The Crystal Structure of Fe(SeO2OH)(SeO4) · H2O

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Summary. The crystal structure of the hydrothermally synthesized compound $Fe(SeO_2OH)$ $(SeO_4) \cdot H_2O$ was determined by single crystal diffraction methods: $a = 8.355(2)$ Å, $b = 8.696(2)$ Å, $c = 9.255(2)$ Å, $\beta = 93.72(1)°$, $V = 670.95$ Å^3; $Z = 4$, space group $P2_1/c$, $R = 0.029$, $R_w = 0.027$ for 2430 independent reflections ($\sin \theta / \lambda \leqslant 0.76$ Å^{-1}). Isolated $FeO_5(H_2O)$-octahedra share five corners with $[SeO_2OH]$ and $[SeO_4]$ groups to form sheets parallel to (100). These sheets are interconnected via hydrogen bonds only.

Keywords. $Fe(SeO_2OH)(SeO_4) \cdot H_2O$; Ferric hydrogenselenite(IV) selenate(VI) monohydrate; Crystal chemistry; Hydrothermal synthesis.

Die Kristallstruktur von Fe(SeO2OH)(SeO4) · H2O

Zusammenfassung. Die Kristallstruktur der hydrothermal dargestellten Verbindung $Fe(SeO_2OH)$ $(SeO_4) \cdot H_2O$ wurde mittels Einkristallbeugungsmethoden bestimmt: $a = 8.355(2)$ Å, $b = 8.696(2)$ Å, $c = 9.255(2)$ Å, $\beta = 93.72(1)°$, $V = 670.95$ Å^3; $Z = 4$, Raumgruppe $P2_1/c$, $R = 0.029$, $R_w = 0.027$ für 2430 unabhängige Reflexe ($\sin \theta / \lambda \leqslant 0.76$ Å^{-1}). Isolierte $FeO_5(H_2O)$-Oktaeder teilen fünf Ecken mit $[SeO_2OH]$- und $[SeO_4]$-Gruppen, wobei sie Schichten parallel (100) bilden. Diese Schichten sind nur über Wasserstoffbrücken miteinander verbunden.

Introduction

The title compound was obtained in the course of hydrothermal experiments [1] in the system selenic acid − iron(II) oxide − water. Preliminary investigations indicated a new compound and a structure determination led to the formula $Fe(SeO_2OH)(SeO_4) \cdot H_2O$. Double salts with selenite and selenate groups, determined by single crystal X-ray work, are known rarely as for the mineral schmiederite [2] $Pb_2Cu_2(OH)_4(SeO_3)(SeO_4)$ and the synthetic compound [3] $Li_2Cu_3(SeO_3)_2$ $(SeO_4)_2$. The title compound is a new type which contains a hydrogenselenite and a selenate group simultaneously.

Experimental Part

Synthesis

$Fe(SeO_2OH)(SeO_4) \cdot H_2O$ was prepared in "Teflon"-lined steel vessels of ~ 50 cm^3 capacity. A mixture of ~ 1 g $FeC_2O_4 \cdot 2H_2O$ (Fa. E. Merck, Darmstadt, FRG), 1 ml H_2SeO_4 (Fa. Fluka Chemie AG,

Buchs, CH) and 2 ml H_2O was heated to 500 K and kept at this temperature for one week. Upon cooling to room temperature (12 h) various phases were isolated, of which the following Fe(III) compounds were identified by X-ray diffraction: $FeH(SeO_3)_2$ [4], $Fe_2(SeO_4)_3$ [5], $Fe(SeO_2OH)$ $(SeO_4) \cdot H_2O$ [present publication] and $Fe_2(SeO_3)_3 \cdot H_2O$ [6].

Yellowish green crystals of $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ had formed in a size up to 1 mm. They showed a perfect cleavage parallel to (100), predominant crystallographic forms of the monoclinic holoedral crystals were {001} and {110}.

Structure Determination

A prismatic chip ($0.06 \times 0.15 \times 0.37$ mm) was chosen for structure determination. The lattice constants were derived from 59 reflections in the range $38° < 2\theta < 46°$ and X-ray intensities were measured at 295 K on a four-circle diffractometer. For a summary of crystal data, X-ray data collection and details of the structure refinement see Table 1. Intensities were corrected for Lorentz and polarisation effects as well as for absorption (empirical correction). Complex scattering curves for neutral atoms were used [7] and a secondary isotropic extinction correction was applied [8]. The structure of $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ was solved by direct methods and Fourier syntheses. The first least-squares refinement (H neglected, position of all other atoms fully occupied) showed a strongly elongated displacement ellipsoid with (longest axis)/(shortest axis) = 3.1 for the atom O7 of the hydrogenselenite group; for the atom Se2 of the SeO_2OH group this value was also considerabely high with 1.7. A

