

## Crystal structure of $\text{Na}_4[\text{Cu}_4\text{O}_2(\text{SO}_4)_4]\cdot\text{MeCl}$ (Me: Na, Cu, $\square$ ) – the synthetic Na-analogue of piypite (caratiite)

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### ABSTRACT

The crystal structure of  $\text{Na}_4[\text{Cu}_4\text{O}_2(\text{SO}_4)_4]\cdot\text{MeCl}$  (Me: Na, Cu,  $\square$ ) has been solved by direct methods and refined to  $R1 = 0.028$  using 2466 independent reflections. The compound is tetragonal with space group  $P4/n$ ,  $a = 18.451(1)$  Å,  $c = 4.9520(2)$  Å,  $Z = 4$ . The two main building units running parallel to the  $c$ -axis comprise: (1) slabs containing  $\text{SO}_4$  and  $\text{OCu}_4$  tetrahedra; and (2) chains of corner sharing  $\text{Me}(\text{Cl},\text{O})_6$  octahedra. The displacement ellipsoids of the atoms occupying the Me sites and of the Cl ions indicate a short-range static disorder. Copper in the slabs exhibits a (4+1) coordination. Both elements form a tunnel structure in which additional Na atoms are incorporated for charge compensation. The structure is closely related to the mineral piypite ( $\text{K}_4\text{Cu}_4\text{O}_2(\text{SO}_4)_4\cdot\text{MeCl}$  (Me: Na, Cu,  $\square$ )):  $a \approx \sqrt{2}\cdot a_{\text{piy.}}$ ;  $c \approx c_{\text{piy.}}$ . Furthermore, the structure has a pronounced pseudo-translational symmetry: apart from some of the oxygen sites, all of the nineteen crystallographically distinct positions are related by a pseudo F centring.

**KEYWORDS:** piypite (caratiite), crystal structure.

### Introduction

To date, only a few detailed crystal structure analyses have been performed on members of the group of alkali chlorosulphates. Chlorothionite ( $\text{K}_2\text{CuCl}_2(\text{SO}_4)$ ; Giacobozzo *et al.*, 1976), kamchatkite ( $\text{KCu}_3\text{OCl}(\text{SO}_4)_2$ ; Varaksina *et al.*, 1990) and caratiite ( $\text{K}_4\text{Cu}_4\text{O}_2(\text{SO}_4)_4\cdot\text{MeCl}$  (Me: Na, Cu,  $\square$ ); Effenberger and Zemmann, 1984) are examples of naturally occurring compounds from this group. The name caratiite has been discredited and the mineral is now called piypite (Jambor and Puziewicz, 1990). Furthermore, Effenberger (1985a) reported the structure of synthetic  $\text{K}_4\text{Cu}_4\text{O}_2(\text{SO}_4)_4\cdot\text{KCl}$  isotypic with piypite. In the course of our crystal chemical investigations on chlorosulphate apatite structures, crystals of a new piypite-related phase were obtained as a by-product. The present paper

reports the crystal structure of this synthetic compound and its relationship to piypite.

### Experimental

#### Crystal growth and chemical analysis

Single crystals were grown in porcelain crucibles. The reagents  $\text{Na}_2\text{SO}_4$  (Aldrich, 99.99%),  $\text{CaSO}_4$  (Merck, p.a.),  $\text{CaCl}_2$  (Fluka, 99%) and  $\text{CuCl}_2$  (Aldrich, 99.99%) were mixed carefully in an agate mortar. A batch of 8 g was placed in a covered 100 ml crucible. The starting material was heated in air from room temperature to 605°C over 6 h, and held at this temperature for 16 h to homogenize the melt. The melt was cooled in two steps, first at a cooling rate of 5°C/h to 570°C, subsequently to 400°C at a rate of 120°C/h and finally quenched. Needle-shaped, transparent, light-green crystals up to 200 µm length were removed from the poly-crystalline matrix.

