The Crystal Structure of Iron(III) Hydrogen Biselenite, $FeH(SeO_3)_2$

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The crystal structure of the title compound has been determined by X-ray methods from 1193 observed reflections collected by counter method. The crystals are monoclinic, space group $P2_1/c$ (No. 14), with unit cell dimensions $a = 6.409(2)$ Å, $b = 9.921(3)$ Å, $c = 8.108(3)$ Å and $\beta = 92.76(3)°$. The structure was solved by direct methods and refined to the conventional R-factor 0.047. The structure consists of edge-sharing pairs of FeO_6-octahedra connected by one of the two non-equivalent Se atoms into layers. The layers are held together by the other Se atom. The range of Se–O bonds is 1.669(7)–1.742(7) Å and the range of Fe–O bonds 1.955(7)–2.137(7) Å.

In our studies on the selenite compounds of divalent manganese the coordination octahedra around the metal atoms were found to be irregularly distorted in $MnSeO_3.D_2O$ and $MnSeO_3.2H_2O$.[1,2] In the first case the distortion was mainly due to the rigidity of the selenite ion, in the latter case to the stretching of the Mn–O bonds by hydrogen bonds. Thus, in these two compounds the spherically distributed d-electron density of the metal ion allows a marked distortion of the MnO_6-octahedron. The question then arose whether the same phenomenon would be encountered in the selenite compounds of the isoelectronic trivalent iron.

EXPERIMENTAL

Preparation of the compound. Dropwise addition of 1 mol/dm^3 solution of $KHSeO_3$ to a 1 mol/dm^3 solution of iron(III) nitrate yielded amorphous, green iron(III) selenite hydrate as a precipitate. After addition of 10–15 cm^3 of 3 mol/dm^3 selenous acid to 0.2 g of the iron(III) selenite hydrate the mixture was sealed in an ampoule and kept for 6–7 weeks at 150 °C.

The ampoule was then broken; among the green bar-like crystals of the title compound a few large enough for X-ray diffraction studies were found and selected for the measurements. The method of preparation is analogous to that described by Pinaev and Volkova for $Fe_2O_3.4SeO_2.H_2O$.[3] All reagents were of analytical grade.

Structure analysis. A computer-controlled Syntex $P2_1$ (Fortran version) four-circle diffractometer with graphite monochromatized Mo$K\alpha$-radiation was utilized in the determination of unit cell parameters and the collection of intensity data. Crystal size was $0.25 \times 0.2 \times 0.1$ mm and the temperature 298 K. Cell dimensions were calculated from diffractometer measurements of setting angles for 24 reflections (Table 1). Intensity data were collected in the interval $5° < 2\theta < 60°$ using the $\theta/2\theta$ technique and a scan speed of 2°/min. Of the 1587

Table 1. Crystal data for $FeH(SeO_3)_2$.

Formula	$FeH(SeO_3)_2$
Formula weight	310.77
Lattice constants	$a = 6.409(2)$ Å
	$b = 9.921(3)$ Å
	$c = 8.108(3)$ Å
	$\beta = 92.76(3)°$
Cell volume	$V = 514.9(3)$ Å^3
Molecules per unit cell	$Z = 4$
Space group	$P2_1/c$ (No. 14)
Density (calc.)	$D_x = 4.01$ g cm^{-3}
Density (pycnometer)	$D_m = 4.0$ g cm^{-3}
Linear absorption coefficient	μ(Mo$K\alpha$) = 168.8 cm^{-1}

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unique reflections measured, 1193 had intensities larger than three times their standard deviations. The space group $P2_1/c$ (No. 14) was determined on the basis of systematic absences in the original intensity data. Empirical absorption corrections were made from the ϕ-scan with 8 different 2θ values after which Lorentz and polarization corrections were applied.

The solving, refinement and drawing of the figures were carried out with the X-Ray 76 program package and a UNIVAC 1108 computer.[4] Scattering factors for neutral atoms were taken from Cromer and Mann.[5] The atomic positions of Fe and Se were determined by direct methods from the E-map calculated with 315 E-values larger than 1.2. The positional parameters of the Fe and the two Se atoms were then refined to an R of 17.9 %, and the subsequent difference Fourier map gave the positions of all the oxygen atoms. After refinement with isotropic temperature factors the value of R was reduced to 5.8 %, and after full-matrix refinement with anisotropic temperature factors the final R-value was 4.7 %. The $|F_o|$ and $|F_c|$ listing is available from the authors upon request.