Table 1. Summary of crystal data, X-ray measurements and structure refinements for $Fe(SeO_2OH)(SeO_4) \cdot H_2O$

a [Å]	8.355 (2)
b [Å]	8.696 (2)
c [Å]	9.255 (2)
β [°]	93.72 (1)
V [Å³]	670.95
space group	$P2_1/c$ (C_{2h}^5)
formula units per cell	4
ρ_{calc} [gcm^{-3}]	3.413
$\mu(MoK\alpha)$[cm^{-1}]	127.32
transmission factors	0.09 − 0.28

Equipment: Stoe four-circle diffractometer AED2; graphite monochromatized MoKα-radiation; program system STRUCSY [9] (Stoe & Cie, Darmstadt, FRG)

Data collection: 2θ-ω scans; 46 steps/reflection, increased for $\alpha_1 - \alpha_2$ splitting; 0.03° and 0.5 − 1.5 s/step; 2 × 7 steps for background measurement; 3 standard reflections each 120 min; $2\theta_{max} = 65°$

extinction coefficient g × 10⁶	4.1 (5)
measured reflections	5 160
internal R(I)	0.051
unique data set	2 430
data with $F_o > 3\sigma(F_o)$	2 071
number of variables	128
reliability index R	0.029
R_w ($w = 1/[\sigma(F_o)]^2$)	0.027

Table 2. Structural parameters of $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ with e.s.d.'s in parentheses. U_{ij} are given in pm^2. $ATF = exp[-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a^*_i a^*_j]$. U_{iso} for the hydrogen atoms were fixed at $200\,pm^2$. Parameters of Se2 and O7 are also listed for the average model

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.19487 (5)	0.50731 (4)	0.32331 (4)	267 (2)	151 (1)	149 (1)	−9 (1)	24 (1)	1 (1)
Se1	0.16755 (3)	0.32471 (3)	0.63783 (3)	184 (1)	156 (1)	169 (1)	−0 (1)	3 (1)	20 (1)
Se2[a]	0.2433 (5)	0.8339 (7)	0.5041 (5)	353 (15)	208 (4)	212 (6)	−26 (10)	37 (7)	−30 (4)
Se2[b]	0.2129 (4)	0.8309 (7)	0.5144 (5)	274 (11)	209 (5)	167 (6)	1 (8)	−20 (7)	−11 (5)
O1	0.1358 (3)	0.3426 (2)	0.4612 (2)	330 (11)	219 (8)	172 (7)	−65 (8)	13 (8)	42 (6)
O2	0.0331 (3)	0.4235 (3)	0.7191 (2)	406 (15)	479 (13)	236 (9)	256 (12)	−7 (10)	−29 (9)
O3	0.1376 (3)	0.1399 (2)	0.6614 (2)	366 (13)	178 (7)	201 (8)	−41 (8)	−25 (8)	44 (6)
O4	0.3440 (3)	0.3728 (3)	0.7038 (2)	278 (12)	410 (12)	369 (12)	−148 (10)	−94 (10)	99 (9)
O5	0.2739 (3)	0.8423 (2)	0.6860 (2)	474 (15)	275 (9)	209 (8)	114 (10)	−34 (9)	−93 (7)
O6	0.2407 (3)	0.6442 (2)	0.4851 (2)	578 (17)	216 (9)	219 (9)	−75 (10)	26 (10)	−55 (7)
O7[a]	0.4381 (10)	0.8520 (11)	0.4602 (13)	312 (39)	569 (48)	750 (55)	−240 (30)	240 (39)	−252 (39)
O7[b]	0.3739 (9)	0.9141 (9)	0.4356 (8)	487 (48)	598 (45)	444 (32)	−222 (33)	61 (34)	70 (32)
O8	0.4238 (3)	0.4199 (3)	0.3469 (3)	240 (12)	290 (10)	385 (11)	−43 (9)	3 (10)	5 (9)
H1	0.483 (5)	0.478 (4)	0.357 (4)						
H2	0.455 (4)	0.334 (4)	0.311 (3)						
H3	0.469 (6)	0.880 (6)	0.478 (6)						
Se2	0.22746 (5)	0.83238 (4)	0.50924 (3)	490 (2)	210 (2)	213 (1)	4 (1)	−62 (1)	−27 (1)
O7	0.4061 (7)	0.8861 (6)	0.4449 (4)	1409 (50)	1443 (47)	657 (25)	−1133 (41)	505 (31)	−410 (28)

