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Synthesis and Crystal Structure of Monoclinic $Fe_2(SeO_4)_3$

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Summary. Crystals of monoclinic $Fe_2(SeO_4)_3$ were synthesized under hydrothermal conditions. The structure was determined by single crystal X-ray methods and refined in space group $P2_1/n$ with 2 646 independent reflections ($\sin\theta/\lambda < 0.7\,Å^{-1}$) to $R = 0.033$, $R_w = 0.037$: $a = 8.530(2)\,Å$, $b = 8.888(2)\,Å$, $c = 11.952(2)\,Å$, $\beta = 91.13(1)°$, $V = 906.0\,Å^3$, $Z = 4$. The crystal structure is isotypic with the monoclinic modification of $Fe_2(SO_4)_3$, containing two different Fe(III) and three Se(VI) atomic positions. The FeO_6 and SeO_4 polyhedra are only slightly distorted, the mean Fe – O bond lengths are 1.986 Å and 2.004 Å, the average distances within the SeO_4 tetrahedra are each 1.628 Å. The isolated FeO_6 octahedra only share corners with SeO_4 tetrahedra to build a framework structure.

Keywords. $Fe_2(SeO_4)_3$; Anhydrous ferric selenate(VI); Crystal structure; Crystal chemistry; Hydrothermal synthesis.

Synthese und Kristallstruktur von monoklinem $Fe_2(SeO_4)_3$

Zusammenfassung. Kristalle von monoklinem $Fe_2(SeO_4)_3$ wurden unter Hydrothermalbedingungen gezüchtet. Die Struktur wurde mit Einkristall-Röntgenmethoden bestimmt und in der Raumgruppe $P2_1/n$ mit 2 646 unabhängigen Reflexen ($\sin\theta/\lambda < 0.7\,Å^{-1}$) auf $R = 0.033$, $R_w = 0.037$ verfeinert: $a = 8.530(2)\,Å$, $b = 8.888(2)\,Å$, $c = 11.952(2)\,Å$, $\beta = 91.13(1)°$, $V = 906.0\,Å^3$, $Z = 4$. Die Kristallstruktur ist isotyp mit der monoklinen Modifikation von $Fe_2(SO_4)_3$, sie enthält zwei unterschiedliche Fe(III) und drei Se(VI) Atompositionen. Die FeO_6-Polyeder sind nur gering verzerrt, die mittleren Fe – O Bindungslängen sind 1.986 Å und 2.004 Å, die mittleren Abstände in den SeO_4-Tetraedern sind jeweils 1.628 Å. Die isolierten FeO_6-Oktaeder sind nur über gemeinsame Ecken mit SeO_4-Tetraedern verbunden, wobei eine Gerüststruktur entsteht.

Introduction

In course of investigations on the kieserite type compounds $Me^{2+}XO_4 \cdot H_2O$ (Me^{2+} = Mg, Mn, Fe, Co, Ni, Zn; X = S, Se) [1, 2] hydrothermal synthesis experiments in the system $FeO - H_2SO_4$ or $H_2SeO_4 - H_2O$ were made and crystals of $Fe(II)Fe(III)_2(SO_4)_4 \cdot 2\,H_2O$ [3], $Fe(SO_4) \cdot H_2O$ [1] and $Fe_2(SeO_4)_3$ were obtained. The present work deals with the determination and description of the crystal structure of $Fe_2(SeO_4)_3$, which proved to be isotypic with the monoclinic polymorph of anhydrous ferric sulfate: $Fe_2(SO_4)_3$ crystallizes in two different modifications with space group $R\bar{3}$ and $P2_1/n$, respectively [4 – 8]. The corresponding rhombohedral selenate compound $Fe_2(SeO_4)_3$ was not obtained yet.

Table 1. Crystal data, X-ray measurement and structure refinement of $Fe_2(SeO_4)_3$

Space group	$P2_1/n$
a [Å]	8.530(2)
b [Å]	8.888(2)
c [Å]	11.952(2)
β [°]	91.13(1)
V [Å^3]	906.0
Formula units per cell	4
Calculated density ρ_{calc} [gcm^{-3}]	3.963
Absorption coefficient μ(MoKα) [cm^{-1}]	148.9

Stoe four-circle diffractometer AED2; graphite monochromatized MoKα-radiation; program system STRUCSY (Stoe & Cie, Darmstadt, FRG).

