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Notes

Iron(II) Triflate Salts as Convenient Substitutes for Perchlorate Salts: Crystal Structures of $[Fe(H_2O)_6](CF_3SO_3)_2$ and $Fe(MeCN)_4(CF_3SO_3)_2$

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Introduction

The preparation of coordination complexes of labile transition metals is simplified when the starting material is the metal salt of a noncoordinating anion. The traditional non- or weakly coordinating anion has been perchlorate. However, there is a recognized danger of explosions with the ClO_4^- salts of coordination complexes. This is particularly true of redox active iron(II) and manganese(II) complexes containing organic ligands and of acetonitrile solvates of lanthanides.[1] The triflate (trifluoromethanesonate, OTf) ion has been demonstrated to be a labile ligand on substitutionally inert Cr(III) and Co(III) complexes[2,3] and has found general utility in the synthesis of a variety of Co(III), Cr(III), Pt(IV), Rh(III), Ir(III), Ru(III), and Os(III) amine complexes.[4]

General preparations of simple metal triflates have been described from the halide salts and neat triflic acid,[5,6] or AgOTf,[7] or the sulfates and $Ba(OTf)_2$.[8] Hydrated Co(II) and Ni(II) triflates have been prepared by reaction of the metal carbonates with triflic acid. These hydrated salts were dried and subsequently dehydrated in organic solvent with 2,2-dimethoxypropane and reacted with pyridine and substituted pyridines to form $M(II)L_4(OTf)_2$ complexes.[9] Hydrated $Fe(OTf)_2$ has been prepared in water, although the product was not characterized.[10] The reaction of finely divided metal with triflic acid in dry acetonitrile is very convenient for the synthesis of dry Mn(II),[11] Fe(II), Co(II), and Cu(I)[12] triflate salts containing various amounts of coordinated acetonitriles. Here are presented details of the preparation and characterization of $Fe(OTf)_2 \cdot x MeCN$, the hydrate, $[Fe(H_2O)_6](OTf)_2$, and the affinity of the former for water.

Table 1. Crystallographic Data for $[Fe(H_2O)_6](OTf)_2$ and $Fe(MeCN)_4(OTf)_2$

	$[Fe(H_2O)_6](OTf)_2$	$Fe(MeCN)_4(OTf)_2$
formula	$C_2H_{12}F_6FeO_{12}S_2$	$C_{10}H_{12}F_6FeN_4O_6S_2$
fw	462.09	518.21
temp, °C	25	−100
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
space group, No.	$C2/c$, 15	$P\bar{1}$, 2
Z	2	1
a, Å	18.664 (2)	6.7333(10)
b, Å	6.9289(8)	8.5229(12)
c, Å	6.5958(9)	8.9480(13)
α, deg		84.858(13)
β, deg	104.917(9)	86.042(12)
γ, deg		80.120(12)
V, Å^3	824.24(17)	503.10(13)
ρ_{calcd}, g cm^{-3}	1.862	1.710
μ, cm^{-1}	0.128	0.104
$R(F_o)$ [a]	0.0395	0.0289
$R_w(F_o^2)$ [a]	0.104	0.070

[a] $R1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]\}^{1/2}$, $[I > 2\sigma(I)]$.

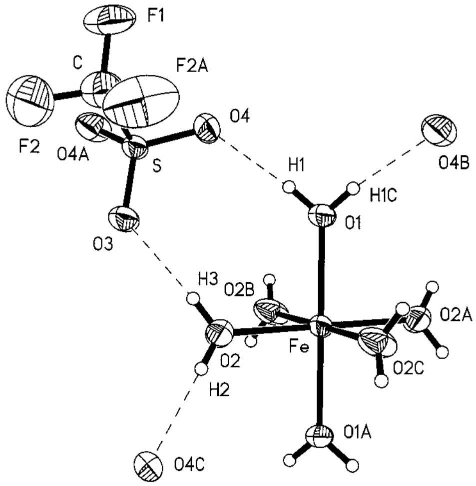

Figure 1. ORTEP (30% probability ellipsoids) of $[Fe(H_2O)_6](OTf)_2$ showing hydrogen bonds.

Experimental Section

All operations were performed under a pure dinitrogen atmosphere in a glovebox or on a Schlenk line. Anhydrous grade acetonitrile and iron powder (<10 μm) were obtained from Aldrich and stored in a glovebox under dinitrogen. Triflic acid was used as obtained from 3M Co.

