Hentschelite, $CuFe_2(PO_4)_2(OH)_2$, a new member of the lazulite group, and reichenbachite, $Cu_5(PO_4)_2(OH)_4$, a polymorph of pseudomalachite, two new copper phosphate minerals from Reichenbach, Germany

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Abstract

The minerals hentschelite and reichenbachite have been found as secondary minerals in a silicified barite vein at Reichenbach, Odenwald, Germany. They occur as dark green translucent crystals with a light green streak. Both minerals are nonfluorescent; they have no cleavage, a vitreous luster, and a hardness about 3.5. The analytical formula for hentschelite, based on 18 negative charges, is $Cu_{1.03}(Fe_{1.87}Al_{0.12})_{\Sigma 1.99}(P_{1.92}As_{0.08})_{\Sigma 2.00}O_8(OH)_2$, and the idealized formula is $CuFe_2(PO_4)_2(OH)_2$. Hentschelite is monoclinic, $P2_1/n$, with $a = 6.984(3)$ Å, $b = 7.786(3)$ Å, $c = 7.266(3)$ Å, $\beta = 117.68(2)°$, $Z = 2$, and $D_{calc} = 3.79$ g/cm³ for the ideal formula. The axial ratio $a:b:c = 0.8970:1:0.9332$. The strongest lines in the X-ray powder-diffraction pattern are $(d(Å),I,hkl)$ $4.81(50)(11\bar{1})$, $3.33(100)(111,021)$, $3.27(50)(11\bar{2},12\bar{1})$, $3.06(20)(20\bar{2})$, $2.400(20)(031,22\bar{2},130)$, $2.112(20)(13\bar{2})$, $1.669(20)(222,042)$, and $1.648(20)(22\bar{4})$. The mineral is biaxial positive with $\alpha = 1.843(3)$, $\beta = 1.848(3)$, and $\gamma = 1.945(3)$ ($\lambda = 589$ nm). The orientation is $Y = \mathbf{b}$, $X \approx [101]$; $2V_{obs}$ is small; and axial dispersion is strong with $r \gg v$.

The analytical formula for reichenbachite, based on 20 negative charges, is $Cu_{5.07}(P_{1.86}As_{0.11}Si_{0.01})_{\Sigma 1.98}O_8(OH)_4$, and the theoretical formula is $Cu_5(PO_4)_2(OH)_4$. Reichenbachite is monoclinic, $P2_1/a$, with $a = 9.198(3)$ Å, $b = 10.691(3)$ Å, $c = 4.476(2)$ Å, $\beta = 92.42(2)°$, $Z = 2$, and $D_{calc} = 4.35$ g/cm³ for the ideal formula. The axial ratio $a:b:c = 0.8603:1:0.4187$. The strongest lines in the X-ray powder-diffraction pattern are $(d(Å),I,hkl)$ $4.470(100)(001)$, $3.132(30)(21\bar{1})$, $3.012(30)(211)$, $2.945(20)(310)$, $2.814(25)(230)$, $2.410(100)(311,23\bar{1})$, $2.357(20)(231)$, $2.238(20)(14\bar{1})$, and $2.235(20)(002)$. The mineral is biaxial negative with $\alpha = 1.782(2)$, $\beta_{calc} = 1.833$, $\gamma = 1.867(5)$ ($\lambda = 589$ nm); $2V_{obs} = 76.3(4)°$ (from extinction curves). The orientation is $Y = \mathbf{b}$, $Z \wedge \mathbf{a} = 29°$ (in the obtuse angle of β), and dispersion is weak with $r < v$.

Introduction

The rare copper phosphate hydroxide minerals hentschelite and reichenbachite were found in 1984 by Mr. Klaus Petitjean in a silicified barite vein near Reichenbach, Odenwald, Federal Republic of Germany (FRG). The powder pattern of reichenbachite is practically identical with that of a pale blue, botryoidal crust from Brown's Prospect, Rum Jungle, Northern Territory, Australia, found with pseudomalachite in 1977 (Birch, 1979, and pers. comm., 1985). Reichenbachite was named after the locality, and hentschelite was named after Dr. Gerhard Hentschel, Hessisches Landesamt für Bodenforschung, Wiesbaden, FRG. Both minerals and their names have been approved prior to publication by the IMA Commission on New Minerals and Mineral Names. Type specimens of both minerals have been deposited at the

Naturhistorisches Museum, Mainz, FRG, and at the Mineralogisches Museum der Universität, Würzburg, FRG.

