

Contribution from the Institute of Materials Science and Department of Chemistry,
University of Connecticut, Storrs, Connecticut 06268

Crystal Structures of Two Isomorphs of Arsenoclasite: $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ and $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$

F. A. RUSZALA, J. B. ANDERSON, and E. KOSTINER*

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Single crystals of $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ and $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$ have been prepared hydrothermally and their crystal structures determined and refined by full-matrix least-squares procedures using automatic diffractometer data to an isotropic residual $R = 0.059$ ($R_w = 0.076$) for $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ and an anisotropic residual $R = 0.033$ ($R_w = 0.043$) for $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$. These compounds are isostructural with the mineral arsenoclasite [$\text{Mn}_5(\text{AsO}_4)_2(\text{OH})_4$], crystallizing in the space group $P2_12_12_1$ with $a = 8.903$ (2), $b = 17.397$ (2), and $c = 5.5154$ (4) Å for the cobalt compound and $a = 9.110$ (1), $b = 18.032$ (4), and $c = 5.6923$ (6) Å for the manganese compound. In these compounds the divalent metal ions occupy five unique octahedrally coordinated positions. The structure is constructed from two elements, a ladder-like chain of edge-shared octahedra and a chain of edge- and corner-shared octahedra coupled by phosphate tetrahedra.

Introduction

Three different structure types are known for compounds with the stoichiometry $\text{M}_5(\text{XO}_4)_2(\text{OH})_4$, where M is a divalent metal ion and X is P or As. $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ is dimorphous; the mineral pseudomalachite^{1,2} has a synthetic dimorph with an interestingly related structure.³ (Cornwallite, $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$, is said⁴ to be isostructural to pseudomalachite.) The third structure type, represented by the mineral arsenoclasite, $\text{Mn}_5(\text{AsO}_4)_2(\text{OH})_4$, has been reported⁵ to have a structural element similar to one found in pseudomalachite.

During our continuing investigations into the syntheses and structures of hydroxyphosphates of this and other stoichiometries, we have observed the formation of two phases, $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ and $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$, which we have determined to be isostructural with the mineral arsenoclasite. This paper reports the results of our structure determination and presents a description of the structure type.

Experimental Section

Synthesis. Crystals of $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ and $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$ were prepared in sealed 5 mm diameter gold tubes (5 cm long) contained in cold-seal autoclaves (TempPress MRA 114R) operating at 55 000 psi and 400 °C over a period of 2 weeks in a two-zone furnace.⁶

Treatment of 0.11 mmol of $\text{Co}_3(\text{PO}_4)_2$ with 0.1 mL of 1.8 M KOH solution yielded deep purple crystals of $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ up to $1.2 \times 0.2 \times 0.2$ mm in dimension. Secondary products included microcrystalline CoO and intensely blue, highly twinned crystals of KCoPO_4 . When the solution was made less basic (0.09 M KOH), burgundy crystals of the cobalt isomorph of triploidite⁷ [$\text{Co}_2\text{PO}_4(\text{OH})$] also appeared.

Treatment of 0.10 mmol of $\text{Mn}_3(\text{PO}_4)_2$ with 0.3 mL of 1.8 M KOH solution yielded light brown crystals of $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$ up to a size of $3.0 \times 1.1 \times 1.1$ mm. If the amount of basic solution was decreased to less than or equal to 0.2 mL, pale rose crystals of manganese triploidite formed. Occasionally, a dark brown coating of Mn_2O_4 formed on the walls of the gold capsule.

Both isomorphs of arsenoclasite are retrograde soluble, while the triploidite phases display normal solubility under these conditions.

Attempts to synthesize the ferrous and nickel isomorphs of $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ using similar chemical and physical conditions were unsuccessful. Similar conditions also failed to produce arsenoclasite. However, we were able to prepare ferrous triploidite using a mixture of powdered iron in excess, FePO_4 , and KOH solution.

All starting materials either were reagent grade or were synthesized from reagent grade materials by sintering ammonium dihydrogen phosphate with the appropriate metal oxide or carbonate at 900 °C in platinum.

Structure Determination. X-ray precession photographs revealed that both compounds had orthorhombic symmetry with systematic extinctions corresponding to the space group $P2_12_12_1$. Crystals of the cobalt phase were found to be highly fractured making it necessary

Table I. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ ^a

	10^4x	10^4y	10^4z	$B, \text{Å}^2$
Co(1)	1272 (1)	8759.7 (6)	1963 (2)	0.37 (1)
Co(2)	1315 (1)	7820.6 (6)	7033 (2)	0.39 (2)
Co(3)	1066 (1)	9717.3 (6)	6809 (2)	0.40 (2)
Co(4)	4996 (1)	6813.0 (6)	5171 (2)	0.44 (2)
Co(5)	2566 (1)	5719.0 (6)	8364 (2)	0.46 (2)
P(1)	4301 (2)	8703 (1)	5606 (3)	0.24 (2)
P(2)	1793 (2)	6218 (1)	3750 (3)	0.26 (2)
O(1)	4922 (6)	6082 (3)	8179 (9)	0.43 (6)
O(2)	2576 (6)	8727 (3)	5288 (9)	0.41 (6)
O(3)	4777 (6)	9235 (3)	7713 (10)	0.56 (7)
O(4)	4773 (6)	7899 (3)	6466 (10)	0.47 (7)
O(5)	57 (6)	6231 (3)	3703 (9)	0.37 (6)
O(6)	2472 (7)	6793 (3)	5610 (10)	0.67 (7)
O(7)	2343 (6)	6405 (3)	1211 (10)	0.50 (7)
O(8)	2315 (6)	5428 (3)	4720 (10)	0.55 (7)
O(9)	2166 (6)	9699 (3)	31 (10)	0.51 (7)
O(10)	115 (6)	5472 (3)	8715 (10)	0.52 (7)
O(11)	76 (6)	7912 (3)	3885 (10)	0.43 (7)
O(12)	2659 (6)	8012 (3)	175 (10)	0.46 (7)

^a Numbers in parentheses are esd's in the last significant figure.

to slowly air quench the autoclave to room temperature over a 6-h period. Since this material had well-developed cleavage planes, we were unable to grind a sphere. A cleavage fragment (0.38 mm long) of $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ bounded by the planes {043}, a low pyramidal cap on one end, and a somewhat uneven fracture on the other was selected for x-ray analysis. The manganese isomorph, on the other hand, was not as highly fractured nor were the cleavages as well developed; thus a suitable sphere could be ground.

