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The Crystal Structure of $Fe_2(SeO_3)_3 \cdot H_2O$

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Crystals of $Fe_2(SeO_3)_3 \cdot H_2O$, obtained by hydrothermal synthesis, were structurally investigated by single crystal X-ray diffraction methods: $a = 7.955(2)$Å, $b = 9.890(2)$Å, $c = 11.538(3)$Å, $\beta = 101.65(1)°$, $V = 889.05$Å^3, $Z = 4$, space group $P2_1/n$, $R = 0.042$, $R_w = 0.037$ for 2188 independent reflections ($\sin \Theta/\lambda \leq 0.7$Å^{-1}). $[Fe1^{[6O]}Fe2^{[5O+1Ow]}O_{10}]$-groups of edge-sharing Fe(III)-polyhedra are corner connected via $Se(IV)O_3$ pyramids to a framework structure. Octahedral Fe–O distances are in the range 1.954–2.102Å for Fe1 and 1.928–2.117Å for Fe2 with mean bond lengths of 2.007 and 2.015Å. The selenite groups are moderately distorted; the mean Se–O lengths are 1.681, 1.695, and 1.708Å.

Introduction

A series of phases containing ferric iron and $Se(IV)O_3$ groups is known; among them the following have been structurally investigated: $FeH(SeO_3)_2$ (*1*), $Fe_2(SeO_3)_3 \cdot 6H_2O$ (*2*), $Fe(HSeO_3)(Se_2O_5)$ (*3*), $Fe(HSeO_3)_3$ (*3*), and the Se(IV)–Se(VI) compound $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ (*4*). The title compound was obtained in the course of hydrothermal experiments on kieserite-type compounds (*5, 6*) in the system selenic acid–iron–water. The formula $Fe_2(SeO_3)_3 \cdot H_2O$ was established by crystal structure determination.

Experimental

Synthesis. The crystals were grown hydrothermally in Teflon-lined steel vessels of ~50 cm^3 capacity. Mixtures of ~1 g $FeC_2O_4 \cdot 2H_2O$ (Fa. E. Merck, Darmstadt, FRG), 1 ml concentrated H_2SeO_4 (Fa. Fluka Chemie AG, Buchs, CH), and 2 ml H_2O were held for one week at 500 K. Finally the vessels were cooled to room temperature within 12 hr. A mixture of various compounds was obtained, of which the Fe(III) compounds $FeH(SeO_3)_2$, $Fe_2(SeO_4)_3$ (*7*), and $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ could be identified by X-ray powder diffraction. Yellowish green, prismatic crystals of $Fe_2(SeO_3)_3 \cdot H_2O$ were up to 0.4 mm in size.

Structure determination. A prismatic crystal with the monoclinic forms {001}, {010}, and {110} was chosen for further investigation on a four-circle diffractometer. The lattice constants were refined from 52 reflections in the range $37° < 2\Theta < 49°$ and the X-ray intensities were measured at 295 K. A summary of crystal data, X-ray data collection, and details of the structure refinement is listed in Table I. Intensities were corrected for Lorentz and polarization effects and for absorption according to the shape of the crystal. Complex scattering

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TABLE I

SUMMARY OF CRYSTAL DATA, X-RAY MEASUREMENTS, AND STRUCTURE REFINEMENTS FOR $Fe_2(SeO_3)_3 \cdot H_2O$

a [Å]	7.955(2)
b [Å]	9.890(2)
c [Å]	11.538(3)
β [°]	101.65(1)
V [Å^3]	889.05
Space group	$P2_1/n$
Formula units per cell	4
ρ_{calc} [g cm^{-3}]	3.815
μ(Mo$K\alpha$) [cm^{-1}]	151.53
Transmission factors	0.22–0.33
Crystal dimensions [mm]	0.09 × 0.12 × 0.18

Equipment: Stoe four-circle diffractometer AED2; graphite monochromatized Mo$K\alpha$ – radiation; program system STRUCSY (9).

