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Hexagonal Tungsten Bronze-Type Fe^{III} Fluoride: $(H_2O)_{0.33}FeF_3$; Crystal Structure, Magnetic Properties, Dehydration to a New Form of Iron Trifluoride

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$(H_2O)_{0.33}FeF_3$, grown by hydrothermal synthesis, crystallizes in the orthorhombic system with cell dimensions $a = 7.423(3)$ Å, $b = 12.730(4)$ Å, $c = 7.526(3)$ Å, and space group *Cmcm*, $Z = 12$. The structure, derived from single crystal X-ray diffraction data (605 independent reflections) is refined to $R = 0.019$ ($R_\omega = 0.021$). The framework of the $Fe^{III}F_6$ octahedra is related to that of hexagonal tungsten bronze (HTB) $Rb_{0.29}WO_3$. At 122°C, zeolithic water is evolved from hexagonal tunnels without any noticeable change of the fluorine skeleton. The related anhydrous compound represents a new form of iron trifluoride which is denoted HTB–FeF_3; at 525°C, it transforms into the cubic form of ReO_3-type. $(H_2O)_{0.33}FeF_3$ and HTB–FeF_3 are antiferromagnetic, with Néel temperatures of $T_N = 128^\circ 7 \pm 0.5$ K and $T_N = 97 \pm 2$ K, respectively.

Introduction

During the thermal decomposition of tetragonal β-FeF_3, 3 H_2O, Macheteau and Charpin (*1*) isolated an intermediate hydrate to which they assigned the formula FeF_3, H_2O. Its X-ray spectrum was indexed in a hexagonal cell with parameters $a = 7.395$ Å, $c = 7.557$ Å; however, the product always contained some amounts of α-Fe_2O_3 and α-$FeF_3 \cdot 3\ H_2O$. This fact cast some doubt on the chemical composition given by these authors and led us to reexamine this compound.

Hydrothermal conditions were systematically applied to FeF_3 (*2*) in order to render the previous results more precise: anhydrous or hydrated phases appear, depending on the temperature and fluorine concentration of the solvent; the trihydrate β-$FeF_3 \cdot 3\ H_2O$ is obtained at 250°C from aqueous solutions, while at 380°C in 49% HF, anhydrous FeF_3 crystals are grown. For intermediate conditions, a new compound $(H_2O)_{0.33}FeF_3$ is isolated. Its structure is related to that of the hexagonal tungsten bronze (HTB) $Rb_{0.29}WO_3$ (*3*).

Preparation and Characterization

Light-green crystals of $(H_2O)_{0.33}FeF_3$ are grown by hydrothermal synthesis (FeF_3: 1.2 g, H_2O: 2.2 cm^3) at 360°C, 200 MPa, for 4 days. They present a pseudo-hexagonal

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prismatic habit and frequent (110) twinning. Their powder X-Ray diffraction pattern is indexed in an ideal hexagonal bronze-type cell $a = 7.39$ Å, $c = 7.56$ Å; the orthorhombic deformation, described later, is not observed.

ATG experiments show the easy dehydration of $(H_2O)_{0.33}FeF_3$ at 122°C (heating rate: 2°C min^{-1}). The weight loss, 5.3%, is close to theorical loss, 5.1%, corresponding to 0.33 H_2O per 1 FeF_3 molecule. The resulting anhydrous compound represents a new form of iron trifluoride and will be denoted HTB–FeF_3. X-Ray diffraction spectra of HTB–FeF_3, from room temperature to 300°C, are very similar to those of $(H_2O)_{0.33}FeF_3$: only very small intensity differences are observed; lattice spacings are identical. At higher temperature, hydrolysis begins to occur on the heating stage. However, thermal analysis (DTA, DSC) indicates that at 60°C, HTB–FeF_3 undergoes an endothermic reversible phase transition, probably due to small reorientations of the iron octahedra. Furthermore, at 525°C under argon, an endothermic peak is observed: HTB–FeF_3 irreversibly transforms to ReO_3-type $FeFe_3$, cubic at this temperature, rhombohedral at $T < 394$°C (*4*).

The infrared spectrum of $(H_2O)_{0.33}FeF_3$ crystals shows the presence of intense and narrow peaks at 1625, 3550, and 3625 cm^{-1} associated with weak and broad bands around 1600 and 3250 cm^{-1}. The absorption close to 1600 and 3500 cm^{-1} may be assigned, respectively, to the bending δ_{H_2O} and to the symmetrical or antisymmetrical stretching ν_{OH} vibrations. The presence at 1625 cm^{-1} of an intense and narrow peak proves unquestionably that structural water is present as H_2O molecules. If structural water were coordinated to iron atoms as hydroxyl groups, only ν_{OH} would be expected. Due to the method of preparation, some adsorbed water, which contributes to the broad bands, is in evidence.

