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Iron-Mediated Cleavage of Coordinated 1,1,1,5,5,5-Hexafluoropentane-2,4-dione by the 2,2,6,6-Tetramethylpiperidine-1-oxyl Nitroxyl Radical[†]

Caroline Ahlers and Michael H. Dickman*

Department of Chemistry, Georgetown University, Washington, D.C. 20057

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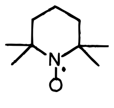
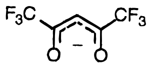
The nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) reacts with diaquobis(hfac)iron(II) (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato) in organic solvents to form the salt 2,2,6,6-tetramethylpiperidinium trifluoroacetate (**1**) as a major product. Crystals of **1** contain hydrogen-bonded dimers. At 123 K, **1** is monoclinic, $C2/c$, with $a = 19.9528(12)$ Å, $b = 8.4100(5)$ Å, $c = 15.6966(9)$ Å, $\beta = 91.4600(10)°$, and $Z = 8$. Refinement with 3092 reflections gave $R_1 = 0.063$. From the reaction in hexane or heptane, crystals of the iron complex salt 2,2,6,6-tetramethylpiperidinium (bis(hfac-*O,O′*)(2,2,6,6-tetramethylpiperidinium-1-oxo-*O*)ferrate(III))(μ-oxo)(bis(hfac-*O,O′*)(formato-*O*)ferrate(III)) (**2**) were also obtained. Crystals of **2** at 173 K are monoclinic, $P2_1/n$, with $a = 19.60790(10)$ Å, $b = 12.4155(2)$ Å, $c = 22.4199(4)$ Å, $\beta = 90.9380(10)°$, and $Z = 4$. Refinement with 12 993 reflections gave $R_1 = 0.065$. The μ-oxo iron dimer has an Fe−O−Fe angle of 146.28(14)° with asymmetric Fe−O distances of 1.802(2) and 1.783(2) Å. TEMPO reduced to the hydroxylamine is coordinated to iron through oxygen. The nitrogen is protonated, forming an apparent hydrogen bond to the μ-oxo group.

Introduction

The stable nitroxyl free radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) forms adducts with $\mathrm{M(hfac)_2}$ complexes ($\mathrm{M^{2+}}$ = Mn, Co, V═O, Cu; hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato).[1−4] These adducts, which generally exhibit strong magnetic interactions between the nitroxyl unpaired electron and the metal d electrons, can be isolated from organic solvents.


TEMPO



hfac

Attempts to isolate a TEMPO adduct of $\mathrm{Fe(hfac)_2}$ under similar conditions failed. Instead, mixtures were formed containing colorless and red crystalline solids. Single-crystal X-ray analysis of the crystalline products resulted in identification of the organic salt 2,2,6,6-tetramethylpiperidinium trifluoroacetate (**1**) and a novel $\mathrm{Fe^{3+}}$ dimer, 2,2,6,6-tetramethylpiperidinium (bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O,O′*)(2,2,6,6-tetramethylpiperidinium-1-oxo-*O*)ferrate(III))(μ-oxo)(bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O,O′*)(formato-*O*)ferrate(III)) (**2**).

Experimental Section

General Considerations. The free radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (Aldrich, 98%), 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Aldrich, 99%), trifluoroacetic acid (Aldrich, 99%), and 2,2,6,6-tetramethylpiperidine (Acros Organics, 98%) were used without further purification. $\mathrm{Fe(hfac)_2(H_2O)_2}$ was prepared using standard procedures.[5,6] Reagent grade solvents were used. A Nicolet 7000 FTIR instrument was used for IR measurements. Elemental analysis was performed by the E+R Microanalytical Laboratory, Inc., Corona, NY 11368. Melting points are uncorrected.

