

A new copper(II) basic sulfate: poly-[3-aminopyridinium μ_3 -hydroxido-di- μ_3 -sulfato-bis[aquacopper(II)]]

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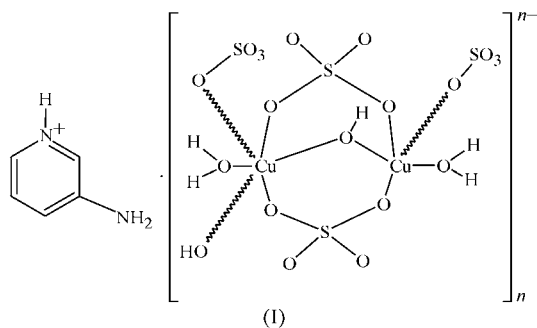
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The crystal structure of the title basic copper(II) sulfate, $\{(C_5H_7N_2)[Cu_2(OH)(SO_4)_2(H_2O)_2]\}_n$, shows an unprecedented structural arrangement of two distinct copper centres. CuO_6 and CuO_5 polyhedra are linked through bridging hydroxide and sulfate anions to form negatively charged infinite chains propagated along the a axis. The negative charge is balanced by 3-aminopyridinium cations that are held in the structure by extensive hydrogen bonding to the inorganic chains. Additionally, the cationic arrangement features π - π stacking.

Comment

In the course of our studies of copper carboxylates with organic amines, we have investigated the $CuSO_4$ /suberic acid/3-aminopyridine system. Attempts to prepare a new polymeric copper(II) dicarboxylate failed. Instead, the synthesis yielded prismatic orange-green crystals which proved to be the title new Cu^{II} basic sulfate species, $L^+ \cdot [Cu_2(OH)(SO_4)_2(H_2O)_2]^-$, (I) (L^+ is the 3-aminopyridinium cation). At first glance, the stoichiometry is reminiscent of that of the mineral natrochalcite, $Na^+ \cdot [Cu_2(OH)(SO_4)(H_2O)]^-$, from the tsumcorite

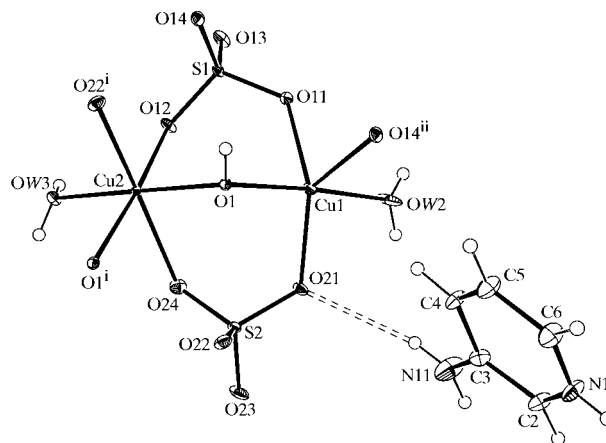


group minerals, but detailed structural analysis reveals a novel structural arrangement that cannot be related to any of the known minerals containing tetrahedral XO_4^{2-} anions ($X = S, Se, Mo, As, P, etc.$).

The basic building unit of (I) is composed of two distinct Cu centres, bridged by two bidentate sulfate groups and by the hydroxide anion (Fig. 1). Additionally, a water molecule is coordinated to each of the two independent Cu atoms. The dimeric $Cu_2(OH)(SO_4)(H_2O)_2$ unit bears a negative charge, which is balanced by one 3-aminopyridinium cation per dimeric unit. Two dimeric units, related by an inversion centre, are further connected by a sulfate O atom and an OH^- anion to form a centrosymmetric tetranuclear entity (Fig. 2a). Negatively charged linear chains of tetramers are then generated by translation along [100] (Fig. 2b). Both sulfate anions thus connect three metal centres in a $\mu_3-O:O':O''$ binding mode. The shortest contact between Cu centres is observed for the two Cu2 atoms related by an inversion centre [$Cu2 \cdots Cu2(-x, -y + 1, -z + 1) = 3.0015(4) \text{ \AA}$].

The crystallographically independent Cu atoms have distinct coordination environments. Atom Cu2 has a typical slightly distorted octahedral geometry of six O atoms (four belonging to sulfate groups, a water O atom and a hydroxide O atom). Atom Cu1 is five-coordinated by three sulfate O atoms, a water O atom and a hydroxide O atom, thus forming a polyhedron that could be described as a distorted trigonal bipyramid rather than a distorted square pyramid [the parameter τ (Addison *et al.*, 1984) has a value of 0.62]. A pair of octahedra, related by an inversion centre and sharing a common edge, are connected to the trigonal bipyramid through a corner common to all three polyhedra (the triply bridging OH^- group) and through the corners of sulfate tetrahedra, generating linear chains propagated along the a axis (Fig. 3a).

