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Crystal Structure and Magnetic Characterization of $[C(NH_2)_3]_3FeF_6$

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The compound $[C(NH_2)_3]_3FeF_6$ is prepared in closed bombs by digestion of FeF_3 and $C(NH_2)_3F$ in aqueous HF solutions. The material is cubic, space group $Pa3$, $a = 14.130(5)$ Å, $Z = 8$. The crystal structure is determined from single-crystal diffraction intensity data refined to the conventional values of the indexes $R = 0.0409$ and $R_w = 0.0409$ for the model containing the nonhydrogen atoms. All the hydrogen atoms are located by the final difference-Fourier map and lie near N atoms at distances in the range 1.02 to 1.09 Å. The structure is characterized by two different sets of regular isolated (FeF_6) octahedra. Guanidinium cations are located on general 24-fold positions. The N–H . . . F hydrogen-bonding network is discussed. As expected, the compound is paramagnetic ($\mu_{exp} = 6.01\mu_B$, $\vartheta_p = -5.6$ K) and characterized by Mössbauer spectroscopy. © 1987 Academic Press, Inc.

Introduction

Some fluorinated compounds of guanidinium cation $-[C(NH_2)_3]^+$, hereafter referred to as Gu^+–, and metal atoms are known (*1–3*). In an attempt to encounter new structural types involving MF_6 octahedra, we started a study in the system $GuF–FeF_3–HF_{aq}$. We report here the structure of the complex Gu_3FeF_6, isostructural with the phases Gu_3MF_6 (M = Al, Ga, In, Mn) first isolated by Bukovec (*1, 2*). We describe the positions of all the hydrogen atoms, discuss the N–H . . . F hydrogen-bonding network, and report the magnetic properties of the complex.

Experimental

Single crystals of Gu_3FeF_6 are obtained by digestion, at 200°C in a closed Teflon vessel (filling rate 0.80), of a mixture of 11 mmole of $FeF_3 \cdot 3H_2O$ and 11.5 mmole of Gu_2CO_3, with 10 cm^3 of a 5 M HF aqueous solution (final pH ≈ 1). After 12 hr of heating, the bomb cools naturally. Many colorless, cubic-shaped single crystals are isolated and washed rapidly with a dilute HF solution and dried in air.

Crystallographic Study and Data Collection

The powder diffraction pattern is readily indexed in a primitive cubic cell with a = 14.130 Å. It reveals that Gu_3FeF_6 is isostructural with the phases Gu_3MF_6 described by Bukovec (*1, 2*). Standard photographic analysis by X-ray diffraction on single crystals reveals the $m3$ Laüe group and systematic absences for $0kl$ with $k \neq 2n$, thus leading to the space group $Pa3$. A small crystal—0.099 mm on each edge—is chosen for the structure determination. Table I gathers the experimental conditions of the data collection.

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TABLE I

CONDITIONS OF THE DATA COLLECTION (NONIUS CAD4)

$[C(NH_2)_3]_3FeF_6$ Molecular weight: 350.07 g
Space group: $Pa\bar{3}$
$a = 14.130(5)$ Å
$V = 2821.15$ Å^3, $Z = 8$ $\rho_{calc} = 1.648$ g · cm^{-3}
$\rho_{obs} = 1.640(3)$ g · cm^{-3} (flotation method)
$\mu(MoK_\alpha) = 11.03$ cm^{-1}
Radiation: MoK_α (graphite monochromatized)
$T = 20$°C
Scanning: $\omega/2\vartheta$
Angular range: $2° \leq \vartheta \leq 35°$
Part of the reciprocal space explored: $-19 \leq h \leq 19$, $0 \leq k \leq 19$, $0 \leq l \leq 19$
Number of reflections measured before average operation: 1545
Number of independent reflections used after absorption correction and average operation: 379 (with $\sigma(I)/I < 0.33$)
Maximum and minimum transmission factors: 0.9180, 0.8922.
$R_{int} = 0.0299$

The cell parameter $a = 14.130(5)$ Å is refined by least-squares from the 25 most intense reflections measured on the diffractometer.

