

Structure of Hentschelite, $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$, a New Member of the Lazulite Group

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Abstract. $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$, $M_r = 399.198$, monoclinic, $P2_1/n$, $a = 6.984$ (3), $b = 7.786$ (3), $c = 7.266$ (3) Å, $\beta = 117.68$ (2)°, $V = 349.9$ (5) Å³, $Z = 2$, $D_x = 3.79$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 7.58$ mm⁻¹, $F(000) = 394$, $T = 293$ K, final $R = 0.037$ for 2157 unique reflections including the 320 unobserved ones ($I < 2\sigma_I$). $\text{Fe}(\text{OH})_2\text{O}_4$ octahedra and distorted $\text{Cu}(\text{OH})_2\text{O}_4$ polyhedra share faces to form $\text{Cu}_2\text{Fe}_2(\text{OH})_4\text{O}_8$ triple octahedral groups. These groups form a three-dimensional framework *via* common corners with phosphorus in tetrahedral interstices. Hentschelite is isostructural with the minerals of the lazulite group, lazulite, scorzalite and barbosalite. The coordination around copper is elongated tetragonal bipyramidal (Jahn–Teller effect), as is often observed for divalent copper. The small angle (16°) of the direction of elongation with [010] explains the rather large difference between the b axis of hentschelite and those of the other lazulite group minerals.

Introduction. The rare copper phosphate mineral hentschelite was found in 1984 by Mr K. Petitjean, Worms, in a silicified barite vein near Reichenbach, Odenwald, Federal Republic of Germany. The mineral was named after Dr Gerhard Hentschel, Hessisches Landesamt für Bodenforschung, Wiesbaden, Federal Republic of Germany. A mineralogical description of hentschelite has been given by Sieber, Tillmanns & Medenbach (1987).

Experimental. Preliminary peak-search and indexing routines and subsequent precession photographs yielded a monoclinic unit cell with extinction conditions $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ reflections consistent with space group $P2_1/n$. A crystal with dimensions $0.2 \times 0.3 \times 0.2$ mm, faces indexable as $\{011\}$, $\{\bar{1}11\}$ and $\{11\bar{1}\}$, was selected for three-dimensional data collection with an automatic four-circle diffractometer (Enraf–Nonius CAD-4), scintillation counter, monochromatized Mo $K\alpha$ radiation (graphite monochromator), $\omega/2\theta$ step scan mode, scan

width in θ : $(0.6 + 0.5 \tan \theta)^\circ$. The lattice constants were refined from the settings of 25 reflections with $20 < \theta < 27^\circ$. Intensity and orientation of three standard reflections were regularly monitored, measurement instability (Stout & Jensen, 1968) was less than 0.008 for all three reference reflections. A total of 2758 reflections with $\theta < 40^\circ$ were measured ($0 \leq h \leq 13$, $0 \leq k \leq 14$, $-12 \leq l \leq 12$). Corrections were made for Lorentz–polarization and absorption effects (linear absorption coefficient 7.58 mm⁻¹, minimum and maximum transmission factors 0.42 and 0.49). The averaging of symmetrically equivalent reflections gave 2157 unique reflections, 320 of which were considered to be unobserved ($I < 2\sigma_I$), $R_{\text{int}} = 0.017$. The structure was solved by Patterson and Fourier methods. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$; after a secondary-extinction correction [Zachariasen (1963), $g = 0.012$] final $R = 0.026$ ($wR = 0.032$) for 1837 observed reflections and $R = 0.037$ ($wR = 0.036$) for all 2157 reflections including the unobserved ones. Largest shift/e.s.d. ratio was less than 0.001 in the last cycle of refinement; H atoms could not be located in the final difference map which showed a maximum of $1.5 \text{ e } \text{Å}^{-3}$ close to the P position and a minimum of $-1 \text{ e } \text{Å}^{-3}$. Atomic scattering factors and correction factors for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974). Fractional atomic parameters and equivalent isotropic displacement factors are given in Table 1.* Interatomic distances and angles are shown in Table 2. For the determination and refinement of the crystal structure the program *SHELX76* (Sheldrick, 1976) was used; distances and angles were calculated with *SADIAN69* (Baur & Wenninger, 1969) and the structure plot was made with the program *STRUPLO84* (Fischer, 1985).