The lattice parameters of $\text{Co}_5(\text{PO}_4)_2(\text{OH})_4$ were determined in a PICK-II least-squares refinement program, using 48 reflections within the angular range $35 < 2\theta < 48^\circ$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation ($\lambda 0.70930 \text{ Å}$). At 25 °C the lattice parameters were found to be $a = 8.903$ (2), $b = 17.397$ (2), $c = 5.5154$ (4) Å, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 4$, was 4.296 g cm^{-3} .

Diffractometer intensities were measured using Zr-filtered Mo $K\alpha$ radiation at a takeoff angle of 2.5° with the diffractometer operating in the θ - 2θ scan mode. Scans were made at $1^\circ/\text{min}$ over 1.4° with allowance for dispersion and with 20-s background counts taken at the both ends the scan. Of the 2294 independent data investigated in the angular range $2\theta < 71^\circ$, 2176 were considered observable according to the criterion $|F_o| > 1.58\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C , k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than $\pm 2\%$ over the data collection period.

Table II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters for $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4^a$

	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	1273.4 (8)	8744.3 (4)	1964 (1)	0.99 (2)	1.07 (2)	0.92 (2)	0.04 (2)	-0.01 (2)	-0.02 (2)
Mn(2)	1404.4 (8)	7789.2 (4)	6993 (1)	1.10 (2)	0.97 (2)	0.99 (2)	-0.09 (2)	0.03 (2)	0.00 (2)
Mn(3)	1009.3 (8)	9750.3 (4)	6850 (1)	1.13 (2)	1.10 (2)	0.95 (2)	-0.09 (2)	0.10 (2)	-0.04 (2)
Mn(4)	4972.5 (8)	6828.6 (4)	5153 (1)	1.02 (2)	1.03 (2)	1.00 (2)	0.01 (2)	-0.04 (2)	0.00 (2)
Mn(5)	2531.8 (8)	5698.4 (4)	8360 (1)	1.11 (2)	1.23 (2)	0.94 (2)	0.08 (2)	-0.02 (2)	-0.05 (2)
P(1)	4287 (1)	8724.3 (7)	5552 (2)	0.72 (4)	0.99 (4)	0.70 (4)	0.05 (3)	0.02 (3)	-0.06 (3)
P(2)	1797 (1)	6234.9 (7)	3697 (2)	0.83 (4)	0.91 (4)	0.76 (4)	0.05 (3)	-0.01 (3)	0.02 (3)
O(1)	4940 (4)	6066 (2)	8242 (6)	0.96 (11)	1.17 (11)	1.01 (11)	-0.12 (10)	0.01 (11)	0.02 (9)
O(2)	2593 (4)	8771 (2)	5260 (6)	0.91 (11)	1.39 (11)	1.13 (12)	-0.19 (11)	-0.15 (10)	0.09 (9)
O(3)	4760 (4)	9213 (2)	7610 (6)	0.91 (11)	1.15 (11)	1.12 (12)	0.13 (10)	-0.17 (9)	-0.11 (9)
O(4)	4677 (4)	7924 (2)	6303 (7)	1.36 (12)	0.86 (11)	1.03 (11)	0.07 (9)	-0.08 (10)	-0.13 (9)
O(5)	103 (4)	6255 (2)	3695 (6)	0.88 (11)	1.29 (12)	1.01 (11)	-0.10 (10)	0.05 (10)	-0.11 (10)
O(6)	2459 (4)	6797 (2)	5444 (7)	1.01 (11)	1.38 (12)	1.29 (12)	0.08 (11)	-0.08 (11)	-0.29 (10)
O(7)	2333 (4)	6408 (2)	1215 (6)	1.02 (11)	1.20 (11)	0.87 (11)	-0.02 (9)	0.02 (10)	0.11 (9)
O(8)	2320 (4)	5476 (2)	4613 (6)	1.17 (11)	0.95 (10)	1.02 (11)	0.04 (10)	0.06 (10)	0.00 (9)
O(9)	2175 (4)	9675 (2)	38 (6)	1.05 (11)	1.12 (11)	0.88 (11)	-0.16 (10)	0.02 (10)	0.00 (9)
O(10)	148 (4)	5450 (2)	8690 (7)	1.18 (11)	1.11 (11)	1.07 (11)	-0.04 (10)	-0.05 (10)	-0.15 (10)
O(11)	45 (4)	7934 (2)	3927 (7)	1.25 (12)	1.13 (11)	1.00 (11)	0.02 (9)	0.05 (11)	-0.02 (10)
O(12)	2681 (4)	7981 (2)	204 (7)	1.05 (11)	0.99 (11)	1.13 (11)	0.22 (10)	-0.12 (11)	-0.04 (9)

^a Numbers in parentheses are estimated standard deviations in the last significant figure. The B 's are defined by the general temperature factor $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Bond Distances, Polyhedral Edge Lengths, and Bond Angles for the Metal Polyhedra