Structure Resolution

All the calculations are performed with SHELX 76 (*4*) in the centric space group $Pa\bar{3}$. An absorption correction is applied before the average operation. Atomic scattering factors and $\Delta f'$ and $\Delta f''$ values are from "International Tables for X-Ray Crystallography" (*5*). The Patterson function analysis gives immediately the positions of the eight Fe atoms located in 4a and 4b particular positions (Fe2 and Fe1). The Fourier-synthesis reveals that all the nonhydrogen atoms are located in six groups of 24d general positions (C, F1, F2, N1, N2, N3). At this stage, and in the anisotropic thermal motion approximation, the values of the conventional indexes are $R = 0.0409$ and $R_w = 0.0409$ with the weighting scheme $w = 2.1315/[\sigma^2 \times F + 1.98 \times 10^{-3}F^2]$. The last Fourier-difference synthesis reveals then all the 144 hydrogen atoms located in six groups of 24d general positions, near the N atoms at distances in the range 1.02–1.09 Å. We did not take into account further refinement including the 24 new hydrogen parameters—leading to best R and R_w values of 0.0262 and 0.0235, respectively—because of the enlargement of the ratio number of adjustable parameters/number of independent reflections.

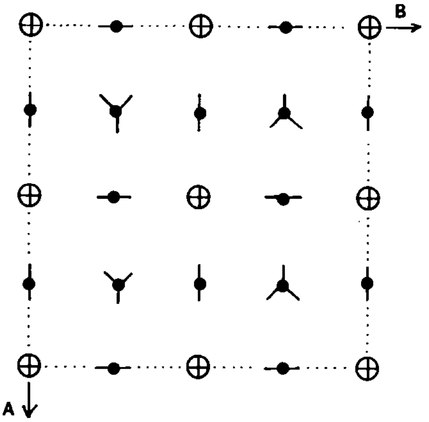

FIG. 1. Idealized projection on the (001) plane. Centers of (FeF_6) octahedra are at $z = 0$ and $\frac{1}{2}$ (open circles). Gu^+ ions are located at $z \approx 0$ and $\frac{1}{2}$ (triangles) and at $z \approx \frac{1}{4}$ and $\frac{3}{4}$ (H atoms are omitted).

Table II gathers the best set of the 58 adjustable parameters (in fact 59, including the overall scale factor) and the atomic coordinates of the hydrogen atoms found on the Fourier-difference map.[1]

Structure Description

Figure 1 shows the idealized projection of the structure on the (001) plane. It con-

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[1] F_0 and F_c values may be obtained on request from J. L. Fourquet.

TABLE II

STRUCTURAL PARAMETERS OF Gu_3FeF_6

Atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq} (Å^2)
C	2648(5)	2511(9)	263(6)	224(51)	290(41)	420(51)	110(73)	−5(33)	−78(92)	2.46
Fe2	0(0)	0(0)	0(0)	71(25)	71(25)	71(25)	0(8)	0(8)	0(8)	0.56
Fe1	5000(0)	5000(0)	5000(0)	242(42)	242(42)	242(42)	12(10)	12(10)	12(10)	1.91
F1	8670(5)	267(6)	4795(5)	163(40)	344(35)	284(41)	−46(39)	−5(29)	46(32)	2.08
F2	5286(5)	3683(5)	237(5)	292(32)	161(40)	292(37)	9(31)	−59(41)	37(33)	1.96
N1	2179(6)	3319(6)	385(7)	372(68)	142(53)	479(55)	1(47)	66(45)	79(42)	2.61
N2	3600(5)	2532(8)	231(6)	200(33)	362(39)	617(63)	17(61)	26(33)	128(71)	3.10
N3	2199(6)	1692(7)	153(6)	353(64)	264(59)	494(62)	−55(43)	−5(45)	−83(40)	2.92
H1	2649	3847	199							
H2	1433	3370	194							
H3	1451	1705	28							
H4	2604	1178	−178							
H5	3852	1848	107							
H6	3883	3170	41							

