inorganic papers

Copper(II) selenate pentahydrate, CuSeO$_4$·5H$_2$O

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Se–O) = 0.001 Å
R factor = 0.018
wR factor = 0.047
Data-to-parameter ratio = 15.2

For details of how these key indicators were
automatically derived from the article, see
http://journals.iucr.org/e.

Copper(II) selenate pentahydrate is isotypic with its sulfate
analogue. All atoms are on general positions except Cu1 and
Cu2 (both with site symmetry $\bar{1}$). The Jahn–Teller distortion of
the CuO$_2$(H$_2$O)$_4$ 'octahedra' is slightly less pronounced than
in the sulfate analogue. The average Se—O bond length is
1.640 Å.

Comment

The title compound copper(II) selenate pentahydrate,
CuSeO$_4$·5H$_2$O, (I), is isotypic with its sulfate analogue
CuSO$_4$·5H$_2$O (*e.g.*, Varghese & Maslen, 1985), known in
nature as the mineral chalcanthite. It is also isotypic with
a selenate–sulfate solid-solution member Cu(SeO$_4$)$_{0.63}$-
(SO$_4$)$_{0.37}$·5H$_2$O (Mestres *et al.*, 1987). The unit-cell volume of
the title compound is about 5.1% larger than that of the
sulfate analogue. Mestres *et al.* (1987) reported the existence
of a complete solid-solution series between CuSeO$_4$·5H$_2$O and
CuSO$_4$·5H$_2$O without any evidence of S–Se ordering. The
presently determined unit-cell volume for the title compound,
382.43 (11) Å^3, is very close to that reported by Mestres *et al.*
(1987), 382.8 Å^3. A determination of the unit-cell parameters
at 120 K indicated no structural change in the title compound.

The compound contains infinite undulating chains of Jahn–
Teller-distorted CuO$_2$(H$_2$O)$_4$ 'octahedra' and SeO$_4$ tetra-
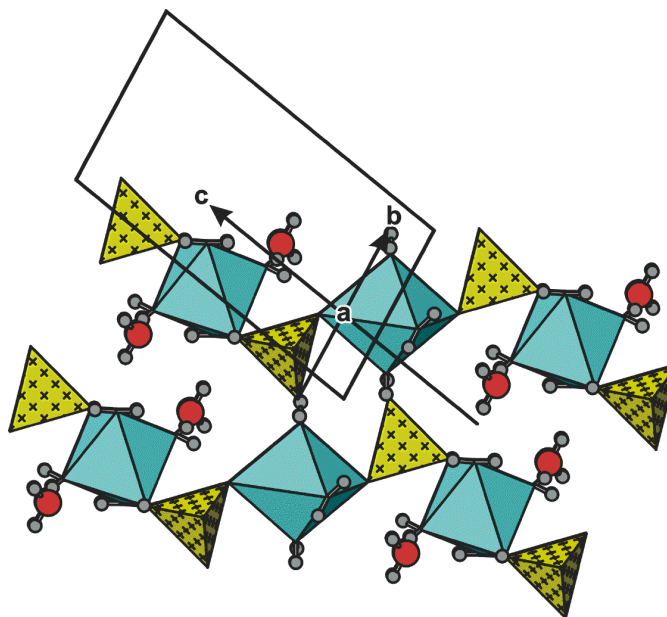
Figure 1
Polyhedral view of CuSeO$_4$·5H$_2$O along [100]. CuO$_2$(H$_2$O)$_4$ 'octahedra'
(blue) are each sharing two opposite O vertices with two neighbouring
SeO$_4$ tetrahedra (yellow) to form chains. The oxygen of the single water
molecule is shown in red.

hedra, which run along $[0\bar{1}1]$. Each $CuO_2(H_2O)_4$ 'octahedron' shares two opposite O vertices with two neighbouring SeO_4 tetrahedra (Fig. 1). The average Se—O bond length, 1.640 Å, is close to expected values. The water ligands are involved in medium–strong to weak hydrogen bonding, ensuring a connection to neighbouring chains. Further hydrogen bonding is provided by the single water molecule located in the space between the chains (Fig. 1). Hydrogen-bonding distances $(O\cdots O = 2.67$ to 3.00 Å) are very similar to those in $CuSO_4\cdot5H_2O$. The two non-equivalent Cu atoms have site symmetry $\bar{1}$, whereas the remaining atoms have site symmetry 1. The Jahn–Teller distortion observed in the two $CuO_2(H_2O)_4$ 'octahedra' is close to that expected for 'ideally' [4+2]-coordinated Cu^{2+} cations (Lambert, 1988; Eby & Hawthorne, 1993). The distortion is slightly less pronounced than that in $CuSO_4\cdot5H_2O$ (Varghese & Maslen, 1985), and average Cu—O bond lengths are also slightly smaller in the selenate (2.099 and 2.100 Å) than in the sulfate (2.106 and 2.109 Å).