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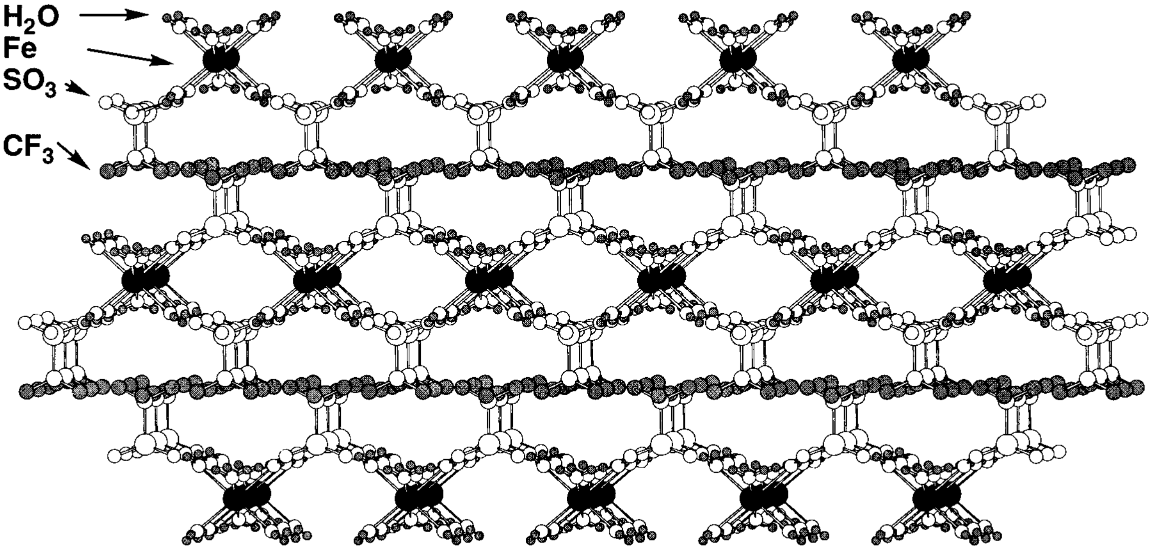

Figure 2. Chem3D representation of layered structure of $[Fe(H_2O)_6](OTf)_2$ viewed approximately down the *c*-axis with the *a*-axis vertical.

Synthesis. 1. $Fe(CF_3SO_3)_2·2CH_3CN$. To a mixture of 5.58 g of finely divided Fe powder (100 mmol) in 100 mL of dry acetonitrile 32.0 g of triflic acid (210 mmol) was carefully added as the reaction is highly exothermic. The flask was fitted with a coldfinger and, after the initial effervescence subsided (1 h), warmed to 60 °C. When the effervescence had stopped, the unreacted iron powder was removed by filtration through a Celite pad. The volume of the solution was condensed to approximately 80 mL under vacuum. Cooling the pale green solution to −25 °C overnight afforded very pale blue-green crystals. The product was washed with anhydrous ether (3 × 20 mL) and dried under 1 atm dinitrogen (33.9 g). The very pale blue-green crystals were shown by X-ray crystallography to be $Fe(MeCN)_4(OTf)_2$. When dried under a vacuum, two of the coordinated solvent molecules are lost, resulting in a fine white, free-flowing powder (28.7 g, 66% yield). The ether washings were added to the filtrate and cooled to −25 °C to precipitate a second crop (10.0 g 23% yield after drying in vacuo). The product can be recrystallized from 60 mL of dry acetonitrile treated with 20 mL of Et_2O and cooled to −25 °C to afford 33.6 g of crystalline $Fe(MeCN)_4(OTf)_2$ and 28.1 g of $Fe(OTf)_2·2MeCN$ after drying under a vacuum overnight. A second crop of 6.7 g of $Fe(MeCN)_4(OTf)_2$ was obtained and was dried to 5.5 g of $Fe(OTf)_2·2MeCN$. Anal. Calcd for $C_2F_6FeO_6S_2·2MeCN$: C, 16.41; H, 1.38; N, 6.38. Found: C, 16.6; H, 1.3; N, 6.4.

