

Crystal structure of hydrated diphenylguanidinium hexafluoroferrate (III)

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Abstract

The crystal structure of $3\text{C}_{13}\text{H}_{14}\text{N}_3^+\text{FeF}_6^{3-}\cdot 3.5\text{H}_2\text{O}$ was determined. Both phenyl rings of the diphenylguanidine cation are oriented *syn* to the central $\text{C}=\text{NH}_2$ group. The anions and cations are held together by a three-dimensional network of hydrogen bonds. In the synthesis of this compound, a second phase (iron trifluoride trihydrate) was formed and identified by powder diffraction data. Mössbauer results show two different iron environments compatible with the two phases reported. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Metal-ion-based paramagnetic systems hold considerable potential for magnetic relaxation agents that may be used in medical magnetic imaging [1]. These contrast agents generally serve the same purpose as the iodine-containing materials used in X-radiography; they increase the sensitivity and accuracy of an examination. The agent most commonly used is gadolinium-diethylenetriaminepentaacetate (Gd-DTPA), also called Magnevist [2].

The contrast of the ^1H NMR imaging, largely composed of the NMR signal of the water protons, is dependent on nuclear relaxation times. Paramagnetic complexes, in particular those of Gd(III), Fe(III) and Mn(II) which have high magnetic moments and relaxation efficiency, can decrease the relaxation times of nearby nuclei via dipolar interactions and so enhance the image contrast.

The lanthanide and even the transition metal atoms are relatively toxic at doses required for a significant change of the NMR relaxation rate. Therefore, investigation has focused on the development of stable paramagnetic ion complexes. The toxicity of the free ligand also becomes a factor in the event of dissociation. A compound based on a thermodynamically and kinetically stable metal complex is much less toxic. Iron(III) may be advantageous because of its reduced toxicity. It is commonly used as a gastrointestinal contrast agent; orally administered ferric chloride was the first paramagnetic agent ever used in humans [3]. Long electron relaxation times were found for Fe bonded to

benzene tetraphosphonic cyclopentents [4], for FeF_2 bonded to porphyrin complexes [5] and for FeF_6 in zeolite cages [6]. In this latter study, it is stated that for high symmetry iron, the electron spin relaxation time may be considerably longer than commonly found.

Single crystals of diphenylguanidinium hexafluoroferrate, a water soluble and shelf stable compound, were isolated during recrystallisation and their crystal structure was determined. In the synthesis of this compound, a minor second phase (iron trifluoride trihydrate) was formed and identified through powder diffraction data. Mössbauer spectroscopy was used to investigate the environment of the iron atoms and susceptibility measurements were performed to check the paramagnetic state at room temperature and possible low-temperature magnetic ordering.

2. Crystal structure of $3\text{DPG}^+\text{FeF}_6^{3-}\cdot 3.5\text{H}_2\text{O}$ (DPG = $\text{C}_{13}\text{H}_{13}\text{N}_3$) and powder X-ray diffraction results

The title compound (1) crystallises in the space group $R\bar{3}c$ with six formula units per cell and unit cell parameters given on Table 1. The guanidinium group of the cation has a geometry close to that expected for a central C_{sp^2} atom. The N2–C1 bond length is [1.335(2) Å] while N1–C1 is slightly shorter [1.316(3) Å]. The former length is close to the expected value for a delocalised $\text{C}=\text{N}$ double bond (1.339 Å) while the latter indicates some charge delocalisation occurring on the guanidine fragment upon protonation, since it is larger than the value expected for a $\text{C}_{\text{sp}^2}=\text{N}$ bond (1.295 Å) [7]. The N2–C2 [1.421(2) Å] bond length, between the N

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Table 1
Crystal data and structure refinement of the title compound

