

The Crystal Structures of the Isotypic Compounds $M_3^{2+}Fe_2^{3+}(SeO_3)_6$ ($M=Cu,Zn$)

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The crystal structures of $M_3^{2+}Fe_2^{3+}(SeO_3)_6$ ($M=Cu,Zn$), synthesized at 500 K, have been solved by single-crystal X-ray diffraction methods. $Cu_3Fe_2(SeO_3)_6$ and $Zn_3Fe_2(SeO_3)_6$ are isotypic, the unit cell data are $a=12.417(9)$, $12.491(8)$, $b=8.269(4)$, $8.331(5)$, $c=7.627(6)$, $7.696(5)$ Å, $\beta=96.31(5)$, $95.96(4)^\circ$, $V=778.4$, 796.5 Å³, $Z=2$, space group $P2_1/c$. The structure consists of FeO_6 octahedra, MO_5 trigonal bipyramids and MO_6 polyhedra as well as trigonal pyramidal SeO_3 groups. These polyhedra are combined by common corners and edges to a complicated framework.

Synthesis and crystal chemistry of iron(III)–selenium(IV) oxosalts have been the subject of detailed investigations within the last few years; dozens of new phases result therefrom, for a survey of the literature see Ref. 1. Most recently, the compounds $Rb_4MgFe_8(SeO_3)_{14}(SeO_2OH)_2 \cdot 2H_2O$ and $Rb_4CuFe_8(SeO_3)_{14}(SeO_2OH)_2 \cdot 2H_2O$,² $KFe_2(SeO_3)_3(SeO_2OH)$,³ $NaFe(SeO_3)_2$,⁴ as well as $ZnFe_2(SeO_3)_4$,⁵ $Zn_3Fe_2(SeO_3)_6$ and $Cu_3Fe_2(SeO_3)_6$, were obtained, the last two of which are characterized in the present paper.

Synthesis

The preparation of the title compounds was carried out in Teflon-lined steel vessels (50 cm³ capacity, filling rate ca. 30%) at temperatures of 500 K within the period of one week: aqueous solutions of mixtures of SeO_2 , $FeC_2O_4 \cdot 2H_2O$ and $Cu(OH)_2 \cdot 2H_2O$ (respectively $ZnSeO_3$) were finally cooled to room temperature within 12 h resulting in a precipitate consisting of individual crystal grains up to 0.5 mm in size. These reaction products could be identified to be a mixture of (a) $Fe_2(SeO_3)_3 \cdot H_2O$ ⁶ and $Cu_3Fe_2(SeO_3)_6$ and (b) $ZnFe_2(SeO_3)_4$ ⁴ and $Zn_3Fe_2(SeO_3)_6$. The crystals of $Cu_3Fe_2(SeO_3)_6$ and $Zn_3Fe_2(SeO_3)_6$ are of brownish- (Cu) or olive green (Zn) color, showing the crystallographic forms $\{100\}$, $\{111\}$ and $\{211\}$.

X-Ray crystallography and structure determination

Single crystals were preliminarily examined using Weissenberg (Cu K α radiation) methods to select appropriate

material for the measurements on the four-circle diffractometer. For a compilation of crystal data, technical details of the data collection and of the structure refinements see Table 1. The lattice constants were derived from accurately measured 2θ values of 46/40 reflections.

The X-ray intensities were corrected for Lorentz and polarization effects, as well as for absorption (ψ -scans). The crystal structure of $Zn_3Fe_2(SeO_3)_6$ was determined by direct (SHELXS-86)⁷ and Fourier methods and was used as a starting model for the refinement of the copper analogue. Complex scattering curves for neutral atoms were taken from Ref. 8. The structure parameters, listed in Table 2, were obtained by full-matrix least-squares techniques (SHELXL-93)⁹ on F^2 . The residual electron densities in final difference Fourier maps were <1.1 (respectively 0.8) e Å⁻³. Selected bond distances and angles are given in Table 3.

