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Posnjakite: ${}^{2}_{\infty}[Cu_4(OH)_6(H_2O)O]$ octahedral sheets in its structure

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Abstract. The crystal structure of posnjakite (space group *Pa*, $a = 10.578$, $b = 6.345$, $c = 7.863$ Å, $\beta = 117.98°$) was determined by direct methods and refined to a final R value of 0.05. The structure is characterized by corrugated sheets of distorted copper octahedra with crystal chemical formula ${}^{2}_{\infty}[Cu_4(OH)_6(H_2O)O]$. Sulphate groups are connected to one side of the octahedral sheet by corner sharing. The resultant composite octahedral-tetrahedral layers are connected to each other by hydrogen bonds. The crystal chemical formula of posnjakite is $Cu_4(SO_4)(OH)_6 \cdot H_2O$ with two such units in the unit cell.

The relations of posnjakite with other copper sulphate hydrates are noted and discussed.

Introduction

Posnjakite was first found in an ore quartz vein of the Nura-Taldinsk tungsten deposit in central Kazachstan by Komkov and Nefedov (1967) who, on the basis of microchemical tests and the supposed paramorphism of the mineral after langite, proposed the chemical formula $Cu_4(SO_4)(OH)_6 \cdot H_2O$; they determined the following unit cell parameters: $a = 9.80(5)$, $b = 6.32(5)$, $c = 7.85(5)$ Å, $\beta = 107(1)°$ (space group not stated). Posnjakite in association with langite was also found at Borovec (Czechoslovakia) and studied by Miskovsky (1975), who also synthesized it, and by Sekanina (1975) who, on the basis of careful goniometric measures, asserted "that (1) posnjakite crystals are limited by their own faces and they are not paramorphs after langite, (2) that they are tabular on $(\bar{1}01)$ and (3) that (231) ist the twin plane"..

Other occurrences of posnjakite were also reported, although without chemical or crystallographic data, from Drakewall Mine, Cornwall (Knight and Barstow, 1970), from Blackcraig (Livingstone, Macpherson, and Jackson, 1976) and from Fowey Consols (Embrey, quoted in Knight and

Barstow, 1970). We thought that a crystal structure investigation of posnjakite would be of value in clarifying its crystal chemical formula and relationships with langite, such as well as its relations with other basic hydrate copper sulphates, as wroewolfeite $Cu_4(SO_4)(OH)_6 \cdot 2\,H_2O$ (Dunn and Rouse, 1975) and ktenasite $Zn_2(Cu,Zn)_8(SO_4)_4(OH)_{12} \cdot 12\,H_2O$ (Mellini and Merlino, 1978). After many trials, we succeeded in finding suitable crystals through the kindness of Dr. J. P. Fuller of the British Museum (Natural History), who sent us a fine specimen of posnjakite from Fowey Consols.

Experimental

Weissenberg and precession photographs showed *2/m* Laue symmetry and systematic absences in $h0l$ for $h = 2n + 1$, indicating Pa or $P2/a$ as possible space groups (this setting was preferred to the standard orientation of a c glide plane for the straightforward relations with the unit cell of other copper sulphate hydroxide hydrate minerals). The unit cell parameters, determined by photographic methods and refined by least squares fitting of 25 θ values, measured by a Philips PW 1100 single crystal automatic diffractometer, using graphite monochromatized Mo$K\alpha$ radiation (λ = 0.7107 Å), were $a = 10.578(5)$, $b = 6.345(3)$, $c = 7.863(3)$, $\beta = 117.98(5)°$. Our unit cell transforms to the cell of Komkov and Nefedov (1967), with $P2/n$ or Pn space group, according to the transformation matrix $[\bar{1}0\bar{1}|0\bar{1}0|001]$. Intensity data were collected on a plate crystal of nearly $0.18 \times 0.10 \times 0.03\ mm^3$, but the same diffractometer and same radiation, using $\theta - 2\theta$ scan, scan speed $0.05°\,s^{-1}$, scan width 1.20°, from 3 to 30° θ. In the intensity data collection step 576, of 1,444 available reflections, were skipped on the basis of a pre-scan test as they had $I_{top} - 2\sqrt{I_{top}} < I_{back}$, with I_{top} and I_{back} indicating peak intensity and background intensity, respectively. The remaining 868 reflections were corrected for Lorentz-polarization factors as well as for absorption by the semi-empirical method of North, Phillips, and Mathews (1968). In the subsequent structure factor calculations the scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography, vol. IV (1974).