(i) Interatomic Distances, Å								
	Co ^a	Mn ^b		Co ^a	Mn ^b		Co ^a	Mn ^b
M(1)-O(12)	2.047	2.131	M(2)-O(11)	2.050	2.157	M(3)-O(9)	2.029	2.107
M(1)-O(10)	2.061	2.181	M(2)-O(11')	2.063	2.156	M(3)-O(10)	2.031	2.116
M(1)-O(11)	2.106	2.153	M(2)-O(12)	2.132	2.193	M(3)-O(8)	2.078	2.173
M(1)-O(9)	2.107	2.166	M(2)-O(2)	2.162	2.299	M(3)-O(3)	2.170	2.210
M(1)-O(5)	2.152	2.244	M(2)-O(6)	2.207	2.214	M(3)-O(5)	2.194	2.328
M(1)-O(2)	2.171	2.229	M(2)-O(5)	2.250	2.407	M(3)-O(2)	2.340	2.453
Average	2.107	2.184	Average	2.144	2.238	Average	2.140	2.231
M(1) octahedron			M(2) octahedron			M(3) octahedron		
O(12)-O(11)	3.083	3.204	O(11)-O(11')	3.111	3.249	O(9)-O(8)	2.947	3.051
O(12)-O(9)	2.969	3.090	O(11)-O(12)	3.003	3.069	O(9)-O(3)	3.201	3.338
O(12)-O(5)	2.871	3.011	O(11)-O(6)	2.945	3.061	O(9)-O(5)	2.659	2.776
O(12)-O(2)	3.084	3.213	O(11)-O(5)	2.926	3.030	O(9)-O(2)	3.135	3.193
O(10)-O(11)	2.819	2.923	O(11')-O(2)	2.751	2.872	O(10)-O(8)	3.067	3.218
O(10)-O(9)	2.888	2.975	O(11')-O(6)	3.041	3.128	O(10)-O(3)	2.918	3.068
O(10)-O(5)	3.064	3.194	O(11')-O(5)	3.050	3.085	O(10)-O(5)	3.053	3.198
O(10)-O(2)	2.904	3.001	O(12)-O(2)	2.970	3.155	O(10)-O(2)	2.904	3.001
O(11)-O(5)	3.226	3.321	O(12)-O(6)	3.296	3.456	O(8)-O(3)	2.875	2.948
O(11)-O(2)	2.751	2.872	O(12)-O(5)	2.871	3.011	O(8)-O(2)	2.961	3.075
O(9)-O(5)	2.659	2.776	O(2)-O(6)	3.371	3.564	O(3)-O(5)	3.562	3.759
O(9)-O(2)	3.376	3.411	O(2)-O(5)	3.008	3.140	O(5)-O(2)	3.008	3.140
	Co ^a	Mn ^b		Co ^a	Mn ^b		Co ^a	Mn ^b
M(4)-O(4)	2.029	2.098	M(5)-O(7)	1.983	2.076			
M(4)-O(1)	2.092	2.233	M(5)-O(9)	1.998	2.076			
M(4)-O(12)	2.110	2.165	M(5)-O(8)	2.085	2.179			
M(4)-O(4')	2.114	2.259	M(5)-O(1)	2.194	2.293			
M(4)-O(6)	2.260	2.297	M(5)-O(10)	2.232	2.225			
M(4)-O(3)	2.281	2.384	M(5)-O(6)	2.410	2.585			
Average	2.148	2.239	Average	2.150	2.239			
M(4) octahedron			M(5) octahedron					
O(4)-O(1)	3.301	3.536	O(7)-O(9)	3.078	3.236			
O(4)-O(12)	2.871	2.975	O(7)-O(1)	2.896	2.981			
O(4)-O(4')	3.113	3.284	O(7)-O(10)	2.910	3.002			
O(4)-O(6)	2.849	2.907	O(7)-O(6)	3.164	3.361			
O(1)-O(12)	3.141	3.262	O(9)-O(8)	3.195	3.401			
O(1)-O(6)	2.880	3.063	O(9)-O(1)	3.197	3.311			
O(1)-O(3)	3.076	3.256	O(9)-O(10)	2.854	2.902			
O(12)-O(4')	2.787	2.871	O(8)-O(1)	3.212	3.331			
O(12)-O(3)	3.152	3.270	O(8)-O(10)	2.949	3.050			
O(4')-O(6)	3.395	3.552	O(8)-O(6)	2.429	2.432			
O(4')-O(3)	2.425	2.441	O(1)-O(6)	2.880	3.063			
O(6)-O(3)	3.428	3.512	O(10)-O(6)	3.553	3.708			

Table III (Continued)