2θ-ω scans; 40 steps/reflection, increased for $\alpha_1-\alpha_2$ splitting; step width 0.03°, 0.5 – 1.5 s/step; 2 × 5 steps for background measurement; 3 standard reflections each 120 min (variation of $I < 2\%$); $2\theta_{max} = 60°$

Extinction coefficient *g* [10]	$5.6(3) \cdot 10^{-6}$
Total measured reflections ($\pm h$, $\pm k$, $+l$)	5520
Unique data set	2646
Reflections with $F_0 > 3\sigma(F_0)$ (refinement)	2503
Number of variables	155
Reliability index *R*	0.033
R_w ($w = 1/[\sigma(F_0)]^2$)	0.037

Table 2. Atomic coordinates of $Fe_2(SeO_4)_3$, e.s.d.'s in parentheses

Atom	*x/a*	*y/b*	*z/c*
Fe1	0.74782(6)	0.46737(7)	0.61732(4)
Fe2	0.75228(7)	0.03181(7)	0.38432(5)
Se1	0.03783(4)	0.25273(5)	0.49341(3)
Se2	0.60362(4)	0.37643(4)	0.34795(3)
Se3	0.61108(4)	0.11770(5)	0.64386(3)
O1	0.0896(4)	0.1223(3)	0.5830(2)
O2	−0.0671(3)	0.1867(4)	0.3883(2)
O3	0.1953(3)	0.3306(4)	0.4455(2)
O4	−0.0598(4)	0.3754(4)	0.5636(3)
O5	0.7287(4)	0.4767(4)	0.2787(2)
O6	0.4250(3)	0.4206(4)	0.3106(2)
O7	0.6290(4)	0.4057(4)	0.4808(2)
O8	0.6210(4)	0.1962(4)	0.3239(2)
O9	0.6267(4)	−0.0044(4)	0.7444(2)
O10	0.7346(4)	0.0746(4)	0.5463(2)
O11	0.4300(3)	0.1123(4)	0.5966(2)
O12	0.6545(4)	0.2846(4)	0.6900(2)

Table 3. Parameters of the anisotropic thermal motion for $Fe_2(SeO_4)_3$; U_{ij} are given in pm^2; ATF $= \exp[-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* a_j^*]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	135 (2)	103 (3)	135 (2)	− 1 (2)	26 (2)	− 6 (2)
Fe2	144 (2)	109 (3)	138 (2)	10 (2)	24 (2)	− 2 (2)
Se1	127 (2)	91 (2)	145 (2)	4 (1)	32 (1)	5 (1)
Se2	127 (2)	98 (2)	117 (2)	3 (1)	19 (1)	1 (1)
Se3	137 (2)	106 (2)	118 (2)	− 12 (1)	18 (1)	5 (1)
O1	212 (14)	144 (16)	201 (13)	54 (12)	57 (11)	68 (11)
O2	204 (13)	189 (16)	183 (12)	− 83 (12)	26 (10)	− 5 (12)
O3	137 (12)	131 (14)	244 (13)	− 9 (11)	69 (10)	34 (12)
O4	185 (14)	174 (17)	268 (14)	23 (11)	83 (12)	− 30 (12)
O5	201 (13)	222 (17)	160 (12)	− 53 (13)	36 (10)	32 (12)
O6	158 (12)	197 (16)	170 (13)	29 (12)	30 (10)	− 20 (11)
O7	208 (14)	250 (18)	137 (12)	− 22 (13)	1 (10)	− 43 (12)
O8	228 (13)	85 (14)	252 (13)	44 (12)	− 22 (11)	− 49 (12)
O9	221 (13)	169 (15)	180 (12)	− 25 (13)	− 41 (11)	63 (12)
O10	213 (14)	271 (18)	155 (12)	− 15 (13)	65 (11)	− 44 (12)
O11	161 (13)	185 (16)	224 (13)	− 20 (12)	− 21 (11)	44 (12)
O12	316 (15)	109 (15)	155 (12)	− 47 (12)	40 (11)	4 (10)