Discussion

$Cu_3Fe_2(SeO_3)_6$ and $Zn_3Fe_2(SeO_3)_6$ form a complicated framework structure as illustrated in Fig. 1. It can be geometrically described to consist of a centrosymmetric group of five edge-sharing polyhedra FeO_6 – M_2O_5 – M_1O_6 – M_2O_5 – FeO_6 , arranged approximately along $[102]$. These formal units are combined by corner- or in addition by edge-linkage with trigonal pyramidal SeO_3 and Se_3O_3 groups and by common corners of M_1O_6 and M_2O_5 polyhedra to a complex sheet parallel to (100), further linked via Se_2O_3 -pyramids to a framework structure.

Table 1. Summary of crystal data, details of X-ray measurements and results of structure refinements for Cu₃Fe₂(SeO₃)₆ and Zn₃Fe₂(SeO₃)₆.^a

	Cu ₃ Fe ₂ (SeO ₃) ₆	Zn ₃ Fe ₂ (SeO ₃) ₆
Space group	P2 ₁ /c	P2 ₁ /c
a/Å	12.417(9)	12.491(8)
b/Å	8.269(4)	8.331(5)
c/Å	7.627(6)	7.696(5)
β/°	96.31(5)	95.96(4)
V/Å ³	778.4	796.5
Z	2	2
ρ _{calc.} /g cm ⁻³	4.54	4.46
μ(Mo Kα)/cm ⁻¹	200	200
(sinθ/λ) _{max} /Å ⁻¹	0.6	0.6
h k l _{min/max}	-14/14; -9/9; -9/9	-14/14; -9/9; -9/9
Reflections measured	5741	5638
Unique reflections	1378	1408
Reflections with F _o > 4σ(F _o)	1132	1003
2θ-range for lattice parameters/°	28–43	25–35
Extinction coefficient	0.0005(3)	0.0011(3)
Variable parameters	134	134
R ₁ , wR ₂	0.025/0.058	0.034/0.072
R ₁ = Σ F _o - F _c / Σ F _o		
wR ₂ = [Σw(F _o ² - F _c ²) ² / ΣwF _o ⁴] ^{1/2}		
w = 1/[σ ² (F _o ²) + a ² P ²]	a ² = 0.0258	0.0328
P = {[max of (0 or F _o ²)] + 2F _c ² } / 3		

^a Equipment: STOE four-circle diffractometer AED2; graphite monochromatized Mo Kα radiation. Data collection: 2θ-ω-scans, 46 steps/reflection, increased for α₁-α₂ dispersion, 2×4 steps for background correction, 0.03° and 0.5–2.0 s/step, 3 standard reflections each 120 min.

Description of coordination polyhedra. The centrosymmetric M1 atom is [4+2]-coordinated to each two O9, O7 and O2 atoms. While the mean M1–O bond lengths are almost the same in both compounds, the Cu1O₆ polyhedron is the more elongated one, which can be attributed to the Jahn–Teller effect of divalent copper. The short intrapolyhedral distances O7–O2 and the rather

small O7–M1–O2 angles are caused by edge-linkage with two adjacent M2O₅ groups.

These M2O₅ polyhedra are distorted bipyramids with O3 and O7 as apices and O2, O9 and O8 in an equatorial arrangement. The O3–M2–O7 angles are 173.9° (Cu) and 171.8° (Zn). The M2O₅ bipyramids have similar bond angle distortions but differ with respect to the in-