(ii) Angles, Deg														
Co ^a			Mn ^b			Co ^a			Mn ^b					
M(1) octahedron			M(2) octahedron			M(3) octahedron			M(4) octahedron			M(5) octahedron		
O(12)-M(1)-O(11)	95.9	96.8	O(11)-M(2)-O(11')	98.3	97.7	O(9)-M(3)-O(8)	91.7	90.9	O(4)-M(4)-O(1)	106.5	109.4	O(7)-M(5)-O(9)	101.3	102.4
O(12)-M(1)-O(9)	91.2	91.9	O(11)-M(2)-O(12)	91.8	89.7	O(9)-M(3)-O(3)	99.3	101.2	O(4)-M(4)-O(12)	87.8	88.5	O(7)-M(5)-O(1)	87.7	85.9
O(12)-M(1)-O(5)	86.2	86.9	O(11)-M(2)-O(6)	87.5	88.9	O(9)-M(3)-O(5)	78.0	77.3	O(4)-M(4)-O(4')	97.4	97.8	O(7)-M(5)-O(10)	87.1	88.4
O(12)-M(1)-O(2)	93.9	94.9	O(11)-M(2)-O(5)	85.6	83.0	O(9)-M(3)-O(2)	91.4	88.6	O(4)-M(4)-O(6)	83.1	82.7	O(7)-M(5)-O(6)	91.7	91.6
O(10)-M(1)-O(11)	85.2	84.8	O(11')-M(2)-O(2)	81.2	80.2	O(10)-M(3)-O(8)	96.6	97.2	O(1)-M(4)-O(12)	96.8	95.8	O(9)-M(5)-O(8)	103.0	106.1
O(10)-M(1)-O(9)	87.7	86.4	O(11')-M(2)-O(6)	90.7	91.4	O(10)-M(3)-O(3)	88.0	90.3	O(1)-M(4)-O(6)	82.8	85.1	O(9)-M(5)-O(1)	99.3	98.4
O(10)-M(1)-O(5)	93.3	92.4	O(11')-M(2)-O(5)	89.9	84.9	O(10)-M(3)-O(5)	92.4	91.9	O(1)-M(4)-O(3)	89.3	89.7	O(9)-M(5)-O(10)	84.7	84.9
O(10)-M(1)-O(2)	86.6	85.8	O(12)-M(2)-O(2)	87.5	89.2	O(10)-M(3)-O(2)	82.9	81.8	O(12)-M(4)-O(4')	82.6	80.9	O(8)-M(5)-O(1)	97.3	96.3
O(11)-M(1)-O(5)	98.5	98.1	O(12)-M(2)-O(6)	98.8	103.2	O(8)-M(3)-O(3)	85.2	84.5	O(12)-M(4)-O(3)	91.7	91.8	O(8)-M(5)-O(10)	86.1	87.7
O(11)-M(1)-O(2)	80.0	81.9	O(12)-M(2)-O(5)	81.8	81.6	O(8)-M(3)-O(2)	83.9	83.1	O(4)-M(4)-O(6)	101.8	102.5	O(8)-M(5)-O(6)	65.0	60.7
O(9)-M(1)-O(5)	77.3	78.0	O(2)-M(2)-O(6)	101.0	104.3	O(3)-M(3)-O(5)	109.4	111.8	O(4)-M(4)-O(3)	66.9	63.4	O(1)-M(5)-O(6)	77.3	77.6
O(9)-M(1)-O(2)	104.2	101.8	O(2)-M(2)-O(5)	85.9	83.7	O(5)-M(3)-O(2)	83.6	82.1	O(6)-M(4)-O(3)	98.0	97.3	O(10)-M(5)-O(6)	99.8	100.6
O(12)-M(1)-O(10)	178.9	178.3	O(11)-M(2)-O(2)	171.5	166.7	O(9)-M(3)-O(10)	169.4	166.5	O(4)-M(4)-O(3)	164.2	160.8	O(7)-M(5)-O(8)	154.0	150.7
O(11)-M(1)-O(9)	171.5	170.2	O(11')-M(2)-O(12)	166.5	163.7	O(8)-M(3)-O(5)	163.1	161.2	O(1)-M(4)-O(4')	156.1	152.6	O(9)-M(5)-O(6)	166.5	165.2
O(5)-M(1)-O(2)	178.5	178.2	O(6)-M(2)-O(5)	173.1	170.5	O(3)-M(3)-O(2)	164.9	164.3	O(12)-M(4)-O(6)	170.3	170.9	O(1)-M(5)-O(10)	174.0	174.0

^a Co \equiv Co₅(PO₄)₂(OH)₄: esd's, Co-O, 0.006 Å; O-O, 0.008 Å; angle, 0.2°. ^b Mn \equiv Mn₅(PO₄)₂(OH)₄: esd's, Mn-O, 0.004 Å; O-O, 0.005 Å; angle, 0.1°.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections ($\mu = 103 \text{ cm}^{-1}$) were made using a computer program written by N. W. Alcock and B. Lee for a crystal of general shape. Input for the program included the indices of the plane faces of the crystal (determined with the aid of precession photography) and the diffraction angles of the crystal coordinates system with respect to the diffractometer coordinate system (obtained from the PICK-II program).

An initial attempt to refine the structure using the positional parameters given for arsenoclasite⁵ failed due to our incorrect symmetry transformation. This led us to solve the structure independently. (Moore⁵ presented the unit cell of arsenoclasite with an unconventional choice of axes in an attempt to relate the structure to that of pseudomalachite; we report the unit cell in the Donnay convention. To transform one set of coordinates to the other, x and z are interchanged and y is made negative.)

Realizing that the cell volume (corrected for relative sizes of PO₄³⁻ and AsO₄³⁻) was very similar to that of arsenoclasite, the unit cell contents Co₂₀(PO₄)₈(OH)₁₆ were used in the multiresolution symbolic addition program MULTAN.⁸ Phases with a probability of being greater than 80% correct were used in the starting set. The five strongest peaks in the best electron density map generated by MULTAN from those reflections proved to be cobalt atoms, all on general positions. Difference Fourier maps revealed the positions of the phosphorus and oxygen atoms.

Using these atomic coordinates, full-matrix least-squares refinement⁹ using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors¹⁰ for Co, P, and O, isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion converged to a residual $R = 0.059$ ($R_w = 0.076$) for 78 independently varied parameters (data:parameter ratio of 28). An anisotropic refinement was attempted, but this resulted in negative temperature factors which we attribute to the approximate

nature of the absorption correction. In the final isotropic refinement, the maximum extinction correction¹¹ was 11% of $|F_o|$ for the 151 reflection.