Experimental

Crystals of $Fe_2(SeO_4)_3$ were hydrothermally synthesized in "Teflon"-lined steel vessels of 50 cm^3 capacity: a mixture of $Fe(II)C_2O_4 \cdot 2\,H_2O$, H_2SeO_4 and H_2O (molar ratio $\approx 2:3:10$) was inserted and heated to 450 K. After one week the vessels were cooled to room temperature. As a result, transparent yellow crystals of the title compound in sizes up to 0.5 mm had formed. They were elongated parallel [010], predominant forms were {100}, {010}, {001} and $\{11\bar{1}\}$.

Preliminary investigations were made by Weissenberg methods; further X-ray measurements were performed on a Stoe four-circle diffractometer AED2. The lattice parameters were derived by least-squares techniques from 36 accurate 2θ values in the range $30° < 2\theta < 42°$. Details of data collection and structure refinement and a summary of crystal data are given in Table 1. The intensities were corrected for Lorentz- and polarisation effects as well as for absorption according to the shape of the crystal. The structure of $Fe_2(SeO_4)_3$ was solved by direct and Fourier methods. The setting was chosen according to [8]. The final structural parameters, obtained by full-matrix least-squares techniques, are summarized in Tables 2 and 3. Complex scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography [9] and a secondary isotropic extinction correction [10] was applied.

Results and Discussion

Selected interatomic distances and bond angles for $Fe_2(SeO_4)_3$ are listed in Table 4, bond strengths [11] are given in Table 5. The atomic arrangement is illustrated in Figs. 1 and 2 in projections parallel to [100] and [010]. The crystal structure of $Fe_2(SeO_4)_3$ is built up by isolated FeO_6 polyhedra, which each share only corners with six selenate groups forming a three-dimensional framework structure.

Table 4. Interatomic distances [Å] and bond angles [°] in $Fe_2(SeO_4)_3$ with e.s.d.'s in parentheses (intrapolyhedral O – O distances are given in brackets)

