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Ionic Liquid Mediated Synthesis and X-ray Crystal Structure of *trans*-Difluorotetrakis(1-methylimidazole)iron(III) Tetrafluoroborate

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Introduction

Iron(III) has a low affinity for simple monodentate nitrogen ligands, and such complexes do not exist in aqueous solution.[1] Indeed, although octahedral iron(II) complexes of 1-methylimidazole (1-Meim)[2] and 2-methylimidazolato (2-Meim$^-$)[3] ligands are known and have been characterized by X-ray crystallography, their corresponding iron(III) analogues are unknown. However, a large number of five- and six-coordinate iron(III) complexes of porphyrins[4,5] and salen type ligands[6] containing imidazole in axial positions have been prepared and characterized by single-crystal X-ray crystallography. The interest shown in the structural characterization of these complexes can be attributed to the prevalence of iron in similar coordination environments in naturally occurring heme and non-heme metalloenzymes.[7] In such complexes it is apparent that the axial ligands play an important role in controlling the spin state of the iron center and hence the binding of substrate molecules.[8] Besides the aforementioned iron porphyrin complexes, a number of simple iron complexes[9] and polynuclear oxoiron clusters[10] with multidentate ligands derived from imidazoles have been characterized, primarily as models of iron centers in non-heme enzymes. However, to our knowledge a simple pseudo-octahedral iron(III) complex of 1-Meim has not been characterized by X-ray crystallography. This paper describes the preparation in an ionic liquid medium[11] and the subsequent structural characterization of such a complex, *trans*-$[Fe(1\text{-}Meim)_4F_2]BF_4$, **1**.

Experimental Section

Tetrafluoroboric acid (48–50%) aqueous solution was purchased from J.T. Baker Chemical Co. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification. Melting points were determined using a Fisher–John apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR, and the UV–Visible spectra of **1** were recorded on a Milton Roy Spectronic 3000 array instrument. NMR spectra were recorded on a Nicolet 360-NB spectrometer at the Atlantic Region Magnetic Resonance Center, and elemental analysis were conducted by Canadian Microanalytical Service, Ltd., Delta, British Columbia, Canada.

Synthesis of [1-MeimJBF$_4$. To a solution of 14.50 g (0.1766 mol) of 1-Meim in 50 mL of ethanol was added dropwise and under stirring 32.29 g (0.1766 mol) of 48% w/w aqueous tetrafluoroboric acid. The mixture was stirred for 3 h before most of the ethanol and water was removed under vacuum in a rotary evaporator. The viscous residue was dehydrated at 80 °C in a vacuum oven for 24 h. The dehydrated residue solidified on cooling to a colorless crystalline solid: Yield 30.00 g (0.1766 mol, 100%); mp 55 °C; IR (KBr reflectance; cm^{-1}) 3153, 2464, 2000 (broad), 1588, 1555, 1526, 1474, 1422, 1376, 1332, 1284, 1236, 1061 (very broad, BF_4^-), 935, 841, 758, and 671; ^{1}H NMR ($CDCl_3$, ppm) 3.62 (s, CH_3–N), 6.87, 7.02, 7.50 (s, 3H, imidazole ring protons); ^{13}C NMR ($CDCl_3$, ppm) 33.5 (CH_3–N), 120.0, 128.7, 137.7 (imidazole ring carbon atoms).

Synthesis of 1. **1** was prepared by reacting 1.520 g (5.002 mmol) of $CpFe(CO)_2I$ and 0.980 g (5.03 mmol) of $AgBF_4$ in 15.0 g of molten $[1\text{-}MeimH]BF_4$in a sealed round-bottom flask on the bench top at 100 °C for 10 h. The reaction mixture was filtered and the residue washed with 50 mL of dichloromethane to remove traces of $[1\text{-}MeimH]BF_4$. The residue was digested with 200 mL of anhydrous acetonitrile and filtered to remove AgI. Upon concentration the filtrate afforded 1.800 g of colorless crystals (3.535 mmol, 71%, mp 190 °C) of the title compound. Single crystals suitable for X-ray structure determination were obtained by recrystallization from acetonitrile. UV–visible: 228 nm (5700 M^{-1}cm^{-1}) with shoulders at 250 and 270 nm. IR (KBr reflectance, cm^{-1}): 3136 (sharp), 2956 (m), 2724, 2553, 2463, 2363, 2182, 2081, 1810, 1719, 1689 (all weak), 1624 (m, C=N), 1529, 1514 (strong), 1473, 1418, 1368, 1332 (weak), 1282, 1227, 1092 and 1052 (BF_4^-), 931, 826, 770, 655 (all strong). Anal. Calcd for $FeC_{16}H_{24}N_8BF_6$: C, 37.74; H, 4.74. Found: C, 37.73; H, 4.73.