A sphere of diameter 0.20 (1) mm was chosen for the x-ray investigation of Mn₅(PO₄)₂(OH)₄. The lattice parameters were determined in the PICK-II least-squares refinement program, using 48 independent reflections within the angular range $36^\circ < 2\theta < 38^\circ$. At 25 °C the lattice parameters are $a = 9.110$ (1), $b = 18.032$ (4), and $c = 5.6923$ (6) Å, where the figures in the parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 4$, is 3.783 g cm^{-3} .

Diffractometer intensities were measured with the diffractometer operating in the ω scan mode with 10-s background counts taken at the ends of a $1.4^\circ \theta$ - 2θ scan corrected for dispersion. This technique was used because a splitting in ω was observed at high 2θ values on the diffractometer which was not observed on precession photographs. We attributed this splitting to minute cracks in the crystal and felt that an ω scan data collection would yield more accurate intensities. Of the 2430 data investigated, 2132 were considered observable according to the above criterion.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections¹² were applied for a spherical crystal with $\mu R = 0.729 \text{ cm}^{-1}$. The maximum absorption correction was 3% of $|F_o|$.

Least-squares refinement using the atomic coordinates obtained for Co₅(PO₄)₂(OH)₄ as a trial structure, a $1/\sigma^2$ weighting scheme, zerovalent scattering factors¹⁰ for Mn, P, and O, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.038$ ($R_w = 0.047$). The anisotropic refinement, based on a data:parameter ratio of 12 with 173 independently varied parameters converged to a final $R = 0.033$ ($R_w = 0.043$). The maximum extinction correction¹¹ was 12% of $|F_o|$ for the 151 reflection.

Table IV. Bond Distances, Polyhedral Edge Lengths, and Bond Angles for the Phosphate Tetrahedra

	Co ^a	Mn ^b	Co ^a	Mn ^b
(i) Interatomic Distances, Å				
P(1)-O(4)	1.537	1.547	P(2)-O(7)	1.519
P(1)-O(3)	1.545	1.528	P(2)-O(8)	1.545
P(1)-O(2)	1.547	1.554	P(2)-O(5)	1.546
P(1)-O(1)	1.552	1.539	P(2)-O(6)	1.555
P(1) tetrahedron			P(2) tetrahedron	
O(4)-O(3)	2.425	2.442	O(7)-O(8)	2.576
O(4)-O(2)	2.516	2.509	O(7)-O(5)	2.474
O(4)-O(1)	2.551	2.545	O(7)-O(6)	2.521
O(3)-O(2)	2.532	2.514	O(8)-O(5)	2.511
O(3)-O(1)	2.575	2.552	O(8)-O(6)	2.429
O(2)-O(1)	2.535	2.541	O(5)-O(6)	2.586
(ii) Angles, Deg				
O(4)-P(1)-O(3)	103.8	105.1	O(7)-P(2)-O(8)	114.4
O(4)-P(1)-O(2)	109.4	108.0	O(7)-P(2)-O(5)	107.7
O(4)-P(1)-O(1)	111.3	111.1	O(7)-P(2)-O(6)	110.2
O(3)-P(1)-O(2)	110.0	109.3	O(8)-P(2)-O(5)	108.6
O(3)-P(1)-O(1)	112.5	112.6	O(8)-P(2)-O(6)	103.1
O(2)-P(1)-O(1)	109.8	110.5	O(5)-P(2)-O(6)	113.0

^a Co ≡ Co₅(PO₄)₂(OH)₄; esd's, Co-O, 0.006 Å; O-O, 0.008 Å; angle, 0.2°. ^b Mn ≡ Mn₅(PO₄)₂(OH)₄; esd's, Mn-O, 0.004 Å; O-O, 0.005 Å; angle, 0.1°.

Results and Discussion

The final atomic coordinates and isotropic thermal parameters for Co₅(PO₄)₂(OH)₄ are presented in Table I; Table II lists the atomic coordinates and anisotropic thermal parameters for Mn₅(PO₄)₂(OH)₄. Oxygens 9, 10, 11, and 12 are the hydroxyl oxygens.

Each of the five unique divalent metal ions in this structure is octahedrally coordinated by oxygen atoms. Table III lists the bond distances and angles and the polyhedral edge lengths for these five ions in both structures. The standard deviations for all distances and angles were computed by the function and error program ORFFE.¹³ The average metal-oxygen distances (for all sites) are 2.138 Å (Co) and 2.226 Å (Mn). The difference between these averages (0.088 Å) agrees with the difference between Shannon and Prewitt's values¹⁴ for high-spin six-coordinated radii for Co²⁺ and Mn²⁺ (0.085 Å). The M(1)-O average distance (Table III) is significantly less than for the other metal sites, most probably due to the position of the M(1) octahedron in the structure (vide infra).

The two phosphate tetrahedra are fairly distorted (Table IV) with an average P-O distance of 1.543 Å (Co) and 1.540 Å (Mn); the average O-P-O angle is 109.5° for all sites. The shortest polyhedral edges about P(1) (O(3)-O(4)) and P(2) (O(6)-O(8)) are involved in edge sharing (vide infra). Table V presents the relevant angles and distances about the oxygen atoms.

Moore⁵ considered the structure of arsenoclasite to be "constructed of a double hexagonal close-packed array of oxygen atoms" with a stacking sequence (...ch...). However, such a model for this structure then forces certain cation coordinations to be less than six, an assumption in direct contradiction to the results in this study. Recalculation of bond distances using Moore's positional parameters confirms the fact that all of the Mn ions in arsenoclasite are six-coordinated and that these structures are indeed isomorphs. The true sixfold coordination about each of the cations causes severe distortions in the double hexagonal net, with the result that the structure can no longer be properly considered as being based on a simple close-packed array. Indeed, the inclusion of all of the bonding interactions relieves most of the underbonding about the oxygen atoms which Moore reports for arsenoclasite.

