Synthesis and Crystal Structure of the New Polymorph $Cu_3Fe_2(SeO_3)_6$-II

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The new polymorph $Cu_3Fe_2(SeO_3)_6$-II was obtained at low hydrothermal conditions as a subordinate coprecipitate of $Cu_3Fe_2(SeO_3)_6$-I. The crystal structure was determined by direct methods from single-crystal X-ray diffraction data in the space group $P2_1/n$: $Z=2$, $a=5.362(1)$, $b=18.840(4)$, $c=7.612(2)$ Å, $\beta=92.72(1)°$, $V=768.1(3)$ Å^3 and refined to $R_1 =0.029$. The crystal structure of $Cu_3Fe_2(SeO_3)_6$-II is built up by CuO_4 squares, dimers of edgesharing CuO_5 trigonal bipyramids and FeO_6 octahedra, corner-linked with three different SeO_3 groups to a framework.

Recently the new compounds $M_3Fe_2(SeO_3)_6$ (M = Cu, Zn) were described[1] as a contribution to our work on the synthesis and stereochemistry of Fe^{III} selenites. A compilation of this class of compounds is given in Ref. 2. $Cu_3Fe_2(SeO_3)_6$-I, associated with $Fe_2(SeO_3)_3 \cdot H_2O$,[3] had been obtained[1] from mixtures of $FeC_2O_4 \cdot 2H_2O$, $Cu(OH)_2 \cdot 2H_2O$ and SeO_2. The new polymorph described in the present paper was synthesized in a system slightly different in chemical composition but under similar conditions.

Synthesis

The samples were prepared from the starting materials $FeC_2O_4 \cdot 2H_2O$ (0.2 g), 0.4 g CuO rods, 0.5 ml 25% NH_3 and 0.5 g SeO_2, added to 15 ml H_2O. This mixture was filled in a Teflon-lined steel autoclave of 50 cm^3 capacity. After treatment for one week at 500 K, the vessel was cooled to room temperature within 12 h. The crystalline precipitate was filtered, suspended several times in an aqueous solution of methanol by means of an ultrasonic cleaner and finally washed with acetone and dried at 330 K. The major product is $Cu_3Fe_2(SeO_3)_6$-I, which forms compact brownish crystals. In small quantities green nonpleochroic crystals, strongly elongated parallel to [100], were also found, which finally proved to be a new modification of $Cu_3Fe_2(SeO_3)_6$ as derived from the crystal structure determination.

X-Ray crystallography and structure determination

A single crystal with the approximate dimensions $0.07 \times 0.08 \times 0.33$ mm^3 was chosen for X-ray data collec-

tion at room temperature on a Stoe AED2 four-circle diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $2\theta - \omega$ scans; 35 steps per reflection, increased for $\alpha_1-\alpha_2$ splitting, 2×4 steps for background correction; $0.03°$ step width, 0.5–2 s per step; three standard reflections every 120 min, lattice parameters refined from 46 reflections in the 2θ-range 26–33°). A summary of crystal data and details of the structure refinement are given in Table 1. The measured intensities were corrected for Lorentz and polarization effects and for absorption by evaluation of ψ-scans. The crystal

Table 1. Crystal data and details of the intensity measurements and structure refinements for $Cu_3Fe_2(SeO_3)_6$-II.

Space group	$P2_1/n$
a/Å	5.362(1)
b/Å	18.840(4)
c/Å	7.612(2)
β/°	92.72(1)
V/Å^3	768.1(3)
Z	2
ρ_{calc}/g cm^{-3}	4.601(5)
μ(Mo $K\alpha$)/cm^{-1}	202.5
$2\theta_{max}$/°	70
Measured reflections	7608
Unique data set	3411
$R_{int.}$	0.058
Data with $F_o > 4\sigma(F_o)$	2113
Variables	134
Extinction coefficient	0.0011(1)
R_1 [for $F_o > 4\sigma(F_o)$]	0.029
wR_2 (for all F_o^2)	0.048

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
$P = \{[\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2\}/3$