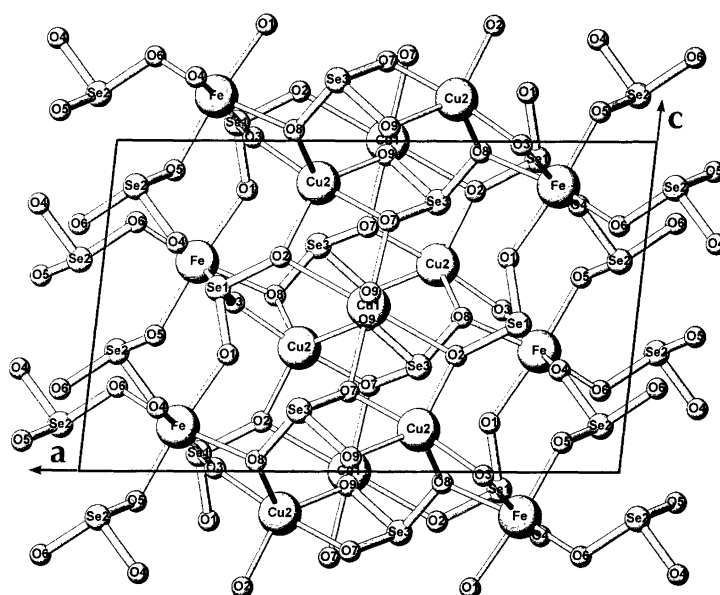


Fig. 1. Crystal structure of Cu₃Fe₂(SeO₃)₆, projection parallel to [010]. The figure was drawn with the program ATOMS.¹⁰

Table 2. Structural parameters of $\text{Cu}_3\text{Fe}_2(\text{SeO}_3)_6$ and $\text{Zn}_3\text{Fe}_2(\text{SeO}_3)_6$ with e.s.d.s in parentheses.

Atom	x	y	z	U_{eq}^a
Cu1	0.5	0.0	0.5	0.0204(2)
Zn1	0.5	0.0	0.5	0.0250(4)
Cu2	0.38122(6)	0.12065(7)	0.12658(8)	0.0211(2)
Zn2	0.37701(7)	0.10203(11)	0.11502(14)	0.0192(3)
Fe	0.82585(7) 0.82909(9)	0.00531(8) 0.00379(13)	0.13429(9) 0.1418(2)	0.0167(2) 0.0170(3)
Se1	0.21809(5) 0.22028(6)	0.09841(6) 0.09796(9)	0.44642(6) 0.44156(12)	0.0167(2) 0.0155(2)
Se2	0.95538(5) 0.95417(6)	0.19829(5) 0.19788(9)	0.86081(6) 0.86374(12)	0.0180(2) 0.0173(2)
Se3	0.60546(5) 0.60487(6)	0.18448(5) 0.17947(9)	0.18332(6) 0.18258(12)	0.0168(2) 0.0161(2)
O1	0.2510(4) 0.2473(4)	0.0168(4) 0.0209(6)	0.6479(4) 0.6426(8)	0.0248(9) 0.0236(15)
O2	0.3274(3) 0.3355(4)	0.0370(4) 0.0431(6)	0.3506(4) 0.3572(8)	0.0219(8) 0.0175(13)
O3	0.2512(3) 0.2465(4)	0.2999(4) 0.2995(6)	0.4899(5) 0.4805(9)	0.0209(9) 0.0223(14)
O4	0.8679(3) 0.8673(5)	0.2687(4) 0.2692(6)	0.6919(4) 0.6973(9)	0.0211(8) 0.0234(15)
O5	0.8874(3) 0.8849(4)	0.0292(4) 0.0300(6)	0.9099(4) 0.9142(8)	0.0193(8) 0.0185(14)
O6	0.0529(3) 0.0481(4)	0.1143(4) 0.1122(6)	0.7463(5) 0.7460(8)	0.0223(8) 0.0236(14)
O7	0.5185(3) 0.5251(4)	0.0339(4) 0.0265(6)	0.2408(4) 0.2402(8)	0.0201(8) 0.0205(14)
O8	0.6747(3) 0.6778(4)	0.0928(4) 0.0887(6)	0.0326(4) 0.0342(8)	0.0185(8) 0.0167(13)
O9	0.5002(3) 0.5022(4)	0.2650(4) 0.2604(6)	0.0423(4) 0.0443(8)	0.0176(8) 0.0190(14)

^a $U_{\text{eq}} = 1/3 [U_{22} + 1/\sin^2 \beta (U_{11} + U_{33} + 2U_{13}\cos\beta)]$. Anisotropic displacement factors can be obtained from the author upon request.

dividual M2–O bond lengths, which vary from 1.938 to 2.210 Å (Cu) and only from 2.013 to 2.159 Å (Zn). In the copper compound the two near oxygen atoms (O3 and O7) are more distinctly separated from the three equatorial oxygen atoms, a feature commonly known in the stereochemistry of divalent copper.¹¹ Polyhedral distortions can again be explained by the presence of further common edges with neighbouring polyhedra: O7–O9 and O3–O8 are common with the Se_3O_3 and the FeO_6 polyhedra, respectively.