The composition of the crystals obtained was determined using a Cameca SX50 electron beam microprobe operating at 15 kV, with a beam current of 10 nA and a counting time of 20 s. The

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standards used were CaSO<sub>4</sub> (Ca,S), NaCl (Na,Cl) as well as CuO (Cu). No incorporation of Ca could be detected. The intensities were corrected for electron scattering, absorption and fluorescence radiation (ZAF-correction). Chemical analyses yielded an average composition of 15.76 ( $\pm 0.21$ ) wt.% Na<sub>2</sub>O, 41.19 ( $\pm 0.21$ ) wt.% CuO, 4.33 wt.% ( $\pm 0.11$ ) Cl and 38.87 wt.% ( $\pm 0.25$ ) SO<sub>3</sub> (numbers in brackets are standard deviations for 12 spot analyses). The formula derived from the chemical analysis based on 18 O pfu is Na<sub>4.22</sub>Cu<sub>4.30</sub>S<sub>4.03</sub>O<sub>18</sub>Cl<sub>1.01</sub>. This empirical formula was interpreted in terms of the simplified structural formula as Na<sub>4</sub>[Cu<sub>4</sub>O<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]·MeCl (Me: Na,Cu,□), with partially vacant Me sites.

#### Single crystal data collection

A tetragonal prismatic crystal of good optical quality was selected for the structure investigations. Precession photographs indicated Laue symmetry  $4/m$ . Diffraction intensities were obtained using a Nonius Kappa CCD four circle diffractometer (see Table 1). Data reduction included Lorentz and polarization corrections as well as an analytical absorption correction based on the indexed faces of the crystal using the program PLATON (Spek, 1999). Systematic absences ( $hkl0$ ),  $h+k \neq 2n$  indicated the centrosymmetric space group  $P4/n$ .

TABLE 1. Experimental details for the synthetic Na piypite.

Crystal cell data	
$a$ (Å)	18.451(1)
$b$ (Å)	18.451(1)
$c$ (Å)	4.9520(2)
$V$ (Å <sup>3</sup> )	1685.86(15)
Temperature (°C)	20
Space group	$P4/n$
$Z$	4
Formula	Na <sub>4</sub> [Cu <sub>4</sub> O <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ](Na <sub>0.26</sub> Cu <sub>0.37</sub> □ <sub>0.37</sub> )Cl
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	3.23
$\mu$ (cm <sup>-1</sup> )	58.6
Intensity measurements	
Crystal shape	Tetragonal prism
Crystal dimensions	0.250 × 0.05 × 0.05 mm <sup>3</sup>
Diffractometer	Nonius Kappa-CCD
Monochromator	Graphite
Rotation axis and width	$\phi/\omega$ 2°
$\theta$ range	2.2–30.0°
Reflection range	$ h  \leq 25;  k  \leq 25;  l  \leq 6$
Measured reflections	18772
Observed reflections ( $I > 4 \sigma(F)$ )	17753
Unique reflections in $4/m$	2466
$R_{\text{int}}$ for $4/m$	0.0422
Max./min. transmission	0.765/0.416
Refinement of the structure	
Parameters used in the refinement	149
No. of restraints	1
$R1$ ( $F_o > 4 \sigma(F_o)$ ), $R1$ (all reflections)	0.028, 0.047
$wR2$ (all reflections)	0.085
Weighting parameters $a, b$	0.041, 0.868
Goodness of Fit	1.042
Final $\Delta\rho_{\text{min}}$ (e/Å <sup>3</sup> )	−0.85
Final $\Delta\rho_{\text{max}}$ (e/Å <sup>3</sup> )	0.70

$$R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$$

$$wR2 = \frac{(\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}}$$

$$P = (2F_c^2 + \max(F_o^2, 0)) / 3$$

CRYSTAL STRUCTURE OF PIYPITE

*Structure solution and refinement*

The structure was solved by direct methods using the program SIR92 (Altomare *et al.*, 1992) by multiresolution techniques. The phase set with the maximum combined figure of merit provided an E-map, the most intense peaks of which could be interpreted to give a sensible crystal chemical model. This model was the starting point for the refinement calculations performed with the program SHELXL-93 (Sheldrick, 1993). X-ray scattering factors for the different cations in their respective valence state, together with real and imaginary anomalous-dispersion coefficients, were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974); the values for  $O^{2-}$  were taken from Hovestreydt (1983). The final least squares calculations using anisotropic displacement parameters converged to  $R1 = 0.028$  for 149 parameters and 2466 independent reflections (cf. Table 1). The refined atomic coordinates, anisotropic displacement factors as well as selected interatomic distances and angles are given in Tables 2–4. Structure factor lists have been deposited with the Principal Editor of

*Mineralogical Magazine* and are available on request. The figures showing structural details were drawn using the programs ATOMS (Dowty, 1997) and ORTEP-3 (Farrugia, 1997).