RESULTS AND DISCUSSION

The positional and thermal parameters of the Fe, Se and O atoms are given in Table 2 and some selected bond lengths and angles in Table 3. There are two non-equivalent Se atoms in the compound, and all the O atoms are bonded to one or the other of the Se atoms. Thus, no water of crystallization is present (*cf.* Ref. 3) and the formula of the compound is written as $Fe(HSeO_3)$ (SeO_3) or more shortly as $FeH(SeO_3)_2$.

A characteristic feature of the structure is that the FeO_6-octahedra appear as edge-sharing pairs,

Table 2. Atomic coordinates and anisotropic temperature coefficients with their estimated standard deviations. The temperature coefficients are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$, and have been multiplied by 10^4.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se1	0.0691(1)	0.9074(1)	0.2016(1)	44(4)	99(4)	125(4)	−7(4)	−15(4)	−6(4)
Se2	0.5940(1)	0.7132(1)	0.0213(1)	55(4)	30(4)	11(4)	6(4)	−13(4)	0(4)
Fe	0.4448(2)	0.5066(1)	0.2989(2)	25(5)	26(5)	3(5)	0(4)	−7(4)	−2(4)
O1	0.2488(10)	0.0279(7)	0.2313(9)	69(30)	31(30)	136(33)	−3(24)	−10(25)	−42(26)
O2	0.0257(14)	0.8640(12)	0.4043(12)	177(42)	604(73)	220(45)	−135(45)	−71(35)	279(49)
O3	0.8560(11)	0.0021(9)	0.1598(10)	38(21)	212(39)	174(36)	30(28)	0(26)	55(31)
O4	0.3938(11)	0.6250(7)	0.1076(9)	99(31)	71(31)	89(31)	−11(25)	−4(25)	50(25)
O5	0.4774(11)	0.8714(7)	0.0024(8)	142(32)	30(28)	12(26)	16(24)	−35(23)	−4(23)
O6	0.5632(12)	0.6640(7)	0.8219(8)	257(40)	42(30)	18(28)	9(27)	−18(26)	−26(23)

Table 3. Bond lengths (Å) and selected angles (°) with standard deviations in parentheses.

Fe−O1	2.002(7)	O1−Fe−O3	174.5(3)
Fe−O3	1.973(7)	O4−Fe−O5	175.3(3)
Fe−O4	1.961(7)	O5^a−Fe−O6	156.1(3)
Fe−O5	2.137(7)	O1−Fe−O5	87.9(3)
Fe−O5^a	2.049(7)	O3−Fe−O6	93.6(3)
Fe−O6	1.955(7)	O4−Fe−O5^a	106.8(3)
Se1−O1	1.669(7)	O1−Se1−O2	100.5(4)
Se1−O2	1.734(10)	O1−Se1−O3	100.2(4)
Se1−O3	1.679(8)	O2−Se1−O3	99.5(4)
Se2−O4	1.728(7)	O4−Se2−O5	99.7(3)
Se2−O5	1.742(7)	O4−Se2−O6	100.7(4)
Se2−O6	1.691(7)	O5−Se2−O6	98.4(3)

^{a} $-x,-y,-z$.

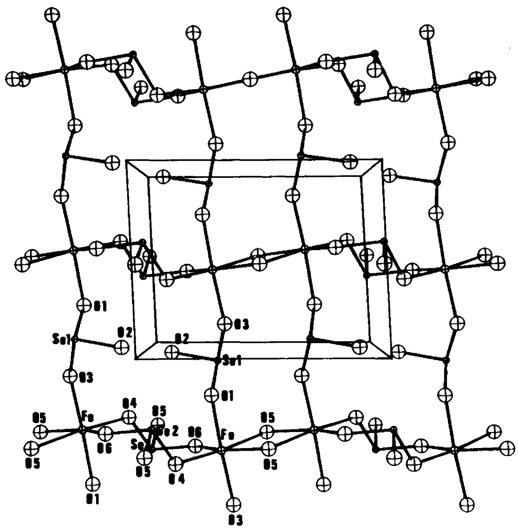

Fig. 1. Perspective view of the layer structure along *b*-axis. The *c*-axis is horizontal.

