.470
H(2)	0.245	0.150	0.100
H(3)	0.205	0.351	0.012
H(4)	0.418	0.098	0.207
H(5)	0.035	0.468	0.353

scattering factors were obtained by interpolation of the values given by Cromer & Waber (1965); for hydrogen the values given by Stewart, Davidson & Simpson (1965) were used. Anomalous dispersion corrections for the heavy atom [ $\Delta f'$  and  $\Delta f''$  published by Cromer & Liberman (1970)] were taken into account in the structure-factor calculation.

### Structure determination and refinement

A three-dimensional Patterson synthesis was computed from the complete set of observed reflexions. In  $C2/c$  the general position is eightfold; thus the only indication from the cell content is that two Mn atoms are

likely to lie on general positions and the remaining one on a special position.\* The Patterson analysis unambiguously revealed the positions of three independent manganese and one phosphorus atom. At this stage the  $R$  index ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) was nearly 0.40. The subsequent Fourier synthesis revealed all the non-hydrogen atoms, although some peaks were poorly resolved.

The refinement of the structure (least-squares method with equal weight for all observed reflexions) was begun with isotropic and concluded with anisotropic tem-

\* Henceforth, for simplicity Mn denotes (Mn, Fe, Mg, Ca) and  $W$ , the water oxygen.

Table 4. Thermal parameters with e.s.d.'s

The  $\beta_i$  values ( $\times 10^5$  for Mn and  $\times 10^4$  for P and O atoms) are in the form  
 $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B_{eq}$
Mn(1)	103 (5)	251 (20)	348 (33)	0	62 (9)	0	1.09
Mn(2)	108 (4)	295 (15)	401 (24)	5 (6)	65 (7)	-7 (13)	1.22
Mn(3)	105 (4)	287 (14)	338 (24)	1 (6)	57 (7)	-18 (13)	1.13
P(1)	7 (1)	20 (2)	23 (4)	1 (1)	6 (1)	-5 (2)	0.75
P(2)	8 (1)	16 (2)	13 (4)	0 (1)	6 (1)	3 (2)	0.61
O(1)	12 (2)	50 (7)	45 (11)	12 (3)	-1 (3)	-8 (6)	1.62
O(2)	12 (2)	36 (7)	54 (10)	-5 (3)	5 (3)	8 (6)	1.53
O(3)	10 (2)	33 (6)	36 (10)	-8 (3)	8 (3)	-9 (6)	1.18
O(4)	10 (2)	47 (7)	36 (10)	2 (3)	0 (3)	-14 (6)	1.35
O(5)	18 (2)	26 (7)	43 (12)	-3 (3)	1 (3)	-7 (6)	1.57
O(6)	12 (2)	24 (7)	50 (10)	-6 (3)	10 (3)	-11 (6)	1.33
O(7)	13 (2)	28 (7)	53 (10)	-1 (3)	11 (3)	6 (6)	1.42
O(8)	10 (2)	37 (7)	43 (10)	0 (3)	10 (3)	3 (6)	1.29
W(1)	12 (2)	36 (7)	41 (10)	-2 (3)	7 (3)	0 (6)	1.34
W(2)	12 (2)	42 (8)	83 (12)	0 (3)	16 (3)	-7 (6)	1.86