Fe1 – O3	2.010 (3)	O3 – Fe1 – O4	92.3 (1)	[2.859 (5)]	O1 – Fe2 – O2	87.2 (1)	[2.775 (5)]
Fe1 – O4	1.953 (3)	O3 – Fe1 – O6	84.3 (1)	[2.684 (4)]	O1 – Fe2 – O5	87.4 (1)	[2.746 (4)]
Fe1 – O6	1.989 (2)	O3 – Fe1 – O7	93.6 (1)	[2.909 (4)]	O1 – Fe2 – O10	90.3 (1)	[2.792 (4)]
Fe1 – O7	1.981 (2)	O3 – Fe1 – O9	93.9 (1)	[2.907 (4)]	O1 – Fe2 – O11	93.6 (1)	[2.906 (4)]
Fe1 – O9	1.967 (2)	O4 – Fe1 – O7	91.9 (1)	[2.827 (4)]	O2 – Fe2 – O5	96.3 (1)	[3.043 (4)]
Fe1 – O12	2.014 (3)	O4 – Fe1 – O9	83.3 (1)	[2.605 (4)]	O2 – Fe2 – O8	86.1 (1)	[2.756 (4)]
⟨Fe1 – O⟩	1.986	O4 – Fe1 – O12	98.4 (1)	[3.003 (4)]	O2 – Fe2 – O10	85.5 (1)	[2.747 (4)]
		O6 – Fe1 – O7	97.1 (1)	[2.976 (4)]	O8 – Fe2 – O5	83.2 (1)	[2.648 (4)]
Fe2 – O1	1.956 (3)	O6 – Fe1 – O9	88.2 (1)	[2.753 (4)]	O8 – Fe2 – O10	99.4 (1)	[3.013 (4)]
Fe2 – O2	2.066 (3)	O6 – Fe1 – O12	85.1 (1)	[2.707 (4)]	O8 – Fe2 – O11	94.5 (1)	[2.937 (4)]
Fe2 – O5	2.019 (2)	O12 – Fe1 – O7	86.1 (1)	[2.727 (4)]	O11 – Fe2 – O5	91.8 (1)	[2.908 (4)]
Fe2 – O8	1.969 (3)	O12 – Fe1 – O9	87.3 (1)	[2.749 (4)]	O11 – Fe2 – O10	86.5 (1)	[2.748 (4)]
Fe2 – O10	1.982 (2)	⟨O – Fe1 – O⟩		[2.809]	⟨O – Fe2 – O⟩		[2.835]
Fe2 – O11	2.031 (3)						
⟨Fe2 – O⟩	2.004						
		O1 – Se1 – O2	112.7 (2)	[2.723 (4)]	O5 – Se2 – O6	110.4 (2)	[2.673 (4)]
		O1 – Se1 – O3	108.5 (2)	[2.645 (4)]	O5 – Se2 – O7	109.5 (2)	[2.653 (4)]
		O1 – Se1 – O4	105.9 (2)	[2.593 (4)]	O5 – Se2 – O8	112.6 (2)	[2.715 (5)]
		O2 – Se1 – O3	109.0 (1)	[2.656 (4)]	O6 – Se2 – O7	109.7 (2)	[2.655 (4)]
Se1 – O1	1.633 (2)	O2 – Se1 – O4	111.1 (2)	[2.683 (4)]	O6 – Se2 – O8	106.0 (2)	[2.606 (4)]
Se1 – O2	1.637 (2)	O3 – Se1 – O4	109.5 (2)	[2.647 (4)]	O7 – Se2 – O8	108.6 (2)	[2.643 (4)]
Se1 – O3	1.625 (2)	⟨O – Se1 – O⟩	109.46	[2.658]	⟨O – Se2 – O⟩	109.46	[2.658]
Se1 – O4	1.616 (3)						
⟨Se1 – O⟩	1.628				O9 – Se3 – O10	109.1 (2)	[2.652 (4)]
					O9 – Se3 – O11	107.4 (2)	[2.626 (4)]
Se2 – O5	1.629 (3)	Se3 – O9	1.623 (3)		O9 – Se3 – O12	110.1 (2)	[2.661 (5)]
Se2 – O6	1.627 (2)	Se3 – O10	1.632 (3)		O10 – Se3 – O11	111.4 (2)	[2.699 (4)]
Se2 – O7	1.620 (2)	Se3 – O11	1.635 (2)		O10 – Se3 – O12	108.1 (2)	[2.636 (4)]
Se2 – O8	1.635 (3)	Se3 – O12	1.623 (3)		O11 – Se3 – O12	110.6 (2)	[2.679 (4)]
⟨Se2 – O⟩	1.628	⟨Se3 – O⟩	1.628		⟨O – Se3 – O⟩	109.47	[2.659]

Table 5. Bond valence calculations v [v.u.] [11] for $Fe_2(SeO_4)_3$

	Fe1	Fe2	Se1	Se2	Se3	Σv
O1		0.59	1.52			2.11
O2		0.44	1.50			1.94
O3	0.51		1.55			2.06
O4	0.59		1.59			2.18
O5		0.49		1.54		2.03
O6	0.54			1.55		2.08
O7	0.55			1.57		2.12
O8		0.57		1.51		2.08
O9	0.57				1.56	2.13
O10		0.55			1.52	2.07
O11		0.48			1.51	1.99
O12	0.50				1.56	2.06
Σv	3.26	3.11	6.17	6.17	6.16	