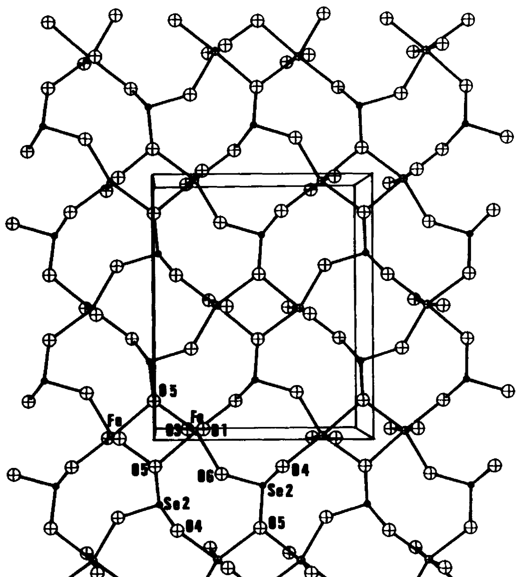

Fig. 2. Perspective view of the layer structure along *a*-axis. The *c*-axis is horizontal.

and these pairs of coordination polyhedra are then knitted by the Se2 atoms into layers parallel to the *ab*-plane (Figs. 1 and 2). One Se2 atom links together three pairs of FeO_6-octahedra. This

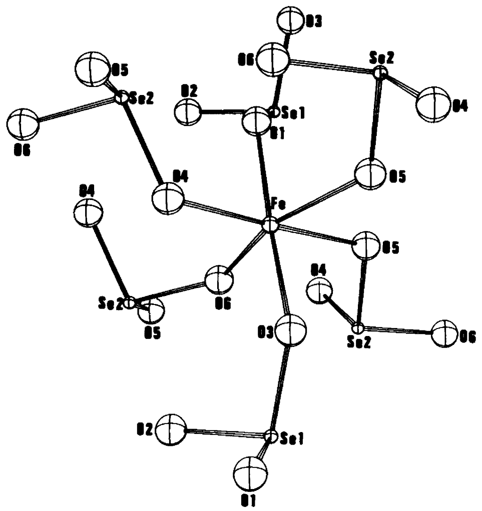

Fig. 3. Bonding scheme of the selenite groups to iron.

structural arrangement is possible because O5, which forms the two vertices of the shared edge, is within bonding distance of three atoms. The angles in the pyramidal arrangement of the bonds of O5 are 104.3(3), 114.6(3) and 129.0(4)° for Fe-O5-Fe′, Fe-O5-Se and Se-O5-Fe′, respectively. In $MnSeO_3.D_2O$, which also has an oxygen simultaneously coordinated to two metal atoms and to one selenium atom, the angles, in corresponding order, are 119.8, 125.0 and 97.9°.[1]

The layers are connected by Se1 atoms into a three-dimensional network. Both the non-equivalent selenite groups act as bridging ligands. The selenite group formed by Se2 joins four Fe atoms and that by Se1 two Fe atoms. Thus, one Fe atom is joined to ten others *via* six different selenite groups (Fig. 3).

The Se1 – O2 bond is stretched as compared with the other two bonds in the $Se1O_3$-group. Since O2 is not coordinated to Fe, it is plausible to assume that this oxygen has the hydrogen atom attached to it and is thus capable of acting as hydrogen bond donor. Such stretching is frequently observed in compounds containing hydrogenselenite groupings, and the relative difference between the shortest and longest bond in the group in the present case is compatible with the difference detected in $PrH_3(SeO_3)_2(Se_2O_5)$ and $MnH(SeO_3)(Se_2O_5)$ for a hydrogenselenite group likewise involved in hydrogen bonding.[6,7] The O – O distances around O2 (less than 3.0 Å) are O2–O1 2.617 Å, O2–O3 2.604 Å and O2–O4 2.814 Å of which the first two are in the same selenite group. Thus it might be possible that the hydrogen atoms exists between O2 and O4, which would explain the stretching of the Se2–O4 bond.

The Se2O_3-pyramid is more distorted than the Se1O_3-pyramid, and also more distorted than the selenite group in $MnSeO_3.D_2O$. In both compounds the bond between the Se and the three-coordinated oxygen is the longest: 1.742(7) Å in the present case and 1.720(8) Å in the latter.

The two bond distances Fe–O5 [2.137(7) and 2.049(7) Å] are significantly longer than the other Fe–O distances in the compound, and especially the former distance approaches the bond lengths detected in compounds of divalent iron. It is notable that the metal-oxygen bond was found to be stretched also in $MnSeO_3.D_2O$, when the coordination number of the oxygen atom was three.[1] This structurally plausible stretching of the Fe–O bonds distorts the regularity of the FeO_6-octahedron and the angle O5–Fe–O5′ deviates from 90° to a smaller value by 14.3(3)°. The mean of the four short bonds is 1.973 Å, which agrees well with the mean bond length found in regular FeO_6-octahedra, for example 1.986 Å reported for $[Fe(H_2O)_6](NO_3)_3.3H_2O$.[8]

Acknowledgement. We are indebted to Professor Lauri Niinistö for his interest in this work.

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Received February 15, 1978.