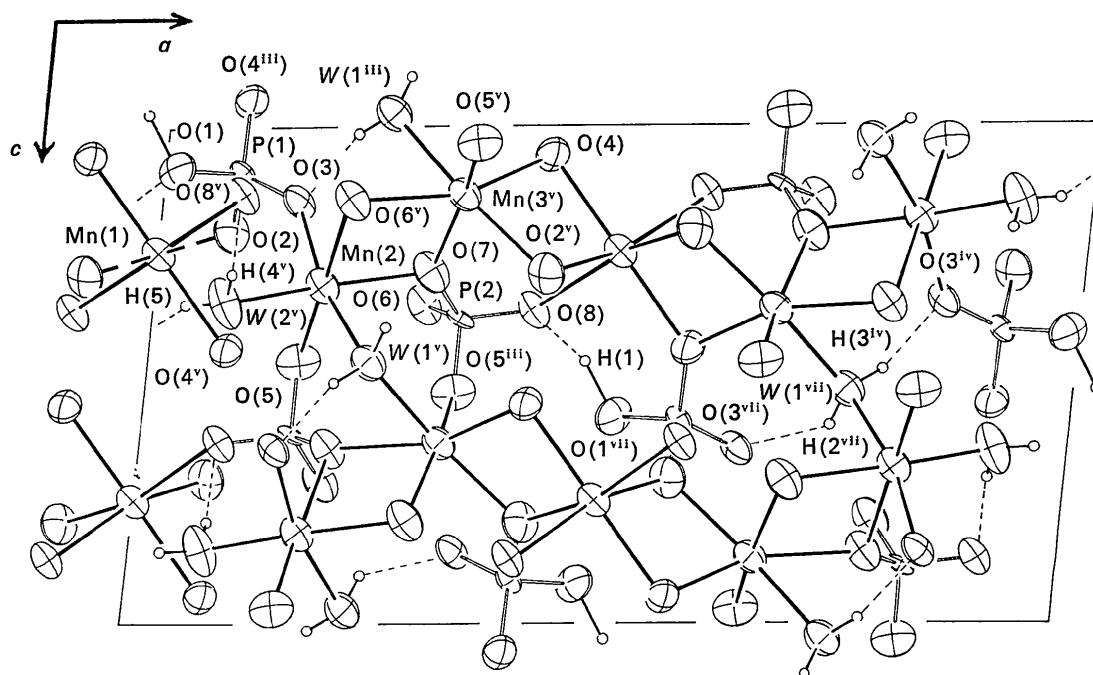


Fig. 1. A projection of the structure along the  $b$  axis.

perature factors. Towards the end of the refinement ( $R=0.07$ ) a difference Fourier synthesis was computed in order to locate the hydrogen atoms. The strongest positive peaks fitted well the expected positions of the five independent H atoms.

The Mn-O distances and thermal parameters showed no evidence of any cation position in which Fe preferably substitutes for Mn. Because of the unreliable variations of the H parameters in the least-squares refinement, coordinates from the difference Fourier

Table 5. Observed and calculated structure factors

The column headings are  $h, k, l, F_o, F_c, A$  and  $B$ . The asterisk marks the unobserved reflexions.

$h$	$k$	$l$	$F_o$	$F_c$	$A$	$B$
0	0	0	1000	1000	1000	1000
0	0	1	1000	1000	1000	1000
0	0	2	1000	1000	1000	1000
0	0	3	1000	1000	1000	1000
0	0	4	1000	1000	1000	1000
0	0	5	1000	1000	1000	1000
0	0	6	1000	1000	1000	1000
0	0	7	1000	1000	1000	1000
0	0	8	1000	1000	1000	1000
0	0	9	1000	1000	1000	1000
0	0	10	1000	1000	1000	1000
0	0	11	1000	1000	1000	1000
0	0	12	1000	1000	1000	1000
0	0	13	1000	1000	1000	1000
0	0	14	1000	1000	1000	1000
0	0	15	1000	1000	1000	1000
0	0	16	1000	1000	1000	1000
0	0	17	1000	1000	1000	1000
0	0	18	1000	1000	1000	1000
0	0	19	1000	1000	1000	1000
0	0	20	1000	1000	1000	1000
0	0	21	1000	1000	1000	1000
0	0	22	1000	1000	1000	1000
0	0	23	1000	1000	1000	1000
0	0	24	1000	1000	1000	1000
0	0	25	1000	1000	1000	1000
0	0	26	1000	1000	1000	1000
0	0	27	1000	1000	1000	1000
0	0	28	1000	1000	1000	1000
0	0	29	1000	1000	1000	1000
0	0	30	1000	1000	1000	1000
0	0	31	1000	1000	1000	1000
0	0	32	1000	1000	1000	1000
0	0	33	1000	1000	1000	1000
0	0	34	1000	1000	1000	1000
0	0	35	1000	1000	1000	1000