[a] All values are ×10^4. Estimated standard deviations are in parentheses. The vibrational coefficients are relative to the expression $T = \exp[-2\pi^2(h^2a^{*2}u_{11} + k^2b^{*2}u_{22} + l^cc^{*2}u_{33} + 2klb^*c^*u_{23} + 2hla^*c^*u_{13} + 2hka^*b^*u_{12})]$.

sists of isolated, regular (FeF_6) octahedra surrounded by 12 Gu^+ ions. The F1–Fe1–F1 angle values are 90.85 and 89.16°, and for F2–Fe2–F2 are 90.10 and 89.90°. As shown previously, there are in fact two sets of Fe, the distances Fe–F being Fe1–F1 = 1.938(9) Å and Fe2–F2 = 1.933(9) Å. The mean Fe–F distance is 1.935 Å, very close to the sum of ionic radii (*6*) of hexacoordinated Fe^{3+} (0.645 Å) and dicoordinated F^- (1.285 Å) and to the mean Fe–F distance in ferric fluorides (1.922 Å) (*7*). The characteristics of the Gu^+ ion are shown in Table III. The mean C–N and N–N distances and the mean N–C–N angle are very close to those reported in other structural determinations: 1.33(3) Å, 2.30(3) Å, and 120(2)° respectively for $Gu_5Th(CO_3)_3F_3$ (*8*) and 1.366(5) Å, 2.35(3) Å, and 119.98(1.9)° respectively for $Gu_2AlF_5 \cdot 2H_2O$ (*3*).

The Hydrogen-Bonding Network

In fact, the (FeF_6) octahedra are tilted as shown in Fig. 2. These tilts are caused by hydrogen bonding between F^- and Gu^+ ions. This representation shows the proposed hydrogen-bonding network based on N–H . . . F hydrogen linking. The short N–F distances lie in the range 2.81–3.20 Å and can be compared to short N–F distances in other compounds containing N–H

TABLE III

CHARACTERISTICS OF THE Gu^+ CATION IN Gu_3FeF_6

d, C–N (Å)		d, N–N (Å)		N–C–N (°)	
C–N1	1.332(12)	N1–N2	2.306(11)	N1–C–N2	118.8(1.0)
C–N2	1.347(9)	N1–N3	2.323(9)	N1–C–N3	121.7(0.7)
C–N3	1.329(12)	N3–N2	2.311(12)	N2–C–N3	119.5(1.1)
Mean C–N	1.336(11)	Mean N–N	2.313(11)	Mean N–C–N	120.0(0.93)

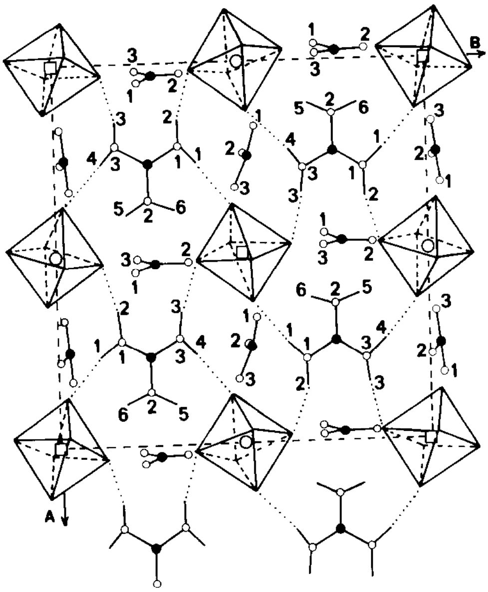

FIG. 2. Part of the projection on the (001) plane. Open squares: Fe1, centers of $[Fe1(F1)_6]$ octahedra ($z = 0$). Large open circles: Fe2, centers of $[Fe_2(F2)_6]$ octahedra ($z = 0$). Solid circles: C atoms ($z \approx 0$ and $\frac{1}{2}$). (See Fig. 1.) Small open circles: N atoms ($z \approx 0$ and $\frac{1}{2}$). (See Fig. 1.) For clarity, H atoms are only figurated for the Gu^+ ions lying near $z \approx 0$. Dotted lines show the proposed N–H . . . F bonding network.