The 3-aminopyridinium cations are arranged between the chains with the ring plane almost perpendicular to the [100] direction. The pyridine rings of neighbouring cations are alternately slipped with respect to each other, but a substantial


Figure 1

A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The coordination around the Cu atoms is completed by O atoms of symmetry-related units. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$].

overlap of the aromatic rings still exists, so that the interaction can be considered as π - π stacking. The plane-to-plane distance is 3.64 Å, whereas the centroid-to-centroid distance is

only slightly longer (3.98 Å). There are a number of possible hydrogen-bond donors and acceptors, as illustrated by a rather complex hydrogen-bonding pattern, the details of which are listed in Table 2.

Taking the stoichiometry into account, the reported compound is closely related to the natrochalcite-type compounds $M^+ \cdot [\text{Cu}_2(\text{OH})(\text{SO}_4/\text{SeO}_4)_2]^- \cdot \text{H}_2\text{O}$, with the tsumcorite parent structure $M^I M^{II}(\text{XO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ (Tillmanns & Gebert, 1973; Giester & Zemann, 1987; Mihajlovic & Effenberger, 2004, and references therein). However, the structures differ significantly. Natrochalcite contains six-coordinated Cu centres in a distorted octahedral environment. Pairs of octahedra are edge-connected to form chains, which are linked by sulfate tetrahedra to form $[\text{Cu}_2(\text{OH})(\text{SO}_4)(\text{H}_2\text{O})]^-$ sheets, interconnected by Na^+ ions and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. There are several structural variations of the members of the parent tsumcorite type of compounds, although in all the reported structures, the M^{II} metal is six-coordinated, whereas in the structure reported here, one of the Cu atoms is five-coordinated. Trigonal-bipyramidal CuO_5 coordination in minerals is rather rare. To the best of our knowledge, it has only been observed in the mineral dolerophanite, $\text{Cu}_2\text{O}(\text{SO}_4)$ (Effenberger, 1989). There is an additional distinct difference: all the compounds listed above contain two-dimensional layers that are further connected by monovalent cations and hydrogen bonds, while the title compound contains linear chains of $[\text{Cu}_2(\text{OH})(\text{SO}_4)_2(\text{H}_2\text{O})_2]^-$ composition. The organic 3-aminopyridinium cation lacks coordination ability and, through its size, apparently prevents closer contacts between the chains.

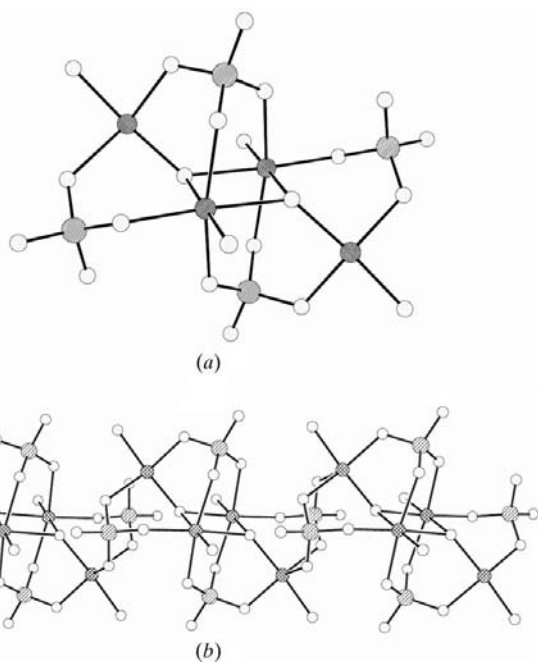


Figure 2
(a) The assembly of two dimeric units of (I) to form a centrosymmetric tetranuclear entity and (b) the connection of tetranuclear units into infinite chains.