0	0	36	1000	1000	1000	1000
0	0	37	1000	1000	1000	1000
0	0	38	1000	1000	1000	1000
0	0	39	1000	1000	1000	1000
0	0	40	1000	1000	1000	1000
0	0	41	1000	1000	1000	1000
0	0	42	1000	1000	1000	1000
0	0	43	1000	1000	1000	1000
0	0	44	1000	1000	1000	1000
0	0	45	1000	1000	1000	1000
0	0	46	1000	1000	1000	1000
0	0	47	1000	1000	1000	1000
0	0	48	1000	1000	1000	1000
0	0	49	1000	1000	1000	1000
0	0	50	1000	1000	1000	1000
0	0	51	1000	1000	1000	1000
0	0	52	1000	1000	1000	1000
0	0	53	1000	1000	1000	1000
0	0	54	1000	1000	1000	1000
0	0	55	1000	1000	1000	1000
0	0	56	1000	1000	1000	1000
0	0	57	1000	1000	1000	1000
0	0	58	1000	1000	1000	1000
0	0	59	1000	1000	1000	1000
0	0	60	1000	1000	1000	1000
0	0	61	1000	1000	1000	1000
0	0	62	1000	1000	1000	1000
0	0	63	1000	1000	1000	1000
0	0	64	1000	1000	1000	1000
0	0	65	1000	1000	1000	1000
0	0	66	1000	1000	1000	1000
0	0	67	1000	1000	1000	1000
0	0	68	1000	1000	1000	1000
0	0	69	1000	1000	1000	1000
0	0	70	1000	1000	1000	1000
0	0	71	1000	1000	1000	1000
0	0	72	1000	1000	1000	1000
0	0	73	1000	1000	1000	1000
0	0	74	1000	1000	1000	1000
0	0	75	1000	1000	1000	1000
0	0	76	1000	1000	1000	1000
0	0	77	1000	1000	1000	1000
0	0	78	1000	1000	1000	1000
0	0	79	1000	1000	1000	1000
0	0	80	1000	1000	1000	1000
0	0	81	1000	1000	1000	1000
0	0	82	1000	1000	1000	1000
0	0	83	1000	1000	1000	1000
0	0	84	1000	1000	1000	1000
0	0	85	1000	1000	1000	1000
0	0	86	1000	1000	1000	1000
0	0	87	1000	1000	1000	1000
0	0	88	1000	1000	1000	1000
0	0	89	1000	1000	1000	1000
0	0	90	1000	1000	1000	1000
0	0	91	1000	1000	1000	1000
0	0	92	1000	1000	1000	1000
0	0	93	1000	1000	1000	1000
0	0	94	1000	1000	1000	1000
0	0	95	1000	1000	1000	1000
0	0	96	1000	1000	1000	1000
0	0	97	1000	1000	1000	1000
0	0	98	1000	1000	1000	1000
0	0	99	1000	1000	1000	1000
0	0	100	1000	1000	1000	1000