**Description and discussion of the structure**

*Basic building units*

$Na_4[Cu_4O_2(SO_4)_4] \cdot MeCl$  (Me: Na, Cu, □) has two main structural units running parallel to [001]: (1) slabs of  $Cu_2O(SO_4)_2$  units; and (2) chains of  $MeO_6$  octahedra. The backbone of the slabs consists of chains of  $O1Cu_4$  tetrahedra with a mean  $O1-Cu$  distance of 1.920 Å. The tetrahedra share edges to form infinite chains parallel to [001]. Whereas the average value of the  $Cu-O1-Cu$  angles is close to the ideal value of  $109.47^\circ$ , the individual angles range from  $98.8$  to  $126.5^\circ$ . The bond distances and bond angles are in good agreement with the values observed in inorganic crystal structures where O atoms are coordinated by four Cu(II) atoms (Effenberger, 1985b; Krivovichev *et al.*, 1998). The copper cations in the chains are coordinated by four oxygens (two O1 oxo anions and two oxygens

TABLE 2. Positional parameters in fractional coordinates, Wyckoff-sites and equivalent isotropic displacement parameters.  $U_{eq}$  is defined as one third of the trace of orthogonalized  $U_{ij}$  tensor. The Me1 and Me2 sites are only partially occupied by Na ( $26 \pm 2\%$ ) and Cu ( $37 \pm 2\%$ ).

Atom	X	y	z	Wyckoff site	$U_{eq}$
Cu1	0.05189(2)	0.05935(2)	0.47175(6)	8(g)	0.0124(1)
Cu2	0.55123(2)	0.05974(2)	0.97817(6)	8(g)	0.0129(1)
Cl1	$\frac{3}{4}$	$\frac{1}{4}$	0	2(a)	0.0300(3)
Cl2	$\frac{1}{4}$	$\frac{1}{4}$	0.5068(3)	2(c)	0.0301(4)
S1	0.41831(4)	0.34183(4)	0.9690(1)	8(g)	0.0134(2)
S2	0.91906(5)	0.34094(5)	0.4896(1)	8(g)	0.0134(2)
Me1	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2(b)	0.0328(6)
Me2	$\frac{1}{4}$	$\frac{1}{4}$	0.0043(3)	2(c)	0.0325(6)
Na1	0.60386(9)	0.27820(9)	0.01600(2)	8(g)	0.0301(4)
Na2	0.10444(8)	0.27925(9)	0.4694(3)	8(g)	0.0306(4)
O1	0.4996(1)	0.5088(1)	0.2501(4)	8(g)	0.0131(3)
O2	0.3927(1)	0.4008(1)	0.1495(4)	8(g)	0.0209(4)
O3	0.6015(1)	0.3911(1)	0.3315(4)	8(g)	0.0216(4)
O4	0.4008(1)	0.3621(1)	0.6823(3)	8(g)	0.0186(4)
O5	0.9040(1)	0.3615(1)	0.2015(4)	8(g)	0.0233(4)
O6	0.6651(2)	0.4972(1)	0.4698(4)	8(g)	0.0238(5)
O7	0.1661(2)	0.4967(2)	0.9976(4)	8(g)	0.0265(6)
O8	0.7273(1)	0.3819(2)	0.4617(4)	8(g)	0.0263(6)
O9	0.2253(1)	0.3799(2)	0.0261(4)	8(g)	0.0284(6)