Reaction of $\mathbf{Fe(hfac)_2(H_2O)_2}$ with TEMPO. In a typical reaction, $\mathrm{Fe(hfac)_2(H_2O)_2}$ (0.25 g, 0.5 mmol) and excess TEMPO (0.25 g, 1.6 mmol) were placed in a 25 mL round-bottom flask with 10 mL of *n*-hexane (similar results were achieved with *n*-heptane) and a magnetic stir bar. The stirred mixture was brought to reflux using a heating mantle. When reflux was reached, the flask was removed from the heat; the deep red solution was allowed to cool briefly and was filtered to remove a small amount of an orange powder. The filtrate was placed in a beaker which was then sealed with paraffin film and allowed to stand. Crystals of **1** started to form almost immediately. Red crystals of **2** formed subsequently. The resulting mixture (ca. 0.2 g) was collected the next day by filtration and washed with *n*-hexane. These crystals were used for the X-ray crystal structure determinations. From microscopic examination of the sample, it appeared that only two crystalline components were present. Some of the red crystals were hand-sorted for an IR spectrum. IR peaks (KBr pellet, $\mathrm{cm^{-1}}$): 1652 s (C═O), 1619 m, 1558 m, 1529 w, 1477 m, 1388 w, 1257 s ($\mathrm{CF_3}$), 1211 s ($\mathrm{CF_3}$), 1145 s ($\mathrm{CF_3}$), 817 w, 798 m, 655 m, 590 w. The reaction was also tried in chloroform and acetonitrile. In these solvents, **1** eventually formed but no other crystalline products were isolated from the red solutions.

Synthesis of 1. A sample of 2,2,6,6-tetramethylpiperidinium trifluoroacetate was prepared for bulk characterization. Equimolar amounts of trifluoroacetic acid and 2,2,6,6-tetramethylpiperidine were mixed in a minimum amount of 95% ethanol, and the crystalline product was obtained in quantitative yield after filtration, washing with ethanol, and air-drying. Mp: 253 °C dec. Anal. Calcd for $\mathrm{C_{11}H_{20}F_3NO_2}$: C, 51.75; H, 7.90; N, 5.49. Found: C, 51.71; H, 8.11; N, 5.41. IR (KBr pellet, $\mathrm{cm^{-1}}$): 1695 s (C═O), 1685 s (C═O), 1205 s ($\mathrm{CF_3}$), 1182 s

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Table 1. Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_{11}H_{20}F_3NO$	$C_{39}H_{44}F_{24}Fe_2N_2O_{12}$
fw	255.28	1300.46
space group, Z	$C2/c$, 8	$P2_1/n$, 4
a (Å)	19.9528(12)	19.60790(10)
b (Å)	8.4100(5)	12.4155(2)
c (Å)	15.6966(9)	22.4199(4)
β (deg)	91.4600(10)	90.9380(10)
unit cell vol (Å^3)	2633.1(3)	5457.21(13)
ρ_{calc} (g cm^{-3})	1.288	1.583
μ (cm^{-1})	1.15	6.69
T (°C)	−150	−100
final R^a	$R_1 = 0.063$; $R_2 = 0.148$	$R_1 = 0.065$; $R_2 = 0.156$

[a] Definitions of R: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

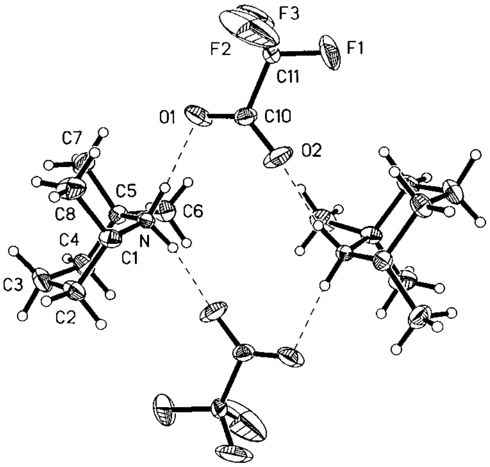

Figure 1. View of a dimer of **1** with 50% displacement ellipsoids. Two methyl groups have been omitted for clarity. Hydrogen atoms are shown as circles of arbitrary radius. Hydrogen-bonding interactions are shown as dashed lines.

(CF_3), 1130 s (CF_3), 979 m, 958 m, 914 m, 829 m, 800 s, 719 s, 596 m, 507 m, 476 m.