Data collection: 2Θ–ω scans; 60 steps/reflection, increased for α_1–α_2 splitting; 0.03° and 0.5–1.5 sec/step; 2 × 10 steps for background measurement; 3 standard reflections each 120 min; $2\Theta_{max} = 60°$

Measured reflections	5924
Internal R(I)	0.058
Unique data set	2595
Data with $F_0 > 3\sigma(F_0)$	2188
Number of variables	136
Reliability index R	0.042
R_w ($w = 1/[\sigma(F_0)]^2$)	0.037

curves for neutral atoms were used (*8*); an extinction correction was not necessary. The structure of $Fe_2(SeO_3)_3 \cdot H_2O$ was solved by direct methods and Fourier syntheses. Unfortunately the positions of the hydrogen atoms, approximately localized by a final difference Fourier map, could not be definitely refined. Structural parameters for the nonhydrogen atoms were obtained by full-matrix least-squares techniques (*9*); they are presented in Table II.

To support the chemical composition $Fe_2(SeO_3)_3 \cdot H_2O$ with respect to the H_2O content, 24.5 mg of the compound were quantitatively analyzed with a Du Pont Moisture Evolution Analyzer 903 H. As a result, 3.5(1)wt.% of water were measured, in excellent agreement with the theoretical value (3.53%).

Discussion

In $Fe_2(SeO_3)_3 \cdot H_2O$ there are three nonequivalent selenium, two iron, and ten oxygen positions, all atoms occupying general sites. Selected bond lengths and angles as well as bond valence calculations (*10*) are given in Table III. Details of the crystal structure are shown in Figs. 1a and 2a in projections along [100] and [001].

The Fe atoms are 6-coordinated to oxygen atoms with Fe–O distances ranging from 1.928 to 2.117Å. ⟨Fe–O⟩ bond lengths for Fe1 and Fe2 are 2.007 and 2.015Å, which agree well with the mean value of 2.011Å, known for ferric iron (*11*). $Fe1O_6$ and $Fe2O_6$ form pairs of edge-sharing, rather distorted octahedra. The common edge O4–O9 forms by far the shortest O–O distance within the $[Fe1^{[6O]}Fe2^{[5O+Ow]}O_{10}]$ group. Eight selenite groups share nine corners with the Fe_2O_{10} pair; one corner belongs to a water molecule. The longitudinal direction of Fe_2O_{10} pairs is oriented parallel to [100]. These Fe_2O_{10} groups are cornerconnected with the selenite pyramids to a framework structure with "channels" along the a-axis, obviously meeting the space requirements of the lone pair electrons of the selenite groups.

The Se atoms are each bound to three oxygens, forming trigonal pyramidal groups as characteristic for Se(IV)O_3 coordinations. The $Se1O_3$ pyramid is linked with two oxygens of one Fe_2O_{10} pair and with one oxygen of a second Fe_2O_{10} dimer, the selenite groups $Se2O_3$ and $Se3O_3$ each are connected to three Fe_2O_{10} pairs. This atomic arrangement is illustrated in detail in Fig. 2a. Distortions of bond lengths and angles within the polyhedra are well correlated with the specific environment of each polyhedron: the quite large bond angle O1–Se–O3 is due to the fact that the edge O1–O3 combines two corners of the iron