Occurrence

The silicified barite vein at Reichenbach, near Bensheim, Hessen, West Germany, is the largest among a number of similar silicified veins occurring in the crystalline rocks of the northwestern Odenwald area. Because of its peculiar pseudomorphic structures, the vein material is quarried in some places for use as an ornamental stone. The vein strikes west-northwest and dips vertically to steeply southward. Locally it reaches thicknesses of more than 10 m, and it can be traced in the field for about 5 km, within which distance it forms some prominent cliffs (for example, Teufelstein, Borstein, Hohenstein).

The wallrocks of the vein are composed of various diorites and gabbros as well as ortho- and paragneisses.

TABLE 1. Mineral phases of the silicified barite vein at Reichenbach, Odenwald, FRG

Elements	Carbonates	Phosphates
copper	azurite	(arsenates, vanadates)
silver	bismutite	agardite/mixite
	calcite	bayldonite
Sulfides	cerussite	carminite
chalcopyrite	malachite	clinobisvanite
chalcocite		cornubite
covellite	Sulfates	cornwallite
enargite	(chromates,	descloizite
tetrahedrite	molybdates,	duftite
galena	tungstates)	hentschelite
luzonite	barite	mimetite
	beudantite	mottramite
Oxides and	chalcanthite	olivenite
Hydroxides	linarite	pharmacosiderite
cuprite	vauquelinite	pseudomalachite
goethite	wulfenite	pucherite
hematite		pyromorphite
lepidocrocite	Halides	reichenbachite
pyrolusite	chlorargyrite	scorodite
quartz	iodargyrite	vanadinite
tenorite		weinschenkite

The vein-filling quartz is not massive, but displays an irregular pattern of crystallites of different shapes and sizes. According to Baier and Venzlaff (1961), this structure resulted from quartz overgrowths on a previously formed framework of thin, platy barite crystals. Subsequently, barite dissolved and left open spaces. These casts and also remaining voids between former barite crystals were filled with quartz. The pseudomorphous crystals show a preferred orientation perpendicular to the walls of the vein and occur in several generations separated by dense cryptocrystalline quartz. In the latter, occasional small stringers of galena, chalcopyrite, and minor tetrahedrite are observed, whereas within the pseudomorphous crystals, only isolated grains of ore minerals can be found. Under weathering conditions, these primary ore minerals have been partially oxidized, leading to a rich assemblage of secondary minerals, predominantly phosphates, arsenates, and vanadates (Table 1). These occur as disseminations and as drusy crusts.

At one locality near Katzenstein and Hohenstein [map coordinates r: 34 799070 h: 55 08230 map sheet 6218

TABLE 2. Electron-microprobe analyses (wt%)

	Reichenbachite $Cu_5(PO_4)_2(OH)_4$	Hentschelite $CuFe_2(PO_4)_2(OH)_2$
CuO	68.19	19.89
Fe_2O_3	—	36.37
Al_2O_3	—	1.52
SiO_2	0.10	0.03
P_2O_5	22.25	33.24
As_2O_5	2.11	2.11
H_2O^*	6.09	4.40
Sum	98.74	97.56

* Calculated with 4.0 (OH) per formula unit for reichenbachite and 2.0 (OH) per formula unit for hentschelite.

TABLE 3. Bond-strength sums (v.u.) of oxygen atoms in hentschelite and reichenbachite

	Hentschelite		Reichenbachite	
	Σ_1	Σ_2	Σ_1	Σ_2
O(1)	1.75	1.89	1.91	1.89
O(2)	1.75	1.95	1.98	2.03
O(3)	2.08	2.11	1.92	1.54
O(4)	2.08	1.96	1.98	1.87
O(5)	1.33	1.23	1.13	1.33
O(6)			1.07	1.32

Note: Calculated after Pauling (1960) (Σ_1) and Brown (1981) (Σ_2).

(Neunkirchen)], a block of rock was found containing clusters of hentschelite crystals, together with mimetite, beudantite, geothite, and quartz. Hentschelite is a very rare mineral, and only two specimens containing crystals of the mineral have been recovered so far.

Reichenbachite crystals have been found at several places near Borstein [map coordinates r: 34 77260 h: 55 08500 and r: 34 76920 h: 55 08650 on topographic map sheet 6218 (Neunkirchen)]. The mineral is associated with quartz, bayldonite, mimetite, malachite, duftite, goethite, and especially pseudomalachite. The close association of pseudomalachite with what is believed to be reichenbachite has also been reported by Birch (1979) from Brown's Prospect, Australia.

