Crystal Structures, Thermal Behaviour and IR Spectra of Iron(III) Diselenite Hydrogenselenite and Iron(III) Tris(hydrogenselenite)

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Crystal structures of iron(III) diselenite hydrogenselenite, $Fe(HSeO_3)(Se_2O_5)$, and iron(III) tris(hydrogenselenite), $Fe(HSeO_3)_3$, have been determined from X-ray single crystal diffraction data. Unit cell data for iron(III) tris(hydrogenselenite): a = 7.460(1), b = 11.597(3), c = 11.360(8) Å and β = 124.48(4)°, Z = 4, space group $P2_1/c$ (No. 14). Results for iron(III) diselenite hydrogenselenite: a = 7.470(8), b = 12.668(5), c = 10.456(12) Å and β = 133.82(5)°, Z = 4, space group $P2_1/c$. Both structures form a three-dimensional network and in both compounds the coordination around Fe(III) is octahedral. The compounds are also similar in decomposing to iron(III) oxide between 200 and 600 °C with loss of selenium dioxide and water. IR spectra have been assigned.

There are many reports in the literature of iron(III)-selenium(IV)-oxygen compounds with the empirical formulas: $Fe_2O_3 \cdot 6SeO_2 \cdot 2H_2O$, $Fe_2O_3 \cdot 6SeO_2 \cdot H_2O$, and $Fe_2O_3 \cdot 4SeO_2 \cdot H_2O$.[1-3] Although oxide formulas are easily assigned on the basis of the analytical results they fail to give any structural information. In many cases the selenite structures are complex and include more than one kind of selenite anion. Examples of such formulas are $Fe(HSeO_3)(Se_2O_5)$ (= $Fe_2O_3 \cdot 6SeO_2 \cdot H_2O$) and $Fe(HSeO_3)(SeO_3)$ (= $Fe_2O_3 \cdot 4SeO_2 \cdot H_2O$).[4] This is not unique for iron; an identical situation exists for praseodymium, manganese and calcium.[5-8]

Experimental

Syntheses. Iron(III) tris(hydrogenselenite) crystallizes from a solution containing 2 cm^3 of 0.25 mol dm^{-3} $Fe(NO_3)_3$, 10 cm^3 of 2 mol dm^{-3} H_2SeO_3 and 10 cm^3 of concentrated nitric acid on slow evaporation at 60–70 °C. When the evaporation takes place at 80–90 °C, the product is iron(III) diselenite hydrogenselenite. Crystals of both compounds are pale green prisms.

Thermal analysis and IR spectra. Thermal behaviour was determined with a Perkin-Elmer TG-2 thermobalance. Sample size was about 10 mg, heating rate 10 °C min^{-1} and air flow 70 cm^3 min^{-1}.

The IR spectra were recorded with a Perkin-Elmer 283 IR spectrometer. The KBr method was used with a scan time of 12 min and scan range from 4000 to 200 cm^{-1}.

Crystal structure determination. X-ray measurements were made using an Enraf-Nonius CAD4 automatic four-circle diffractometer equipped with a graphite monochromator. Cell constants were obtained from a least-squares refinement. Conditions for unit cell determination and data collection are summarized in Table 1. The ratio of peak counting time to background counting time was 2:1. Two test reflections measured hourly during data collection did not show any significant variation in intensity. Lorentz and polarization corrections were applied to the data and

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Table 1. Conditions for unit cell determination and data collection.