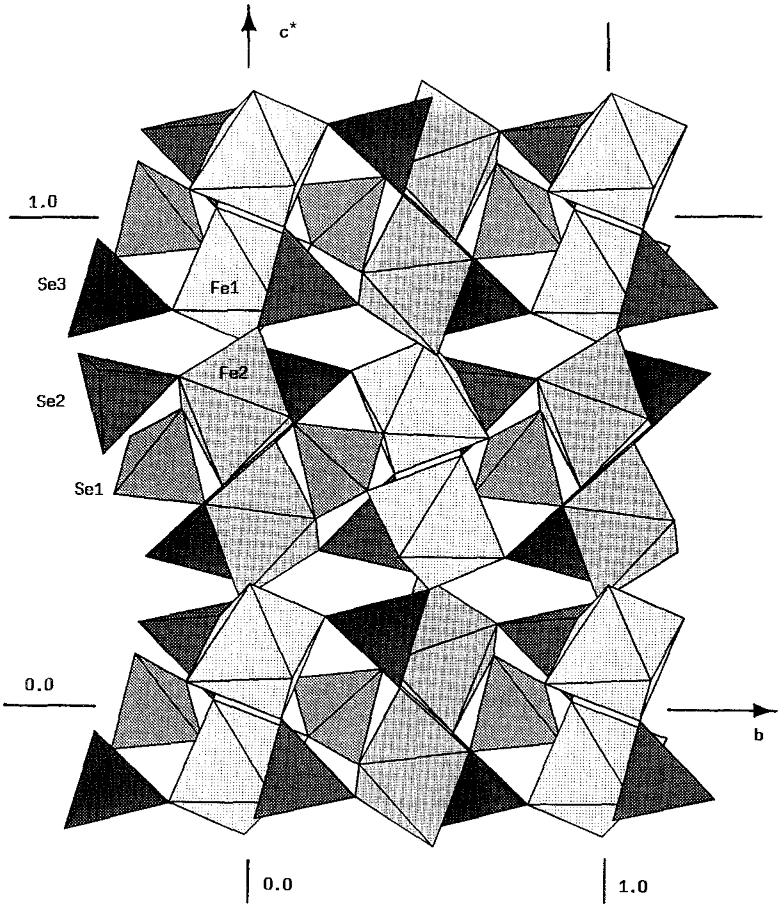

Fig. 1. Crystal structure of $Fe_2(SeO_4)_3$ in a projection parallel to [100]; Figs. 1 and 2 were drawn with the computer program ATOMS [12]