X-ray Crystallography. A single crystal suitable for X-ray crystallography was selected, sealed in a thin-walled glass capillary, and placed on an Enraf-Nonius CAD-4 diffractometer. Pertinent experimental parameters related to X-ray crystallography are presented in Table I. The structure was solved by direct methods using the PC version of the NRCVAX program package[12] implemented on an 80486-based IBM-compatible computer. The cation was found to lie around a crystallographic inversion center whereas the anion resides around a 2-fold axis. A weighting scheme based upon counting statistics was used. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as follows: 1-Meim ring hydrogen atoms were fixed in calculated positions (C–H = 1.08 Å) and assigned isotropic thermal parameters the basis of the atom to which they are bonded; methyl and nitrogen hydrogen atoms were located via difference Fourier map inspection and fixed during least-squares refinement. Neutral-atom scattering factors were taken

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Table I. Crystallographic Data for *trans*-[Fe(1-Meim)$_4$F$_2$]BF$_4$

compd	[Fe(1-MeIm)$_4$F$_2$]BF$_4$
color	colorless
fw	509.1
cryst system	monoclinic
space group	$I2/a$
temp, °C	17
cell constants[a]	
a, Å	13.606(3)
b, Å	12.5840(10)
c, Å	14.738(3)
β, deg	116.817(10)
V, Å^3	2252.0(7)
F(000)	1044
Z	4
D_{calc}, g cm^{-3}	1.50
μ_{calc}, cm^{-1}	7.4
scan type	$\omega/2\theta$
radiation	Mo Kα
max xtal dimens, mm	0.35 × 0.35 × 0.85
scan width	0.80 + 0.35 tan θ
transm range	0.865, 0.999
decay of stds	±2%
reflcns measd	1548
2θ range, deg	2–45
unique reflcns	1473
reflcns obsd[b]	1204
computer programs	NRCVAX
struct solution	direct
no. of params	147
weight modifier, k	0.000 008
GOF	4.33
R	0.043
R_w	0.043
final diff map, e/Å^3	0.30

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections $\theta > 14°$. [b] $I > 2.5\sigma(I)$. Corrections: Lorentz–polarization and absorption (empirical ψ scan).

Table II. Fractional Atomic Coordinates x, y, z and B_{iso} Values (Å^2) for *trans*-[Fe(Meim)$_4$F$_2$]BF$_4$

	x	y	z	B_{iso}[a]
Fe	0	0	0	3.25(4)
F(1)	0.12378(18)	0.07863(18)	0.07574(17)	4.24(13)
N(1)	0.0350(3)	0.0106(3)	–0.12610(24)	3.44(20)
N(2)	0.0968(3)	0.0715(3)	–0.2302(3)	3.79(21)
N(3)	–0.0928(3)	0.1437(3)	–0.04924(25)	3.47(21)
N(4)	–0.2312(3)	0.2542(3)	–0.1150(3)	4.22(23)
C(1)	0.1031(3)	0.0784(4)	–0.1365(3)	3.53(24)
C(2)	0.0205(4)	–0.0050(4)	–0.2824(3)	4.3(3)
C(3)	–0.0184(4)	–0.0424(4)	–0.2188(4)	3.97(25)
C(4)	0.1584(4)	0.1387(4)	–0.2687(4)	5.6(3)
C(5)	–0.2007(4)	0.1524(3)	–0.0960(3)	3.6(3)
C(6)	–0.1375(5)	0.3132(4)	–0.0791(4)	4.9(3)
C(7)	–0.0514(4)	0.2458(4)	–0.0381(4)	4.4(3)
C(8)	–0.3442(5)	0.2936(5)	–0.1669(4)	6.5(4)
B	$^1/_4$	0.3844(6)	0.00000	4.6(5)
F(2)	0.3193(4)	0.4460(3)	–0.0185(3)	11.5(3)
F(3)	0.3072(3)	0.3238(3)	0.0821(3)	9.1(3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

from ref 13. The final least-squares cycle was calculated with 29 atoms and 147 parameters and afforded $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.043$ and $R_w = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2} = 0.043$.