Table 2. Atomic coordinates and anisotropic displacement parameters with e.s.d.s in parentheses for $Cu_3Fe_2(SeO_3)_6$-II.[a]

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0	0	½	0.01190(1)	0.0154(3)	0.0125(3)	0.0078(2)	0.00031(19)	0.0004(2)	−0.0051(2)
Cu2	0.39495(10)	0.00699(3)	0.17958(6)	0.02426(12)	0.0206(2)	0.0406(3)	0.01226(19)	−0.01254(18)	0.00861(17)	−0.0182(2)
Fe	0.97516(9)	0.15697(2)	0.74255(6)	0.00917(9)	0.0089(2)	0.01044(19)	0.00815(18)	−0.00015(16)	0.00032(16)	−0.00112(17)
Se1	0.88137(6)	0.097989(17)	0.14034(4)	0.01013(6)	0.01205(14)	0.01051(13)	0.00771(12)	0.00006(10)	−0.00065(11)	−0.00130(12)
Se2	0.48197(6)	0.221800(17)	0.94122(4)	0.01115(7)	0.01139(15)	0.01011(14)	0.01176(13)	−0.00174(11)	−0.00141(11)	0.00059(12)
Se3	0.45730(6)	0.116950(18)	0.52537(4)	0.01014(6)	0.00903(14)	0.01410(14)	0.00731(12)	−0.00038(11)	0.00076(10)	−0.00075(12)
O1	0.0684(5)	0.10858(13)	−0.0293(3)	0.0157(5)	0.0134(12)	0.0215(13)	0.0122(10)	0.0067(9)	0.0006(9)	−0.0036(10)
O2	0.0587(5)	0.03926(14)	0.2623(3)	0.0159(5)	0.0152(12)	0.0224(12)	0.0103(10)	0.0047(9)	0.0024(9)	0.0038(10)
O3	0.6621(5)	0.04323(15)	0.0424(3)	0.0201(6)	0.0175(13)	0.0349(15)	0.0082(10)	−0.0052(10)	0.0043(9)	−0.0175(12)
O4	0.4254(5)	0.30717(12)	0.9959(3)	0.0123(4)	0.0155(12)	0.0106(10)	0.0106(10)	−0.0046(8)	−0.0015(9)	0.0046(9)
O5	0.7571(5)	0.23052(14)	0.8408(4)	0.0201(5)	0.0113(12)	0.0184(13)	0.0310(14)	−0.0098(10)	0.0073(11)	−0.0015(10)
O6	0.2793(5)	0.21494(13)	0.7632(3)	0.0138(5)	0.0129(11)	0.0166(11)	0.0116(10)	−0.0018(8)	−0.0027(9)	−0.0032(9)
O7	0.5501(5)	0.05767(16)	0.3777(3)	0.0255(6)	0.0169(13)	0.0402(16)	0.0199(12)	−0.0202(12)	0.0070(11)	−0.0129(13)
O8	0.6758(5)	0.09252(13)	0.6891(3)	0.0128(4)	0.0122(11)	0.0125(11)	0.0134(10)	0.0027(8)	−0.0036(9)	−0.0037(9)
O9	0.1968(4)	0.07798(12)	0.6140(3)	0.0119(4)	0.0097(11)	0.0144(10)	0.0119(10)	−0.0028(8)	0.0028(9)	−0.0018(9)

[a]The anisotropic displacement parameter is defined as $\exp(-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* a_j^*)$. $U_{eq} = 1/3[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{12}\cos\beta)]$.
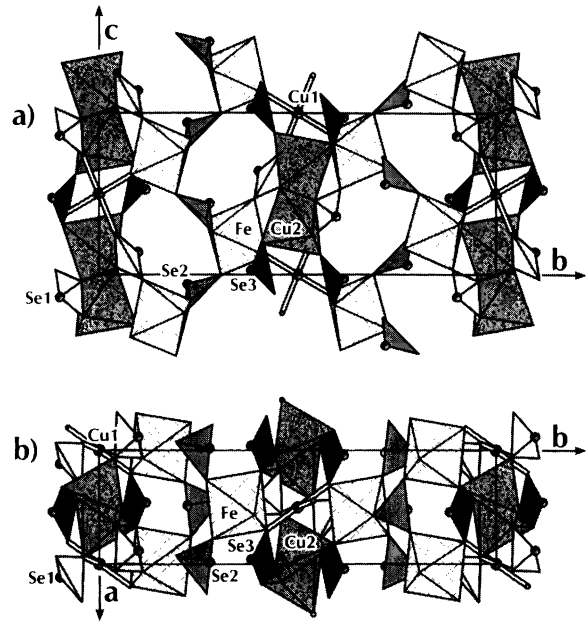