map were assumed, and thermal parameters were fixed at  $3.0 \text{ \AA}^2$ . The final  $R$  index, computed with all atoms for the observed reflexions, is 0.053; including the non-observed reflexions the same index is 0.059.

Final atomic coordinates and anisotropic, with equivalent isotropic, thermal parameters are given in Tables 3 and 4 respectively. Table 5 lists the observed and calculated structure factors.

Table 6. *Interatomic distances (Å) and angles (°) with e.s.d.'s*

Superscripts for symmetry-related atoms.			
None	$x$	$y$	$z$
i	$\frac{1}{2} + x$	$\frac{1}{2} + y$	$z$
ii	$1 - x$	$1 - y$	$1 - z$
iii	$\frac{1}{2} - x$	$\frac{1}{2} - y$	$1 - z$
iv	$1 - x$	$y$	$\frac{1}{2} - z$
v	$\frac{1}{2} - x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$
vi	$x$	$1 - y$	$\frac{1}{2} + z$
vii	$\frac{1}{2} + x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$

An asterisk denotes atoms of adjacent cells.

<b>Mn(1) octahedron</b>			
Mn(1)—O(4) <sup>i</sup> *	2.235 (7)	O(4) <sup>i</sup> *—Mn(1)—O(8 <sup>v</sup> )	92.1 (2)
Mn(1)—O(8 <sup>i</sup> )*	2.251 (6)	O(4) <sup>i</sup> *—Mn(1)—O(8 <sup>i</sup> )*	86.2 (2)
Mn(1)—O(2)*	2.133 (6)	O(4) <sup>i</sup> *—Mn(1)—O(2)*	103.6 (3)
		O(4 <sup>v</sup> )—Mn(1)—O(2)*	78.2 (2)
O(4 <sup>i</sup> )*—O(8 <sup>v</sup> )	3.231 (8)	O(8 <sup>i</sup> )*—Mn(1)—O(8 <sup>v</sup> )	97.4 (3)
O(4 <sup>i</sup> )*—O(8 <sup>i</sup> )*	3.066 (9)	O(8 <sup>v</sup> )—Mn(1)—O(2)*	88.7 (2)
O(4 <sup>i</sup> )*—O(2)*	3.434 (9)	O(2)*—Mn(1)—O(2 <sup>iv</sup> )*	87.1 (3)
O(4 <sup>v</sup> )—O(2)*	2.756 (10)	O(2)*—Mn(1)—O(8 <sup>i</sup> )*	168.2 (3)
O(8 <sup>i</sup> )*—O(8 <sup>v</sup> )	3.383 (12)	O(4 <sup>i</sup> )*—Mn(1)—O(4 <sup>v</sup> )	177.6 (3)
O(8 <sup>v</sup> )—O(2)*	3.066 (8)		
O(2)*—O(2 <sup>iv</sup> )*	2.938 (12)		
<b>Mn(2) octahedron</b>			
Mn(2)—O(3)	2.158 (7)	O(5)—Mn(2)—O(3)	93.2 (2)
Mn(2)—O(6 <sup>v</sup> )	2.218 (6)	O(5)—Mn(2)—O(7)	98.4 (2)
Mn(2)—O(5)	2.209 (7)	O(5)—Mn(2)— $W(1^v)$	98.9 (2)
Mn(2)—O(7)	2.136 (6)	O(5)—Mn(2)— $W(2^v)$	91.2 (2)
Mn(2)— $W(2^v)$	2.109 (6)	O(6 <sup>v</sup> )—Mn(2)—O(3)	90.2 (2)
Mn(2)— $W(1^v)$	2.297 (6)	O(6 <sup>v</sup> )—Mn(2)—O(7)	82.0 (2)
		O(6 <sup>v</sup> )—Mn(2)— $W(1^v)$	77.8 (2)
O(5)—O(3)	3.173 (10)	O(6 <sup>v</sup> )—Mn(2)— $W(2^v)$	87.7 (2)
O(5)—O(7)	3.290 (9)	O(3)—Mn(2)—O(7)	85.6 (2)
O(5)— $W(1^v)$	3.423 (8)	O(3)—Mn(2)— $W(2^v)$	104.9 (2)
O(5)— $W(2^v)$	3.087 (9)	$W(1^v)$ —Mn(2)— $W(2^v)$	86.8 (2)
O(6 <sup>v</sup> )—O(3)	3.101 (8)	$W(1^v)$ —Mn(2)—O(7)	80.9 (2)
O(6 <sup>v</sup> )—O(7)	2.858 (8)	O(5)—Mn(2)—O(6 <sup>v</sup> )	176.5 (2)
O(6 <sup>v</sup> )— $W(1^v)$	2.837 (10)	O(7)—Mn(2)— $W(2^v)$	165.4 (2)
O(6 <sup>v</sup> )— $W(2^v)$	3.000 (9)	$W(1^v)$ —Mn(2)—O(3)	163.0 (2)
O(3)—O(7)	2.917 (8)		
O(3)— $W(2^v)$	3.384 (9)		
$W(1^v)$ — $W(2^v)$	3.031 (9)		
$W(1^v)$ —O(7)	2.879 (9)		
<b>Mn(3) octahedron</b>			
Mn(3)—O(2)	2.183 (7)	O(5)—Mn(3)—O(6)	87.9 (2)
Mn(3)—O(7 <sup>v</sup> )*	2.181 (7)	O(5)—Mn(3)— $W(1^{vi})$ *	99.1 (2)
Mn(3)—O(5)	2.154 (6)	O(5)—Mn(3)—O(4 <sup>v</sup> )*	103.8 (2)
Mn(3)—O(6)	2.348 (6)	O(5)—Mn(3)—O(2)	93.9 (2)
Mn(3)—O(4 <sup>v</sup> )*	2.211 (6)	O(7 <sup>v</sup> )*—Mn(3)—O(6)	78.2 (2)
Mn(3)— $W(1^{vi})$ *	2.266 (6)	O(7 <sup>v</sup> )*—Mn(3)— $W(1^{vi})$ *	89.1 (2)
		O(7 <sup>v</sup> )*—Mn(3)—O(4 <sup>v</sup> )*	94.0 (2)
O(5)—O(6)	3.128 (8)	O(7 <sup>v</sup> )*—Mn(3)—O(2)	82.1 (2)
O(5)— $W(1^{vi})$ *	3.364 (8)	O(6)—Mn(3)— $W(1^{vi})$ *	70.5 (2)
O(5)—O(4 <sup>v</sup> )*	3.434 (8)	$W(1^{vi})$ *—Mn(3)—O(4 <sup>v</sup> )*	88.3 (2)
O(5)—O(2)	3.170 (10)	O(4 <sup>v</sup> )*—Mn(3)—O(2)	77.7 (2)
O(7 <sup>v</sup> )*—O(6)	2.858 (8)	O(2)—Mn(3)—O(6)	121.5 (2)
O(7 <sup>v</sup> )*— $W(1^{vi})$ *	3.120 (10)	O(5)—Mn(3)—O(7 <sup>v</sup> )*	160.5 (3)
O(7 <sup>v</sup> )*—O(4 <sup>v</sup> )*	3.213 (9)	$W(1^{vi})$ *—Mn(3)—O(2)	162.8 (2)
O(7 <sup>v</sup> )*—O(2)	2.867 (8)	O(4 <sup>v</sup> )*—Mn(3)—O(6)	157.2 (2)
O(6)— $W(1^{vi})$ *	2.662 (9)		
$W(1^{vi})$ *—O(4 <sup>v</sup> )*	3.117 (8)		
O(4 <sup>v</sup> )*—O(2)	2.756 (10)		
O(2)—O(6)	3.955 (8)		

Table 6 (cont.)