Experimental

Laue and precession photographs show that $(H_2O)_{0.33}FeF_3$ crystals are orthorhombic with space group *Cmcm* (No. 63) (Table I). The cell derives from the hexagonal bronze-type cell (dashed unit cell in Fig. 1: $a = b = 7.370$ Å, $\gamma = 119°52$). Intensity data are collected on a CAD 4 Nonius diffractometer.[1] Operating features are as follows: Mo$K\alpha$ radiation; graphite monochromator; scan-mode ω; sweep $s = (0.80 + 0.35 \text{ tg } \theta)°$; scintillation counter aperture $D = (1.50 + 1.00 \tan \theta)$ mm; scanning speed $v = (20.1166/NV)° \text{ min}^{-1}$ with NV integer; range measured: $3° \leq \theta \leq 40°$, $0 \leq h \leq +14$, $-22 \leq k \leq +22$, $-12 \leq l \leq +12$ with C restrictions; reflections measured: total = 1778, *mmm* symmetry independent and $|F| \geq 6\sigma(|F|) = 605$. Corrections for Lorentz and polarization effects and for absorption are applied, using, for all calculations, the SHELX program (*5*). The transmission factor varies from 0.615 to 0.724. Atomic scat-

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TABLE I

Experimental Data for $(H_2O)_{0.33}FeF_3$ Crystals

Symmetry: orthorhombic Z = 12	Cell parameters: $a = 7.423(3)$ Å
Space group: *Cmcm*	$b = 12.730(4)$ Å
Conditions: $hkl\ h + k = 2n$	$c = 7.526(3)$ Å
$h0l\ l = 2n (h = 2n)$	
$\rho_{exp} = 3.25(10)$ g cm^{-3}	$\mu(\text{Mo}K\alpha) = 61.7\ \text{cm}^{-1}$
$\rho_{calc} = 3.33$ g cm^{-3}	Crystal dimensions: $(0.07 \times 0.10 \times 0.06)\ \text{mm}^3$

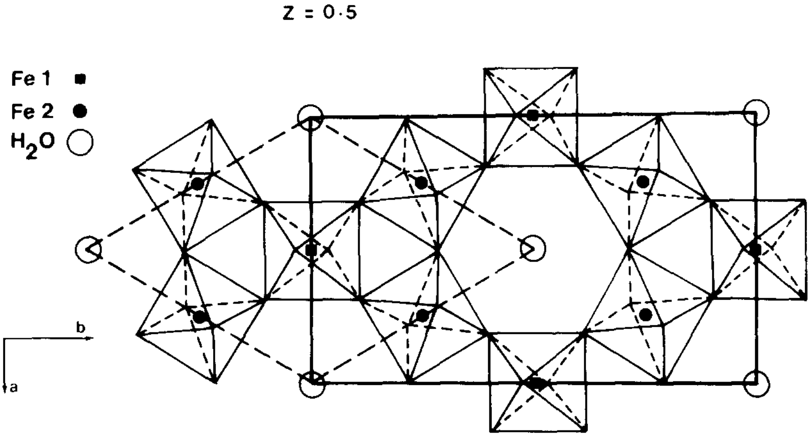

FIG. 1. (001) projection of $(H_2O)_{0.33}FeF_3$.

tering factors are taken from the "International Tables for X-Ray Crystallography" (1968) for Fe^{3+}, O, and F^- (*6*).

Structure Determination

Examination of Fe–Fe interactions in the Patterson map built from I_{hkl} clearly points out that iron atoms occupy a pseudo-hexagonal bronze-type array. Fe–F interactions further indicate that FeF_6 octahedra are tilted from the **c** axis; in particular, some of these octahedra strictly rotate around **a**. Thus, a solution is based on a model, giving to the $Fe(1)F_6$ octahedron a tilt around **a** and correlated tilts to $Fe(2)F_6$ octahedra. The water molecules are placed at the center of the hexagonal cavities. Refinement of this set of atomic coordinates, weighting, secondary extinction, and isotropic thermal parameters easily converges to $R = 0.035$ ($R_\omega = 0.041$). The residual falls to $R = 0.019$ ($R_\omega = 0.021$) when applying anisotropic thermal motion for all nonhydrogen atoms.[2]

Table II presents the final results for the seven independent positions; characteristic distances are listed in Table III. The refinement of the site occupancy factor for oxygen atoms in 4*a* (0 0 0) or 4*c* (0, *y*, $\frac{1}{4}$) really indicates that the 4*c* site is fully occupied and the 4*a* site, empty.