TABLE 3. Anisotropic displacement parameters ( $\text{\AA}^2$ ) given as  $-2\pi^2[h^2 a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu1	0.0148(2)	0.0145(2)	0.0080(15)	0.0003(1)	0.0003(1)	-0.0028(2)
Cu2	0.0151(2)	0.0146(2)	0.0091(16)	0.0009(1)	0.0001(1)	-0.0028(2)
Cl1	0.0173(6)	0.0173(6)	0.0554(11)	0	0	0
Cl2	0.0174(6)	0.0174(6)	0.0556(11)	0	0	0
S1	0.0154(4)	0.0132(4)	0.0117(27)	0.0009(2)	-0.0020(2)	-0.0020(3)
S2	0.0154(4)	0.0135(4)	0.0114(29)	0.0002(2)	0.0006(2)	-0.0026(3)
Me1	0.0415(9)	0.0415(9)	0.0153(8)	0	0	0
Me2	0.0404(9)	0.0404(9)	0.0166(8)	0	0	0
Na1	0.0195(9)	0.0254(9)	0.0453(8)	0.0004(5)	0.0008(5)	0.0045(7)
Na2	0.0197(8)	0.0291(9)	0.0431(7)	-0.0084(5)	0.0002(5)	0.0067(7)
O1	0.0142(10)	0.0180(9)	0.0073(7)	-0.0001(6)	-0.0006(5)	-0.0012(9)
O2	0.0204(10)	0.0283(11)	0.0138(8)	-0.0073(7)	-0.0014(7)	-0.0011(8)
O3	0.0288(11)	0.0197(10)	0.0161(9)	0.0018(7)	-0.0092(8)	-0.0008(8)
O4	0.0234(10)	0.0219(10)	0.0104(8)	0.0009(7)	-0.0026(7)	-0.0066(8)
O5	0.0313(11)	0.0271(11)	0.0114(8)	0.0013(7)	-0.0022(8)	-0.0102(9)
O6	0.0247(14)	0.0164(13)	0.0303(11)	-0.0004(8)	0.0005(8)	-0.0038(11)
O7	0.0247(15)	0.0152(14)	0.0397(14)	-0.0066(7)	0.0041(8)	-0.0039(11)
O8	0.0169(13)	0.0324(15)	0.0297(11)	0.0003(9)	0.0058(8)	0.0078(11)
O9	0.0209(14)	0.0333(16)	0.0309(11)	-0.0073(9)	-0.0106(8)	0.0126

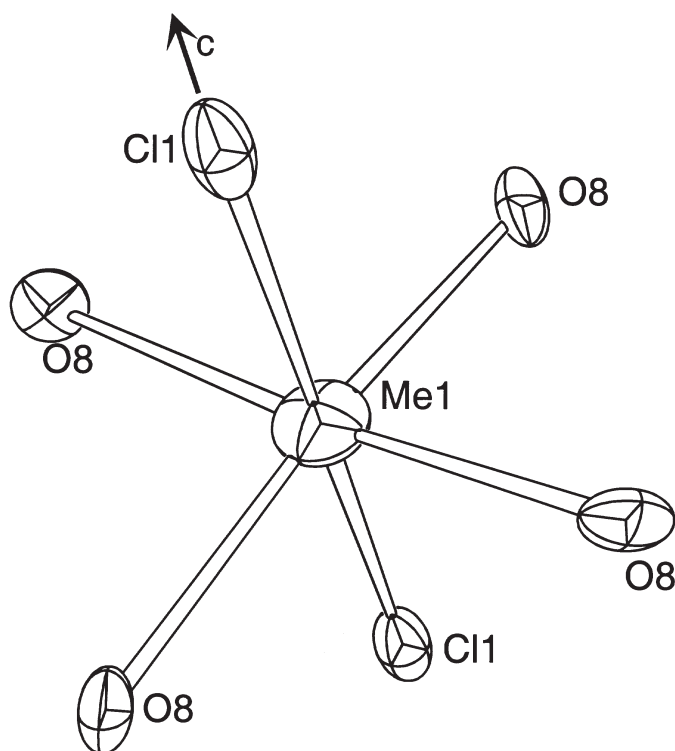


FIG. 1. Side view of the octahedron surrounding Me1 with the displacement ellipsoids drawn at the 50% probability level.

## CRYSTAL STRUCTURE OF PIYPITE

TABLE 4. Bond distances (Å) and angles (°).