X-ray Crystal Structure Determinations. Crystals were mounted on glass fibers and placed in a cold nitrogen stream on a Siemens SMART CCD diffractometer having a normal-focus X-ray tube with a Mo anode and graphite monochromator (wavelength = 0.710 73 Å). For **1**, a colorless block of approximate dimensions 0.26 × 0.24 × 0.22 mm was used; for **2**, a red block of about 0.34 × 0.26 × 0.16 mm was used. Procedures and programs for indexing, data collection, and solution and refinement of the structures have been described.[7-9] Full-matrix least-squares refinement was used on F^2 over all independent reflections. Hydrogen atoms were refined isotropically in observed positions except where disordered, in which case fixed, calculated positions were used. Additional crystal data are contained in Table 1.

Results and Discussion

Structure of 1. The organic salt 2,2,6,6-tetramethylpiperidinium trifluoroacetate crystallized as a hydrogen-bonded dimer (Figure 1). The CF_3COO^- anion was disordered 75−25% over two postions. The disorder can be described as a twist around the C10−C11 bond plus a rotation around the carboxylate carbon C10, the rotation axis being approximately parallel to a line passing through the carboxylate oxygens. The resulting

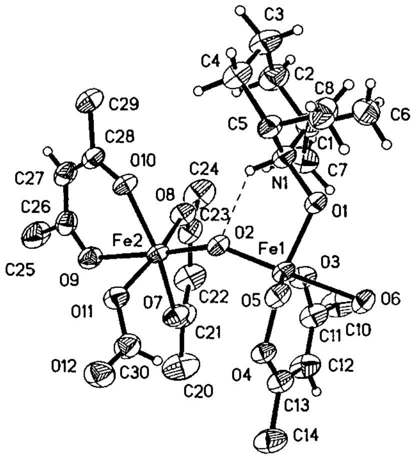

Figure 2. View of the μ-oxo dimer anion of **2** with 50% displacement ellipsoids. CF_3 groups, a methyl group, and one hfac ring have been omitted for clarity. Hydrogen atoms are shown as circles of arbitrary radius. The N1- -O2 possible hydrogen-bonding interaction is shown as a dashed line.

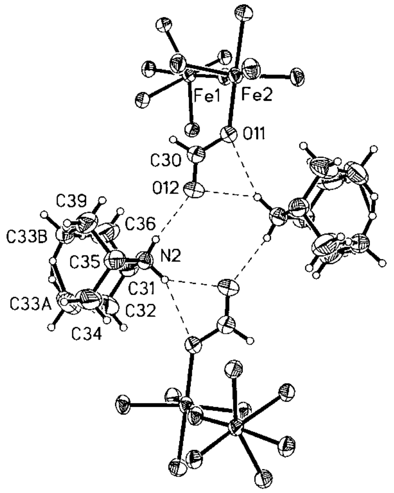

Figure 3. View of **2** showing the coordinated formate and its hydrogen-bonding interactions with the tetramethylpiperidinium cation. Possible hydrogen-bonding interactions are shown as dashed lines. Displacement ellipsoids encompass 50% probability except for hydrogen atoms, which are shown as circles of arbitrary radius. Chelate rings and the coordinated hydroxylamine are omitted for clarity. The chair−chair disorder of the cation is shown; the other methyl groups are omitted for clarity.

dihedral angle between the O1−O2−C10−C11 and the O1′−O2′−C10−C11′ planes is 20.9(7)°. Bond distances and angles are otherwise as expected. The average N−O hydrogen-bonding distance is 2.80(2) Å with an average N−H distance of 0.92(3) Å and an average N−H- -O angle of 169(3)°. Structures of other tetramethylpiperidinium salts have been reported. The bromide salt forms hydrogen-bonded chains,[10] while the structure of the thiocyanate salt contains both chains and dimers.[11]

Structure of 2. X-ray analysis of a red crystal chosen from the hexane reaction mixture resulted in identification of compound **2** as a μ-oxo dimer of Fe^{3+} (Figure 2). The iron dimer carries a negative charge which is balanced by a tetramethylpiperidinium cation. Each cation is hydrogen-bonded to formate groups on two centrosymmetrically related anions,