Empirical formula	C ₃₉ H ₄₉ F ₆ Fe ₁ N ₉ O _{3.5}
Formula weight	869.68
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal size	0.49 mm×0.37 mm×0.25 mm
Crystal system	Trigonal
Space group	$R\bar{3}c$
Unit cell dimensions (hexagonal axes)	$a=9.7211(11)$ Å $c=77.872(18)$ Å $V=6373.0(18)$ Å ³
Z	6
Final R indices ($I>2$ sigma (I))	$R=0.0322$, $wR=0.0847$
R indices all data	$R=0.0709$, $wR=0.1011$

atom and its substituent ring, compares well with other diphenylguanidium (DPG) salts. The dihedral angle between the central planar guanidine moiety and the phenyl rings is 42.28(9)°. The angle between the least-squares planes of the two phenyl rings is 82.47(7)° close to the value observed in DPG⁺ nitrate [81.49(11)°]. Both phenyl rings are oriented *syn* to the terminal unsubstituted N1 atom. Different conformations of the cation have been found in other DPG compounds, namely *anti-anti* [8] and *syn-anti* [9] conformations which have been explained by the low potential barrier for rotation of the rings about the C–N bonds.

The transition metal atoms are located at the 6a special positions. Each iron is octahedrally co-ordinated by six fluorine ions at distance 1.9335(9) Å, such that the ion has an exact 32 symmetry. Similar Fe–F distances (1.879–1.956 Å) are found in piperazinium oxonium hexafluoro iron(III) [10–12], where the fluorine ions are also involved in H-bonding. The Fe–F distance is larger than the reported value in K₃FeF₆ (1.85 Å) which lacks H-bonding. However, the much shorter distance may be also due to either thermal shrinkage or disorder.

The anions and cations are held together by a three-dimensional network of hydrogen bonds. Both diphenylguanidine NH and NH₂ groups donate their hydrogens to the fluorine ions, exhausting DPG potential for hydrogen bonding. Each DPG cation links two different FeF₆³⁻, in such a way that all fluorine ions accept two hydrogens coming from guanidine fragments (N1–H1...F 2.738(2) Å, N2–H2...F 2.688(3) Å).

Two independent positions for solvent water molecules were located, their refined occupation being close to one third and one quarter, which corresponds to 3.5 water molecules per unit formula. These water molecules are disordered through positions related by the three-fold axis. The atomic displacement parameters of the oxygens were refined isotropically but the disorder prevented the water hydrogens to be located.

PLATON [13] indicates that there are no voids in the structure capable of holding solvent molecules.

An X-ray powder diffractogram showed the existence of an additional phase in the synthesised polycrystalline material. The extra peaks were identified as belonging to iron trifluoride trihydrate [14]. In this second phase, each iron atom is surrounded by six ligands in the form of a nearly regular octahedron. Octahedron apices are fluorine atoms shared between different iron atoms. The four other ligands of each octahedron are two fluorine atoms and two water molecules which occupy statistically the four positions of the square around the iron atom.

3. Mössbauer and magnetic susceptibility results

Fig. 3 shows the ⁵⁷Fe Mössbauer spectrum at room temperature for a sample of the polycrystalline material. The spectrum was fitted with a single peak and a doublet, which are also shown in the figure. The fitted parameters are listed in Table 4.

The single peak subspectrum can be ascribed to FeF₆ [15] and the obtained spectral parameters of the doublet agree with those obtained for FeF₃·3H₂O [16].

Magnetic susceptibility measurements were performed down to 4 K, in an applied field of 200 Oe. The variation of the induced magnetic moment with temperature shows a paramagnetic behaviour down to the lowest temperature with no sign of magnetic ordering.

4. Experimental

4.1. Synthesis

The pure metal (Aldrich, 99.99%) was dissolved in concentrated hydrofluoric acid (Merck, 40%). Diphenylguanidine (Aldrich, 98%) dissolved in ethanol was then added to the solution. After a few months, the inhomogeneous solid formed was dissolved in water. Crystals with different shades of pink grew from the solution within a few weeks.

4.2. Structure determination of the title compound

A single crystal was selected and tested by photographic methods prior to data collection. The diffraction data were collected at room temperature, using a CAD-4 ENRAF-NONIUS diffractometer [17] with Mo K α radiation up to a θ limit of 28°. Intensity values of 5138 for one hemisphere of data were collected, from which a total of 1717 were independent.

Three intensity and orientation control reflections measured every 3 h of X-ray exposure time showed a decay of 1%, and a linear correction was applied to compensate. A Ψ -scan absorption correction [18] based on the measurement of high χ reflections was applied, $T_{\max}=0.9645$ and $T_{\min}=0.9212$.