Formula	$Fe(HSeO_3)_3$	$Fe(HSeO_3)(Se_2O_5)$
Formula weight	439.75	421.73
a/Å	7.460(1)	7.470(8)
b/Å	11.597(3)	12.668(5)
c/Å	11.360(8)	10.456(12)
β/°	124.48(4)	133.82(5)
V/Å^3	801.1	713.9
Space group[a]	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
d_{calc}/g cm^{-3}	3.61	3.92
Z	4	4
μ/cm^{-1}	152.3	172.7
F(000)	812	772
Crystal size/mm	0.2×0.08×0.08	0.15×0.07×0.07
Temperature/°C	23±1	23±1
Mo*K*α/Å	0.71073	0.71073
Number of reflections used in unit cell determination	25	25
Range of reflections used in unit cell determination/θ	20–28	11–21
Data collection method	ω–2θ	ω–2θ
Scan speed/° min^{-1}	1.6–16.5	1.6–8.2
Scan width (in omega)/°	0.8+0.34 tanθ	0.7+0.34 tanθ
Range of data collection/θ	2–30	1–30
Number of collected reflections	2488	2177
Number of refined reflections [$I>3\sigma(I)$]	1690	1485
$R_{(iso)}$ (no absorption corr.)	10.2	10.1
$R_{(iso)}$ (with absorption corr.)	4.5	3.1
$R_{(aniso)}$ (with absorption corr.)	3.2	2.4
$R_{(aniso)}$ (with absorption corr. with extinct. corr.)	3.0	2.2

[a]Dimensions in the $P2_1/n$ setting: a = 7.460(1), b = 11.517(3), c = 9.421(8) Å, β = 96.27(4)° and a = 7.470(8), b = 12.668(5), c = 7.548(12) Å, β = 91.75°.

an empirical absorption correction was calculated.[9] Maximum and minimum absorption coefficients were 1.40 and 0.85 for $Fe(HSeO_3)_3$ and 1.35 and 0.81 for $Fe(HSeO_3)(Se_2O_5)$.

All calculations were performed with a micro VAX I computer using the Enraf-Nonius structure determination package SDP-Plus.[10] This package incorporates the direct methods program MULTAN and the plotting program ORTEP.

Positions of iron and selenium atoms were established by direct methods and the remaining atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were not included in the calculations, and refinement was based on structure factors and unit weights. The function minimized was $\Sigma(|F_o| - |F_c|)^2$.

Scattering factors were taken from Cromer and Waber,[11] and the anomalous dispersion correction method of Ibers and Hamilton[12] was employed using coefficients from Cromer.[13] In final anisotropic refinement a secondary extinction correction (coefficient 0.0000003 for both compounds) was also applied.[14] The final electron densities in the difference Fourier maps were 1.28 and 0.83 e Å^{-3} for $Fe(HSeO_3)_3$ and $Fe(HSeO_3)(Se_2O_5)$, respectively. Lists of F_o, F_c and anisotropic temperature factors are available from the authors upon request.

Results and discussion

Thermal analysis. Iron(III) tris(hydrogenselenite) decomposes in a first stage to iron(III) diselenite hydrogenselenite. The temperature range is 200–270 °C and observed weight loss 4.0 % [theoretical value 4.1 %, eqn. (1)]. In a second stage, the iron(III) diselenite hydrogense-

Table 2. IR spectral data (cm^{-1}) of $Fe(HSeO_3)_3$ and $Fe(HSeO_3)(Se_2O_5)$.

Assignment	$Fe(HSeO_3)_3$	$Fe(HSeO_3)(Se_2O_5)$
ν(O–H)	2900 b	2853 b
	2303 m	2395 m
δ(Se–O–H)	1231 sh	1233 m
	1175 m	
	1145 m	
ν_s(Se–O)	886 s	877 s
ν_{as}(Se–O)	829 sh	830 s
	751 vs	745 vs
ν(Se–OH)	674 s	649 s
ν(Se–O–Se)	–	592 s
δ(O–Se–O)	487 s	471 s
δ_{as}(O–Se–OH)	365 w	397 s
δ_s(O–Se–OH)	324 s	324 s

vs = very strong, s = strong, m = medium, sh = shoulder, b = broad, w = weak.

lenite loses water and selenium dioxide and decomposes to iron(III) oxide [eqn. (2)]. The temperature range is 300–600 °C and the observed and calculated weight losses are 77.5 % and 77.7 %, respectively.

$$Fe(HSeO_3)_3 \rightarrow Fe(HSeO_3)(Se_2O_5) + H_2O \quad (1)$$

$$2Fe(HSeO_3)(Se_2O_5) \rightarrow Fe_2O_3 + 6SeO_2 + H_2O \quad (2)$$

Pure, crystalline iron(III) diselenite hydrogenselenite decomposes directly according to eqn. (2). The temperature range is the same, 300–600 °C, and observed and calculated weight losses are 80.9 and 81.0, respectively. The high decomposition temperatures indicate stable structures, as was confirmed by structure analysis.