Results and Discussion

Final fractional atomic coordinates and important interatomic bond lengths and angles for **1** are presented in Tables II and III, respectively. An ORTEP[14] perspective view of the cation is shown in Figure 1. It reveals that the iron(III) center exists in a pseudo-octahedral environment with two axial fluoride ligands and four equatorial 1-Meim ligands. The fluoride ligands are presumably abstracted from tetrafluoroborate anions by the reactive organometallic fragment generated when iodide is removed from CpFe(CO)$_2$I by AgBF$_4$. The ability of transition metal Lewis acid moieties to abstract fluoride from fluoroanions is quite well established.[15] One tetrafluoroborate anion exists as the counterion. The iron center resides on a crystallographic inversion center, making the F–Fe–F angle precisely 180°. The Fe–F distance is 1.8609(22) Å. There are two crystallographically independent 1-Meim molecules with Fe–N distances of 2.102(3) and 2.136(3) Å, respectively. The N–Fe–N angles are 88.91(12) and 91.09(12)°. The coordinated nitrogen atoms and the iron center are coplanar because of crystallographic symmetry.

Table III. Listing of Bond Distances (Å) and Angles (deg) for *trans*-[Fe(1-Meim)$_4$F$_2$]BF$_4$

	Distances		
Fe–F(1)	1.8609(22)	N(3)–C(7)	1.383(6)
Fe–N(1)	2.120(3)	N(4)–C(5)	1.336(6)
Fe–N(3)	2.136(3)	N(4)–C(6)	1.360(7)
N(1)–C(1)	1.319(6)	N(4)–C(8)	1.460(7)
N(1)–C(3)	1.394(6)	C(2)–C(3)	1.351(7)
N(2)–C(1)	1.348(6)	C(6)–C(7)	1.349(7)
N(2)–C(2)	1.370(6)	B–F(2)	1.340(6)
N(2)–C(4)	1.472(6)	B–F(3)	1.342(6)
N(3)–C(5)	1.316(6)		
	Angles		
F(1)–Fe(F(1)[a]	180.0	C(2)–N(2)–C(4)	127.4(4)
F(1)–Fe–N(1)	88.76(12)	Fe–N(3)–C(5)	126.7(3)
F(1)–Fe–N(1)[a]	91.24(12)	Fe–N(3)–C(7)	126.8(3)
F(1)–Fe–N(3)	89.97(12)	C(5)–N(3)–C(7)	106.5(4)
F(1)–Fe–N(3)[a]	90.03(12)	C(5)–N(4)–C(6)	107.1(4)
F(1)[a]–Fe–N(1)	91.24(12)	C(5)–N(4)–C(8)	126.1(4)
F(1)[a]–Fe–N(1)[a]	88.76(12)	C(6)–N(4)–C(8)	126.7(4)
F(1)[a]–Fe–N(3)	90.03(12)	N(1)–C(1)–N(2)	110.8(4)
F(1)[a]–Fe–N(3)[a]	89.97(12)	N(2)–C(2)–C(3)	106.9(4)
N(1)–Fe–N(1)[a]	180.0	N(1)–C(3)–C(2)	108.6(4)
N(1)–Fe–N(3)	88.91(12)	N(3)–C(5)–N(4)	110.9(4)
N(1)–Fe–N(3)[a]	91.09(12)	N(4)–C(6)–C(7)	107.6(4)
N(1)[a]–Fe–N(3)	91.09(12)	N(3)–C(7)–C(6)	107.8(4)
N(1)[a]–Fe–N(3)[a]	88.91(12)	F(2)–B–F(2)[b]	109.2(6)
N(3)–Fe–N(3)[a]	180.0	F(2)–B–F(3)	109.7(3)
Fe–N(1)–C(1)	126.2(3)	F(2)–B–F(3)[b]	108.73(23)
Fe–N(1)–C(3)	127.2(3)	F(2)[b]–B–F(3)	108.73(23)
C(1)–N(1)–C(3)	106.2(3)	F(2)[b]–B–F(3)[b]	109.7(3)
C(1)–N(2)–C(2)	107.5(4)	F(3)–B–F(3)[b]	110.8(6)
C(1)–N(2)–C(4)	125.0(4)		

[a] $-x, -y, -z$. [b] $0.5 - x, y, -z$.