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44024 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Iron and copper ions are octahedrally coordinated by oxygen atoms and hydroxyl ions; the Cu(OH)₂O₄ polyhedron exhibits the characteristic Jahn–Teller distortion of four short and two longer bonds which is often found for divalent copper (Zemann, 1972). The arrangement of the four closer O atoms around copper is planar with a value of 360° for the sum of the four O–Cu–O angles and an average Cu–O distance of 1.975 Å. The two longer bonds have a length of 2.395 Å. The average Fe–O distance in the Fe(OH)₂O₄ octahedron is 2.010 Å. One Cu(OH)₂O₄ polyhedron and two Fe(OH)₂O₄ polyhedra share faces to form triple groups of composition CuFe₂(OH)₄O₈. These groups are linked together *via* hydroxyl ions as common corners; P atoms occupy tetrahedral interstices in the framework of triple groups. The individual phosphate groups are slightly distorted with P–O distances between 1.522 and 1.559 Å and an average tetrahedral angle of 109.5°. Every CuFe₂(OH)₄O₈ group is connected to four other identical groups and to eight PO₄ tetrahedra *via* common corners; each PO₄ tetrahedron is linked to four CuFe₂(OH)₄O₈ groups. Fig. 1 shows a polyhedral representation of the crystal structure.

There are five crystallographically different oxygen positions in the crystal structure. O1–O4 are bonded to phosphorus in the PO₄ group and to Fe³⁺ or Cu²⁺ with bond-strengths sums (Pauling, 1960) of 1.75–2.08, while O5 is only bonded to one Cu²⁺ and two Fe³⁺ with a bond-strengths sum of 1.33. It is this oxygen position to which the proton is assigned. A possible hydrogen bond is formed between O5 and O1 which have a short separation of 2.726 Å, but do not belong to the same coordination polyhedron.

Hentschelite is isostructural with the minerals of the lazulite group: lazulite, MgAl₂(OH)₂(PO₄)₂, scorzalite, FeAl₂(OH)₂(PO₄)₂ and barbosalite, FeFe₂(OH)₂(PO₄)₂ (Lindberg & Christ, 1959) and represents the Cu²⁺–Fe³⁺ member. Table 3 shows the lattice constants for the lazulite group minerals. The setting corresponds to space group *P*2₁/*n* with the shortest non-parallel vectors in the plane perpendicular to the twofold axis chosen as *a* and *c* (reduced cell), while the setting of Lindberg & Christ corresponds to space group *P*2₁/*c*.

There are rather large differences between the *a* and *b* lattice constants of hentschelite and those of the other minerals; this is due to the Jahn–Teller distortion of the Cu²⁺(OH)₂O₄ octahedron. The octahedron is elongated along O4–Cu–O4 with an angle of about 16° between this direction and the *b* axis, the length of which is therefore strongly increased by the distortion. O–O distances in the distorted square plane of the [4 + 2]-coordination around Cu are 2.596 Å for the edges shared with the FeO₄(OH)₂ octahedra and 2.976 Å for the unshared edges. The latter ones are considerably shorter than in lazulite which causes the decrease of the *a* lattice constant.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement factors (Å² × 10³)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*]
Cu	0.0	0.0	0.0	9.0 (1)
Fe	0.2799 (1)	0.2738 (1)	0.0122 (1)	6.8 (1)
P	0.5002 (1)	0.0970 (1)	0.7485 (1)	4.7 (2)
O1	0.2928 (2)	−0.0102 (2)	0.6348 (2)	9.3 (5)
O2	0.4751 (2)	0.2153 (2)	0.9026 (2)	11.3 (5)
O3	0.6901 (2)	−0.0318 (2)	0.8626 (2)	9.3 (5)
O4	0.5503 (2)	0.2035 (2)	0.5990 (2)	10.3 (5)
OH5	0.5226 (2)	0.3711 (2)	0.2703 (2)	7.2 (4)

$$* U_{eq} = \frac{1}{3}(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j)$$

Table 2. Interatomic distances (Å) and angles (°); estimated standard deviations are 0.002 Å for distances and 0.1° for angles

Cu–O3	1.933 (2×)	Fe–O2	1.926
Cu–OH5	2.016 (2×)	Fe–O1	1.930
Cu–O4	2.395 (2×)	Fe–O4	1.985
O3–O3	180.0	Fe–OH5	2.003
O3–O4	75.4	Fe–O3	2.060
O3–O4	104.6	Fe–OH5	2.158
O3–OH5	97.8	O1–O3	171.2
O3–OH5	82.2	O1–O4	93.1
O4–O4	180.0	O1–OH5	94.6
OH5–O4	106.7	O1–OH5	95.7
OH5–O4	73.3	O2–O1	91.8
OH5–OH5	180.0	O2–O3	91.1
		O2–O4	169.7
P–O2	1.522	O2–OH5	91.3
P–O4	1.531	O2–OH5	91.2
P–O1	1.538	O3–OH5	75.9
P–O3	1.559	O4–O3	82.7
O1–O3	107.0	O4–OH5	97.2
O2–O1	108.8	O4–OH5	79.4
O2–O3	111.0	OH5–O3	93.7
O2–O4	109.7	OH5–OH5	169.4
O4–O1	112.4		4.143
O4–O3	107.9	OH5...O1	2.726
		OH5...O2	3.459

Table 3. Lattice constants of the lazulite group minerals (setting *P*2₁/*n*)

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
Lazulite	7.16 (2)	7.26 (2)	7.13 (2)	119.11 (9)
Scorzalite	7.15 (2)	7.31 (2)	7.14 (2)	119.01 (9)
Barbosalite	7.25 (2)	7.46 (2)	7.35 (2)	118.25 (9)
Hentschelite	6.984 (3)	7.786 (3)	7.266 (3)	117.68 (2)

Transformation matrix *P*2₁/*c* to *P*2₁/*n*: 100/010/101̄.