Cu2—O1	1.904(2)	Cu1—O1	1.920(2)
O1	1.933(2)	O1	1.924(2)
O5	2.005(2)	O4	1.987(2)
O3	2.019(2)	O2	2.034(2)
O7	2.420(2)	O6	2.400(2)
S1—O9	1.454(3)	S2—O8	1.454(2)
O7	1.461(3)	O6	1.459(3)
O2	1.485(2)	O3	1.476(2)
O4	1.504(2)	O5	1.502(2)
Mean	1.476	Mean	1.473
Me1—C11	2.476 × 2	Me2—O9	2.444(3) × 4
O8	2.477(3) × 4	C12	2.464(2)
		C12	2.488(2)
Mean	2.478	Mean	2.455
Na1—O7	2.230(3)	Na2—O6	2.250(3)
O8	2.558(2)	O9	2.427(2)
O3	2.605(2)	O4	2.554(2)
O5	2.637(3)	O2	2.626(2)
O5	2.740(2)	C12	2.746(2)
C11	2.747(2)	O4	2.815(2)
O8	2.764(2)	O9	2.945(2)
O1—Cu2	1.904(2)		
Cu1	1.920(2)		
Cu1'	1.924(2)		
Cu2'	1.933(2)		
Mean	1.920		
O9—S1—O7	112.21(17)	O8—S(2)—O6	112.09(16)
O9—S1—O2	110.58(14)	O8—S(2)—O3	111.03(14)
O9—S1—O4	106.91(12)	O8—S(2)—O5	106.79(12)
O7—S1—O2	109.30(13)	O6—S(2)—O3	108.50(13)
O7—S1—O4	109.22(12)	O6—S(2)—O5	109.46(12)
O2—S1—O4	108.53(12)	O3—S(2)—O5	108.92(12)
O1—Cu1—O1'	81.00(9)	O1—Cu2—O1'	81.24(9)
O1—Cu1—O4	174.03(8)	O1—Cu2—O5	101.32(8)
O1—Cu1—O2	92.13(8)	O1—Cu2—O3	166.75(8)
O1—Cu1—O6	100.74(8)	O1—Cu2—O7	92.82(7)
O1'—Cu1—O4	101.47(7)	O1'—Cu2—O5	167.22(8)
O1'—Cu1—O2	171.91(8)	O1'—Cu2—O3	94.40(8)
O1'—Cu1—O6	96.80(8)	O1'—Cu2—O7	104.74(8)
O4—Cu1—O2	85.79(8)	O5—Cu2—O3	85.70(8)
O4—Cu1—O6	84.44(8)	O5—Cu2—O7	87.72(9)
O2—Cu1—O6	80.21(8)	O3—Cu2—O7	76.10(8)
Cu2—O1—Cu1	112.93(8)		
Cu2—O1—Cu1'	126.51(9)		
Cu2—O1—Cu2'	98.76(9)		
Cu1—O1—Cu1'	99.00(9)		
Cu1—O1—Cu2'	104.11(8)		
Cu1'—O1—Cu2'	114.10(8)		
Mean	109.24		