P(1) tetrahedron			
P(1)-O(1)	1.574 (6)	O(1)-P(1)-O(2)	109.1 (4)
P(1)-O(2)	1.519 (7)	O(1)-P(1)-O(3)	107.8 (3)
P(1)-O(3)	1.531 (6)	O(1)-P(1)-O(4 <sup>iii</sup> )*	108.2 (4)
P(1)-O(4 <sup>iii</sup> )*	1.531 (7)	O(2)-P(1)-O(3)	106.8 (4)
		O(2)-P(1)-O(4 <sup>iii</sup> )*	112.5 (4)
O(1)-O(2)	2.520 (9)	O(3)-P(1)-O(4 <sup>iii</sup> )*	112.4 (4)
O(1)-O(3)	2.510 (8)		
O(1)-O(4 <sup>iii</sup> )*	2.515 (9)		
O(2)-O(3)	2.448 (8)		
O(2)-O(4 <sup>iii</sup> )*	2.536 (10)		
O(3)-O(4 <sup>iii</sup> )*	2.544 (9)		
P(2) tetrahedron			
P(2)-O(5 <sup>iii</sup> )	1.541 (8)	O(5 <sup>iii</sup> )-P(2)-O(6)	109.4 (4)
P(2)-O(6)	1.522 (6)	O(5 <sup>iii</sup> )-P(2)-O(7)	109.1 (4)
P(2)-O(7)	1.526 (6)	O(5 <sup>iii</sup> )-P(2)-O(8)	109.1 (4)
P(2)-O(8)	1.550 (6)	O(6)-P(2)-O(7)	108.5 (3)
		O(6)-P(2)-O(8)	111.0 (3)
O(5 <sup>iii</sup> )-O(6)	2.500 (9)	O(7)-P(2)-O(8)	109.7 (3)
O(5 <sup>iii</sup> )-O(7)	2.499 (10)		
O(5 <sup>iii</sup> )-O(8)	2.517 (9)		
O(6)-O(7)	2.474 (8)		
O(6)-O(8)	2.532 (8)		
O(7)-O(8)	2.515 (8)		

### Description and discussion of the structure

In a recent paper on the crystal chemistry of phosphate and arsenate minerals, Keller (1971) reported for hureaulite the three following crystal-chemical formulae:  $(\text{Mn, Fe})_5(\text{H}_3\text{O})_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ ;  $(\text{Mn, Fe})_5[(\text{OH})_2(\text{HOPO}_3)_4] \cdot 2\text{H}_2\text{O}$ ;  $(\text{Mn, Fe})_5[(\text{HOPO}_3)_2(\text{PO}_4)_2] \cdot 4\text{H}_2\text{O}$ . The infrared study (Keller, 1971) gave no clear evidence of the presence of  $\text{HOPO}_3$  groups, but indicated the probable presence of the  $\text{H}_3\text{O}$  ion. Therefore the first of the above formulae would seem the preferred one. In the present investigation on the crystal structure of hureaulite the crystal-chemical formula is well established as the third of those given by Keller.

The structure of hureaulite projected along  $[010]$  is shown in Fig. 1, where, for clarity, about half the cell content is represented. The simultaneous presence of  $\text{HOPO}_3$  and  $\text{PO}_4$  groups is evident. A similar feature is shown by the mineral sainfeldite,  $\text{Ca}_3(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , the structure of which is described in a paper (Ferraris & Abbona, 1972) that appeared during the refinement of the structure of hureaulite. The bond distances and bond angles show that hureaulite and sainfeldite are structurally very closely related and that Ca-As and Mn-P pairs are quite interchangeable with no difference other than a variation of related bond distances. Interatomic distances and angles of hureaulite are given in Table 6, and the thermal ellipsoid parameters with their standard deviations are presented in Table 7.

The  $(\text{HOPO}_3)^{2-}$  group is related to P(1) and  $(\text{PO}_4)^{3-}$  is related to P(2); O(1) is the oxygen atom to which the acidic hydrogen is linked. The average P-O distance in the  $\text{HOPO}_3$  tetrahedron is not significantly different from the average P-O value in the  $\text{PO}_4$  tetrahedron.