TABLE II

STRUCTURAL PARAMETERS OF $Fe_2(SeO_3)_3 \cdot H_2O$ WITH E.S.D.'S IN PARENTHESES

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Fe1	.30603(10)	.23496(8)	.77293(7)	88(3)	121(4)	168(4)	−1(3)	11(3)	3(3)	1.01
Fe2	.19622(10)	.25712(8)	.22924(7)	95(4)	120(4)	223(4)	6(3)	37(3)	16(3)	1.15
Se1	.13430(8)	.33798(7)	.49342(5)	148(3)	227(3)	205(3)	−5(2)	−6(2)	40(2)	1.57
Se2	.00379(7)	.45139(5)	.83314(5)	109(3)	101(2)	222(3)	5(2)	45(2)	7(2)	1.12
Se3	.50711(7)	.47572(5)	.18731(5)	96(2)	100(2)	209(3)	4(2)	33(2)	11(2)	1.07
O1	−.0648(6)	.2804(5)	.4396(3)	154(21)	438(28)	128(20)	−17(20)	−36(16)	−23(19)	1.97
O2	.1934(6)	.2314(5)	.6060(4)	264(24)	290(24)	191(21)	−61(20)	−45(18)	96(18)	2.06
O3	.2594(6)	.2736(5)	.4036(4)	122(21)	424(28)	270(23)	32(20)	25(18)	22(21)	2.16
O4	.0075(5)	.6107(4)	.7717(4)	105(19)	100(18)	297(22)	−26(15)	20(16)	32(16)	1.34
O5	.2004(5)	.3995(4)	.8223(4)	107(20)	152(19)	386(26)	17(16)	67(18)	−26(18)	1.68
O6	−.1191(5)	.3663(4)	.7209(4)	152(20)	157(19)	321(24)	−30(16)	48(18)	−43(17)	1.66
O7	.6302(5)	.3913(4)	.3019(4)	154(20)	177(20)	205(20)	68(16)	76(16)	23(16)	1.37
O8	.3089(5)	.4211(4)	.1904(4)	106(19)	172(19)	404(27)	−21(17)	90(18)	20(19)	1.75
O9	.5022(5)	.6317(4)	.2584(4)	123(19)	98(17)	316(24)	−10(15)	88(17)	−36(16)	1.37
Ow	.1215(7)	.2254(6)	.0446(4)	378(30)	459(30)	174(23)	59(25)	33(21)	6(21)	2.69
H1	.216	.247	.005							
H2	.038	.194	.003							

Note. U_{ij} are given in pm^2. ATF = $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij} h_i h_j a_i^* a_j^*]$. The positions of the hydrogen atoms H1 and H2 were not refined.

octahedra within one Fe_2O_{10} group. The $Se2O_3$ and $Se3O_3$ pyramids have each one relatively long Se–O bond length. These oxygen atoms (O4 and O9) are those further bound to two Fe atoms each, forming the common edge of the Fe_2O_{10} pair.

With the exception of O4, O9, and Ow, all oxygen atoms are coordinated to one iron and one selenium atom with Fe–O–Se bond angles ranging from 120.1° to 139.3°. O4 and O9 are fairly planar or slightly pyramidal 3-coordinated (sums of the three bond angles are 358.2° and 347.4° for O4 and O9, respectively). The oxygen atom Ow is bound to only one Fe2 atom with a distance of 2.117Å. A bond valence calculation for Ow leads to a value of 0.38 v.u., definitely proving the presence of a water molecule. Neglecting Ow–O bonds within the Fe2 polyhedron, there are four Ow–O contacts <3.64Å, which come into consideration for hydrogen bonding. Bond lengths, bond valence calculations, and the bond angles Se–O–Fe for these atoms are as follows:

Ow–O1:	2.986Å	1.96 v.u.	130.2°
Ow–O3:	3.009Å	1.91 v.u.	126.2°
Ow–O7:	3.041Å	1.95 v.u.	120.1°
Ow–O5:	3.254Å	2.02 v.u.	137.3°.

Figure 3 illustrates the atomic arrangement in the region of the water molecule: Ow is nearly coplanar with the atoms Fe2, O1, and O3, the sum of the three angles Fe2–Ow–O1, Fe2–Ow–O3, and O1–Ow–O3 (124.6°) being 359.5°. O1 and O3 are considered (in accordance to the positions of the weak peaks H1 and H2 in the difference Fourier synthesis) to be acceptor atoms of hydrogen bonds. Additionally, at least O7 might have a subordinate influence on the hydrogen atoms.