Table 2

Atomic fractional co-ordinates, equivalent displacement parameter and occupancy factor of non-hydrogen atoms (\AA , \AA^2)

Atom	x	y	z	U_{eq}	Occupancy
N1	0.2820(2)	0.3333	0.0833	0.0521(7)	1
N2	0.0796(2)	0.3426(2)	0.06874(2)	0.0386(4)	1
C1	0.1466(2)	0.3333	0.0833	0.0349(6)	1
C2	0.1295(2)	0.3376(2)	0.05172(2)	0.0348(4)	1
C3	0.1135(3)	0.4315(2)	0.03950(3)	0.0438(5)	1
C4	0.1531(3)	0.4249(3)	0.02270(3)	0.0539(6)	1
C5	0.2099(3)	0.3264(3)	0.01803(3)	0.0577(6)	1
C6	0.2260(3)	0.2334(3)	0.03008(3)	0.0571(6)	1
C7	0.1844(3)	0.2362(3)	0.04690(3)	0.0461(5)	1
Fe	0.6667	0.3333	0.0833	0.02675(18)	1
F	0.57177(13)	0.14528(11)	0.069081(13)	0.0368(3)	1
O1	0.689(3)	0.3854(13)	0.03685(8)	0.140(5)	0.338(6)
O2	0.7439(16)	0.353(2)	0.01158(13)	0.147(7)	0.246(7)

The structure was solved by direct methods using SHELXS97 [19], which gave the positions of most of the atoms. The rest of the atoms were then located from a difference-Fourier map, and the entire structure was anisotropically refined (with exception of the water molecules) by SHELXL97 [20] to a final agreement factor of 3.22%. All hydrogen atoms except those of the water molecules were placed at calculated idealised positions and refined as riding with an isotropic temperature factor of $1.2U_{\text{eq}}$ of the parent atoms. The crystal and structure refinement data, atomic co-ordinates and selected bond distances and angles of (1) are summarised in Tables 1–3, respectively. The structure of the individual anion and cation and the hydrogen bonding network are shown in Figs. 1 and 2, respectively.

All calculations were performed on a Pentium 333 MHz PC running LINUX.

Table 3

Selected bond distances (\AA) and angles ($^\circ$)

N1–C1	1.316(3)
N2–C1	1.335(2)
N2–C2	1.421(2)
Fe–F	1.9335(9)
F–Fe–F ^a	90.02(6)
F–Fe–F ^b	179.50(7)
F–Fe–F ^c	89.31(7)
C1–N2–C2	127.22(17)
N1–C1–N2 ^b	121.45(11)
N1–C1–N2	21.45(11)
N2–C1–N2 ^b	117.1(2)
C2–N2–C1–N1	6.8(2)
C2–N2–C1–N2 ^b	–173.2(2)

^a $-x+4/3, -x+y+2/3, -z+1/6$.

^b $x-y+1/3, -y+2/3, -z+1/6$.

^c $y+1/3, x-1/3, -z-1/6$.

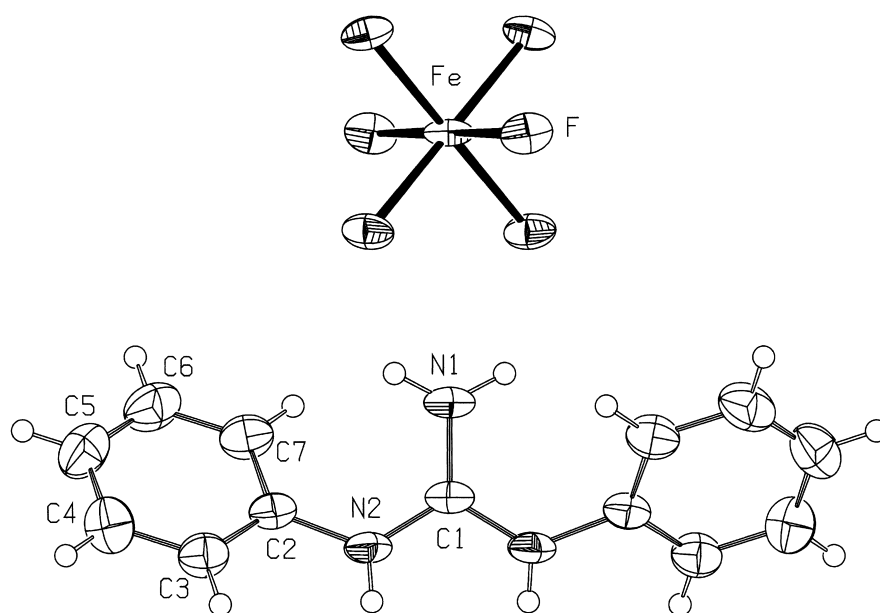


Fig. 1. ORTEP [21] plot of the anion and cation of the title compound. Displacement ellipsoids are drawn at the 50% level.