The thermal behaviour of iron(III) selenites differs from that of other diselenites and hydrogenselenites described in the literature. Manganese and alkaline earth hydrogenselenites form in the first stage diselenite, which then decomposes to normal selenite.[6,15] No corresponding intermediate products are formed with the iron(III) selenites.

IR spectra. IR spectral data for the two compounds are listed in Table 2. Assignments were made according to the literature.[16] The data are very similar to those reported by Volkova *et al.* for $Fe_2O_3 \cdot 6SeO_2 \cdot 2H_2O$ and $Fe_2O_3 \cdot 6SeO_2 \cdot H_2O$; however, our results suggest that the former formula should be $Fe_2O_3 \cdot 6SeO_2 \cdot 3H_2O$ [= $Fe(HSeO_3)_3$].

Both compounds display typical Se–O stretching, O–Se–O bending, Se–OH stretching and O–Se–OH bending vibrations. The main difference

Table 3. Positional parameters and their estimated standard deviations for $Fe(HSeO_3)_3$.

Atom	*x*	*y*	*z*	B/Å^2 [a]
Se1	0.69789(9)	0.16271(6)	0.56750(6)	0.87(1)
Se2	0.09680(9)	0.31530(6)	0.49902(6)	1.05(2)
Se3	0.71880(9)	0.45911(6)	0.73701(6)	0.80(1)
Fe1	0.5258(1)	0.29606(8)	0.26984(8)	0.69(2)
O1	0.4834(7)	0.2000(5)	0.4014(4)	1.19(9)
O2	0.5620(7)	0.1075(4)	0.6348(4)	1.18(9)
O3	0.7756(7)	0.0338(5)	0.5294(5)	1.7(1)
O4	0.2090(6)	0.2140(4)	0.6269(4)	1.05(9)
O5	−0.1650(7)	0.2938(5)	0.4302(5)	1.6(1)
O6	0.0947(8)	0.2457(7)	0.3622(5)	2.4(1)
O7	0.5654(7)	0.3393(5)	0.6737(5)	1.3(1)
O8	0.5181(7)	0.5584(4)	0.6544(4)	1.2(1)
O9	0.8127(7)	0.4646(5)	0.6279(5)	1.6(1)

[a]Parameters for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
$\frac{4}{3}[a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + a \cdot b \cdot (\cos\gamma) \cdot B(1,2) + a \cdot c \cdot (\cos\beta) \cdot B(1,3) + b \cdot c \cdot (\cos\alpha) \cdot B(2,3)]$.

Table 4. Positional parameters and their estimated standard deviations for $Fe(HSeO_3)(Se_2O_5)$.

Atom	*x*	*y*	*z*	B/Å^{2a}
Se1	0.98989(6)	0.86895(4)	0.56846(4)	0.857(7)
Se2	0.65803(6)	0.69877(4)	0.55111(4)	0.866(7)
Se3	0.30134(6)	0.50941(4)	0.73232(4)	0.913(8)
Fe1	0.13082(8)	0.67671(5)	0.44284(6)	0.77(1)
O1	1.1007(5)	0.9062(3)	0.7656(3)	1.31(7)
O2	1.1572(5)	0.7612(3)	0.6180(3)	1.17(6)
O3	0.6941(5)	0.8131(3)	0.4688(3)	1.49(7)
O4	0.9128(5)	0.7055(3)	0.7674(3)	1.14(6)
O5	0.4334(4)	0.7556(3)	0.5290(3)	1.05(6)
O6	0.1533(5)	0.3986(3)	0.6139(3)	1.26(6)
O7	0.3628(4)	0.5666(3)	0.6221(3)	1.07(6)
O8	0.5972(5)	0.4542(3)	0.9024(4)	1.73(8)

[a]See footnote to Table 3.