Comparison with other Fe(III) selenites. In $FeH(SeO_3)_2$ (*1*), $Fe_2(SeO_3)_3 \cdot 6H_2O$ (*2*), $Fe(HSeO_3)(Se_2O_5)$ (*3*), $Fe(HSeO_3)_3$ (*3*), and $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ (*4*), as well as in the title compound $Fe_2(SeO_3)_3 \cdot H_2O$, ferric iron is 6-coordinated to oxygen atoms. These octahedra are either isolated or form,

TABLE III

Interatomic Bond Lenghts [Å], Bond Angles [°] (with e.s.d.'s in Parentheses; Intrapolyhedral O–O Distances Are Given in Brackets) and Bond Valences ν [v.u.] in $Fe_2(SeO_3)_3 \cdot H_2O$

	[Å]	[v.u.]
Fe1–O1	1.995(4)	0.53
Fe1–O2	1.954(4)	0.59
Fe1–O4	2.070(4)	0.43
Fe1–O5	1.968(4)	0.57
Fe1–O7	1.954(4)	0.59
Fe1–O9	2.102(4)	0.40
⟨Fe1–O⟩	⟨2.007⟩	3.10

	[°]	[Å]
O1–Fe1–O4	86.5(2)	[2.785(6)]
O1–Fe1–O5	87.2(2)	[2.733(6)]
O1–Fe1–O7	91.9(2)	[2.839(6)]
O1–Fe1–O9	87.9(2)	[2.845(6)]
O2–Fe1–O4	87.3(2)	[2.779(6)]
O2–Fe1–O5	99.4(2)	[2.990(6)]
O2–Fe1–O7	87.5(2)	[2.702(6)]
O2–Fe1–O9	92.6(2)	[2.935(6)]
O4–Fe1–O7	103.7(2)	[3.165(6)]
O4–Fe1–O9	75.4(2)	[2.552(5)]
O5–Fe1–O7	96.7(2)	[2.931(6)]
O5–Fe1–O9	84.2(2)	[2.730(6)]
		⟨2.832⟩

	[Å]	[v.u.]
Fe2–O3	1.979(4)	0.55
Fe2–O4	2.081(3)	0.42
Fe2–O6	1.928(4)	0.63
Fe2–O8	1.948(4)	0.60
Fe2–O9	2.035(4)	0.47
Fe2–Ow	2.117(4)	0.38
⟨Fe2–O⟩	⟨2.015⟩	3.06

	[°]	[Å]
O3–Fe2–O4	89.5(2)	[2.859(6)]
O3–Fe2–O6	93.6(2)	[2.849(6)]
O3–Fe2–O8	97.5(2)	[2.953(7)]
O3–Fe2–O9	91.2(2)	[2.868(6)]
O4–Fe2–O8	82.5(2)	[2.659(6)]
O4–Fe2–O9	76.6(2)	[2.552(5)]
O4–Fe2–Ow	91.6(2)	[3.010(6)]
O6–Fe2–O8	97.2(2)	[2.907(6)]
O6–Fe2–O9	103.1(2)	[3.104(6)]
O6–Fe2–Ow	85.3(2)	[2.743(7)]
O8–Fe2–Ow	86.6(2)	[2.791(7)]
O9–Fe2–Ow	85.2(2)	[2.810(6)]
		⟨2.842⟩

	[Å]	[v.u.]
Se1–O1	1.679(4)	1.43
Se1–O2	1.665(4)	1.48
Se1–O3	1.699(4)	1.35
⟨Se1–O⟩	⟨1.681⟩	4.26

	[°]	[Å]
O1–Se1–O2	99.8(2)	2.559(6)
O1–Se1–O3	105.8(2)	2.694(6)
O2–Se1–O3	97.5(2)	2.530(6)
⟨O–Se1–O⟩	⟨101.0⟩	⟨2.594⟩

	[Å]	[v.u.]
Se2–O4	1.730(3)	1.24
Se2–O5	1.674(4)	1.45
Se2–O6	1.682(4)	1.42
⟨Se2–O⟩	⟨1.695⟩	4.11

	[°]	[Å]
O4–Se2–O5	98.9(2)	2.587(6)
O4–Se2–O6	101.2(2)	2.638(6)
O5–Se2–O6	101.3(2)	2.595(6)
⟨O–Se2–O⟩	⟨100.5⟩	⟨2.607⟩