TABLE 4. Observed (FeKα radiation) and calculated X-ray powder-diffraction data for hentschelite

d_{calc}	I_{calc}	hkl	d_{obs}	I_{obs}
6.091	15	$10\bar{1}$	6.09	10
4.960	17	011	4.92	15
4.798	38	$11\bar{1}$	4.81	50
3.331	100	111, 021	3.33	100
3.287	58	$11\bar{2}$	} 3.27	50
3.280	13	$12\bar{1}$		
3.217	9	002	3.22	10
3.186	12	$21\bar{1}$	3.18	10
3.046	14	$20\bar{2}$	3.06	20
2.676	13	121	2.685	15
2.599	15	$22\bar{1}$	2.597	15
2.480	7	022	2.484	10
2.421	6	220	2.420	10
2.407	12	031		
2.399	5	$22\bar{2}$	} 2.400	20
2.393	5	130		
2.388	8	$13\bar{1}$	2.386	10
2.283	8	211	2.292	10
2.204	9	$31\bar{1}$	2.208	10
2.110	15	$13\bar{2}$	2.112	20
2.035	8	221	2.037	10
1.965	10	$31\bar{3}$	1.959	10
1.947	6	040	—	
1.746	5	$40\bar{2}$	1.746	10
1.665	24	222, 042	1.669	20
1.644	18	$22\bar{4}$	1.648	20
1.599	7	$33\bar{3}$	1.604	10
1.546	9	400	1.540	10
1.523	5	$40\bar{4}$	1.520	5
1.471	7	133	1.475	10
1.422	4	$25\bar{1}$	1.421	5
1.300	11	$44\bar{2}$	1.301	10

TABLE 5. Observed (Cu$K\alpha$ radiation) and calculated X-ray powder-diffraction data for reichenbachite

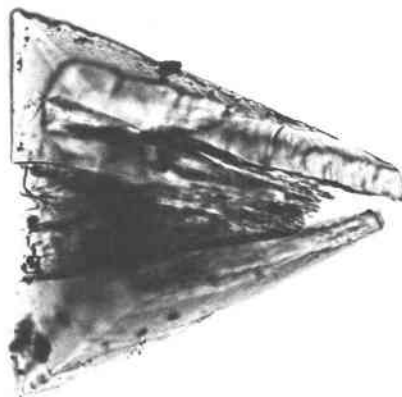| d_{calc}	I_{calc}	hkl	d_{obs}	I_{obs}
5.345	13	020	5.340	10
4.472	100	001	4.470	100
3.485	7	220	3.480	5
3.430	17	021	3.427	15
3.248	18	12$\bar{1}$	3.252	5
3.180	17	121	—	
3.131	31	21$\bar{1}$	3.132	30
3.012	31	211	3.012	30
2.945	19	310	2.945	20
2.816	22	230	2.814	25
2.792	16	22$\bar{1}$	2.795	15
2.687	6	13$\bar{1}$	2.683	5
2.648	17	131	2.650	10
2.566	15	140	2.569	10
2.507	11	31$\bar{1}$	2.505	5
2.415	29	311	} 2.410	100
2.411	87	23$\bar{1}$		
2.356	13	231	2.357	20
2.297	9	400	2.298	10
2.294	9	041	2.290	10
2.249	11	321	2.246	10
2.237	16	14$\bar{1}$	2.238	20
2.236	15	002	2.235	20
2.029	4	12$\bar{2}$	2.029	10
2.014	6	340	2.017	10
2.009	11	401	2.010	10
1.817	8	31$\bar{2}$	1.817	5
1.811	7	510	1.810	5
1.782	6	060	1.781	10
1.774	10	23$\bar{2}$	1.778	10
1.729	15	232	1.729	5
1.696	9	14$\bar{2}$	—	
1.676	4	142	1.677	5
1.655	9	061	1.653	5
1.569	10	402	1.569	10
1.531	8	15$\bar{2}$	1.533	5
1.514	8	540	1.512	5
1.507	7	170	1.505	5
1.431	5	17$\bar{1}$	1.429	5
1.425	6	171	1.421	5
1.408	9	460	1.407	5
1.357	7	63$\bar{1}$	1.357	5
1.353	6	46$\bar{1}$	1.353	5
1.333	12	461	1.333	10
1.304	9	233	—	

Fig. 1. Twinned crystal of hentschelite. For orientation and morphology, see Fig. 2; scale bar is 0.1 mm.