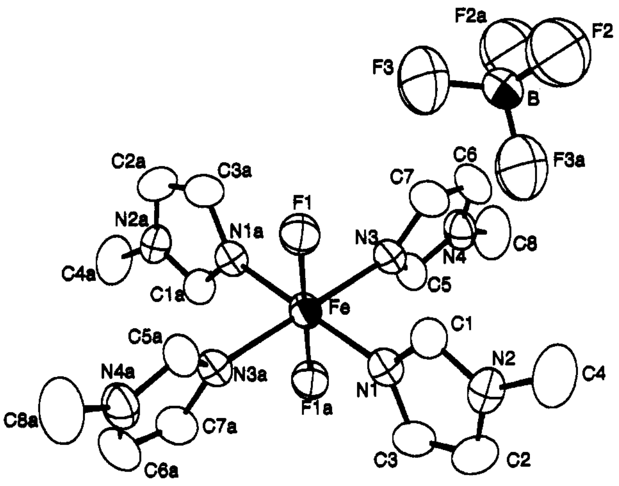

Figure 1. Perspective ORTEP view of *trans*-[Fe(1-Meim)$_4$F$_2$][BF$_4$]. The cation lies around a crystallographic inversion center whereas the anion resides around a 2-fold axis.

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The 1-Meim planes are oriented roughly perpendicular to the equatorial Fe–N_4 plane, angles between the two crystallographically independent 1-Meim ligands and the Fe–N_4 plane being 77.16(16) and 76.57(18)°. The methyl groups on the two crystallographically independent imidazoles are oriented above and below the Fe–N_4(1-Meim) plane. The geometries of the 1-Meim ligands do not show any significant variation compared to 1-Meim ligands found in other coordination complexes.[6] A review of the literature reveals that Fe–N(imidazole) distances in iron complexes vary significantly depending upon both the oxidation and spin state of iron and also the nature and structure of the ligands *trans* and *cis* to an imidazole ligand.[4–10] Hence, unless identical oxidation and spin states exist with a similar ligand environment, such distances are not comparable. However, it should be noted that the distances around the iron atom closely resemble those observed for the high-spin cation *trans*-$[Fe(salen)(Im)_2]^+$.[6] The title compound is colorless in the solid state and gives a yellow solution in acetonitrile or water. **1** is stable in acetonitrile solution and exhibits an intense charge-transfer band with shoulders (see synthesis of **1**) that tail into the visible region, thereby obscuring the recognition of a distinct d–d band. This is characteristic of high-spin Fe(III) complexes, and such behavior is consistent with high-spin d^5 configuration, which, as for the high-spin Mn(II) complexes, makes the d–d transitions spin forbidden and very weak.[16] The high-spin nature was confirmed from an ESR spectrum of a solid sample of **1** in MgO matrix. At ambient temperatures (293 K) a very broad signal centered at 2.310 g was observed.[17] No discernible hyperfine splitting patterns that might be attributed to F and N nuclei were observed. Simple high-spin complexes such as $Fe(ClO_4)_3$ in aqueous solution are known to give similar types of broad signals.[18] The aqueous solution of **1** is unstable and decomposes within minutes to deposit a brown precipitate.

Finally, the preparation of the complex deserves some mention. In recent years, ionic liquids based on organic cations (particularly tetrachloroaluminate salts) have been extensively used as reaction media.[19] In particular, the photo- and electrochemistry of iron(II) diimine complexes has been studied in organic cation ionic liquids and formation of the corresponding iron(III) diimine complexes by electron transfer to the organic cation has been reported.[20] It is conceivable that **1** formed via a similar mechanism. In light of the relative instability of iron(III)–monodentate nitrogen complexes, the successful isolation of the title complex can be attributed to the nonaqueous ionic conditions used in the preparation. Organic cation low-melting salts clearly offer a convenient medium for synthesis and subsequent study of hitherto inaccessible inorganic complexes from low-valent organometal complexes.

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Supplementary Material Available: Listings of hydrogen atom positional and thermal parameters, anisotropic thermal parameters for nonhydrogen atoms, complete bond distances and angles, and best planes calculations (7 pages). Ordering information is given on any current masthead page.

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