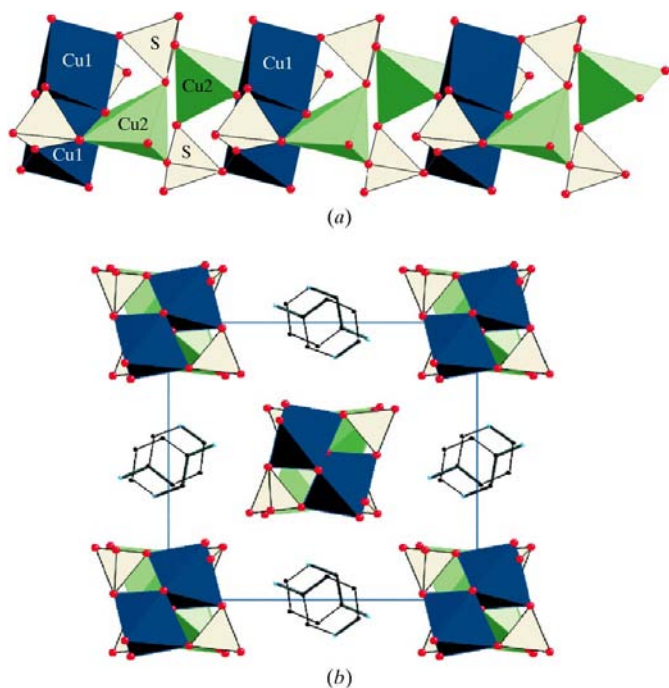


Figure 3
(a) The connection of CuO_6 octahedra (Cu1) and CuO_5 trigonal bipyramids (Cu2) through sulfate tetrahedra (S) into linear chains. (b) A packing diagram for (I), viewed along $[100]$. Note the π - π stacking arrangement of the 3-aminopyridinium cations.

Experimental

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.10 g, 0.4 mmol) and suberic acid (0.07 g, 0.4 mmol) were combined in water (15 ml). The mixture was stirred and heated to boiling. The addition of 3-aminopyridine (0.19 g, 2.0 mmol) resulted in a green solution. Upon cooling to room temperature, a turquoise precipitate of unknown composition was formed. On standing at ambient temperature, orange-green single crystals of (I) appeared within three weeks. The crystals are extremely sensitive and decompose rapidly when removed from the solution.

Crystal data

$(\text{C}_5\text{H}_7\text{N}_2)[\text{Cu}_2(\text{OH})(\text{SO}_4)_2(\text{H}_2\text{O})_2]$	$V = 1312.16 (8) \text{ \AA}^3$
$M_r = 467.41$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.4094 (2) \text{ \AA}$	$\mu = 3.62 \text{ mm}^{-1}$
$b = 12.6262 (5) \text{ \AA}$	$T = 150 (1) \text{ K}$
$c = 14.0648 (5) \text{ \AA}$	$0.12 \times 0.12 \times 0.10 \text{ mm}$
$\beta = 94.2600 (10)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	2976 independent reflections
5582 measured reflections	2897 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.011$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.053$	$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
2976 reflections	
223 parameters	

Table 1

Selected bond lengths (Å).

Cu1—OW2	1.9355 (16)	Cu2—O1	1.9475 (13)
Cu1—O1	1.9422 (13)	Cu2—O12	2.0821 (13)
Cu1—O21	1.9771 (13)	Cu2—O24	2.1877 (13)
Cu1—O11	2.0843 (13)	Cu2—O22 ⁱⁱ	2.1975 (13)
Cu1—O14 ⁱ	2.1061 (13)	Cu2—O1 ⁱⁱ	2.2097 (13)
Cu2—OW3	1.9288 (13)	Cu2—Cu2 ⁱⁱ	3.0015 (4)

 Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11—H11A \cdots O24 ⁱⁱⁱ	0.86	2.37	3.132 (2)	148
N11—H11B \cdots O21	0.86	2.49	3.326 (3)	165
N11—H11B \cdots O13 ^{iv}	0.86	2.64	3.122 (3)	117
OW3—H1A \cdots O23 ^v	0.78 (3)	1.90 (3)	2.6697 (19)	174 (3)
N1—H1N \cdots O22 ^{vi}	0.76 (3)	2.07 (3)	2.796 (2)	160 (3)
O1—H1 \cdots O11 ⁱ	0.71 (3)	2.22 (3)	2.8616 (18)	152 (3)
OW3—H1B \cdots O13 ^{vii}	0.78 (3)	1.90 (3)	2.6657 (19)	168 (3)
OW2—H2A \cdots O13 ^{iv}	0.81 (3)	1.83 (4)	2.637 (2)	176 (3)
OW2—H2B \cdots O23 ^{viii}	0.67 (3)	2.09 (3)	2.739 (2)	165 (4)

 Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (iii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x, -y + 2, -z + 1$; (vii) $x - 1, y, z$; (viii) $x + 1, y, z$.

Aromatic and amino group H atoms of the 3-apyH cation were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. All other H atoms were found in a difference Fourier map and refined freely, with O—H distances ranging from 0.67 (3) to 0.81 (3) Å and an N—H distance of 0.76 (3) Å.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3034). Services for accessing these data are described at the back of the journal.

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