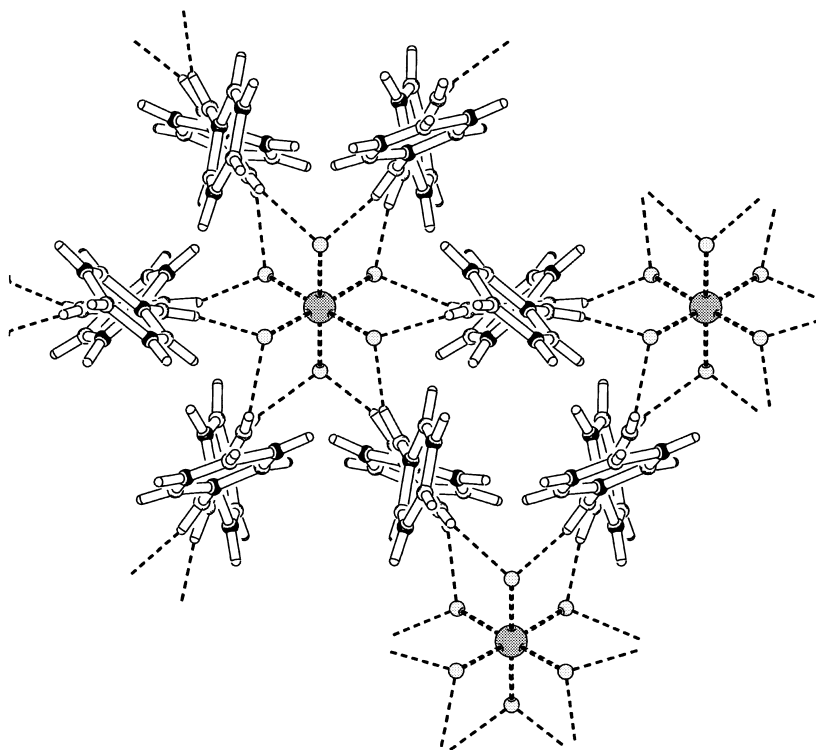


Fig. 2. Fluorine hydrogen bonding network.

4.3. Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectrum was recorded at room temperature in a transmission geometry with a $^{57}\text{Co}/\text{Rh}$ source of about 30 mCi. The sample was powdered by means of a grinding mortar. The evaluation of the spectrum was made using a least-squares-minimum computer fit to a superposition of Lorentzian shape lines (Fig. 3, Table 4).

4.4. Powder diffraction

A glass capillary was filled with the powder obtained by grinding the solid described in Section 4.1. The sample was

mounted on an ENRAF-NONIUS powder diffractometer (equipped with a CPS120 detector by INEL) and data were collected for 24 h using Debye–Scherrer geometry. $\text{Cu K}\alpha_1$ radiation was used ($\lambda=1.540598 \text{ \AA}$). Potassium aluminium sulphate dodecahydrate was chosen as an external calibrant. The diffractogram shows two different phases: the title compound and iron trifluoride trihydrate. A calculated diffractogram of these two phases agrees well with the experimental diffractogram (Fig. 4).

4.5. Susceptibility measurements

Susceptibility measurements were performed as function of temperature (4–300 K) on a SQUID Quantum Design magnetometer, applying a magnetic field of 200 Oe to a powder sample. The powder was free to rotate under the field.