	[Å]	[v.u.]
Se3–O7	1.697(4)	1.36
Se3–O8	1.674(4)	1.45
Se3–O9	1.752(3)	1.17
⟨Se3–O⟩	⟨1.708⟩	3.98

	[°]	[Å]
O7–Se3–O8	102.8(2)	2.635(6)
O7–Se3–O9	97.6(2)	2.595(6)
O8–Se3–O9	99.4(2)	2.614(6)
⟨O–Se3–O⟩	⟨99.9⟩	⟨2.615⟩

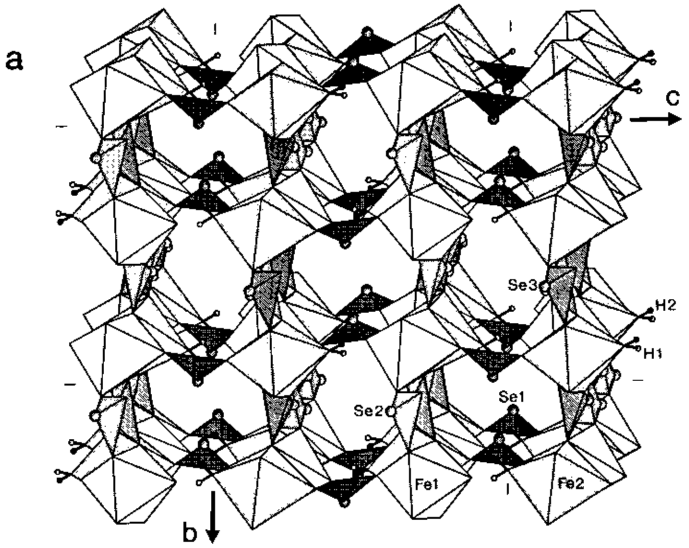

FIG. 1a. Crystal structure of $Fe_2(SeO_3)_3 \cdot H_2O$ in a projection slightly inclined to [100]. The figures were drawn with the program ATOMS. The selenium atoms are symbolized as large circles; the hydrogen atoms H1 and H2, indicated as small circles, represent the unrefined maxima ($\sim 1e/\text{Å}^3$) of the difference Fourier map.

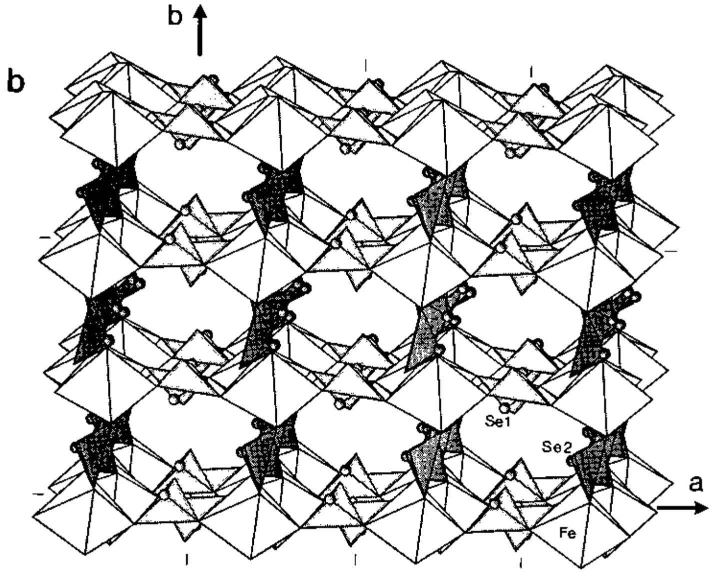

FIG. 1b. Comparable section of $FeH(SeO_3)_2$ projected slightly inclined to [001]. All drawings of $FeH(SeO_3)_2$ were done based on the structure determination by (1). The hydrogen atom of the hydrogen selenite group $Se1O_2OH$ has not been located.