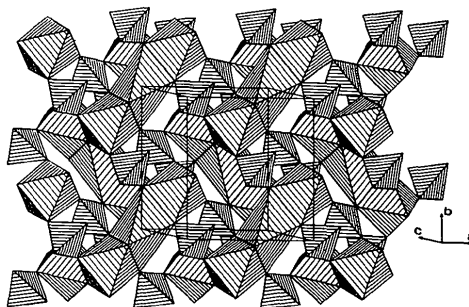


Fig. 1. Polyhedral representation of the crystal structure of hentschelite. Origin of the right-handed coordinate system is in the lower left rear corner.

Computing time was provided by the University Computer Centres at Würzburg and Mainz; crystals of hentschelite were supplied by Mr K. Petitjean.

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Tetrachlorophosphonium(V) Tetrachloroaurate(III)

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Abstract. $[\text{PCl}_4][\text{AuCl}_4]$, $M_r = 511.6$, orthorhombic, *Imma*, $a = 15.734$ (5), $b = 12.433$ (4), $c = 11.646$ (3) Å, $V = 2278$ Å³, $Z = 8$, $D_x = 2.98$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 14.9$ mm⁻¹, $F(000) = 1840$, $T = 293$ K, $R = 0.045$, $wR = 0.047$ for 1325 unique observed reflections [$F > 4\sigma(F)$]. The structure consists of isolated PCl_4^+ and AuCl_4^- ions with crystallographic symmetry 2 and *mm*2 respectively; there are two independent anions. The cations and anions form independent layers near $x = 0.25$, 0.75 and 0 , 0.5 respectively. $[\text{PCl}_4][\text{AuCl}_4]$ is isostructural with $[\text{PCl}_4][\text{ICl}_4]$. The independent bond lengths are P–Cl 1.924 (2), 1.930 (2), Au–Cl 2.274 (3), 2.273 (3), 2.270 (3), 2.277 (5) and 2.293 (4) Å.

Introduction. Continuing our study of the salts $\text{MCl}_x \cdot \text{AuCl}_4^-$, we here present the structure of $\text{PCl}_4^+ \cdot \text{AuCl}_4^-$. Yellow prisms and octahedra were obtained by a slight modification of the method of Lindet (1887), coated with an inert oil and mounted in glass capillaries. The compound is extremely moisture-sensitive.

Experimental. A yellow prism $0.35 \times 0.27 \times 0.27$ mm was used to measure 3205 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer with monochromated Mo $K\alpha$ radiation ($2\theta_{\text{max}} 60^\circ$, octants $+h + k + l$ and $-h - k - l$). Three check

reflections showed no significant intensity change. An empirical absorption based on ψ scans was applied; transmission factors 0.27–0.54. Of 1790 unique reflections ($R_{\text{int}} 0.027$), 1325 with $F > 4\sigma(F)$ were used for all calculations with *SHELX76* (Sheldrick, 1976). The index ranges after merging were: $h 0 \rightarrow 22$, $k 0 \rightarrow 17$, $l 0 \rightarrow 16$. Cell constants were refined from 2θ values of 59 reflections in the range $20\text{--}23^\circ$.

The structure was solved by the heavy-atom method and refined anisotropically on F (full matrix) to $R = 0.045$, $wR = 0.047$. The weighting scheme was $w^{-1} = \sigma^2(F_o) + 0.0003F_o^2$. An extinction correction of the form $F_{\text{corr}} = F_c/[1 + xF^2/\sin\theta]^{0.25}$ was employed, where x refined to $6.4(2) \times 10^{-7}$. 59 parameters, $S = 1.7$, max. $\Delta/\sigma 0.006$, max. features in final $\Delta\rho$ map $2 \text{ e } \text{Å}^{-3}$ (close to Au2). Atomic scattering factors those of *SHELX76*.

Discussion. Final atomic coordinates are given in Table 1,† with derived bond lengths and angles in Table 2. The structure consists of independent PCl_4^+ and AuCl_4^- ions. The cations are tetrahedral, although the crystallographic symmetry is only 2 (the P atom lies on the

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44065 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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