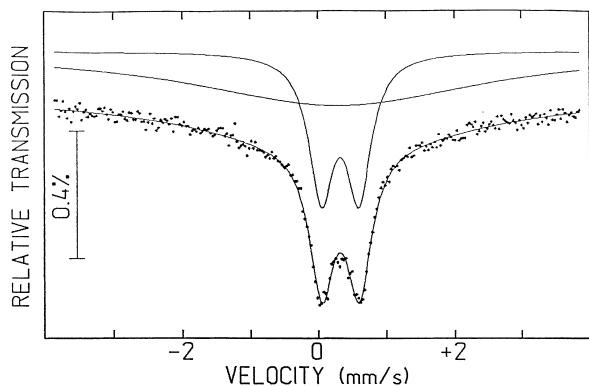


Fig. 3. Room temperature ^{57}Fe Mössbauer spectrum of a sample of the polycrystalline material.

Table 4
Best-fit values of spectral parameters obtained from the ^{57}Fe Mössbauer spectrum^a

Single peak			Doublet			
IS (mm/s)	Γ (mm/s)	%	IS (mm/s)	QS (mm/s)	Γ (mm/s)	%
0.44	1.5	76.7	0.45	0.61	0.29	23.3

^a The meaning of the symbols — IS: isomer shift; QS: quadrupole splitting; Γ : width at half maximum and %: relative percentage. The IS is given relative to $\alpha\text{-Fe}$.

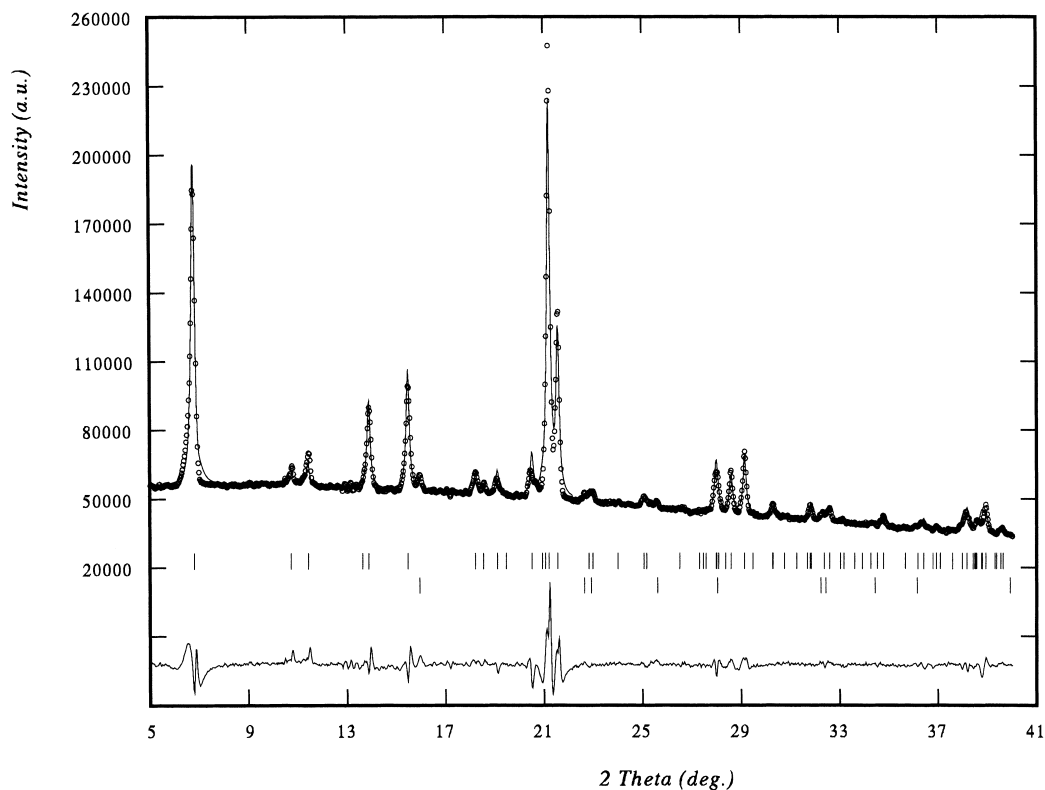


Fig. 4. X-ray powder diffractogram of a sample of the polycrystalline material. The solid line is the calculated diffractogram from single crystal data for diphenylguanidinium hexafluoroferrate and iron trifluoride [14]. Only global parameters defining the peak shape, zero-offset and scale were allowed to refine. Bottom line is the difference between the experimental and calculated diffractogram. Bragg peak positions for both phases are indicated.

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