The FeO_6 octahedra are very similar in both compounds, the mean Fe–O bond distances of 2.015 and 2.020 Å comply well with the data known for ferric iron in an octahedral coordination. The small angle O3–Fe–O8 of ca. 76° is caused by the linkage with the M_2O_5 bipyramids.

Three different SeO_3 groups are in typical trigonal pyramidal coordination with mean Se–O bond lengths and bond angles varying from 1.702 to 1.719 Å; 97.1 to 99.9° (Cu) and 1.703 to 1.710 Å; 98.1 to 100.0° (Zn). While the

Se_1O_3 and Se_2O_3 groups are rather regular, the Se_3O_3 pyramids in both compounds have quite small O7–Se3–O9 bond angles owing to the common edge with the M_2O_5 bipyramids.

Each oxygen atom is bound to one selenium atom and in addition belongs to one iron atom only or to one M2 atom and a further metal ion. The analogous bond angles are quite similar for both compounds: the oxygen atoms O1, O4, O5 and O6 are two-coordinated with respective Se–O–Fe angles of 134.3/137.2°, 128.7/128.0°, 121.9/121.9° and 121.4/121.8°. O2, O3, O7, O8 and O9 are three-coordinated with bond angle sums of 347.7/354.6°, 359.1/358.8°, 325.4/323.7°, 337.8/338.5° and 343.3/346.3° in $\text{Cu}_3\text{Fe}_2(\text{SeO}_3)_6$ and $\text{Zn}_3\text{Fe}_2(\text{SeO}_3)_6$, respectively.

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Table 3. Interatomic distances and bond angles with intrapolyhedral O–O edges (given in brackets) in Cu₃Fe₂(SeO₃)₆ and Zn₃Fe₂(SeO₃)₆.