The structure of M₅(PO₄)₂(OH)₄ (M = Co, Mn) can be considered as being built up of two major elements. One is

a ladder-like chain consisting of edge sharing occupied by M(1), M(2), and M(3) atoms; the second consists of a chain of edge and corner shared M(4) and M(5) containing octahedra coupled by P(1)O₄ and P(2)O₄ tetrahedra. Both chains run parallel to the *c* axis.

The M(1) octahedron (labeled a in the figure) shares its O(2)-O(10) edge with an M(3) octahedron (labeled c) and the trans edge (O(5)-O(12)) with an M(2) octahedron (labeled b) as illustrated in Figure 1. Similarly, the O(5)-O(9)

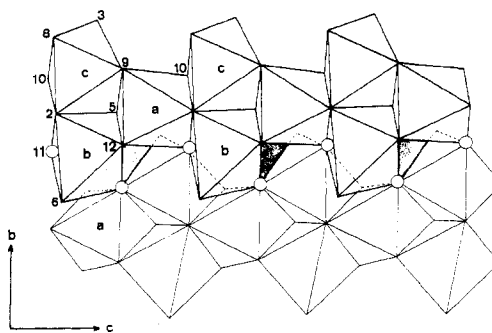


Figure 1. A portion of the structure of M₅(PO₄)₂(OH)₄ projected down the *a* axis illustrating the ladder-like chain of M(1), M(2), and M(3) octahedra (labeled a, b, and c, respectively). Oxygen atoms are numbered.

edge of the M(1) polyhedron is shared with an M(2) polyhedron and the trans edge (O(2)-O(11)) is shared with an M(2) polyhedron. The M(2) and M(3) octahedra further link by sharing the O(2)-O(5) edge to form the ladder-like chain. Two such chains are related by a 2₁ screw axis parallel to the *c* axis and are linked together by corner sharing through O(11). We previously noted that in both the Co and Mn compound the octahedron with the shortest average M-O distance contains M(1). This is undoubtedly due to its central location in the M(1), M(2), M(3) chain.

The core of the second chain is composed of M(4) octahedra (labeled d) which share cis O(4) corners with each other (Figure 2). The P(1) tetrahedra are attached to this core by sharing the O(3)-O(4) edge with one M(4) octahedron and the O(1) corner with another. The M(5) octahedra (labeled e) link to the M(4) octahedra by sharing the O(1)-O(6) edge.

Table V. Bond Distances (Å) and Bond Angles (deg) for the Anion Polyhedra

Bond distances ^a			Bond angles ^b		
Atoms	Co ^c	Mn ^d	Atoms	Co ^c	Mn ^d
(i) O(1) Polyhedron					
O(1)-P(1)	1.552	1.539	P(1)-O(1)-M(4)	121.6 (3)	121.0 (2)
O(1)-M(4)	2.091	2.233	P(1)-O(1)-M(5)	117.1 (3)	119.0 (2)
O(1)-M(5)	2.193	2.293	M(4)-O(1)-M(5)	104.0 (2)	102.3 (1)
(ii) O(2) Polyhedron					
O(2)-P(1)	1.546	1.554	P(1)-O(2)-M(2)	116.4 (3)	112.3 (2)
O(2)-M(2)	2.162	2.299	P(1)-O(2)-M(1)	128.8 (3)	128.6 (2)
O(2)-M(1)	2.171	2.229	P(1)-O(2)-M(3)	123.4 (3)	125.7 (2)
O(2)-M(3)	2.340	2.453	M(2)-O(2)-M(1)	96.7 (2)	95.2 (1)
			M(2)-O(2)-M(3)	94.6 (2)	96.8 (1)
			M(1)-O(2)-M(3)	88.7 (2)	90.5 (1)
(iii) O(3) Polyhedron					
O(3)-P(1)	1.545	1.528	P(1)-O(3)-M(3)	137.7 (3)	137.7 (2)
O(3)-M(3)	2.169	2.210	P(1)-O(3)-M(4)	89.6 (3)	92.3 (2)
O(3)-M(4)	2.281	2.384	M(3)-O(3)-M(4)	123.5 (3)	122.0 (2)
(iv) O(4) Polyhedron					
O(4)-P(1)	1.547	1.547	P(1)-O(4)-M(4)	140.0 (4)	145.2 (2)
O(4)-M(4)	2.029	2.098	P(1)-O(4)-M(4')	96.3 (3)	96.7 (2)
O(4)-M(4')	2.114	2.259	M(4)-O(4)-M(4')	123.5 (3)	118.1 (2)
(v) O(5) Polyhedron					
O(5)-P(2)	1.546	1.544	P(2)-O(5)-M(1)	122.4 (3)	123.9 (2)
O(5)-M(1)	2.152	2.244	P(2)-O(5)-M(3)	116.9 (3)	114.6 (2)
O(5)-M(3)	2.194	2.328	P(2)-O(5)-M(2)	124.1 (3)	126.0 (2)
O(5)-M(2)	2.250	2.407	M(1)-O(5)-M(3)	98.8 (3)	97.5 (1)
			M(1)-O(5)-M(2)	92.2 (2)	90.8 (1)
			M(3)-O(5)-M(2)	96.2 (2)	97.3 (1)
(vi) O(6) Polyhedron					
O(6)-P(2)	1.555	1.542	P(2)-O(6)-M(2)	125.0 (3)	128.2 (2)
O(6)-M(2)	2.207	2.214	P(2)-O(6)-M(4)	109.0 (3)	111.1 (2)
O(6)-M(4)	2.260	2.297	P(2)-O(6)-M(5)	86.0 (3)	85.4 (2)
O(6)-M(5)	2.410	2.585	M(2)-O(6)-M(4)	119.3 (3)	116.2 (2)
			M(2)-O(6)-M(5)	114.8 (2)	112.0 (1)
			M(4)-O(6)-M(5)	92.6 (2)	92.3 (1)
(vii) O(7) Polyhedron					
O(7)-P(2)	1.519	1.527	P(2)-O(7)-M(5)	129.3 (3)	128.8 (2)
O(7)-M(5)	1.983	2.076			
(viii) O(8) Polyhedron					
O(8)-P(2)	1.545	1.540	P(2)-O(8)-M(3)	126.7 (3)	128.5 (2)
O(8)-M(3)	2.078	2.173	P(2)-O(8)-M(5)	98.6 (3)	101.2 (2)
O(8)-M(5)	2.085	2.179	M(3)-O(8)-M(5)	117.5 (3)	115.1 (2)
(ix) O(9) Polyhedron					
O(9)-M(5)	1.997	2.076	M(5)-O(9)-M(3)	115.6 (3)	112.7 (1)
O(9)-M(3)	2.029	2.107	M(5)-O(9)-M(1)	120.7 (3)	121.0 (2)
O(9)-M(1)	2.107	2.166	M(3)-O(9)-M(1)	105.8 (2)	107.1 (1)
(x) O(10) Polyhedron					
O(10)-M(3)	2.031	2.116	M(3)-O(10)-M(1)	100.9 (2)	101.5 (1)
O(10)-M(1)	2.061	2.181	M(3)-O(10)-M(5)	127.6 (3)	126.3 (2)
O(10)-M(5)	2.232	2.226	M(1)-O(10)-M(5)	114.8 (2)	114.0 (2)
(xi) O(11) Polyhedron					
O(11)-M(2)	2.049	2.157	M(2)-O(11)-M(2')	134.0 (3)	133.8 (2)
O(11)-M(2')	2.063	2.156	M(2)-O(11)-M(1)	119.4 (3)	117.6 (2)
O(11)-M(1)	2.106	2.153	M(2')-O(11)-M(1)	101.9 (2)	101.8 (1)
(xii) O(12) Polyhedron					
O(12)-M(1)	2.047	2.131	M(1)-O(12)-M(4)	120.4 (3)	119.9 (2)
O(12)-M(4)	2.110	2.165	M(1)-O(12)-M(2)	98.8 (2)	100.0 (1)
O(12)-M(2)	2.132	2.194	M(4)-O(12)-M(2)	125.2 (3)	122.5 (2)