Structure determination

The crystal structure of posnjakite was solved by MULTAN program (Main, Woolfson, and Germain, 1971) in the Pa space group, as the statistical averages and distribution of E_{hkl} values indicated a non-centrosymmetric distribution of atoms in the unit cell. The application of direct methods pointed to locating all the atoms, apart from the hydrogen atoms, as an asymmetric unit. Full matrix least squares refinement, with individual isotropic thermal parameters, led to $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.066$ and $R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2} = 0.069$, where w was assigned as the reciprocal of the variance on F_o, estimated from counting statistics. The introduction of anisotropic thermal parameters for copper and sulphur atoms lowered R_1 to 0.052. A ΔF synthesis, calculated at this stage, located the hydrogen atoms, apart from that one bonded to O(5) atom. They were introduced in the structure factor calculation, with a fixed $B = 2\,\text{Å}^2$, obtaining $R_1 = 0.050$ and $R_2 = 0.054$. The final atomic positional and thermal parameters are reported in Table 1. Observed and calculated structure factors were deposited at Akademische Verlagsgesellschaft, Wiesbaden.

Structure description

The crystal structure of posnjakite, shown in Figure 1, is made up by sheets of six-coordinated copper atoms, parallel to (001). The copper coordination is strongly distorted from the octahedron toward the elongated tetragonal bipyramid (Table 2). The ligands making up the sheet are hydroxyl groups, water molecules, and oxygen atoms. Sulphate groups are linked on one side of the pseudo-octahedral sheet by corner sharing. The connection between successive sheets is assured by hydrogen bonds.

Copper coordination: Four independent copper atoms are present in the unit cell. All of them are six-coordinated, with remarkable distortions from the octahedral geometry, due to the Jahn-Teller effect. Among these four polyhedra, that surrounding Cu(3) is the most regular, with the minor value of the difference between the average values of axial and equatorial bond distances. Whereas Cu(3) is surrounded by six hydroxyl anions, Cu(2) and Cu(4) cations are surrounded by four hydroxyl anions [O(1) to O(6) atoms], a water molecule, O(8), and an oxygen atom belonging to a sulphate group, O(7). Within Cu(1), Cu(2), and Cu(4) coordination polyhedra, the maximum bond distance is associated with the O(8) water molecule (2.472, 2,948, and 2.751 Å, respectively); the other axial bond is formed with the O(7) sulphur linked atom (2.351, 2.275, and 2.311 Å, respectively); all the shortest bond distances are with hydroxyl anions.

The resulting sheet has crystal chemical formula ${}^{2}_{\infty}[Cu_4(OH)_6(H_2O)O]$. It can be derived from the pseudo-octahedral sheets present in ktenasite, serpierite, and devillite (Mellini and Merlino, 1978), with ${}^{2}_{\infty}[Cu_4(OH)_6O_2]^{2-}$ crystal chemical formula, by substituting one of the two oxygen atoms with a water molecule, with consequent halving of the number of sulphate groups linked to the sheet. While the ktenasite sheet is negatively charged, the posnjakite sheet is neutral. Therefore, whereas in posnjakite equal sheets succeed each other in the [001] direction, in ktenasite they alternate with insulated $Zn(H_2O)_6^{2+}$ octahedra and in serpierite and devillite calcium octahedra are formed by three intersheet water molecules and three oxygen atoms of the sulphate groups.

Table 1. Positional and thermal parameters for heavy atoms, with e.s.d.'s in parentheses. Positional parameters of the hydrogen atoms as found by ΔF synthesis. Anisotropic thermal parameters are in the form exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$