Discussion of the Structure

The structure determination and the light-green color of the crystals prove that $(H_2O)_{0.33}FeF_3$ represents the first hexagonal tungsten bronze-type fluoride with only one metallic species and no mixed-metal valencies. Figure 1 presents a projection of the structure at $z = 0.5$ and shows its similarity to $Cs_{0.4}\ Zn_{0.4}\ Fe_{1.6}\ F_6$ (*7*). Iron atoms occupy two types of crystallographic sites. The six nearest-neighbor distances around iron atoms (Table III) are consistent with Fe^{3+}–F^- distances ($\bar{d} = 1.947$ Å) and confirm the absence of H_2O or OH groups in the iron coordination polyhedra (*8*). Refinement and Fourier map allow the placing of the oxygen atom of water molecules in the

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[2] See NAPS document No. 04038 for 6 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE II

FINAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS IN $(H_2O)_{0.33}FeF_3$[a,b]

Atom	Site	x	y	z	$U_{11} \cdot 10^4$	$U_{22} \cdot 10^4$	$U_{33} \cdot 10^4$	$U_{23} \cdot 10^4$	$U_{13} \cdot 10^4$	$U_{12} \cdot 10^4$	Beq. (Å^2)
Fe1	4*b*	0	$\frac{1}{2}$	0	84(1)	65(1)	66(1)	−1(2)	0	0	0.57(1)
Fe2	8*d*	$\frac{1}{4}$	$\frac{1}{4}$	0	61(1)	88(1)	73(1)	−1(1)	2(1)	10(1)	0.58(2)
F1	8*f*	0	0.2156(1)	0.5511(2)	72(5)	244(8)	176(6)	17(6)	0	0	1.29(5)
F2	16*h*	0.1876(1)	0.3962(1)	0.0434(2)	193(4)	124(4)	199(4)	−9(4)	−25(4)	62(4)	1.36(3)
F3	4*c*	0	0.5386(2)	$\frac{1}{4}$	230(10)	133(10)	66(8)	0	0	0	1.13(7)
F4	8*g*	0.2101(2)	0.2176(1)	$\frac{1}{4}$	179(7)	201(8)	78(6)	0	0	−2(7)	1.21(6)
H_2O	4*c*	0	−0.0006(4)	$\frac{1}{4}$	519(28)	410(27)	721(40)	0	0	0	4.34(25)

[a] Standard deviations are given in parentheses.

[b] The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

TABLE III

CHARACTERISTIC INTERATOMIC DISTANCES (Å) AND BOND ANGLES

4 × Fe1–F2	1.948(1)	$\bar{d}_{Fe1-F} = 1.947$	
2 × Fe1–F3	1.945(1)	$\bar{d}_{F-F} = 2.753$	
2 × Fe2–F1	1.945(1)	$\bar{d}_{Fe2-F} = 1.946$	
2 × Fe2–F2	1.945(1)	$\bar{d}_{F-F} = 2.752$	
2 × Fe2–F4	1.949(1)		
		Fe1–F3–Fe1	150°7(1)
2 × H_2O–F1	3.119(4)	Fe2–F4–Fe2	149°8(1)
2 × H_2O–F1	3.565(4)	Fe2–F1–Fe2	145°1(1)
4 × H_2O–F2	3.086(5)	Fe1–F2–Fe2	142°3(1)
4 × H_2O–F2	3.467(5)		
2 × H_2O–F3	3.745(4)	F2–Fe1–F2	88°7(1)
2 × H_2O–F4	3.186(5)	F2–Fe1–F3	89°5(1)
2 × H_2O–F4	4.183(4)	F1–Fe2–F2	88°8(1)
		F1–Fe2–F4	89°9(1)

hexagonal cavities, but hydrogen atoms cannot be located.

Orthorhombic symmetry arises mainly from anionic displacements. The nearly regular $Fe(1)F_6$ and $Fe(2)F_6$ octahedra tilt cooperatively from **c** axis (14°1 and 14°9, respectively). These important tilts imply a shortening of $8H_2O$–F distances (Table III). However, the shortest H_2O–F distances (3.09 Å) provide evidence that water molecules are weakly hydrogen bonded. They can move inside the large tunnels, as confirmed by the high values of their thermal motion parameters and by the easy dehydration of the compound.

Recently, Gerand *et al.* (*9*) synthetized $WO_3 \cdot \frac{1}{3}H_2O$. The structure, refined from powder diffraction data, is built up from bronze-type layers in a cell similar to that of $(H_2O)_{0.33}FeF_3$. However, the lattice-centering mode, *F* for $WO_3\frac{1}{3}H_2O$ and *C* for $(H_2O)_{0.33}FeF_3$, implies that the connection of the layers is different for both compounds. In WO_3, $\frac{1}{3}H_2O$, the layers are shifted along **a**. The water molecule, which belongs to the tungsten octahedron, points toward crossed tunnels running along [101] and [10$\bar{1}$]. In $(H_2O)_{0.33}FeF_3$, the layers are superimposed along **c**.