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

Fe1−O1	1.960(2)	Fe2−O8	2.096(2)
Fe1−O2	1.802(2)	Fe2−O9	2.158(2)
Fe1−O3	2.055(2)	Fe2−O10	2.049(2)
Fe1−O4	2.111(2)	Fe2−O11	1.992(2)
Fe1−O5	2.061(2)	O1−N1	1.397(3)
Fe1−O6	2.113(2)	O11−C30	1.274(4)
Fe2−O2	1.783(2)	O12−C30	1.224(5)
Fe2−O7	2.043(2)		
Fe1−O2−Fe2	146.28(14)	O2−Fe2−O11	99.47(10)
O2−Fe1−O1	93.50(10)	O2−Fe2−O7	100.30(10)
O2−Fe1−O3	96.16(10)	O11−Fe2−O7	90.90(10)
O1−Fe1−O3	100.64(10)	O2−Fe2−O10	95.58(10)
O2−Fe1−O5	100.54(10)	O11−Fe2−O10	95.79(10)
O1−Fe1−O5	93.00(10)	O7−Fe2−O10	161.51(10)
O3−Fe1−O5	157.72(10)	O2−Fe2−O8	94.59(10)
O2−Fe1−O4	97.77(10)	O11−Fe2−O8	165.86(10)
O1−Fe1−O4	167.67(9)	O7−Fe2−O8	85.02(10)
O3−Fe1−O4	83.16(9)	O10−Fe2−O8	84.33(10)
O5−Fe1−O4	80.07(9)	O2−Fe2−O9	175.08(10)
O2−Fe1−O6	175.48(10)	O11−Fe2−O9	85.26(10)
O1−Fe1−O6	85.49(10)	O7−Fe2−O9	80.88(10)
O3−Fe1−O6	79.72(10)	O10−Fe2−O9	82.52(10)
O5−Fe1−O6	83.92(9)	O8−Fe2−O9	80.73(10)
O4−Fe1−O6	83.66(9)	O12−C30−O11	124.3(4)

Table 3. Possible Hydrogen Bonds in **2** with Distances *d* (Å) and Angles ∠ (deg)

atoms	d(N−H)	d(H- -O)	∠NHO	*d*(N- -O)
N1−H1N- -O2	0.96(5)	2.07(6)	133(4)	2.812(4)
N2−H2NA- -O12	0.79(4)	2.08(5)	171(4)	2.860(4)
N2−H2NB- -O12[a]	0.95(5)	2.12(5)	144(4)	2.940(4)
N2−H2NB- -O11[a]	0.95(5)	2.35(5)	157(4)	3.249(4)

[a] Symmetry operation: 2 − *x*, 1 − *y*, −*z*.

so that the μ-oxo dimers are further associated into pairs in the solid state (Figure 3). The tetramethylpiperidinium cation exhibited chair−chair disorder. In addition, several CF_3 groups on the anion showed evidence of disorder and were modeled accordingly during refinement. Table 2 contains selected bond distances and angles for the anion. The Fe−O_{oxo} distances are asymmetric, with Fe1−O_{oxo} being longer than Fe2−O_{oxo} by 0.019(2) Å. These Fe−O distances are within the range (1.73−1.82 Å, average 1.77 Å) found for other Fe^{3+}−O−Fe^{3+} μ-oxo dimers.[12] Each iron is coordinated to two hfac ligands in addition to the oxo group. The remaining coordination sites are occupied by a reduced TEMPO ligand on Fe1 and by a formate anion on Fe2. The TEMPO has been reduced to the hydroxylamine as indicated by the N−O distance of 1.397(3) Å, which is about 0.1 Å longer than the analogous distance in nitroxyls. The hydroxylamine oxygen is bound to iron, and nitrogen N1 is apparently protonated. Charge balance considerations require an additional positive charge, and a peak was found near the nitrogen at a position appropriate for a proton. The peak was successfully refined without restraint as hydrogen. The proton forms an apparent hydrogen bond with the μ-oxo oxygen O2. This interaction provides a qualitative explanation for the asymmetric μ-oxo O−Fe distances, which may result from a distortion of the Fe−O−Fe geometry to accommodate N−H- -O_{oxo} hydrogen bonding. Apparent hydrogen-bonding interactions in **2** are summarized in Table 3. Structures of N-protonated hydroxylamines have been reported previously. These include protonated *N*,*N*-diethylhydroxylamine[13] and a series of organoboron compounds in which the hydroxylamine oxygen is bound to boron.[14] Structures containing reduced TEMPO have also been reported previously. For example, reaction of TEMPO with palladium(II) compounds resulted in N,O-bound metallocycle hydroxylamine metal complexes.[15]