^a See Tables III and IV for esd's. ^b Numbers in parentheses are esd's in the last significant figure. ^c Co \equiv Co₅(PO₄)₂(OH)₄. ^d Mn \equiv Mn₅(PO₄)₂(OH)₄.

P(2) tetrahedra then join to the M(5) polyhedra by sharing the O(6)-O(8) edge with one octahedron and the O(7) corner with another. These chains link together by extensive polyhedral corner sharing as seen in Figure 3, a projection of the structure down the *c* axis.

In an attempt to locate the hydrogen bonds we calculated the bond valences (in valence units, vu) about each of the metal atoms using Brown and Shannon's¹⁵ empirical correlation of

bond length and bond valence: $S = S_0(R/R_0)^{-N}$, where *S* is bond valence, *R* is bond length, and *S*₀, *R*₀, and *N* are empirically fit constants for a given atom. Taking Mn₅(P-O₄)₂(OH)₄ as the example and using the values¹⁵ of *S*₀, *R*₀, and *N* for Mn²⁺ and P⁵⁺ as 0.333, 2.186, and 5.5 and 1.25, 1.534, and 3.2, respectively, the individual bond strengths about the oxygen atoms were summed (see Table VI).

O(9) through O(12), the hydroxyl oxygens, have bond

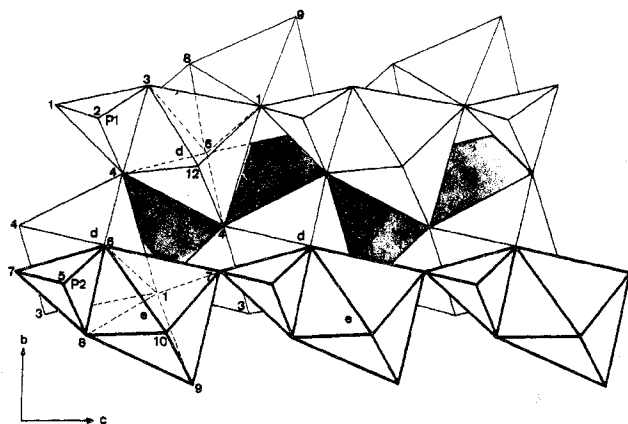


Figure 2. A portion of the structure of $Mn_5(PO_4)_2(OH)_4$ projected down the a axis illustrating the M(4)–P(1) and M(5)–P(2) chains. (M(4) and M(5) octahedra are labeled d and e, respectively.) Oxygen atoms are numbered.