subsequent difference Fourier synthesis of the region of O7 showed this atom split with two maxima of equal height (ca. $6.5\,e\,Å^{-3}$) approximately $0.6\,Å$ apart. Consequently, the atoms Se2 and O7 were split on two positions each (labeled a and b) and refined separately with an occupancy of 0.5, which led to more reasonable thermal ellipsoids and a reduction of R_w from 0.031 (average model) to 0.027 (split model). The two oxygen ligands of the hydrogenselenite group (O5, O6), which both in addition belong to FeO_6 octahedra, remained unsplit. (The accuracy of structure determination did not allow to decide between a structure model with split positions for O5 and O6 or one position with somewhat higher anisotropy of their displacement parameters). In the last stage of structural determination it was tried to localize the hydrogen atoms by a final difference Fourier summation. The hydrogen atoms of the H_2O group could be clearly recognized. The localisation of the hydrogen atom belonging to the hydrogenselenite pyramid should be considered with caution as the oxygen atom O7 acts as donor atom and the refined atomic coordinates of H3 are considered to be an average position of the residual electron density. Structural parameters were obtained by full-matrix least-squares techniques. Final structural parameters of the split model are presented in Table 2. For comparison corresponding values for the unsplit atoms Se2 and O7 are also listed in Table 2.

Results and Discussion

Selected interatomic distances, bond angles and bond valence calculations [10] are given in Table 3 for the split model; values for the $Se(2)O_3$ group in the averaged model are included for comparison. Figs. 1 and 2 illustrate the atomic arrangement of $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ in projections along [100] and [010]. The structure

Table 3. Interatomic bond lengths [Å] and bond angles [°] (with e.s.d.'s in parentheses; intrapolyhedral O−O distances are given in brackets) and bond valences v [v.u.] [10] in Fe(SeO$_2$OH)(SeO$_4$)·H$_2$O. Bond valence calculations of the oxygen atoms were done without considering hydrogens

	[Å]	[v.u.]
Fe−O1	2.001(1)	0.52
Fe−O2	2.012(2)	0.50
Fe−O3	2.005(1)	0.51
Fe−O5	1.968(2)	0.57
Fe−O6	1.931(2)	0.63
Fe−O8	2.057(2)	0.45
<Fe−O>	<1.996>	3.18

	[°]	[Å]
O1−Fe−O2	93.95(10)	[2.934(3)]
O1−Fe−O3	87.87(7)	[2.780(3)]
O1−Fe−O6	89.50(8)	[2.769(3)]
O1−Fe−O8	86.21(10)	[2.773(3)]
O2−Fe−O3	82.43(10)	[2.646(3)]
O2−Fe−O5	91.62(10)	[2.853(4)]
O2−Fe−O6	95.99(11)	[2.930(3)]
O3−Fe−O5	90.89(8)	[2.831(3)]
O3−Fe−O8	91.05(10)	[2.899(3)]
O5−Fe−O6	91.90(9)	[2.803(3)]
O5−Fe−O8	88.02(10)	[2.797(3)]
O6−Fe−O8	90.55(11)	[2.835(3)]
		<2.821>

	[Å]	[v.u.]
Se1−O1	1.646(1)	1.47
Se1−O2	1.636(2)	1.51
Se1−O3	1.643(1)	1.48
Se1−O4	1.614(2)	1.60
<Se1−O>	<1.635>	6.06

	[°]	[Å]
O1−Se1−O2	109.62(11)	[2.682(3)]
O1−Se1−O3	102.03(9)	[2.557(3)]
O1−Se1−O4	115.81(12)	[2.762(3)]
O2−Se1−O3	109.72(13)	[2.681(3)]
O2−Se1−O4	109.14(13)	[2.648(4)]
O3−Se1−O4	110.27(12)	[2.672(3)]
<O−Se1−O>	<109.43>	<2.667>

	[Å]	[v.u.]
Se2^a−O5	1.688(5)	1.40
Se2^a−O6	1.658(6)	1.51
Se2^a−O7^a	1.710(9)	1.31
<Se2^a−O>	<1.685>	4.22

	[°]	[Å]
O5−Se2^a−O6	98.6(3)	2.536(3)
O5−Se2^a−O7^a	98.5(4)	2.575(11)
O6−Se2^a−O7^a	94.2(4)	2.468(9)
<O−Se2^a−O>	<97.1>	<2.526>

	[Å]	[v.u.]
Se2^b−O5	1.639(4)	1.59
Se2^b−O6	1.664(5)	1.49
Se2^b−O7^b	1.730(8)	1.24
<Se2^b−O>	<1.678>	4.32