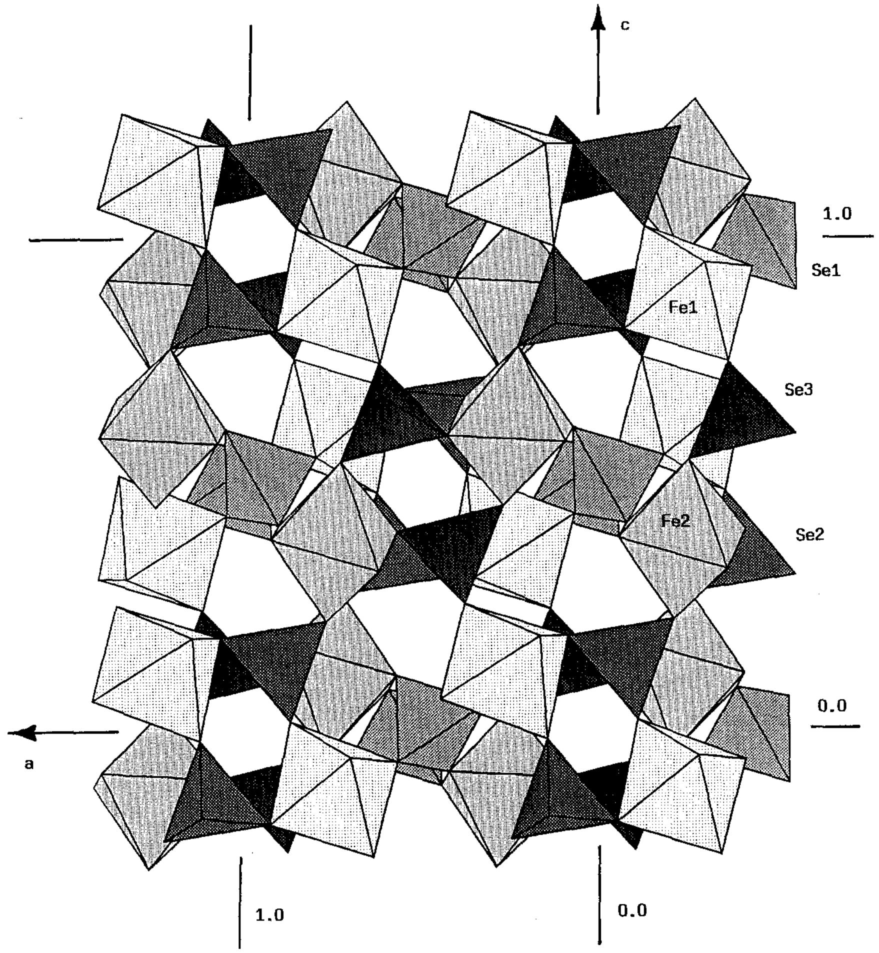

Fig. 2. Crystal structure of $Fe_2(SeO_4)_3$ in a projection on (010)

In $Fe_2(SeO_4)_3$ all atoms occupy the general site with point symmetry 1. The two crystallographically different Fe(III) atoms are coordinated to each six oxygen atoms forming slightly distorted octahedra: Fe – O distances range from 1.953 to 2.066 Å with mean values of 1.986 and 2.004 Å for Fe1 and Fe2, which are in accordance to data given in Ref. [13]. The SeO_4 tetrahedra are rather regular with mean Se – O bond lengths of each 1.628 Å for Se1, Se2, and Se3 and are therefore in the range of short ⟨Se – O⟩ bond lengths as known for SeO_4 groups [14]. The oxygen atoms are bound to each one Fe and one Se atom only; the Fe – O – Se bond angles vary from 130.7° to 155.3°.

A comparison of the isotypic crystal structures of $Fe_2(SeO_4)_3$ and $Fe_2(SO_4)_3$ [8] reveals that there are only minor differences in the geometry of corresponding coordination polyhedra. The average Fe – O bond lengths in $Fe_2(SO_4)_3$ (⟨Fe1 – O⟩ = 1.981 Å, ⟨Fe2 – O⟩ = 1.995 Å) are somewhat smaller than in the title compound. The distortions of corresponding bond lengths and angles within the FeO_6 octahedra are more pronounced in $Fe_2(SeO_4)_3$; the deviations of O – Fe – O angles from 90° do not exceed 7.2° for the sulfate and 9.4° for the selenate compound. For a comparison of distortion parameters see Table 6. As for the selenate com-

Table 6. Distortion parameters of bond distances $\Delta \cdot 10^6$ and bond angles σ for the polyhedra in $Fe_2(SO_4)_3$ and $Fe_2(SeO_4)_3$: $\Delta_{oct} = 1/6\Sigma[(d_i - d_m)/d_m]^2$, $\sigma_{oct} = 1/11\Sigma(\theta_i - 90°)^2$, $\Delta_{tet} = 1/4\Sigma[(d_i - d_m)/d_m]^2$, $\sigma_{tet} = 1/5\Sigma(\theta_i - 109.47°)^2$, where d_i are individual, d_m mean bond lengths; θ_i are individual bond angles

		$Fe_2(SeO_4)_3$	$Fe_2(SO_4)_3$
Fe1	Δ_{oct}	120.2	69.2
	σ_{oct}	25.96	9.91
Fe2	Δ_{oct}	365.7	210.7
	σ_{oct}	24.75	20.67
Se1, S1	Δ_{tet}	24.4	4.2
	σ_{tet}	5.41	1.86
Se2, S2	Δ_{tet}	10.8	10.8
	σ_{tet}	4.64	1.66
Se3, S3	Δ_{tet}	10.8	3.8
	σ_{tet}	2.35	0.80

pound, the average S−O bond lengths−which are each 1.467Å for S1, S2, and S3, respectively−are also smaller than overall mean ⟨S(VI)−O⟩ distances given in Ref. [13]. The variations of the individual S−O and Se−O bond lengths are in good agreement as it holds true for the bond angles: the maximal deviations of the angles O−S−O and O−Se−O from the ideal 109.47° are 2.34° in $Fe_2(SO_4)_3$ and 3.58° in $Fe_2(SeO_4)_3$; distortion parameters for the anion groups are also included in Table 6. On the average, the Fe−O−S bond angles are larger than the corresponding Fe−O−Se angles by about 4.8°, differences ranging from 0.9° (O 4) to 9.4° (O 10).

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