Dehydration of $(H_2O)_{0.33}FeF_3$ and $WO_3 \cdot \frac{1}{3}H_2O$ leads to similar HTB-type compounds. So their dehydration mechanisms must differ. For $(H_2O)_{0.33}FeF_3$, the loss of zeolithic water is achieved at low temperature, and the framework of octahedra remains unchanged. By contrast, for $WO_3 \cdot \frac{1}{3}H_2O$, a shift of the HTB layers must occur; then, the transition is destructive and realized at high temperatures ($T > 300°C$) (*10*).

Magnetic and Mossbauer Studies

For $(H_2O)_{0.33}FeF_3$ crystals and HTB-FeF_3, the thermal variations of inverse susceptibility χ^{-1} (Fig. 2) and magnetization, measured with a vibrating sample magnetometer, are indicative of strong antiferromagnetic interactions. Even at 293 K, the Curie–Weiss law is not obeyed; so θ_p values and molar Curie constants can not be obtained. The very flat χ^{-1} versus T curves present a slight slope discontinuity around $T = 130$ K for $(H_2O)_{0.33}FeF_3$ crystals, $T = 100$ K for anhydrous HTB–FeF_3. Mössbauer experiments show that these temperatures correspond to the magnetic ordering temperatures T_N (128.7 ± 0.5 K for $(H_2O)_{0.33}FeF_3$ and 97 ± 2 K for HTB-FeF_3).

TABLE IV

MÖSSBAUER DATA

T(K)	δ^a (mm s^{-1})	ΔE_Q (mm s^{-1})	$4\varepsilon^b$ (mm s^{-1})	H (kOe)	Γ (mm s^{-1})
295	0.439(2)	0.640(4)	—	—	0.50(1)
129	0.539(2)	0.645(4)	—	—	0.52(1)
77	0.54(1)	—	−0.24(4)	511(2)	0.66(1)
4.2	0.55(1)	—	−0.26(4)	565(2)	0.60(1)

[a] δ = isomer shift relative to Fe metal (T = 300 K).
[b] ε = quadrupolar shift of the outer Zeeman lines.

Experimental Mössbauer data are listed in Table IV. For $(H_2O)_{0.33}FeF_3$ crystals, the two types of iron sites are not distinguished through Mössbauer spectrometry, as could be deduced from considerations of bond lengths (Table III) and angles. The thermal variation of their common hyperfine magnetic field is shown in Fig. 3; the value found at 4.2 K, close to that observed for hexagonal bronze-type A_xFeF_3 (*11*), corroborates the absence of water molecules in the iron coordination polyhedra. From the ε value, the determination of the angle between the magnetic hyperfine field direction and the main electric field gradient axis is ambigous: it could be 63°5 or 46°6, depending on the unknown sign of quadrupole splitting ΔE_Q.

According to the Kanamori (*12*) or Goodenough rules (*13*), the antiferromagnetic exchange between layers is easily rationalized ($\widehat{\text{Fe–F–Fe}}$ = 149°8 or 150°7, Table III), but frustration must exist in the cycles formed by three octahedra linked by corners in the layer plane. Thus, neutron

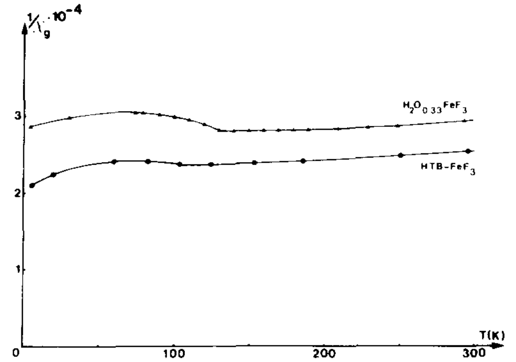

FIG. 2. Thermal variation of the magnetic inverse susceptibility (l/emu g^{-1}).

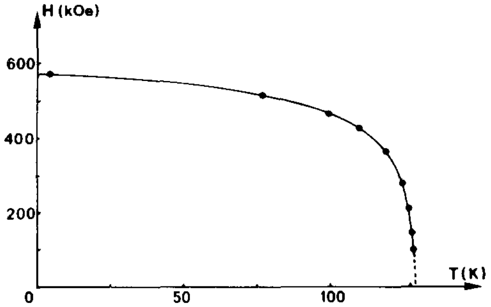

FIG. 3. Thermal variation of the magnetic hyperfine field of $(H_2O)_{0.33}FeF_3$.

diffraction experiments, scheduled at the ILL Grenoble, will have to determine the magnetic structure of $(H_2O)_{0.33}FeF_3$ and both nuclear and magnetic structure of anhydrous HTB–FeF_3. The influence of frustration on magnetic structure and the role of water for structure stability will have to be investigated.

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