Structures of other Fe^{3+}(hfac) derivatives published include $Fe(hfac)_3$,[16] pyridinium (1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol)$(hfac)_2$ferrate,[17] and (μ-oxo)bis(hfac(hydrotris(1-pyrazolyl)borato)iron).[18] This last compound was reported to be a catalyst effective in dioxygen hydroxylation of alkanes and arenes. Structure reports of Fe^{3+} μ-oxo dimers containing organic ligands and with a O_5−Fe−O−Fe−O_5 donor set are uncommon. Other examples involve nitrone[19] or sulfoxide[20] complexes of the $(hfac)_2$Fe−O−Fe$(hfac)_2$ unit and also arise from oxidation of $Fe(hfac)_2$.

Reaction of TEMPO with $Fe(hfac)_2(H_2O)_2$. The organic salt **1** was isolated from the reaction of TEMPO with $Fe(hfac)_2(H_2O)_2$ in several organic solvents. Reduction of TEMPO by Fe^{2+} to the hydroxylamine stage has been previously observed,[21] but this is the first report of reduction to the amine by Fe^{2+}. Reduction of nitroxyls to the amine has been observed before for a variety of other reducing agents including sulfide, metal carbonyls, and Sn^{2+}.[22−24] Reaction of TEMPO with cupric perchlorate in triethyl orthoformate was reported to result in isolation of the amine as a perchlorate salt.[25]

Cleavage of coordinated hfac by a strong base has been reported. With $Cu(OMe)_2$, $Ln(hfac)_3$, and 1,3-bis(dimethylamino)-2-propanol in THF, products containing trifluoroacetate and the ligand 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato were observed.[26] The mechanism of formation of this ligand was proposed to be base-catalyzed retro-Claisen condensation of hfac to trifluoroacetate and 1,1,1-trifluoroacetone followed by hydration of 1,1,1-trifluoroacetone to 1,1,1-trifluoro-2,2-propanediol and cycloaddition of this compound with another hfac. Formate was not reported as a product of the reaction.

In the present case, the details of the role of iron in this obviously complicated reaction are not clear, but in hydrocarbon solvents, the crystalline Fe^{3+} dimer **2** was isolated. Like **1**, **2**

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is a tetramethylpiperidinium salt but also contains a one-electron-reduction product of TEMPO, the hydroxylamine. The coordinated formate in **2** and the trifluoroacetate found in **1** evidently come from cleavage of hfac. Initial formation of an oxygen-bound TEMPO adduct followed by one-electron reduction of TEMPO by Fe^{2+} might afford a sufficiently strong base in the form of deprotonated hydroxylamine to allow a retro-Claisen condensation yielding trifluoroacetate and 1,1,1-trifluoroacetone. However, an additional cleavage is required to yield formate and presumably another trifluoroacetate.

The reaction observed with iron does not readily occur with hfac complexes of manganese, cobalt, or copper, implicating iron in the cleavage mechanism. Additionally, TEMPO loses an oxygen atom in reduction to the amine. These facts suggest that the mechanism of the reaction involves net oxygen transfer from TEMPO to either hfac or trifluoroacetone via iron. Oxygen transfer from iron to hfac might be in addition to, or instead of, a retro-Claisen mechanism. Oxidation states of iron higher than Fe^{3+} may be present. Fe^{5+} has been implicated in Fenton reactions ($Fe^{2+} + H_2O_2$)[27] and "Gif" reactions ($Fe^{2+} + O_2$).[28] The oxidation state of oxygen in TEMPO is formally at the peroxide level, so it is possible that the present reaction is a nonaqueous Fenton analogue.

Conclusion

While redox is not an unexpected result of reacting TEMPO with $Fe(hfac)_2(H_2O)_2$, the extent of fragmentation of the hfac ligand is surprising. Detection of formate as a hfac cleavage product is unprecedented. The mechanism of the reaction is not clear, but iron may act as an oxygen-transfer agent for the reaction between hfac and TEMPO. Compound **2** is an unusual example of hydrogen-bonding to a μ-oxo oxygen in an iron complex and is also noteworthy for containing two reduction products of TEMPO as the coordinated hydroxylamine and a protonated amine counterion. Other oxidation reactions of $Fe(hfac)_2$ are currently under investigation.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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