2. $Fe(CF_3SO_3)_2·6H_2O$. The hydrate was prepared either by reacting iron metal in aqueous triflic acid or by recrystallizing $Fe(OTf)_2·2MeCN$ from water. Very thin plates, that appear very pale green in bulk, grew on evaporation to near dryness. These crystals analyze as $Fe(OTf)_2·5H_2O$ when air-dried (Anal. Calcd for $C_2F_6FeO_6S_2·5H_2O$: C, 5.20; H, 2.62; N, 0. Found: C, 5.6; H, 2.6; N, 0.2) and as $Fe(OTf)_2·H_2O$ when dried under a vacuum (Anal. Calcd for $C_2F_6FeO_6S_2·H_2O$: C, 6.16; H, 1.03; N, 0. Found: C, 6.4; H, 1.4; N, 0.2) and are shown by crystallography to be $Fe(OTf)_2·6H_2O$ when prevented from drying. Exposure of 0.85 mg of powdered $Fe(OTf)_2·2MeCN$ to the atmosphere for several days affords 0.90 mg of white powder of the pentahydrate. (Anal. Calcd for $C_2F_6FeO_6S_2·5H_2O$: C, 5.20; H, 2.62; N, 0. Found: C, 5.3; H, 2.4; N, 0.1.)

Crystallography. Data were collected on a Siemens P4 automated diffractometer equipped with an orientated graphite monochromator and an LT-2 low-temperature attachment. XSCANS and the SHELXTL program package (Bruker Analytical X-ray, Inc., Madison, WI 53711) were used for data collection and processing. All atoms were located by direct methods or Patterson map interpretation and difference Fourier maps. The hydrogen atom positions and thermal parameters were refined. Crystallographic data and discrepancy factors are given in Table 1.

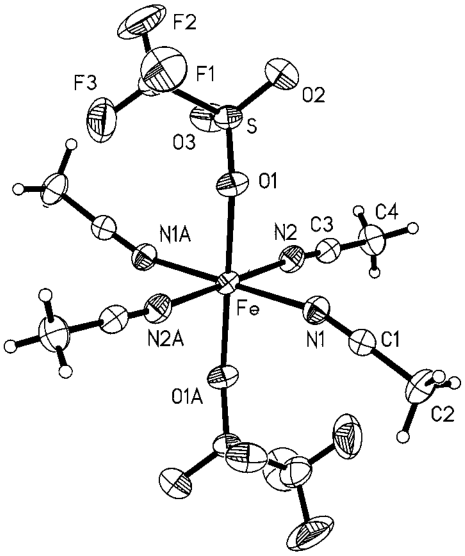

Figure 3. ORTEP (50% probability ellipsoids) of $Fe(MeCN)_4(OTf)_2$.

Results and Discussion

Synthesis. Finely divided iron metal reacts rapidly with anhydrous triflic acid in acetonitrile to form a pale green solution from which $Fe(MeCN)_4(OTf)_2$ is isolated either by cooling a concentrated solution or through addition of ether followed by cooling. The very pale blue-green crystals lose some of the coordinated acetonitrile at atmospheric pressure. The crystallinity is lost when dried under a vacuum resulting in a white powder that contains only two solvent molecules, $Fe(OTf)_2·2MeCN$. This is a convenient source of anhydrous iron(II), but it must be stored in a dry atmosphere as it absorbs water when exposed to a humid atmosphere. It is otherwise stable to oxidation in the solid state. We have found that it is important to use a fresh bottle of iron powder or one that is stored under dinitrogen once opened. Occasional preparations will initially form light to dark orange solutions that contain some oxidized product. The iron(III) species is/are more soluble than $Fe(MeCN)_4(OTf)_2$, and one or two recrystallizations from acetonitrile/ether afford pure product.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Fe(H_2O)_6](OTf)_2$ and $Fe(MeCN)_4(OTf)_2$

$Fe(MeCN)_4(OTf)_2$		$Fe(MeCN)_4(OTf)_2$	
Fe−O1	2.103(3)	Fe−O1	2.091(1)
Fe−O2	2.105(2)	Fe−N1	2.162(2)
		Fe−N2	2.170(2)
O(1)#1−Fe−O(2)#1[a]	91.08(10)	O(1)−Fe−N(1)#1[b]	90.02(6)
O(1)−Fe−O(2)#1	88.92(10)	O(1)−Fe−N(1)	89.98(6)
O(2)#1−Fe−O(2)#2	90.94(15)	O(1)−Fe−N(2)#1	88.70(7)
O(2)−Fe−O(2)#2	89.06(15)	O(1)−Fe−N(2)	91.30(7)
		N(1)−Fe−N(2)#1	93.25(7)
		N(1)−Fe−N(2)	86.75(7)

[a] #1: $-x, -y, -z$. #2: $-x, y, -z$. [b] #1: $-x + 1, -y + 1, -z$.