		Angle/°	Distance/Å			Angle/°	Distance/Å
Cu1–O9 ^{iii,v}	2X		1.970(3)	Zn1–O9 ^{iii,v}	2X		2.025(5)
Cu1–O7 ^{i,iv}	2X		2.034(4)	Zn1–O7 ^{i,iv}	2X		2.067(6)
Cu1–O2 ^{i,iv}	2X		2.334(5)	Zn1–O2 ^{i,iv}	2X		2.256(6)
<Cu1–O>			<2.113>	<Zn1–O>			<2.116>
O9–Cu1–O7	2X	88.6(1)	[2.796(5)]	O9–Zn1–O7	2X	86.8(2)	[2.810(8)]
O9–Cu1–O2	2X	91.4(1)	[2.867(5)]	O9–Zn1–O2	2X	93.3(2)	[2.975(8)]
O9–Cu1–O7	2X	93.7(1)	[3.150(5)]	O9–Zn1–O2	2X	94.5(2)	[3.148(7)]
O9–Cu1–O2	2X	86.3(1)	[2.955(5)]	O9–Zn1–O2	2X	85.5(2)	[2.910(7)]
O7–Cu1–O2	2X	72.7(2)	[2.602(5)]	O7–Zn1–O2	2X	74.6(2)	[2.623(7)]
O7–Cu1–O2	2X	107.3(2)	[3.522(5)]	O7–Zn1–O2	2X	105.4(2)	[3.442(8)]
<O–O>			<2.982>	<O–O>			<2.985>
Cu2–O3 ^{vi}	1X		1.938(4)	Zn2–O3 ^{vi}	1X		2.013(6)
Cu2–O7 ⁱ	1X		1.963(4)	Zn2–O7 ⁱ	1X		2.092(6)
Cu2–O2 ⁱ	1X		2.024(4)	Zn2–O9 ⁱ	1X		2.046(6)
Cu2–O9 ⁱ	1X		2.056(4)	Zn2–O9 ⁱ	1X		2.159(5)
Cu2–O8 ⁱⁱ	1X		2.210(3)	Zn2–O8 ⁱⁱ	1X		2.037(5)
<Cu2–O>			<2.038>	<Zn2–O>			<2.069>
O3–Cu2–O2	1X	103.7(2)	[3.116(5)]	O3–Zn2–O2	1X	107.3(2)	[3.270(8)]
O3–Cu2–O9	1X	102.7(2)	[3.121(5)]	O3–Zn2–O9	1X	101.0(2)	[3.221(7)]
O3–Cu2–O8	1X	77.4(1)	[2.604(5)]	O3–Zn2–O8	1X	79.7(2)	[2.595(7)]
O7–Cu2–O2	1X	81.5(2)	[2.602(5)]	O7–Zn2–O2	1X	78.7(2)	[2.623(7)]
O7–Cu2–O9	1X	74.5(2)	[2.433(5)]	O7–Zn2–O9	1X	70.8(2)	[2.462(8)]
O7–Cu2–O8	1X	99.0(1)	[3.178(5)]	O7–Zn2–O8	1X	104.8(2)	[3.270(8)]
O2–Cu2–O9	1X	141.0(2)	[3.847(5)]	O2–Zn2–O9	1X	129.4(2)	[3.802(8)]
O2–Cu2–O8	1X	94.5(2)	[3.111(5)]	O2–Zn2–O8	1X	103.0(2)	[3.194(8)]
O9–Cu2–O8	1X	119.0(1)	[3.677(5)]	O9–Zn2–O8	1X	123.0(2)	[3.688(7)]
<O–O>			<3.077>	<O–O>			<3.125>
Fe–O6 ^{iv}	1X		1.942(4)	Fe–O6 ^{iv}	1X		1.939(6)
Fe–O5 ^{vii}	1X		1.959(4)	Fe–O5 ^{vii}	1X		1.963(6)
Fe–O4 ^{vi}	1X		1.976(4)	Fe–O4 ^{vi}	1X		1.986(5)
Fe–O1 ^{iv}	1X		2.013(4)	Fe–O1 ^{iv}	1X		2.009(6)
Fe–O8 ⁱ	1X		2.081(4)	Fe–O8 ⁱ	1X		2.105(6)
Fe–O3 ^v	1X		2.121(4)	Fe–O3 ^v	1X		2.118(6)
<Fe–O>			<2.015>	<Fe–O>			<2.020>
O6–Fe–O5	1X	96.0(2)	[2.899(5)]	O6–Fe–O5	1X	96.6(2)	[2.913(9)]
O6–Fe–O4	1X	101.8(2)	[3.041(5)]	O6–Fe–O4	1X	102.6(3)	[3.062(7)]
O6–Fe–O1	1X	88.9(2)	[2.769(5)]	O6–Fe–O1	1X	90.2(3)	[2.796(7)]
O6–Fe–O3	1X	95.2(2)	[3.002(5)]	O6–Fe–O3	1X	95.3(2)	[3.002(8)]
O5–Fe–O4	1X	88.8(1)	[2.755(5)]	O5–Fe–O4	1X	89.2(2)	[2.774(8)]
O5–Fe–O8	1X	93.6(2)	[2.945(5)]	O5–Fe–O8	1X	90.0(2)	[2.877(7)]
O5–Fe–O3	1X	83.7(2)	[2.726(5)]	O5–Fe–O3	1X	82.9(2)	[2.704(7)]
O4–Fe–O1	1X	92.3(2)	[2.876(5)]	O4–Fe–O1	1X	92.5(2)	[2.887(8)]
O4–Fe–O8	1X	87.7(2)	[2.811(5)]	O4–Fe–O8	1X	87.2(2)	[2.822(7)]
O1–Fe–O8	1X	81.3(2)	[2.667(5)]	O1–Fe–O8	1X	82.8(2)	[2.723(8)]
O1–Fe–O3	1X	93.7(2)	[3.017(5)]	O1–Fe–O3	1X	93.3(2)	[3.001(9)]
O8–Fe–O3	1X	76.6(2)	[2.604(5)]	O8–Fe–O3	1X	75.8(2)	[2.595(7)]
<O–O>			<2.843>	<O–O>			<2.846>
Se1–O1 ⁱ	1X		1.687(4)	Se1–O1 ⁱ	1X		1.677(7)
Se1–O2 ⁱ	1X		1.688(4)	Se1–O2 ⁱ	1X		1.701(5)
Se1–O3 ⁱ	1X		1.739(3)	Se1–O3 ⁱ	1X		1.731(5)
<Se1–O>			<1.705>	<Se1–O>			<1.703>
O1–Se1–O2	1X	98.5(2)	[2.558(5)]	O1–Se1–O2	1X	98.7(3)	[2.564(8)]
O1–Se1–O3	1X	100.4(2)	[2.633(5)]	O1–Se1–O3	1X	101.3(3)	[2.634(8)]
O2–Se1–O3	1X	100.7(2)	[2.640(5)]	O2–Se1–O3	1X	100.1(3)	[2.631(7)]
<O–Se1–O>		<99.9>	<2.610>	<O–Se1–O>		<100.0>	<2.610>
Se2–O4 ⁱ	1X		1.695(4)	Se2–O4 ⁱ	1X		1.698(7)
Se2–O5 ⁱ	1X		1.696(3)	Se2–O5 ⁱ	1X		1.710(5)
Se2–O6 ^{viii}	1X		1.716(4)	Se2–O6 ^{viii}	1X		1.710(5)
<Se2–O>			<1.702>	<Se2–O>			<1.706>