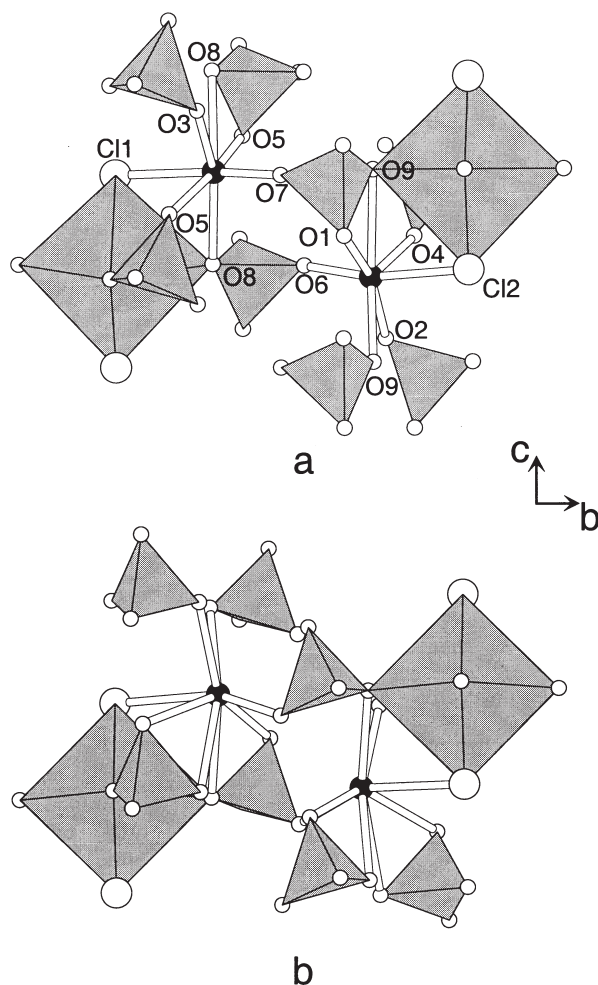


FIG. 2. Side view of the coordination spheres of the large cations within the tunnels: (a)  $\text{Na}_4[\text{Cu}_4\text{O}_2(\text{SO}_4)_4]\cdot\text{MeCl}$ , and (b) piyprite. The black circles correspond to Na and K ions, respectively.

belonging to sulphate groups) with distances between 1.90 Å and 2.03 Å and a fifth more distant sulphate oxygen at ~2.40 Å. The spread in the interatomic S–O distances as well as the O–S–O angles of the  $\text{SO}_4$  tetrahedra is small.

The two octahedral Me1 and Me2 positions are partially occupied by Na and Cu atoms and are surrounded by four oxygens and two chlorines with bond distances between 2.44 and 2.49 Å. These values have to be considered critically in comparison with the well known stereochemistry of Na and Cu(II) in inorganic crystal structures. According to the *International Tables of Crystallography, Vol. C* (Wilson, 1993), bond

distances within this range are typical of Na–O bonds. However, Na–Cl distances are usually close to 2.84 Å and are therefore much larger than the observed metal–ligand distances in the octahedra. On the other hand, a coordination with all six ligands at ~2.45 Å away from the centre of the octahedron contradicts the crystal chemical character of Cu(II), preferring a less regular surrounding with shorter Cu–O bonds. A possible explanation for these discrepancies may be attributed to static disorder on the Me1 and Me2 sites, involving small shifts of the cations away from the mean position determined by the diffraction experiment. This hypothesis is