The values found in hureaulite are 1.539 and 1.535 Å respectively, and are in good agreement with the average values 1.539 and 1.536 Å given by Corbridge (1971) in a work on the structural chemistry of phosphates. The P(1)-O(1) distance (1.574 Å) is characteristically greater than the three remaining ones (mean value 1.527 Å) and the O-P-O angles are also greater than the O-P-OH angles, except O(2)-P(1)-O(3) which is smaller than the tetrahedral value. This again indicates that the sainfeldite and hureaulite structures are closely analogous. In the  $\text{PO}_4$  tetrahedron the bonds P-O(6) and P-O(7) are slightly shorter than the other two, but none of the four independent P-O distances deviates significantly from the mean value, nor do the O-P-O angles. P(1) and P(2) tetrahedra are linked to form a pair by a short (2.612 Å) hydrogen bond, namely O(1)-H(1)  $\cdots$  O(8). In the last section of this paper some considerations are given on the distortion in coordination polyhedra, both for P tetrahedra and for Mn octahedra to be described.

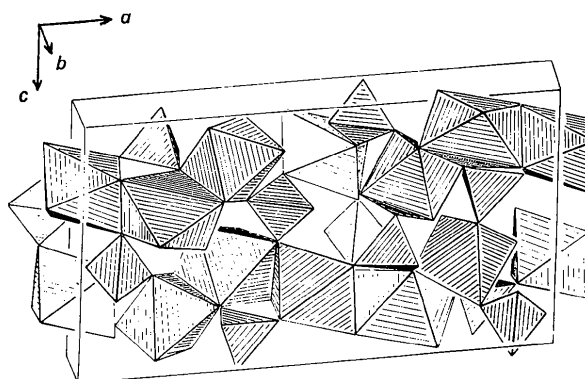


Fig. 2. Packing of polyhedra ( $b$  axis almost vertical).

Table 7. *Parameters for the thermal ellipsoids*

The first column contains the r.m.s. displacement (Å) and the next the three angles (°) between the principal ellipsoid axes and the crystallographic axes.

Mn(1)	0.103 (4)	90	180	90
	0.109 (5)	43 (8)	90	140 (8)
	0.138 (4)	133 (8)	90	130 (8)
Mn(2)	0.111 (3)	72 (16)	157 (21)	105 (14)
	0.117 (3)	42 (12)	67 (21)	129 (8)
	0.143 (3)	126 (6)	90 (4)	137 (6)
Mn(3)	0.107 (3)	67 (99)	141 (33)	122 (72)
	0.114 (3)	56 (14)	51 (24)	127 (15)
	0.136 (3)	136 (7)	86 (5)	127 (7)
	0.070 (8)	125 (7)	57 (10)	48 (8)
P(1)	0.099 (5)	57 (13)	36 (11)	106 (10)
	0.117 (5)	128 (11)	78 (10)	134 (9)
	0.051 (15)	63 (5)	69 (12)	150 (10)
P(2)	0.084 (5)	102 (9)	21 (12)	72 (11)
	0.117 (4)	150 (6)	92 (6)	113 (6)
	0.10 (2)	136 (8)	46 (8)	85 (18)
O(1)	0.14 (2)	76 (16)	75 (17)	26 (13)
	0.18 (1)	130 (7)	132 (8)	64 (13)
	0.10 (1)	121 (12)	144 (12)	71 (11)
O(2)	0.15 (1)	32 (12)	119 (20)	85 (40)
	0.16 (1)	89 (36)	109 (24)	160 (15)
	0.09 (2)	138 (16)	131 (24)	77 (31)
O(3)	0.11 (2)	108 (29)	59 (27)	34 (17)
	0.16 (1)	127 (9)	57 (9)	121 (13)
	0.11 (2)	88 (47)	127 (20)	143 (16)
O(4)	0.12 (1)	18 (13)	104 (33)	84 (40)
	0.16 (1)	108 (13)	140 (12)	54 (13)
	0.10 (2)	98 (7)	160 (15)	107 (16)
O(5)	0.14 (2)	85 (19)	109 (16)	22 (15)
	0.17 (1)	171 (12)	84 (9)	76 (18)
	0.09 (2)	107 (17)	160 (9)	99 (16)
O(6)	0.12 (1)	38 (14)	97 (21)	134 (13)
	0.17 (1)	123 (12)	71 (7)	135 (12)
	0.10 (1)	113 (24)	148 (29)	66 (19)
O(7)	0.12 (1)	41 (22)	121 (30)	119 (16)
	0.17 (1)	122 (13)	97 (9)	141 (12)
	0.10 (2)	146 (15)	96 (26)	50 (13)
O(8)	0.12 (1)	99 (25)	10 (22)	92 (20)
	0.15 (1)	123 (13)	98 (16)	140 (13)
	0.11 (1)	133 (23)	124 (46)	56 (36)
W(1)	0.13 (1)	109 (43)	35 (45)	59 (33)
	0.15 (1)	131 (21)	80 (21)	131 (24)
	0.11 (2)	153 (16)	73 (23)	63 (7)
W(2)	0.13 (1)	72 (22)	18 (22)	92 (12)
	0.20 (1)	110 (7)	84 (6)	153 (7)

Like the Ca atoms in sainfeldite, the three independent Mn atoms in hureaulite are each coordinated to six oxygen atoms in a distorted octahedral arrangement. In Mn(2) and Mn(3) polyhedra there is no distinction between Mn–O and Mn–W distances; Mn(1) is coordinated only to oxygen atoms belonging to PO<sub>4</sub> and HOPO<sub>3</sub> groups.