Fig. 1. Crystal structure of $Cu_3Fe_2(SeO_3)_6$-II in projections parallel to (a) [100] and (b) [001]. The drawings have been made with the program ATOMS.[6]

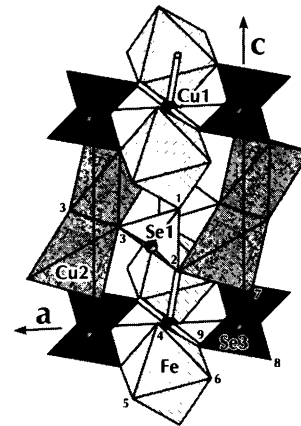Fig. 2. Crystal structure of $Cu_3Fe_2(SeO_3)_6$-II in a projection parallel to [010] illustrating the polyhedral arrangement within the 'sheet'. The Se(2)O₃ pyramids are omitted.

structure was determined by direct methods[4] and subsequent Fourier and difference Fourier syntheses. Final structure parameters of the title compound, obtained by full-matrix least-squares techniques on $|F|^2$ (SHELXL-96),[5] are listed in Table 2; selected interatomic distances and bond angles are given in Table 3. Residual electron densities are $<1.2\ \text{Å}^{-3}$.

Results and discussion

The framework structure of $Cu_3Fe_2(SeO_3)_6$-II, illustrated in Figs. 1a and 1b, consists of planar CuO_4 groups, dimers of edge-sharing, distorted CuO_5 trigonal bipyramids and FeO_6 octahedra, corner-linked with three different SeO_3 groups. The polyhedra of copper and

Table 3. Selected interatomic distances (in Å) and angles (in °) for Cu₃Fe₂(SeO₃)₆-II.

Cu1–O9	2×	1.984(2)	Fe–O6	1.963(2)	Se1–O1	1.684(2)
Cu1–O2	2×	1.994(2)	Fe–O5	1.982(2)	Se1–O2	1.705(2)
⟨Cu1–O⟩		1.989	Fe–O4	2.001(2)	Se1–O3	1.709(2)
			Fe–O1	2.004(2)	⟨Se1–O⟩	1.699
O9–Cu1–O2	2×	88.9(1)	Fe–O8	2.038(2)	O1–Se1–O2	99.1(1)
O9–Cu1–O2	2×	91.1(1)	Fe–O9	2.166(2)	O1–Se1–O3	99.2(1)
			⟨Fe–O⟩	2.026	O2–Se1–O3	101.5(1)
Cu2–O3		1.937(2)			⟨O–Se1–O⟩	99.9
Cu2–O7		1.939(2)	O1–Fe–O8	93.6(1)		
Cu2–O3		1.948(2)	O1–Fe–O9	87.7(1)	Se2–O4	1.692(2)
Cu2–O2		2.031(3)	O4–Fe–O8	86.8(1)	Se2–O6	1.701(2)
Cu2–O8		2.167(2)	O4–Fe–O9	81.9(1)	Se2–O5	1.702(2)
⟨Cu2–O⟩		2.004	O5–Fe–O1	96.8(1)	⟨Se2–O⟩	1.698
			O5–Fe–O4	93.6(1)	O4–Se2–O6	98.8(1)
O3–Cu2–O8		87.5(1)	O5–Fe–O8	91.1(1)	O4–Se2–O5	100.8(1)
O2–Cu2–O8		86.5(1)	O6–Fe–O1	90.7(1)	O6–Se2–O5	100.6(1)
O3–Cu2–O7		86.8(1)	O6–Fe–O5	94.8(1)	⟨O–Se2–O⟩	100.1
O3–Cu2–O3		78.1(1)	O6–Fe–O4	87.7(1)		
O7–Cu2–O2		88.1(1)	O6–Fe–O9	87.0(1)	Se3–O7	1.677(3)
O7–Cu2–O8		98.3(1)	O8–Fe–O9	86.8(1)	Se3–O8	1.732(2)
O3–Cu2–O2		108.0(1)			Se3–O9	1.742(2)
O3–Cu2–O8		134.7(1)	O4–Fe–O1	169.6(1)	⟨Se3–O⟩	1.717
O3–Cu2–O2		138.8(1)	O5–Fe–O9	175.2(1)	O7–Se3–O8	95.3(1)
O7–Cu2–O3		163.3(1)	O6–Fe–O8	172.3(1)	O7–Se3–O9	104.4(1)
					O8–Se3–O9	97.9(1)
					⟨O–Se3–O⟩	99.2