CRYSTAL STRUCTURE OF PIYPITE

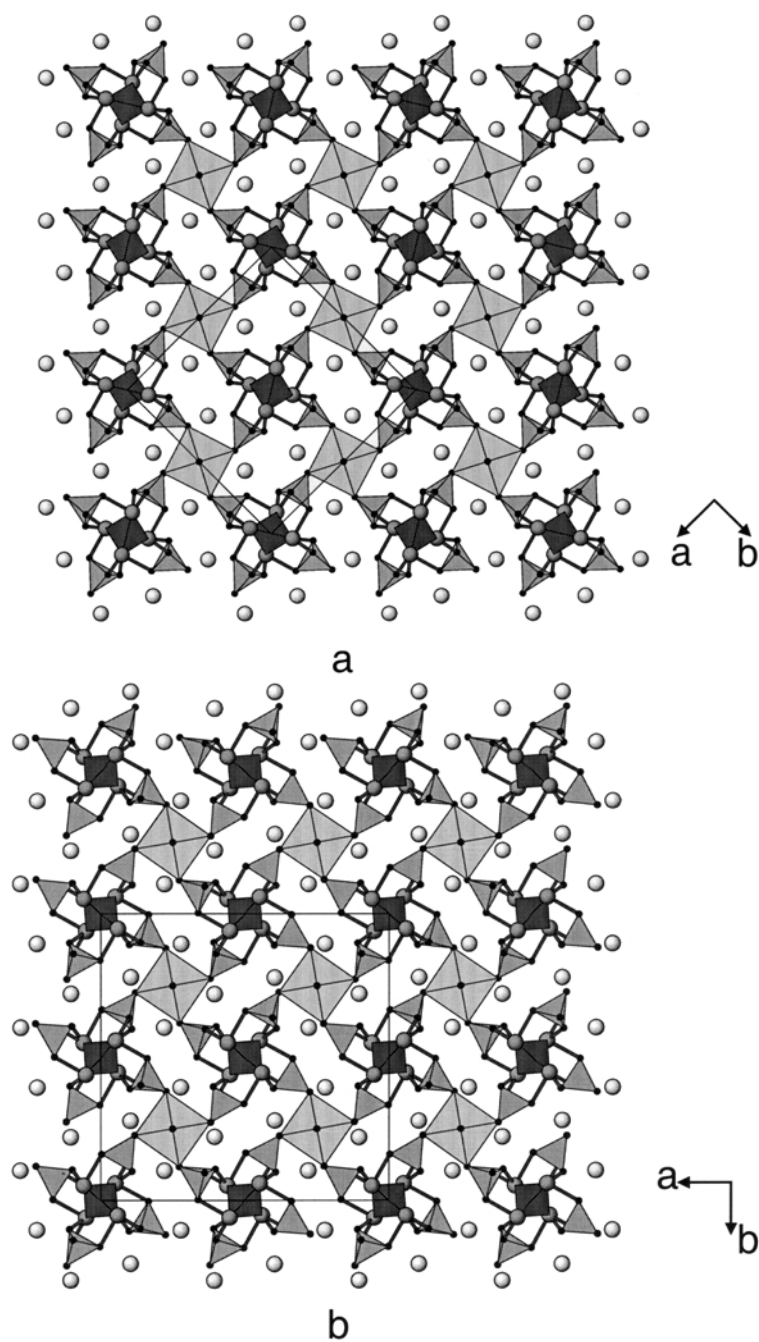


FIG. 3. Projection of the crystal structures of (a) piypite and (b) Na<sub>4</sub>[Cu<sub>4</sub>O<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]·MeCl parallel to [001] with SO<sub>4</sub> groups (medium grey), MeO<sub>6</sub> octahedra (light grey) and OCu<sub>4</sub> tetrahedra (dark grey). Light and dark grey circles represent the Na/K ions in the tunnels of the structures and the Cu atoms at the apices of the OCu<sub>4</sub> groups, respectively. Cu–O bonds linking the OCu<sub>4</sub> tetrahedra with the sulphate groups are indicated by solid lines. The outlines of the unit cells are indicated ( $a \approx \sqrt{2}a_{\text{piy}}$ ;  $c \approx c_{\text{piy}}$ ).

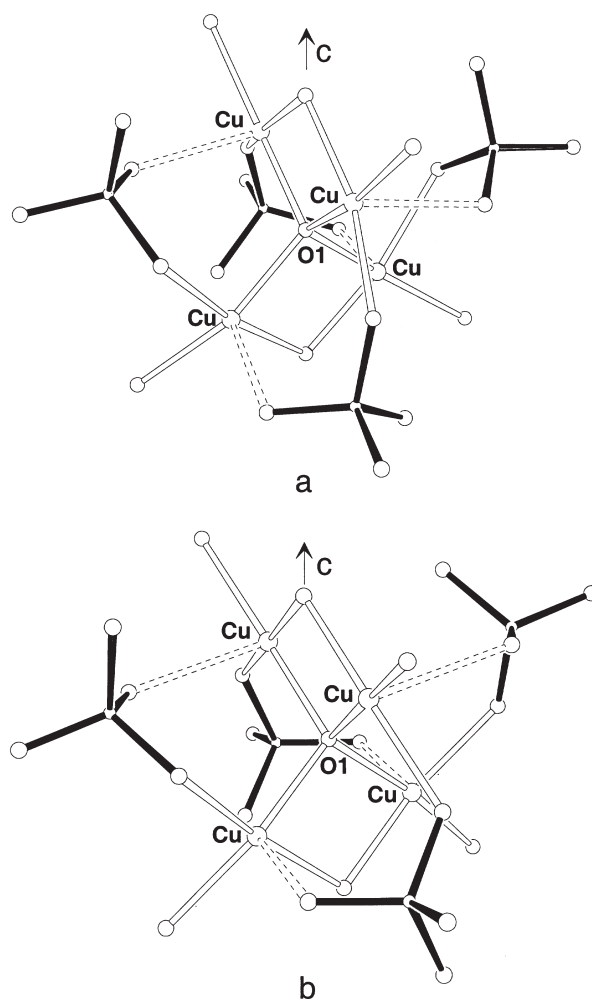


FIG. 4. Detail of the  $\text{Cu}_2\text{O}(\text{SO}_4)_2$  chains for (a) piypite and (b)  $\text{Na}_4[\text{Cu}_4\text{O}_2(\text{SO}_4)_4]\cdot\text{MeCl}$ . S–O bonds of the sulphate groups are shaded. The (4+1) coordination of the Cu cations is indicated by solid and stippled lines for the corresponding bonds.