	[°]	[Å]
O5−Se2^b−O6	100.3(3)	2.536(3)
O5−Se2^b−O7^b	100.5(3)	2.590(8)
O6−Se2^b−O7^b	102.7(3)	2.650(8)
<O−Se2^b−O>	<101.2>	<2.592>

	[Å]	[v.u.]
Se2−O5	1.659(2)	1.51
Se2−O6	1.658(2)	1.51
Se2−O7	1.708(5)	1.32
<Se2−O>	<1.675>	4.34

	[°]	[Å]
O5−Se2−O6	99.8(1)	2.537(3)
O5−Se2−O7	100.1(2)	2.580(5)
O6−Se2−O7	99.0(2)	2.558(6)
<O−Se2−O>	<99.6>	<2.558>

Oxygen:	O1	O2	O3	O4	O5	O6	O7^a	O7^b	O8	O7
v [v.u.]	1.99	2.02	1.99	1.60	2.06	2.13	1.31	1.24	0.45	1.32
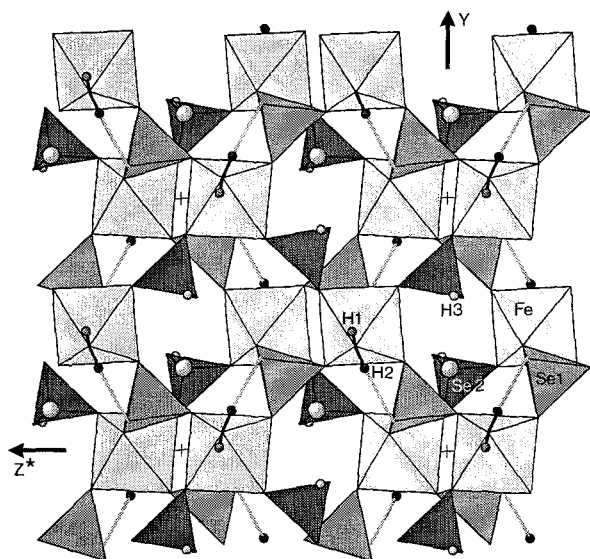
Fig. 1. Crystal structure of Fe(SeO$_2$OH)(SeO$_4$)·H$_2$O in a projection parallel to [100]. The hydrogenselenite group is shown unsplit in Fig. 1 and 2. For H$_2$O the proposed hydrogen bonds are indicated. The hydrogen atoms are indicated as small circles, the selenium atom of the hydrogenselenite group as large one. Both Figures were drawn with the program ATOMS
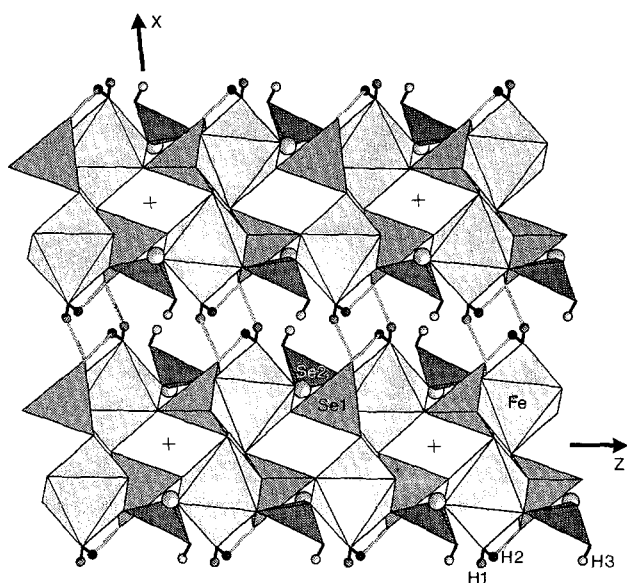
Fig. 2. Crystal structure of Fe(SeO$_2$OH)(SeO$_4$)·H$_2$O in a projection parallel to [010] (see also caption of Fig. 1)

is built up by sheets parallel to (100) consisting of isolated FeO$_6$ octahedra, which are corner connected with selenate and hydrogenselenite groups. The only connection between these sheets are two of the three crystallographically different hydrogen bonds which explains the excellent cleavage // (100).