Table 5. Bond distances (Å) and their estimated standard deviations. Numbers in parentheses are estimated standard deviations in the last significant digits.

$Fe(HSeO_3)_3$			$Fe(HSeO_3)(Se_2O_5)$		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Se1	O1	1.700(3)	Se1	O1	1.672(3)
Se1	O2	1.703(6)	Se1	O2	1.672(4)
Se1	O3	1.745(6)	Se1	O3	1.811(3)
Se2	O4	1.678(5)	Se2	O3	1.798(4)
Se2	O5	1.661(5)	Se2	O4	1.669(2)
Se2	O6	1.743(7)	Se2	O5	1.688(4)
Se3	O7	1.681(5)	Se3	O6	1.683(3)
Se3	O8	1.690(4)	Se3	O7	1.672(4)
Se3	O9	1.736(6)	Se3	O8	1.759(3)
Fe1	O1	2.027(6)	Fe1	O1	2.002(4)
Fe1	O2	2.036(6)	Fe1	O2	2.010(4)
Fe1	O4	1.973(4)	Fe1	O4	2.026(3)
Fe1	O5	1.971(4)	Fe1	O5	2.024(3)
Fe1	O7	2.028(6)	Fe1	O6	2.005(4)
Fe1	O8	2.004(5)	Fe1	O7	1.991(3)

in the spectra is the Se–O stretching vibration of the bridging oxygen in the diselenite group.

Crystal structures. Fractional coordinates are listed in Tables 3 and 4 and bond distances and angles in Tables 5 and 6.

In both compounds iron is six-coordinated and the coordination polyhedron is a regular octahedron. The average Fe–O distance is 2.01 Å (Table 7). The geometry of the selenite groups is also normal. The hydrogen atom in the hydrogenselenite group causes elongation of one selenium-oxygen bond, and the bridging oxygen atom in the diselenite group causes elongation of the selenium-oxygen distances. Each hydrogenselenite group forms a bridge between two different iron atoms, and the oxygen to which hydrogen is bonded is unconnected. The diselenite group forms bridges between three different iron atoms with all oxygen atoms connected. Oxygen O1 and O4 connected to the same iron atom, O2 and O5 are each connected to a different iron

Table 6. Bond angles (°) and their estimated standard deviations. Numbers in parentheses are estimated standard deviations in the last significant digits.

$Fe(HSeO_3)_3$				$Fe(HSeO_3)(Se_2O_5)$			
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Se1	O2	99.7(2)	O1	Se1	O2	102.9(2)
O1	Se1	O3	100.3(2)	O1	Se1	O3	100.6(2)
O2	Se1	O3	98.9(3)	O2	Se1	O3	102.2(2)
O4	Se2	O5	100.3(3)	O3	Se2	O4	101.5(2)
O4	Se2	O6	101.3(3)	O3	Se2	O5	93.2(2)
O5	Se2	O6	95.5(3)	O4	Se2	O5	104.8(2)
O7	Se3	O8	98.7(2)	O6	Se3	O7	102.0(2)
O7	Se3	O9	100.2(3)	O6	Se3	O8	97.9(2)
O8	se3	O9	99.6(3)	O7	Se3	O8	96.7(2)
O1	Fe1	O2	178.9(2)	O1	Fe1	O2	179.2(1)
O1	Fe1	O4	87.7(2)	O1	Fe1	O4	92.5(1)
O1	Fe1	O5	84.3(2)	O1	Fe1	O5	92.6(2)
O1	Fe1	O7	95.9(2)	O1	Fe1	O6	93.4(2)
O1	Fe1	O8	90.8(2)	O1	Fe1	O7	88.3(1)
O2	Fe1	O4	91.1(2)	O2	Fe1	O4	86.7(1)
O2	Fe1	O5	96.8(2)	O2	Fe1	O5	87.5(2)
O2	Fe1	O7	84.1(2)	O2	Fe1	O6	86.5(2)
O2	Fe1	O8	89.1(2)	O2	Fe1	O7	92.5(1)
O4	Fe1	O5	172.0(3)	O4	Fe1	O5	89.4(1)
O4	Fe1	O7	89.0(2)	O4	Fe1	O6	93.4(1)
O4	Fe1	O8	89.6(2)	O4	Fe1	O7	176.5(1)
O5	Fe1	O7	92.1(2)	O5	Fe1	O6	173.2(2)
O5	Fe1	O8	90.3(2)	O5	Fe1	O7	87.2(1)
O7	Fe1	O8	173.0(2)	O6	Fe1	O7	89.9(1)