	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.5621	0.5189(3)	0.9774	0.0007(4)	0.0032(6)	0.0058(8)	0.0000(4)	0.0013(4)	0.0007(6)
Cu(2)	0.0730(2)	0.9856(4)	0.0185(3)	16(4)	46(6)	49(8)	0(4)	8(4)	8(6)
Cu(3)	0.8199(3)	0.7494(5)	0.0027(5)	13(2)	32(5)	56(4)	0(2)	14(2)	6(2)
Cu(4)	0.3193(3)	0.7531(5)	−0.0012(5)	20(2)	42(5)	49(4)	0(2)	16(2)	−3(2)
S	0.6333(6)	0.7179(7)	0.4233(8)	33(4)	93(9)	29(7)	−7(6)	0(5)	0(7)
O(1)	0.361(2)	0.544(2)	0.847(2)	0.9(3)					
O(2)	0.862(2)	0.998(2)	0.885(2)	0.7(3)					
O(3)	0.280(2)	0.953(3)	0.149(2)	0.8(3)					
O(4)	0.034(2)	0.721(3)	0.121(2)	1.1(3)					
O(5)	0.774(2)	0.496(2)	0.119(3)	1.3(3)					
O(6)	0.609(1)	0.776(2)	0.879(2)	0.7(2)					
O(7)	0.561(1)	0.753(2)	0.209(2)	0.9(2)					
O(8)	0.045(2)	0.700(2)	0.707(2)	1.7(2)					
O(9)	0.030(2)	0.251(2)	0.494(3)	3.9(4)					
O(10)	0.256(1)	0.143(2)	0.515(2)	2.6(3)					
O(11)	0.184(2)	0.509(3)	0.458(3)	4.4(4)					
H(1)	0.34	0.51	0.84	2					
H(2)	0.35	0.02	0.79	2					
H(3)	0.32	0.89	0.31	2					
H(4)	0.08	0.71	0.26	2					
H(6)	0.58	0.77	0.81	2					
H(81)	0.01	0.60	0.61	2					
H(82)	0.01	0.72	0.62	2					

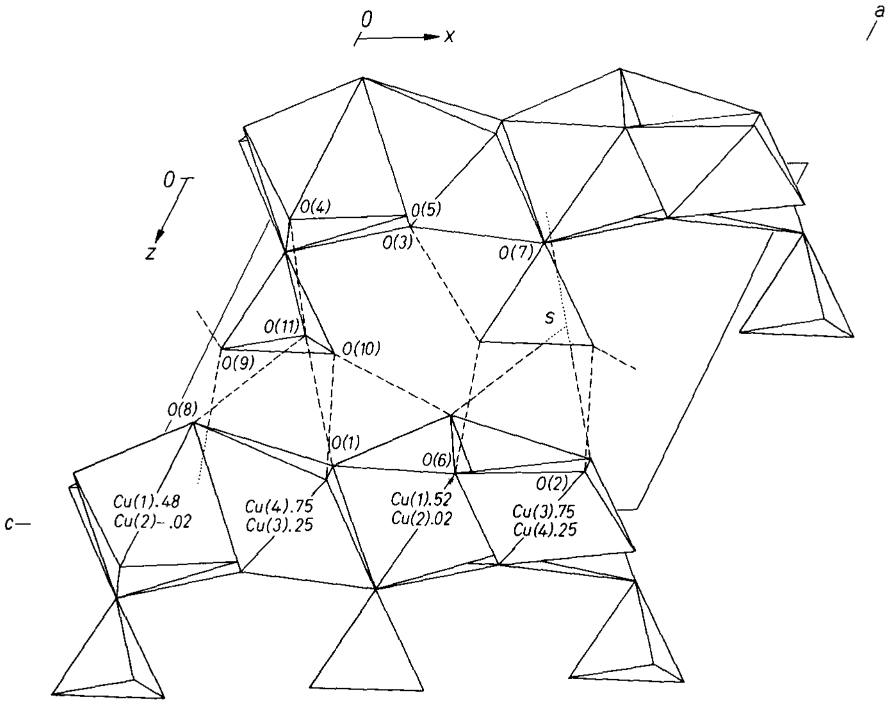

Fig. 1. Crystal structure of posnjakite, as seen along [001]; the y coordinate of copper atoms is given in the figure

Hydrogen bond system and bond valence balance

Table 3 reports all the distances between oxygen atoms not belonging to the same polyhedron and less than 3.2 Å. From these data, as well as from the hydrogen atom positions found in the ΔF synthesis, it is possible to derive the hydrogen bond network illustrated in Figure 1; only O(5) hydroxyl anion is not engaged in hydrogen bonding. Acceptors in the hydrogen bond system are the 'free' oxygen atoms of the sulphate group. Table 4 reports the bond strengths associated with the various bonds, calculated following Brown and Shannon (1973); under column $\Sigma c'_v$ we report the sum of bond strengths reaching the anion after correction for hydrogen bonding, where the strength associated with the various hydrogen bonds was estimated following Donnay and Allmann (1970).