The hydrated salt, $Fe(H_2O)_6(OTf)_2$, can be isolated by recrystallizing the acetonitrile solvate from water to form hygroscopic, white crystals that have a hint of green to them. Some samples will evaporate to a product containing yellow impurities. The reaction between iron powder and triflic acid can be carried out in methanol from which $Fe(OTf)_2 \cdot 2MeCN$ is obtained using the same procedure as for acetonitrile solvate.

The reaction between acetonitrile and triflic acid, which is known to result in the formation of triazine or nitrilium salts,[13] does not seem to interfere with the formation of the metal triflate.

Structures. $[Fe(H_2O)_6](OTf)_2$ crystallizes from water in the monoclinic space group $C2/m$. The hexaquairon(II) cation has crystallographically imposed C_{2h} symmetry with two unique oxygen atoms (Figure 1). The mirror plane contains O(1), Fe, and O(1A) and relates O(2) to O(2C) and O(2A) to O(2B), while the 2-fold axis passes through the Fe and relates O(1) to O(1A), O(2) to O(2B), etc. The bond lengths and angles indicate that the FeO_6 portion of the cation has approximate O_h symmetry. The triflates lie on mirror planes with two unique F atoms and O atoms. Each hydrogen atom on the six water molecules is hydrogen-bonded to a separate triflate oxygen atom, which in turn are each linked by hydrogen bonds to two hydrogen atoms on neighboring hexaquairon(II) cations establishing an extended network of hydrogen bonds that defines layers parallel to the *bc* plane (Figure 2). The $(OTf)[Fe(H_2O)_6](OTf)$ layers are connected through layers of CF_3 groups in which the closest intermolecular interactions are F2···F2′ separations of 2.87 Å. The crystals grow as plates whose large faces are parallel to these planes. Attempts to cool the crystals to −100 °C for data collection caused the crystals to shatter parallel to the planes.

Table 3. Hydrogen Bonds for $[Fe(H_2O)_6](OTf)_2$ and $Fe(MeCN)_4(OTf)_2$ [Å and deg]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1)−H(1)···O(4)	0.83(3)	1.96(3)	2.790(3)	173(3)
O(2)−H(2)···O(4)#5[a]	0.76(4)	2.04(4)	2.805(3)	179(4)
O(2)−H(3)···O(3)	0.81(5)	2.05(4)	2.840(3)	163(4)
C(4)−H(4C)#6···O(1)	1.083[b]	2.51	3.524(3)	156
C(4)−H(2B)#7···O(2)	1.083	2.43	3.493(3)	166
C(2)−H(2B)#8···O(3)	1.083	2.27	3.306(3)	159
C(2)−H(2C)#6···O(3)	1.083	2.58	3.324(4)	125

[a] Symmetry transformations used to generate equivalent atoms. #1: $-x, -y, -z$. #2: $-x, y, -z$. #3: $x, -y, z$. #4: $x, -y + 1, z$. #5: $x, y, z + 1$. #6: $-x, -y + 1, -z$. #7: $x, y, z - 1$. #8: $x, y + 1, z$. [b] C−H bonds normalized to distances obtained by neutron diffraction (1.08 Å).

The crystals grown from an anhydrous acetonitrile/diethyl ether mixture consist of the trans isomer of $Fe(MeCN)_4(OTf)_2$ located on an inversion center (Figure 3). The Fe−N bond lengths are typical of high-spin iron(II) coordinated to nitriles.[14] One of the unique acetonitrile ligands binds in a nearly linear fashion (Fe−N(2)−C(3), 172.8(2)°), while the other is significantly bent (Fe−N(1)−C(1), 158.8(2)°). This is a result of considerable intermolecular interactions. All three triflate oxygen atoms form weak intermolecular hydrogen bonds with the methyl groups of acetonitrile ligands on neighboring complexes (Table 3).[15] The O(3)···H(2B)−C(2) is especially short.[16] The closest F···F interaction is 2.82 Å. There is very little void volume in the crystal, and it is not clear why two of the acetonitrile ligands are readily lost when the crystals are placed in a vacuum.

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Supporting Information Available: Packing diagram for $Fe(MeCN)_4(OTf)_2$ and X-ray crystallographic files in CIF format for complexes $[Fe(H_2O)_6](OTf)_2$ and $Fe(MeCN)_4(OTf)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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