ferric iron share common corners along rows within formal sheets parallel to (010), involving the Se(1)O₃ and Se(3)O₃ groups. These units are linked via the Se(2)O₃ pyramids to the framework; the atomic arrangement of one 'sheet' is shown in Fig. 2.

The centrosymmetric Cu(1)O₄ square, a coordination figure commonly reported for divalent copper, has four further neighbouring oxygen atoms as far as 2.77 Å (2×O7) and 2.89 Å (2×O8). The Cu(2)O₅ trigonal bipyramid is formed by close ligands (O7 and O3) as apices and by O2, O8 and a further O3 atom arranged in the equatorial plane. The bond-angle sum O–Cu(2)–O within the plane is 360°. Each pair of Cu(2)O₅ groups shares a common edge (O3–O3 = 2.45 Å); the respective O3–Cu(2)–O3 bond angle is by far the smallest within the polyhedron. The FeO₆ octahedron is moderately distorted, with a mean bond length of 2.026 Å; it complies well with the geometry of Fe octahedra observed in various selenites of ferric iron.[2] The trigonal pyramids Se(1)O₃ and Se(2)O₃ are quite regular, while the Se(3)O₃ group is significantly more strongly distorted. The mean Se–O bond lengths are in the range 1.699–1.717 Å. The oxygen atoms are each bound to one selenium atom and to one or two further cations. The three-coordinated oxygens are nearly planar (O2, O3, O8) or slightly pyramidal (O9) coordinated, with M–O–M bond sums (M = Cu, Fe, Se) of 359.6–360.0 and 349.3°, respectively. A calculation of bond strengths[7] yields 1.91, 2.13, 2.96, 4.06, 4.07 and 3.88 v.u. for the cations Cu(1), Cu(2), Fe and Se(1–3).

Comparison of Cu₃Fe₂(SeO₃)₆-I and Cu₃Fe₂(SeO₃)₆-II. The geometry of coordination polyhedra of the Cu, Fe

and Se atoms is the same in both compounds, except for the centrosymmetric Cu(1) atom, which is [4+2] coordinated (1.97, 2.03, 2.33 Å) in phase I: the Cu(2)O₅ trigonal bipyramid (1.94–2.21 Å, ⟨2.038 Å⟩), the FeO₆ octahedron (1.94–2.12 Å, ⟨2.015 Å⟩) and the three selenite groups (⟨Se–O⟩ = 1.705, 1.702 and 1.719 Å) in phase I show similar bond-length and bond-angle distortions. However, in the framework structure of phase I centrosymmetric units of five edge-sharing polyhedra of the sequence FeO₆–Cu(2)O₅–Cu(1)O₆–Cu(2)O₅–FeO₆ are formed. These units are linked by corners or edges with Se(1)O₃ and Se(3)O₃ pyramids and by common corners of Cu(1)- and Cu(2)-polyhedra to a sheet parallel to (100) and by the Se(2)O₃ groups to the framework.

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