The title compound shares the parent structure type of $CuSO_4\cdot5H_2O$ also with other $M^{2+}X^{6+}O_4\cdot5H_2O$ compounds, where M = Mg, Cr, Mn, Fe, Co, Zn; X = S and/or Se (e.g. Koleva & Stoilova, 1999, and references therein, and entries in the ICDD–PDF database). The chromate $MgCrO_4\cdot5H_2O$ (Bertrand et al., 1971; Baur & Rolin, 1972) is also isotypic with $CuSO_4\cdot5H_2O$. Compounds with M = Ni and Cd and X = S or Se, and compounds with X = Mo apparently do not form this structure type; although both unit-cell data and chain topology of the molybdate $MgMoO_4\cdot5H_2O$ are fairly similar to those of $CuSO_4\cdot5H_2O$, it crystallizes in a slightly different structure type (Bars et al., 1977).

Chains similar to those in the title compound are also known to occur in the two arsenate minerals liroconite, $Cu_2Al(AsO_4)(OH)_4\cdot4H_2O$, and brassite, $MgHAsO_4\cdot4H_2O$ (see e.g. Hawthorne, 1994).

Experimental

The title compound was prepared by controlled evaporation at room temperature of an aqueous solution containing selenic acid and copper(II) chloride. Pale-blue transparent crystals up to several mm in size formed.

Crystal data

$CuSeO_4\cdot5H_2O$	$Z = 2$
$M_r = 296.58$	$D_x = 2.576$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.083$ (1) Å	Cell parameters from 3095
$b = 6.226$ (1) Å	reflections
$c = 10.867$ (2) Å	$\theta = 3.6$–$30.0°$
$\alpha = 77.14$ (3)$°$	$\mu = 7.63$ mm^{-1}
$\beta = 82.20$ (3)$°$	$T = 293$ (2) K
$\gamma = 72.91$ (3)$°$	Fragment, pale blue
$V = 382.43$ (11) Å^3	$0.27 \times 0.20 \times 0.13$ mm

Data collection

Nonius KappaCCD diffractometer	2194 independent reflections
φ and ω scans	2115 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.012$
(HKL SCALEPACK;	$\theta_{max} = 30.0°$
Otwinowski & Minor, 1997)	$h = -8 \rightarrow 8$
$T_{min} = 0.233$, $T_{max} = 0.437$	$k = -7 \rightarrow 8$
4115 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$+ 0.220P]$
$wR(F^2) = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2194 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
144 parameters	$\Delta\rho_{min} = -0.77$ e Å^{-3}
All H-atom parameters refined	Extinction correction: SHELXL97
	Extinction coefficient: 0.103 (2)

Table 1
Selected interatomic distances (Å).

Se—O1^i	1.6368 (13)	Cu1—OW8	1.9842 (16)
Se—O2^i	1.6375 (13)	Cu1—O2	2.3501 (15)
Se—O3	1.6386 (14)	Cu2—OW5^{ii}	1.9261 (14)
Se—O4	1.6479 (12)	Cu2—OW6	1.9613 (15)
Cu1—OW7^{ii}	1.9632 (14)	Cu2—O3^{ii}	2.4115 (16)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OW5—H51$\cdots$O1	0.73 (4)	1.94 (4)	2.668 (2)	178 (4)
OW5—H52$\cdots$O4^i	0.80 (3)	1.91 (3)	2.703 (2)	167 (3)
OW6—H61$\cdots$O1^{ii}	0.75 (3)	1.95 (3)	2.695 (2)	175 (3)
OW6—H62$\cdots$O4^{ii}	0.79 (3)	1.98 (3)	2.762 (2)	169 (3)
OW7—H71$\cdots$OW9	0.83 (3)	1.95 (3)	2.772 (2)	172 (3)
OW7—H72$\cdots$O4^{iii}	0.80 (3)	2.05 (3)	2.836 (2)	169 (3)
OW8—H81$\cdots$OW9^{ii}	1.04 (4)	1.75 (4)	2.777 (2)	167 (4)
OW8—H82$\cdots$O3^{iv}	0.69 (3)	2.16 (3)	2.814 (2)	159 (3)
OW9—H91$\cdots$O3	0.75 (3)	2.28 (3)	3.003 (2)	162 (3)
OW9—H92$\cdots$O2	0.82 (4)	1.97 (4)	2.778 (2)	168 (3)

Symmetry codes: (i) $1 + x, y - 1, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $-x, 2 - y, 1 - z$; (iv) $1 - x, 1 - y, 1 - z$.

H atoms were refined without constraints. Refined O—H distances range between 0.69 and 1.04 Å.

Data collection: COLLECT (Nonius, 2001); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Shape Software, 1999).

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