$As_{0.08})_{\Sigma 2.00}O_8(OH)_2$, or ideally $CuFe_2(PO_4)_2(OH)_2$. The empirical formula of reichenbachite, calculated on the basis of 20 negative charges, is $Cu_{5.07}(P_{1.86}As_{0.11}Si_{0.01})_{\Sigma 1.98}O_8(OH)_4$, or ideally $Cu_5(PO_4)_2(OH)_4$.

Bond-strength sums for hentschelite and reichenbachite, calculated after Pauling (1960) and Brown (1981), are given in Table 3. Hydrogen atom positions could not be localized in the crystal-structure determination (Sieber et al., 1984), but possible hydroxyl ion positions can be inferred from the individual bond-strength sums. For hentschelite, there are five crystallographically nonequivalent oxygen atoms, four of which are bonded to P in the PO_4 group and to Fe^{3+} or Cu^{2+} with bond-strength sums

CHEMISTRY

An electron microprobe (Cameca, Camebax microbeam, 15 kV, 6 nA) was used for chemical analyses. Table 2 gives average values of 10 wavelength-dispersive measurements with Al_2O_3, SiO_2, $AlPO_4$, $2Fe_2O_3 \cdot As_2O_5$, Fe_3O_4, $SrCuSi_4O_{10}$, and Mn metal as standards. The empirical formula for hentschelite, calculated on the basis of 18 negative charges, is $Cu_{1.03}(Fe_{1.87}Al_{0.12})_{\Sigma 1.99}(P_{1.92}$-

TABLE 6. Lattice constants of the lazulite-group minerals (setting $P2_1/n$)

	a (Å)	b (Å)	c (Å)	β (°)
Lazulite	7.16	7.26	7.13	119.11
Scorzalite	7.15	7.31	7.14	119.01
Barbosalite	7.25	7.46	7.35	118.25
Hentschelite	6.98	7.79	7.27	117.68

Note: Transformation matrix $P2_1/c$ to $P2_1/n$: 100, 0$\bar{1}$0, $\bar{1}$0$\bar{1}$.
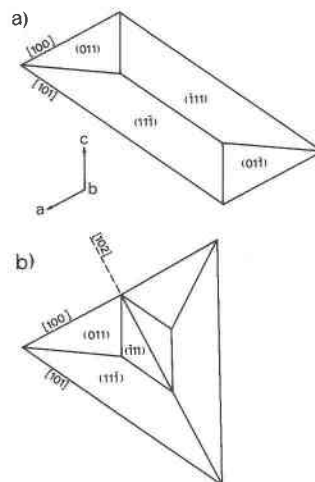