. . . F bonds: 2.900 Å in NH_4AlF_4 (*9*), 2.835 Å in Gu_3MnF_6 (*1*), and 2.804 to 2.901 Å in $Gu_2AlF_5 \cdot 2H_2O$ (*3*).

Magnetic Characterization

Susceptibility Measurement

The magnetic susceptibility is measured on crushed single crystals by the Faraday method in the temperature range 90–300 K. The data are corrected from diamagnetism and then fitted by least-squares to a classical Curie–Weiss law, leading to $\mu_{exp} = 6.01\mu_B$ and $\vartheta_p = -5.6$ K.

Mössbauer Study

^{57}Fe Mössbauer experiments were performed using a classical method with a ^{57}Co source diffused into a rhodium matrix. The Mössbauer sample has been prepared containing 5–6 mg/cm^2 of natural iron.

Two Mössbauer spectra are shown in Fig. 3 and fitted data are given in Table IV.

Both spectra are identical to those obtained for $(NH_4)_3FeF_6$ and for $(NH_4)_2NaFeF_6$ by Morup and Thrane (*10*) and Pebler *et al.* (*11, 12*), In which the FeF_6 octahedra are isolated. They suggest relaxation phenomena.

At 300 K and $H_{ext} = 0$, the spectrum is perfectly symmetric and has been fitted using a single broad Lorentzian line indicating a very small electric field gradient in agreement with the symmetry of the FeF_6 octahedra.

The spectrum at 5 K was recorded using an external field $H_{ext} = 6$ Tesla parallel to the γ-beam direction and consists of two pairs of absorption lines.

The average total hyperfine field ($\overline{H}_{tot} = 350$ kOe) is very far from the value expected at magnetic saturation ($H \approx 600$ kOe). This result is very different from that obtained by Pebler in $(NH_4)_3FeF_6$ (*11*) and

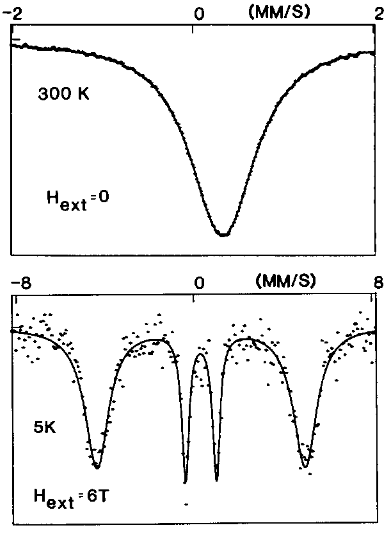

FIG. 3. Mössbauer spectra of Gu_3FeF_6.

TABLE IV

MÖSSBAUER DATA OF $(Gu)_3FeF_6$

	δ^a (mm · sec^{-1})	ΔEQ (mm · sec^{-1})	Γ_o^b (mm · sec^{-1})	Γ_i^b (mm · sec^{-1})	H_{tot} (kOe)
300 K, $H_{ext} = 0$	0.42(1)	0^c	0.85(2)		—
5 K, $H_{ext} = 6$ Tesla	0.44(1)	0^c	1.65(2)	0.40(2)	350(3)

[a] Isomer shift relative to Fe metal (RT).

[b] The linewidths Γ_0 and Γ_i are for the outer and inner line pairs, respectively.

[c] Fixed value.

$(NH_4)_2NaFeF_6$ (*12*) and is surprising in such a compound. Further Mössbauer and magnetic experiments are in progress to explain this phenomenon.

Acknowledgments

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