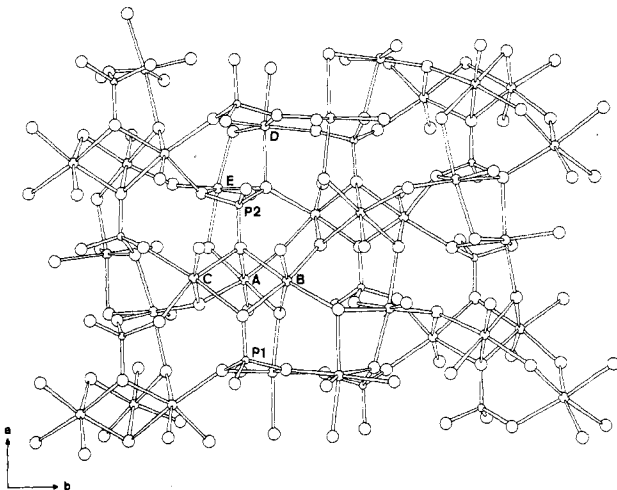


Figure 3. The $Mn_5(PO_4)_2(OH)_4$ structure projected down the c axis. A, B, C, D, and E are M(1), M(2), M(3), M(4), and M(5), respectively. Larger circles represent oxygen atoms.

strength sums near one (the hydrogen atoms have not been included). Of the remaining phosphate oxygens, O(1), O(3), and O(7) are decidedly underbonded. Inspection of the *interpolyhedral* oxygen–oxygen distances shows that the shortest occur between the hydroxyls and these phosphate oxygens: O(9)→O(3), 2.856 Å; O(10)→O(1), 2.952 Å; O(11)→O(7), 2.792 Å; O(12)→O(7), 2.908 Å. We believe that these represent the positions of the hydrogen bonds which further join the ladders and chains of linked polyhedra. A complementary analysis can be made for $Co_5(PO_4)_2(OH)_5$.

We should like to point out the distinct value in using Brown and Shannon's criteria for bond strength in assessing valence sums about oxygen atoms in complex crystal structures. Using Pauling's electrostatic valence balances would indicate, for example, that O(1), O(3), O(4), and O(8) have similar environments. Table VI definitely indicates that of these four oxygens O(1) and O(3) are underbonded and therefore act as recipients of hydrogen bonds.

Although the $Mn_5(PO_4)_2(OH)_4$ structure type is unique, it bears some resemblance to other structures. The M(1), M(2), M(3) ladder chain is, in essence, fused partial strips of the brucite structure. The zigzag grouping of octahedra typified

Table VI. Individual Bond Strengths and Bond Strength Sums about Oxygen Atoms (in ν) for $Mn_5(PO_4)_2(OH)_4$

O(1):	P(1)	1.24	O(5):	P(2)	1.22	O(9):	Mn(5)	0.44
	Mn(4)	0.30		Mn(1)	0.29		Mn(3)	0.41
	Mn(5)	0.26		Mn(3)	0.24		Mn(1)	0.35
	Σ	1.80		Mn(2)	0.20		Σ	1.20
				Σ	1.95			
O(2):	P(1)	1.20	O(6):	P(2)	1.23	O(10):	Mn(3)	0.40
	Mn(1)	0.30		Mn(2)	0.31		Mn(1)	0.34
	Mn(2)	0.25		Mn(4)	0.25		Mn(5)	0.30
	Mn(3)	0.18		Mn(5)	0.13		Σ	1.04
	Σ	1.93		Σ	1.92			
O(3):	P(1)	1.27	O(7):	P(2)	1.27	O(11):	Mn(2)	0.36
	Mn(3)	0.31		Mn(5)	0.44		Mn(2')	0.36
	Mn(4)	0.21		Σ	1.71		Mn(1)	0.36
	Σ	1.79		Σ	1.08			
O(4):	P(1)	1.22	O(8):	P(2)	1.23	O(12):	Mn(1)	0.38
	Mn(4)	0.42		Mn(3)	0.34		Mn(4)	0.35
	Mn(4')	0.28		Mn(5)	0.34		Mn(2)	0.32
	Σ	1.92		Σ	1.91		Σ	1.05

by a strip of this double chain is also observed in hydrozincite [$Zn_5(CO_3)_2(OH)_6$]¹⁶ and pseudomalachite.^{1,5}

The secondary chain of M(4) and M(5) octahedra linked with the phosphate tetrahedra is more typical of anhydrous divalent transition metal phosphates such as $Co_3(PO_4)_2$.¹⁷ The resemblance of the secondary chain to these compounds is far from pronounced, being limited to the phosphate group's edge- and corner-sharing to metal-containing octahedra.

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Registry No. $Co_5(PO_4)_2(OH)_4$, 63301-39-3; $Mn_5(PO_4)_2(OH)_4$, 63301-40-6; $Co_3(PO_4)_2$, 13455-36-2; $Mn_3(PO_4)_2$, 14154-09-7.

Supplementary Material Available: Tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) S. Ghose, *Acta Crystallogr.*, **17**, 1051 (1964).
- (2) G. L. Shoemaker, J. B. Anderson, and E. Kostiner, *Am. Mineral.*, in press.
- (3) J. B. Anderson, G. L. Shoemaker, E. Kostiner, and F. A. Ruszala, *Am. Mineral.*, **62**, 115 (1977).
- (4) L. G. Berry, *Am. Mineral.*, **36**, 484 (1951).
- (5) P. B. Moore and J. Molin-Case, *Am. Mineral.*, **56**, 1539 (1971).
- (6) F. A. Ruszala and E. Kostiner, *J. Cryst. Growth*, **30**, 93 (1975).
- (7) L. Waldrop, *Z. Kristallogr. Kristallgeom., Kristallphys., Kristallchem.*, **131**, 1 (1971).
- (8) G. Germain, P. Main, and M. N. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
- (9) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Report ORNL-TM-305, Oak Ridge, Tenn., 1962.
- (10) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (11) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); *Acta Crystallogr., Sect. B*, **24**, 324 (1968).
- (12) "International Tables for X-Ray Crystallography", Mathematical Tables, Vol. II, Kynoch Press, Birmingham, 1968, p 295.
- (13) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Report ORNL-TM-306, Oak Ridge, Tenn., 1962.
- (14) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).
- (15) I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, **29**, 266 (1973).
- (16) S. Ghose, *Acta Crystallogr.*, **12**, 1051 (1964).
- (17) J. B. Anderson, E. Kostiner, M. C. Miller, and J. R. Rea, *J. Solid State Chem.*, **14**, 372 (1975).