Fig. 2. Typical morphological development of a single crystal of hentschelite (a) constructed from the twinned specimen (b).
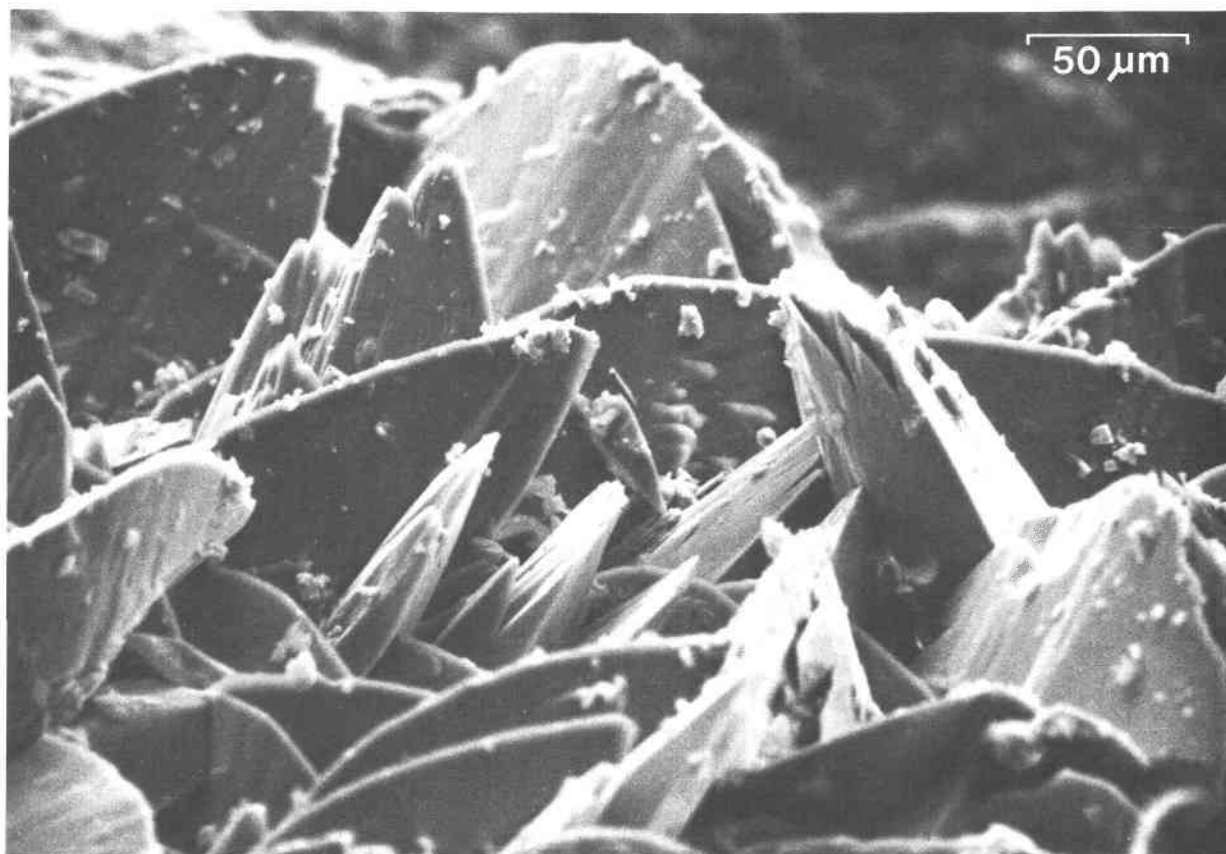
Fig. 3. SEM photomicrograph of reichenbachite crystals.

close to 2.0. The remaining atom is coordinated by one Cu^{2+} and two Fe^{3+} with a bond-strength sum of about 1.25 and is most likely a hydroxyl ion. It is part of a possible hydrogen bond to an oxygen atom of the PO_4 group at a distance of 2.73 Å. The crystal-structure determination of reichenbachite shows six crystallographically nonequivalent oxygen atoms, four of which are bonded to one P and two or three Cu atoms, and the two remaining ones are bonded to three Cu atoms each. From the bond-strength sums, it appears most likely that the former four positions are occupied by oxide ions and the latter two by hydroxyl ions, a distribution which was also suggested by Anderson et al. (1977) in their structure determination of synthetic $Cu_5(PO_4)_2(OH)_4$. The O–H $\cdots$ O distances of possible hydrogen bonds are 2.84 and 2.87 Å.

CRYSTALLOGRAPHY

Hentschelite, $CuFe_2(PO_4)_2(OH)_2$, crystallizes in the monoclinic system, space group $P2_1/n$ with lattice constants $a = 6.984(3)$ Å, $b = 7.786(3)$ Å, $c = 7.266(3)$ Å, $\beta = 117.68(2)°$, $V = 349.9$ Å^3, and $Z = 2$. The lattice constants were refined from the settings of 25 reflections with $20° < \theta < 27°$, which had been centered on an automatic 4-circle diffractometer (Enraf-Nonius CAD IV) using $MoK\alpha$ radiation with a graphite monochromator. The

refinement of the powder data gave much larger standard deviations because only a few crystals were available for a Debye-Scherrer photograph. Table 4 shows the observed and calculated X-ray powder-diffraction data for hentschelite.

Reichenbachite, $Cu_5(PO_4)_2(OH)_4$, crystallizes in the monoclinic system, space group $P2_1/a$, with the lattice constants $a = 9.198(3)$ Å, $b = 10.691(3)$ Å, $c = 4.476(2)$ Å, $\beta = 92.42(2)°$, $V = 439.8$ Å^3 and $Z = 2$. The lattice constants were refined from the settings of 50 reflections with $23° < \theta < 30°$, using the same conditions as for hentschelite. Lattice constants refined from single-crystal and powder data agree within two estimated standard deviations. The observed and calculated powder-diffraction data for reichenbachite are given in Table 5.