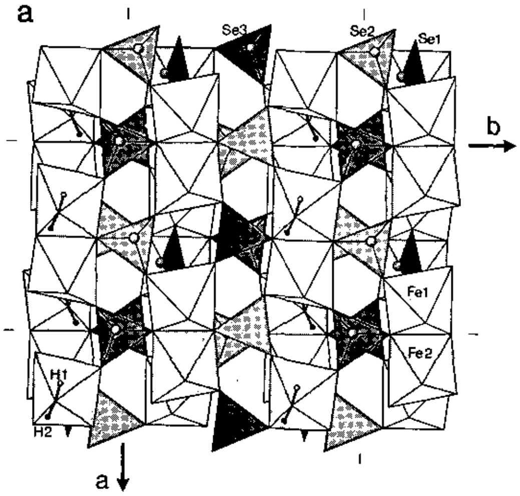

FIG. 2a. Crystal structure of $Fe_2(SeO_3)_3 \cdot H_2O$ in a projection parallel to [001].

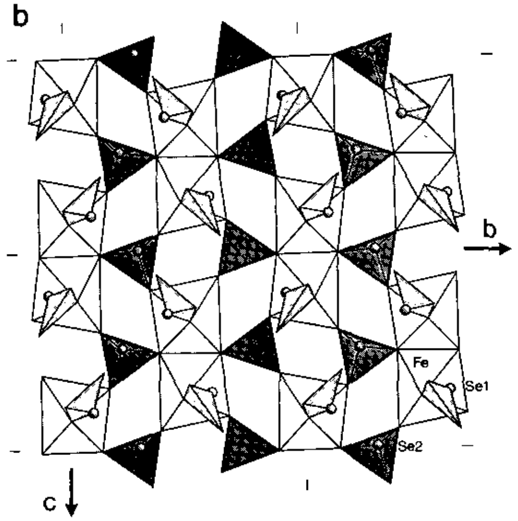

FIG. 2b. Crystal structure of $FeH(SeO_3)_2$ in a projection parallel to [100].

as in the case of $FeH(SeO_3)_2$ and $Fe_2(SeO_3)_3 \cdot H_2O$, pairs of edge-sharing polyhedra. Distortions of bond distances and angles are much smaller for the isolated octahedra than within the Fe_2O_{10} pairs. In $FeH(SeO_3)_2$ the Fe_2O_{10} groups are parallel orientated as in $Fe_2(SeO_3)_3 \cdot H_2O$, but are bound to 10 selenite groups. Within the (100) plane in $FeH(SeO_3)_2$ and the (001) plane in $Fe_2(SeO_3)_3 \cdot H_2O$ polyhedral connections are

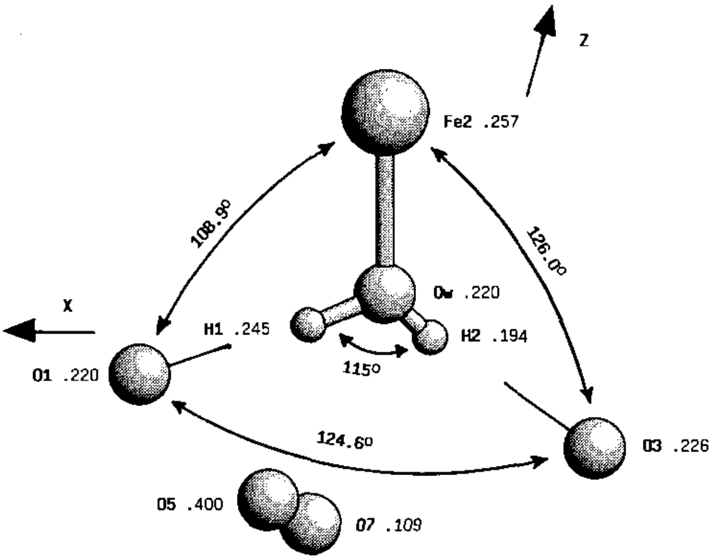

FIG. 3. Proposed hydrogen bonding scheme in $Fe_2(SeO_3)_3 \cdot H_2O$ projected parallel to [010]. The heights *y*/*b* of the atoms are given.

closely related while consecutive sheets are combined differently, as illustrated in Figs. 1a,b and 2a,b.

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