supported by an inspection of the anisotropic displacement factors, as can be seen in Fig. 1. The displacement ellipsoids of the Me sites are disc shaped with a preferred elongation within (001), indicating a static disorder of the Me cations including displacements towards one or two of the four oxygens. The root-mean-square amplitudes of the thermal ellipsoids for Me1, for example, are 0.20 Å parallel to the (001) plane and 0.12 Å perpendicular to the  $a$ – $b$  plane. Furthermore, the two chlorines show definitely prolate spheroids with the longest principal axes parallel to [001]: for the Cl1 anions, the amplitudes of the ellipsoids

are 0.24 Å parallel to [001] and 0.13 Å within (001). This probably arises from static short-range displacements of the Cl ions dependent on the occupancy of the Me sites. Potential long-range order between Na/Cu and vacancies on the Me sites coupled with Cl displacements requires a doubling of the  $c$  lattice parameter. However, even on strongly over-exposed CCD rotation photographs about [001] no additional layer lines could be observed.

The sodium atoms Na1 and Na2, lying within the tunnels, have seven ligands up to 3.0 Å with coordination polyhedra which can be described as



## CRYSTAL STRUCTURE OF PIYPITE

distorted pentagonal bipyramids (Fig. 2a). Six of the ligands are O atoms from the sulphate groups. The coordination sphere is completed by an additional chlorine from the Me octahedra.

### Site occupancies of the Me sites

The result of the chemical analysis summarized in the empirical formula given above can be interpreted in such a way that the Me1 and Me2 sites are occupied by Na and Cu. A linear constraint was applied in the refinement of site occupancies, so that the sum of the charges for all Me1 and Me2 sites inside the unit cell was +4 in order to ensure charge compensation. The occupancies of Na in Me1 and Me2 were constrained to be equal as were those of Cu, otherwise the refinement became unstable due to correlations. The resulting final structural formula is  $\text{Na}_4[(\text{Cu}_4\text{O}_2)(\text{SO}_4)_4](\text{Na}_{0.26}\text{Cu}_{0.37}\square_{0.37})\text{Cl}$ , in good agreement with the chemical analysis.

### Pseudosymmetry

Interestingly, the structure reveals a distinct pseudo-translational symmetry. Among the cation positions as well as the chlorine sites, pairs of atoms can be found which obey the conditions of a F centring to a good approximation. For the O1 site the translations are even approximately fulfilled within the set of symmetry equivalent positions generated by the symmetry operations of  $P4/n$ . The shifts between the real positions in the structure and those calculated assuming that the F centring translations are present are  $<0.3 \text{ \AA}$ . However, the oxygen positions O2, O3, O4 and O5 deviate significantly from the pseudo centring and no pseudo-translational equivalents can be found.

### Relation to the piypite structure

As mentioned above, there is a close relationship between the mineral piypite and our synthetic K-free phase. Piypite adopts space group  $I4$  with  $a = 13.60 \text{ \AA}$  and  $c = 4.98 \text{ \AA}$ . The building elements of both structures are the same, as can be seen from the comparison of the projections of the structures parallel to  $[001]$  as shown in Fig. 3a,b.

Furthermore, the Me positions in both compounds are only partially occupied by Na and Cu. The main difference between the two structures results from the relative orientation of the sulphate tetrahedra within the  $\text{Cu}_2\text{O}(\text{SO}_4)_2$

units and is detailed in Fig. 4a,b. In piypite these rows reside on the  $4_2$  screw axes running parallel to  $[001]$ . The apices of the tetrahedra all point in the same direction, producing a polar crystal structure. On the other hand, the chains in the synthetic K-free compound are located on the inversion centres of space group  $P4/n$ . Therefore, the apices alternate in an up-down-up-down sequence along  $[001]$ . The different orientations of the sulphate tetrahedra in the structures yields a slightly different coordination of the Na and K atoms in tunnels. The K ions in piypite are surrounded by seven oxygens and one chlorine (Fig. 2b), whereas Na in  $\text{Na}_4[\text{Cu}_4\text{O}_2(\text{SO}_4)_4]\cdot\text{MeCl}$  shows a seven-fold coordination.

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