PHYSICAL AND OPTICAL PROPERTIES

Both hentschelite and reichenbachite are dark green with a light green streak; they are translucent and nonfluorescent and have a vitreous luster. No cleavage is observed, and the fracture is irregular. The densities could not be measured owing to the small amounts of both minerals found so far. The calculated density for hentschelite is 3.79 g/cm³ based on the theoretical formula with $Z = 2$. The equivalent for reichenbachite is 4.35 g/cm³. Both minerals have a hardness of about 3.5.

Most crystals of hentschelite from Reichenbach occur as characteristically twinned specimens up to 0.4 mm in diameter (Fig. 1). As illustrated in Figure 2, the crystals are twinned around [102] and the faces of individual crystals may be indexed as $\{011\}$, $\{\bar{1}11\}$ and $\{11\bar{1}\}$. The angle between [102] and c^* is 1.04°.

Hentschelite is biaxial positive with the measured refractive indices $\alpha = 1.843(3)$, $\beta = 1.848(3)$, $\gamma = 1.945(3)$ ($\lambda = 589$ nm), and a small $2V$. The optical orientation is $Y = b$ and $X \approx [101]$, $X \wedge a = 61(2)°$ in the obtuse angle of β. The pleochroism is very weak from $X =$ blue-green to $Y =$ yellow-green, and the axial dispersion is strong with $r \gg v$. On the basis of the Gladstone-Dale relationship (Mandarino, 1981), the compatibility $[1 - (K_P/K_C) = 0.025]$ is excellent.

Reichenbachite crystals are as much as $0.3 \times 0.3 \times 0.06$ mm, are lancet-shaped (Fig. 3), and are often intergrown with pseudomalachite. The mineral is biaxial negative with measured refractive indices $\alpha = 1.782(2)$, $\beta_{calc} = 1.833$, and $\gamma = 1.867(5)$ ($\lambda = 589$ nm), $2V_{meas} = 76.3(4)°$ (from extinction curves). The optical orientation is $Y = b$, $Z \wedge a = 29(2)°$ (in the obtuse angle of β). Dispersion is weak with $r < v$ and pleochroism is very weak from $X =$ bright emerald-green to $Z =$ emerald-green. The compatibility $(1 - (K_P/K_C) = -0.027)$ is excellent.

DISCUSSION

Three polymorphs of $Cu_5(PO_4)_2(OH)_4$ are known, namely the mineral pseudomalachite (Ghose, 1963; Shoemaker et al., 1977) and two synthetic polymorphs, "PPM" (Anderson et al., 1977) and "QPM" (Shoemaker et al., 1981; Shoemaker and Kostiner, 1981). Reichenbachite is identical to "PPM." Indeed, our determination of the crystal structure of reichenbachite gave atomic coordinates that are identical (maximal deviation < 3 esd) to those reported by Anderson et al. (1977) for "PPM." The compound "QPM" has so far not been identified in nature, although Shoemaker and Kostiner (1981) reported the probable occurrence of all three polymorphs on a cornetite-containing specimen (Harvard no. 90308). Closer inspection of other pseudomalachite specimens may reveal the presence of the other polymorphic modifications.

For the analogous arsenate compound, two polymorphs are known, those being the minerals cornubite and cornwallite (Claringbull et al., 1959). Single crystals of cornubite have also been found in Reichenbach (Tillmanns et al., 1985). Although cornwallite is isostructural with pseudomalachite, no known phosphate analogue of cornubite or arsenate analogues of reichenbachite or "QPM" have been reported.

Hentschelite is isostructural with the minerals of the lazulite group—lazulite $MgAl_2(PO_4)_2(OH)_2$, scorzalite $FeAl_2(PO_4)_2(OH)_2$, and barbosalite $FeFe_2(PO_4)_2(OH)_2$ (Lindberg and Christ, 1959)—and represents the Cu^{2+}-

Fe^{3+} member. Table 6 shows the lattice constants for the lazulite-group minerals. The axial setting corresponds to space group $P2_1/n$, with the shortest nonparallel vectors in the plane perpendicular to the twofold axis chosen as a and c (reduced cell). The cell chosen by Lindberg and Christ (1959) corresponds to space group $P2_1/c$ and is not reduced. The large difference between the b cell edge of hentschelite and those of the other minerals is due to the Jahn-Teller distortion of the $Cu^{2+}O_4(OH)_2$ octahedron, which has four Cu–O distances of 1.933–2.016 Å and two of 2.395 Å, with an angle of about 16° between b and the long axis of the octahedron.

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