The assemblage of tetrahedra and octahedra is depicted in Fig. 2. The basis of the structure is provided by a repeat group of five edge-shared Mn octahedra, namely the Mn(1) octahedron on the twofold axis, two symmetrical Mn(3)'s and finally two more symmetrical Mn(2) octahedra. Each of these groups branching out in the *a* direction, is joined by two corners to each of the neighbouring symmetrical groups. P(1) and P(2) tetrahedra occur in this framework, tightly connecting the above-described groups of octahedra to one another.

The H atomic positions were detected by a difference Fourier synthesis. The hydrogen-bonding system, which serves to strengthen the structure, is not completely identical with the one found in sainfeldite. This arises not only from a shortening of all the donor-acceptor distances, but mainly from a lengthening of the W(2)–W(2,4) distance 3.155 Å which seems to prevent the formation of the same bifurcated hydrogen bond as found in sainfeldite. The donor-acceptor distances involved in this bond are 2.948 and 3.035 Å in sainfeldite and 2.738 and 3.155 Å in hureaulite, indicating the presence of a normal H bond. As usual (Corbridge, 1971), the strongest H bond is the one involving the acidic hydrogen, the related O–O distance (2.612 Å) being shorter than the W–O distances, which range from 2.666 to 2.808 Å. Similar O–O and W–O distances have also been found, *e.g.* in newberyite, MgHPO<sub>4</sub>·3H<sub>2</sub>O (Sutor, 1967; Baur, 1970), with O–O = 2.609 Å and W–O ranging from 2.684 to 2.843 Å. If one assumes that the experimental H positions are sufficiently reliable one can conclude that in hureaulite none of the W–H···O or O–H···O bonds is perfectly linear and that H(1), the acidic hydrogen, is farther from the donor than expected.

#### Distortion of the coordination polyhedra

In the previous section it was shown that on substituting the Mn–P pair for the Ca–As pair, in spite of the substantial decrease in ionic radii, the oxygen-atom packing remains unchanged apart from the O–O approach. Thus the coordination polyhedra in sainfeldite and hureaulite are very likely to have similar distortions, rather large especially for octahedra.

Recently Robinson, Gibbs & Ribbe (1971) suggested that the angle variance ( $\sigma^2$ ) and the mean quadratic elongation ( $\lambda$ ) can be convenient quantitative measures of distortion of polyhedra from their holosymmetric

Table 8. *Distances (Å) and angles (°) involving hydrogen atoms*

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>AB</i>	<i>BC</i>	<i>AC</i>	<i>CD</i>	<i>DE</i>	<i>CE</i>	<i>BD</i>
O(3 <sup>III</sup> )*	·····H(3 <sup>III</sup> )*	–W(1)–H(2)·····	O(3)		1.71	0.99	2.666	0.98	2.00	2.808	1.45
O(1 <sup>I</sup> )*	·····H(5 <sup>V</sup> )*	–W(2)–H(4)·····	O(8)		2.00	0.86	2.738	0.96	1.78	2.725	1.59
		O(1)–H(1 <sup>VI</sup> )*	·····O(8 <sup>VI</sup> )*					1.18	1.43	2.612	
					$\angle BCD$	$\angle ACE$	$\angle ABC$	$\angle CDE$			
					96	109.8	160	138			
					122	139.7	143	167			
								174			

geometries. In order to make a further comparison between sainfeldite and hureaulite structures, this method was applied in the present work.

The straight lines shown in Fig. 3 (a) and (b) are those reported by the above authors and represent the linear correlations between  $\sigma^2$  and  $\lambda$  for octahedral and tetrahedral coordination polyhedra respectively. The solid circles represent the experimental values for hureaulite. The open circles are those of sainfeldite, calculated on the basis of atomic coordinates, bond distances and bond angles given by Ferraris & Abbona (1972) [there are two misprints in the original values, namely the distance Ca(1)–O(4) of 2.254 Å which is actually 2.352 Å and the angle O(4)–Ca(1)–O(8,5) = 74.7°, actually 87.5°]. As can easily be seen in Fig. 3, the  $\sigma^2$  and  $\lambda$  values computed for hureaulite and sainfeldite (see Table 9) fit fairly well the correlation found by Robinson *et al.* (1971).