atom, and O3 forms a bridge between two selenium atoms (Figs. 1 and 2).

There are strong hydrogen bonds in both structures. It was not possible to determine the positions of the hydrogen atoms, but the magnitude of the oxygen–oxygen distances clearly indicates the existence of hydrogen bonds. In $Fe(HSeO_3)(Se_2O_5)$ there is one hydrogen bond, O8–H···O5, the oxygen–oxygen distance being 2.670(5) Å. $Fe(HSeO_3)_3$ had hydrogen bonds between oxygen atoms O3–O2, O6–O1 and O9–O8, and O–O distances being 2.681(6), 2.725(8) and 2.736(5) Å, respectively.

Both structures form a three dimensional network, but it can also be seen that they form layers parallel to the *ac* plane (Figs. 1 and 2). A similar situation exists for $Fe(HSeO_3)(SeO_3)$.[4] In fact, the structures of this and the present two iron (III) selenites are very similar: the space group is the same, the layer structure is of the same type

Table 7. Average bond distances (Å) in iron selenites.

	Average Fe–O	Average Se–O	Average Se–O(–H)	Average Se–O(–Se)
$Fe(HSeO_3)_3$	2.007	1.685	1.741	–
$Fe(HSeO_3)(Se_2O_5)$	2.010	1.676	1.759	1.804
$Fe(HSeO_3)(SeO_3)$[a]	2.013	1.702	1.734	–

[a]From. Ref. 4.