Continued.

Table 3. Continued.

		Angle/°	Distance/Å			Angle/°	Distance/Å
O4–Se2–O5	1×	99.1(2)	[2.580(5)]	O4–Se2–O5	1×	99.2(3)	[2.594(8)]
O4–Se2–O6	1×	100.5(2)	[2.622(5)]	O4–Se2–O6	1×	99.6(3)	[2.602(7)]
O5–Se2–O6	1×	100.1(2)	[2.616(5)]	O5–Se2–O6	1×	99.8(3)	[2.616(7)]
<O–Se2–O>		<99.9>	<2.606>	<O–Se2–O>		<99.5>	<2.604>
Se3–O7 ⁱ	1×		1.736(4)	Se3–O7 ⁱ	1×		1.705(5)
Se3–O8 ⁱ	1×		1.689(4)	Se3–O8 ⁱ	1×		1.709(5)
Se3–O9 ⁱ	1×		1.732(4)	Se3–O9 ⁱ	1×		1.717(6)
<Se3–O>			<1.719>	<Se3–O>			<1.710>
O7–Se3–O8	1×	103.1(2)	[2.683(5)]	O7–Se3–O8	1×	102.1(2)	[2.655(7)]
O7–Se3–O9	1×	89.1(2)	[2.433(5)]	O7–Se3–O9	1×	92.1(3)	[2.462(8)]
O8–Se3–O9	1×	99.0(2)	[2.601(5)]	O8–Se3–O9	1×	100.1(3)	[2.626(6)]
<O–Se3–O>		<97.1>	<2.572>	<O–Se3–O>		<98.1>	<2.581>

^a Symmetry operators: ⁱ x, y, z ; ⁱⁱ $1-x, -y, -z$; ⁱⁱⁱ $x, 1/2-y, 1/2+z$; ^{iv} $1-x, -y, 1-z$; ^v $1-x, y-1/2, 1/2-z$; ^{vi} $x, 1/2-y, z-1/2$; ^{vii} $x, y, z-1$; ^{viii} $x+1, y, z$.

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