Table 9. Mean quadratic elongation and angle variance for hureaulite and sainfeldite polyhedra

	$\lambda$	$\sigma^2$		$\lambda$	$\sigma^2$
P(1)	1.0012	5.9	As(1)	1.0031	8.7
P(2)	1.0004	0.7	As(2)	1.0007	1.2
Mn(1)	1.0205	68.4	Ca(1)	1.0190	65.4
Mn(2)	1.0189	64.9	Ca(2)	1.0230	82.1
Mn(3)	1.0588	185.9	Ca(3)	1.0654	208.0

It is interesting to note the continuing persistence of similarities between hureaulite and sainfeldite. Although P and Mn polyhedra are less distorted than the corresponding As and Ca polyhedra [with the exception of Mn(1) with respect to the Ca(1) octahedron] the most important feature is the strict correspondence apparent between P(1) and As(1), P(2) and As(2) and so on. The large separation in  $\sigma^2$  and  $\lambda$  values between the octahedron involving Mn(3) or Ca(3) and the others is also evident. This difference is likely to be related to the various sharing degrees found in the three crystallographically independent octahedra. Indeed the Mn(3) octahedron shares all six of its oxygen atoms with other Mn octahedra through two edges and two corners; moreover five of its oxygen atoms also belong to P tetrahedra. On the other hand Mn(1) and Mn(2) octahedra show, with respect to Mn(3), a fairly lower sharing degree. Owing to the lack of homogeneous and quantitative data on the distortions in other structures, it is impossible to extend the comparison and to further speculate on this matter. A generalized use of the above method seems therefore to be useful and recommendable.

In addition to some local programs, the programs for the CII 10070 computer used in this work were the following: *ORFLS* least-squares program by Busing, Martin & Levy; *ORFFE* function and error program

by Busing, Martin & Levy; *ORTEP* plotting program by Johnson.

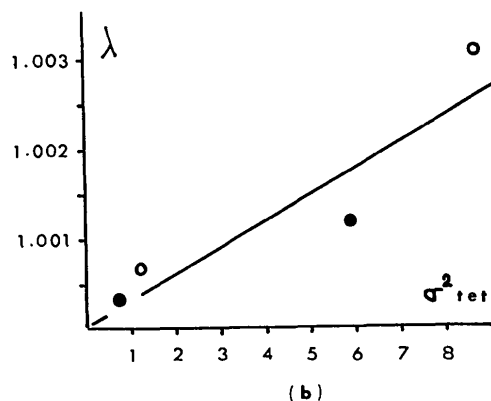
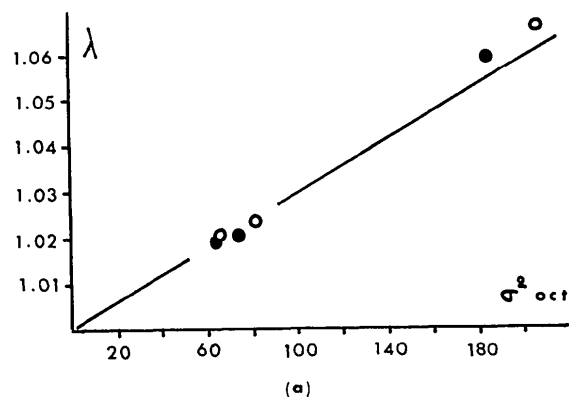


Fig. 3. Mean quadratic elongation plotted against angle variance of octahedra (a) and tetrahedra (b).

#### References

- ALLUAUD, F. (1826). *Ann. Sci. Nat.* **8**, 334–344.  
 BAUR, W. H. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 129–155.  
 CORBRIDGE, D. E. C. (1971). *Bull. Soc. Fr. Minér. Crist.* **94**, 271–299.  
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.  
 FERRARIS, G. & ABBONA, F. (1972). *Bull. Soc. Fr. Minér. Crist.* **95**, 33–41.  
 FISCHER, D. J. (1964). *Amer. Min.* **49**, 398–406.  
 KELLER, P. (1971). *Neues Jb. Miner. Mh.* pp. 491–510.  
 MOORE, P. B. (1965). *Amer. Min.* **50**, 2052–2062.  
 PALACHE, C., BERMAN, H. & FRONDEL, C. (1951). *Dana's System of Mineralogy*, Vol. II, pp. 700–702. New York: John Wiley.  
 ROBINSON, K., GIBBS, G. V. & RIBBE, P. H. (1971). *Science*, **172**, 567–570.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 STRUNZ, H. (1954). *Neues Jb. Miner. Mh.* pp. 166–177.  
 SUTOR, D. J. (1967). *Acta Cryst.* **23**, 418–422.