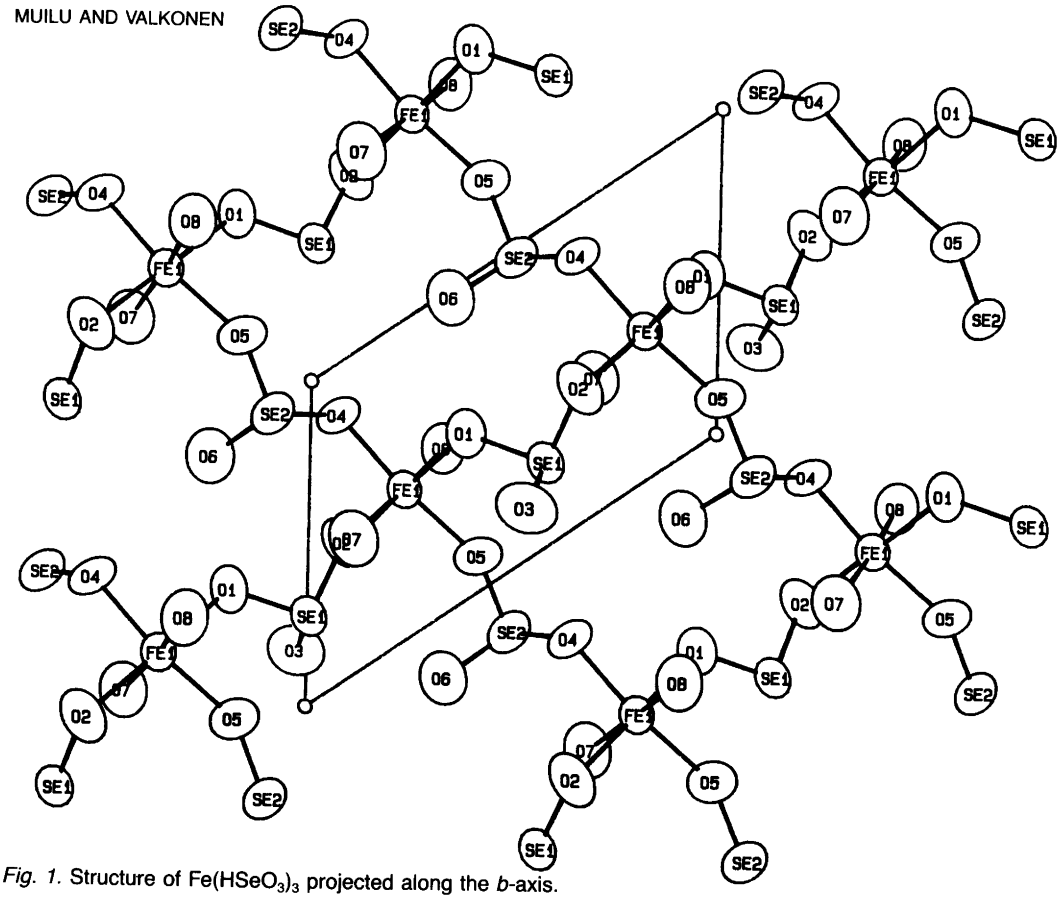

Fig. 1. Structure of $Fe(HSeO_3)_3$ projected along the *b*-axis.

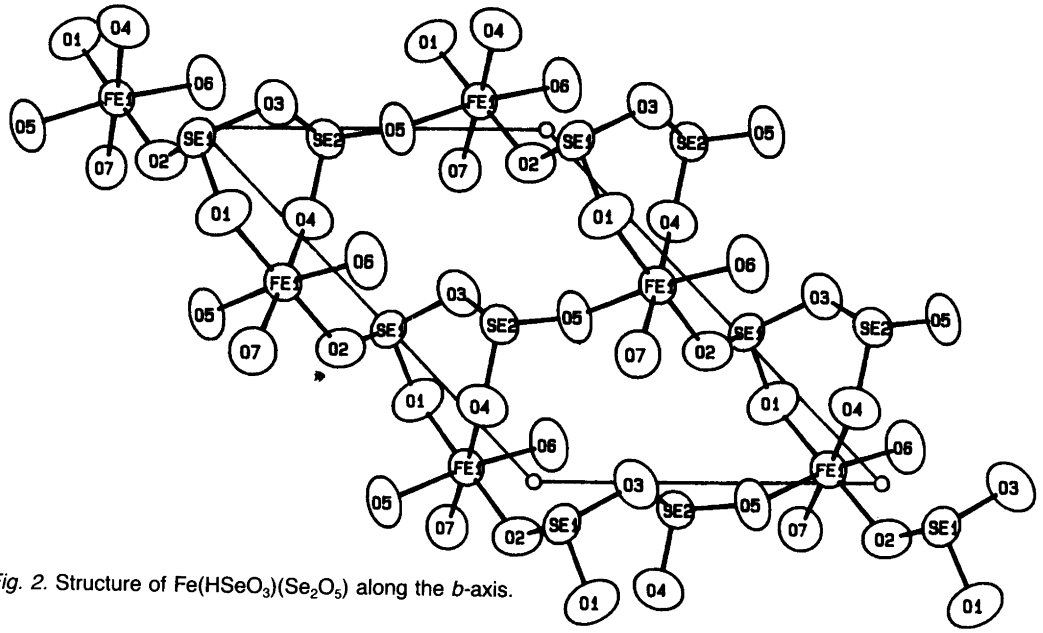

Fig. 2. Structure of $Fe(HSeO_3)(Se_2O_5)$ along the *b*-axis.

and the hydrogenselenite group interconnects the layers. Nevertheless, the details of the structures are different.

The structures of the two selenites described here seem to be stable: all non-hydrogen atoms are bonded together and hydrogen bonds reinforce the structure. The stability is confirmed by the high decomposition temperature observed in the thermal study.

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