Concluding remarks

As already stated, the crystal structures of posnjakite, ktenasite, serpierite, and devillite are characterized by the presence of a distorted octahedral sheet

Table 2. Bond distances (Å) in the coordination polyhedra, with e.s.d.'s in parentheses

Cu(1) – O(1)	1.887(15)	Cu(2) – O(3)	1.945(14)
– O(6)	1.971(14)	– O(2) iv	1.971(14)
– O(5) ii	1.987(16)	– O(4)	1.990(16)
– O(4) vii	1.999(16)	– O(6) x	2.007(14)
– O(7) ii	2.351(15)	– O(7) ix	2.275(15)
– O(8) vi	2.472(16)	– O(8) iii	2.948(16)
Cu(3) – O(6) iii	1.977(15)	Cu(4) – O(3)	1.908(18)
– O(2) iii	1.981(17)	– O(1) iii	1.964(19)
– O(4) i	2.013(16)	– O(2) x	1.973(17)
– O(5)	2.018(19)	– O(5) xi	2.011(17)
– O(3) v	2.351(17)	– O(7)	2.311(12)
– O(1) viii	2.377(17)	– O(8) iii	2.751(12)
S – O(7)	1.505(15)		
– O(9) vi	1.461(26)		
– O(10) vi	1.450(15)		
– O(11) vi	1.516(19)		

Symmetry code:

i	atom at	$1+x$	y	z
ii	atom at	x	y	$1+z$
iii	atom at	x	y	$-1+z$
iv	atom at	$-1+x$	y	$-1+z$
v	atom at	$1/2+x$	$2-y$	z
vi	atom at	$1/2+x$	$1-y$	z
vii	atom at	$1/2+x$	$-1+y$	$1+z$
viii	atom at	$1/2+x$	$1-y$	$-1+z$
ix	atom at	$-1/2+x$	$2-y$	z
x	atom at	$-1/2+x$	$2-y$	$-1+z$
xi	atom at	$-1/2+x$	$1-y$	z

Table 3. Shortest O – O distances (Å) with hydrogen bond strength (v.u.)

	Distance	Hydrogen bond strength
O(1) – O(11)	2.746	0.189
O(2) – O(10)	2.732	0.196
O(3) – O(9)	3.047	0.082
O(4) – O(11)	2.715	0.203
O(6) – O(9)	2.737	0.193
O(8) – O(10)	2.872	0.140
O(8) – O(11)	3.189	0.062

Table 4. Bond strengths balance (v.u.)

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	S	Σc_v	$\Sigma c'_v$
O(1)	0.564		0.166	0.456		1.186	0.997
O(2)		0.447	0.436	0.445		1.328	1.132
O(3)		0.480	0.176	0.532		1.188	1.106
O(4)	0.415	0.425	0.400			1.240	1.037
O(5)	0.429		0.395	0.402		1.226	1.226
O(6)	0.447	0.407	0.440			1.294	1.101
O(7)	0.176	0.209		0.193	1.350	1.928	1.928
O(8)	0.135	0.053		0.076		0.264	0.062
O(9)					1.521	1.521	1.796
O(10)					1.567	1.567	1.903
O(11)					1.312	1.312	1.766
Σa_v	2.166	2.021	2.013	2.104	5.750		

Σc_v: sums of bond strengths reaching the anion
$\Sigma c'_v$: sums of bond strengths reaching the anion after correction for hydrogen bond
Σa_v: sums of bond strengths reaching the cation

with crystal chemical formula $^{2}_{\infty}[Cu_4(OH)_6O_m(H_2O)_{2-m}]^{2(1-m)}$ with $m = 1$ in posnjakite and $m = 2$ in the other three minerals. The substitution $O^{2-} - H_2O$ is related to the number of sulphate groups bonded to the sheet; moreover the sheet is neutral for $m = 1$ but is negatively charged for $m = 2$, which results in the presence of intersheet cations. The crystal chemistry and structure of the mentioned minerals can be easily described by the following formulae:

$[(Cu,Zn)_4(OH)_6(SO_4)_2]^{2-}$	$[Zn(H_2O)_6]^{2+}$	Ktenasite
$[(Cu,Zn)_4(OH)_6(SO_4)_2]^{2-}$	$[Ca(H_2O)_3]^{2+}$	Serpierite
$[Cu_4(OH)_6(SO_4)_2]^{2-}$	$[Ca(H_2O)_3]^{2+}$	Devillite
$[Cu_4(OH)_6(SO_4)(H_2O)]$		Posnjakite