Table 4. Details of the hydrogen bonding system
of the H_2O group in $Fe(SeO_2OH)(SeO_4) \cdot H_2O$

O8 – H1	0.71 (4) Å
O8 – H1 ⋯ O4	157 (5)°
O8 – O4	2.711 (3) Å
O8 – H2	0.86 (3) Å
O8 – H2 ⋯ O4*	138 (2)°
O8 – O4*	2.926 (3) Å
H1 – O8 – H2	116 (4)°
O4 ⋯ O8 ⋯ O4*	130.1 (2)°

In $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ all atoms occupy the general site. The Fe(III) atom is octahedrally coordinated to six oxygen atoms, which belong to three selenate tetrahedra, two hydrogenselenite pyramids and one H_2O group. The Fe – O distances are in good agreement with the literature [11] (<2.011 Å$>$ for trivalent iron).

The Se1 atom is bound to four oxygen atoms forming a slightly distorted tetrahedron. Se1 – O bond lengths comply with common experience [12] for a selenate (VI) tetrahedron. Three of the ligands are further bonded to each one Fe atom, while O4 (with the short Se1 – O distance of 1.614 Å) acts as acceptor atom in the hydrogen bonding system.

There is clear evidence that the hydrogenselenite group [Se(2)O$_2$OH] is disordered. Two of the ligands, the oxygen atoms O5 and O6 (both are considered to be unsplit) additionally belong to one FeO_6 octahedron each. The third, split ligand O7 is the oxygen atom of an OH group [O7 – H3]. O7 and the central atom Se2 could be satisfactorily refined on two positions each with occupancy 0.5; the distances of separation Se2^a – Se2^b and O7^a – O7^b are 0.278(5) Å and 0.784(12) Å, respectively. The geometry (bond lengths and angles, see Table 3) of the resulting two hydrogenselenite groups, of course, does not fully agree with that calculated for the average model. However, it has to be noted that in both models mean Se2-O distances are rather short; bond angles O – Se2 – O are well within the range known for selenite groups [13].

Table 4 gives the proposed hydrogen bonding scheme of the H_2O group in $Fe(SeO_2OH)(SeO_4) \cdot H_2O$. Bond valance calculations (see Table 3) show strong deficiencies for the oxygen atoms O8, O7$^{a, b}$ and for O4. The atom O8, which belongs to the FeO_6 octahedron, is obviously the oxygen atom of a H_2O group. The hydrogen atoms H1 and H2 are well substantiated with O – H distances commonly known for X-ray investigations. Nearest O8 – O distances outside the FeO_6 polyhedron are two O8 – O4 contacts of 2.711 Å and 2.926 Å, respectively, with corresponding hydrogen bonds O8 – H1 ⋯ O4 and O8 – H2 ⋯ O4*. While the arrangement of this H_2O group is clear, problems arise for the hydrogen bond belonging to the hydrogenselenite group. To simplify matters, the average model is a useful approach for preliminary discussion: there is no doubt for stereochemical reasons (e.g. bond strength of 1.32 v.u. for O7) that O7 donates a hydrogen bond. Searching for distances O7 – O < 3Å, which are not an edge of a coordination polyhedron and

can act as possible hydrogen bonds, there is only an $O7 - O7$ contact of 2.686 Å. Next $O7 - O$ contacts are $O7 - O4$ and $O7 - O8$ with distances of 3.082 Å and 3.142 Å, respectively. The two $O7$ oxygen atoms are combined via a symmetry centre at position 2 d. A distance of about 2.7 Å is in the range of "normal" hydrogen bonds, but too long for centrosymmetrically restricted bonding $O7 - H3 - O7$. Additionally, for reasons of balanced charges, the hydrogen atom H3 should occupy a general site with multiplicity four. A difference Fourier summation and subsequent refinements led to an approximate positional determination of the H3 atom with rather limited accuracy. Nevertheless, this refinement of H3 at 4 e (0.45/0.84/0.49; separation distance $H3 - H3 = 2.8$ Å) results in improbable angles for $O7 - H3 \cdots O7$ (2 ×), contradicting an exclusive bonding $O7 - H3 \cdots O7$.

For the split model things become more complicated as three $O7 - O7$ distances result, ranging from 2.708 Å to 2.852 Å. A splitting of H3 on two positions 4 e with occupancy 0.5 each could not be excluded from the discussion but was not proofed — this is not surprising for X-ray work, especially in a compound containing heavy atoms like selenium. H3 was further on refined at one position 4 e (0.47/ 0.88/0.48; separation distance $H3 - H3 = 2.2$ Å), but, as it is likely that H3 is in fact split, bond angles and distances around unsplit H3 cannot be used for deriving details. In addition, recognition of further $O7 - O$ contacts, possibly participating in the hydrogen system, becomes more complex.

Concluding, while general features of hydrogen bonding in Fe(SeO₂OH) (SeO₄) · H₂O seem clarified, there are still some questions open in detail.

Acknowledgements

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