These formulae clearly explain the relationships in the cell parameters and unit cell contents among these minerals, reported and compared in Table 6 of our paper on the crystal structure of ktenasite (Mellini and Merlino, 1978). The same Table 6 gave also the crystal data for langite and wroewolfeite: the cell content assumed for langite is $Cu_8(SO_4)_2(OH)_{12} \cdot 2\,H_2O$, as reported in the literature; the most recent chemical analysis on langite (Pierrot and Sainfield, 1958) gives a water content H_2O^- of 3.7%, which could correspond to two more water molecules in the unit cell. Moreover with the cell data given by Wappler (1971) ($a = 6.05$, $b = 11.25$, $c = 7.14$ Å, $\alpha = 90°$), calculated densities of 3.215 and 3.338 $g\,cm^{-3}$ were obtained for the chemical compositions $Cu_8(SO_4)_2(OH)_{12} \cdot 2\,H_2O$ and $Cu_8(SO_4)_2(OH)_{12} \cdot 4\,H_2O$, respectively. Since Pierrot and Sainfield (1958) gave a measured density of 3.31 g cm^{-3}, strong evidence exists that the last formula is the correct one for langite. Langite thus appears dimorphous to wroewolfeite to which it is crystallographically closely related (Dunn and Rouse, 1975). The crystal structure of langite, studied by Wappler (1971), is built up by distorted octahedral sheets similar to those present in the other minerals of the group. One ligand site is vacant however and three of the four copper atoms in the asymmetric unit are really five-coordinated. As in posnjakite, sulphate groups are linked on one side of the sheets; one water molecule outside the octahedral sheet is linked to the sulphate groups by hydrogen bonding. Although the main features of the structure appear correct, some uncertainties remain concerning the number and position of the ligands: the work was based on the chemical composition $Cu_8(SO_4)_2(OH)_{12} \cdot 2\,H_2O$ and the accuracy of the determination is low (two-dimensional data, with R values of 0.125 and 0.158 for $0kl$ and $hk0$ reflections, respectively). In particular we maintain that the supposed vacant position is occupied by a water molecule directly linked to copper cations, thus obtaining an octahedral sheet with crystal chemical formula $^2_\infty[Cu_4(OH)_6(H_2O)O]$, exactly like that given for posnjakite. By analogy to posnjakite, ktenasite, serpierite, and devillite, the crystal chemistry and structure of langite can be described by the formula

$[Cu_4(OH)_6(SO_4)(H_2O)][H_2O]$ Langite.

This formula probably holds also for wroewolfeite. To definitely prove our proposal, accurate structural studies with full three-dimensional data for langite and wroewolfeite would be necessary.

References

Brown, I. D., Shannon, R. D.: Empirical bond strength- bond length curves for oxides. Acta Crystallogr. **A29**, 266–282 (1973)

Donnay, G., Allmann, R.: How to recognize O^{2-}, OH^- and H_2O in crystal structures determined by X-rays. Amer. Mineral. **55**, 1003–1015 (1970)

Dunn, P. J., Rouse, R. C.: Wroewolfeite, a new copper sulphate hydroxide hydrate. Mineral. Mag. **40**, 1–5 (1975)

International Tables for X-ray Crystallography, Vol. IV, Ed. J. A. Ibers and W. C. Hamilton. Birmingham: Kynoch Press (1974)

Knight, J. R., Barstow, R. W.: Posnjakite from Cornwall. Mineral. Mag. **37**, 740 (1970)

Komkov, A. I., Nefedov, E. I.: Posnjakite, a new mineral (in Russian). Zap. Vses. Min. Obshch **96**, 58–62 (1967)

Livingstone, A., Macpherson, H. G., Jackson, B.: Wroewolfeite and other langite-group minerals from Blackcraig, Kirkcudbrightshire. Mineral. Mag. **40**, 893–894 (1976)

Main, P., Woolfson, M., Germain, G.: MULTAN, a computer program for the automatic solution of crystal structures. University of York (1971)

Mellini, M., Merlino, S.: Ktenasite, another mineral with ${}^{2}[(Cu,Zn)_2(OH)_3O]^-$ octahedral sheets. Z. Kristallogr. **147**, 129–140 (1978)

Miskovsky, J.: Posnjakit a langit z Borovce u Bystrice nad Pernstejnem. Casopis Mineral. Geol. **20**, 75–79 (1975)

North, A. C. T., Phillips, D. C., Scott Mathews, F.: A semi-empirical method of absorption correction. Acta Crystallogr. **A 24**, 351–359 (1968)

Pierrot, R., Sainfield, P.: Sur la langite des Vosges. Bull. Soc. franc. Miner. Crist. **81**, 257–260 (1958)

Sekanina, J.: To the problem of langite and posnjakite. Casopis Mineral. Geol. **20**, 349–358 (1975)

Wappler, G.: Zur Kristallstruktur von Langit, $Cu_4(OH)_6/SO_4H_2O$. Ber. deutsch. Ges. geol. Wiss. B Miner. Lagerstättenf. **16**, 175–203 (1971)