Inorg. Chem. **2005**, *44*, 6918–6920

Inorganic Chemistry
Communication

Unusual Role of Solvents in the Syntheses of $\{Fe–NO\}^{6,7}$ Nitrosyls Derived from a Ligand with Carboxamido Nitrogen and Thiolato Sulfur Donors

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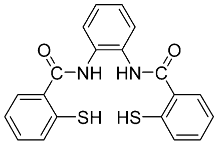
Received April 28, 2005

Reaction of excess NO with the $S = {}^3/_2$ Fe(III) complex $(Et_4N)_2[Fe(PhPepS)(Cl)]$ (**1**) in protic solvents such as MeOH affords the $\{Fe–NO\}^7$ nitrosyl $(Et_4N)_2[Fe(PhPepS)(NO)]$ (**2**). This distorted square-pyramidal $S = {}^1/_2$ complex, a product of reductive nitrosylation, is the first example of an $\{Fe–NO\}^7$ nitrosyl with carboxamido-N and thiolato-S coordination. When the same reaction is performed in aprotic solvents such as MeCN and DMF, the product is a dimeric diamagnetic $\{Fe–NO\}^6$ complex, $(Et_4N)_2[\{Fe(PhPepS)(NO)\}_2]$ (**3**). Both electrochemical and chemical oxidation of **2** leads to the formation of **3** via a transient five-coordinate $\{Fe–NO\}^6$ intermediate. The oxidation is NO-centered. The ligand frame is not attacked by excess NO in these reactions.

The enzyme nitrile hydratase (NHase), involved in the microbial assimilation of organic nitriles, catalyzes the conversion of nitriles into amides.[1] This enzyme contains at its active site a low-spin non-heme Fe(III) or a noncorrinoid Co(III) center ligated to two deprotonated carboxamido nitrogens and three cysteinate sulfurs, two of which are post-translationally modified to sulfenato (−SO) and sulfinato ($-SO_2$) groups.[2] In addition to this unusual coordination, the Fe−NHase is photoregulated via binding of NO at the sixth coordination site.[3] The discovery of a photolabile Fe−NO unit at the active site of Fe−NHase inspired us and other groups to synthesize structural mimics of the active sites and study the affinity of the Fe sites toward NO.[4] However, examples of $\{Fe-NO\}^6$ nitrosyls as models of the NO-bound Fe site of NHase have been scarce. Artaud and co-workers have recently reported the distorted square-pyramidal complex $(Et_4N)[Fe(N_2S_2)(NO)]$ (N_2S_2 = *N*,*N*′-(2-thioacetylisobutyryl)-*o*-phenylenediamine), the only example of such $\{Fe-NO\}^6$ species with carboxamido-N and thiolato-S donors.[5] To determine whether the scarcity is related to the conventional wisdom of synthetic difficulties associated with the susceptibility of both thiolate and carboxamide groups toward attack by NO, we have now studied the reactions of NO with Fe(III) complexes derived from mixed carboxamido-N/thiolato-S ligands. Herein, we report the synthesis and characterization of an $S = {}^3/_2$ Fe(III) complex $(Et_4N)_2[Fe(PhPepS)(Cl)]$ (**1**) and its reactions with NO. The products of these reactions reveal that the solvent plays an important role in the nitrosylation process. For example, in protic solvents such as MeOH, **1** undergoes reductive nitrosylation to afford the $\{Fe-NO\}^7$ species, namely, $(Et_4N)_2[Fe(PhPepS)(NO)]$ (**2**) much like that observed in the case of $[Fe(bpb)(py)_2](ClO_4)$.[6] In contrast, passage of NO through a solution of **1** in MeCN yields the dimeric $\{Fe-NO\}^6$ complex $(Et_4N)_2[\{Fe(PhPepS)(NO)\}_2]$ (**3**). Use of excess NO in these reactions did not lead to any S-nitrosylated product.[7]



PhPepSH$_4$

The starting Fe(III) complex **1** was synthesized by reacting $(Et_4N)[FeCl_4]$ with $PhPepS^{4-}$ (deprotonated with NaH) in

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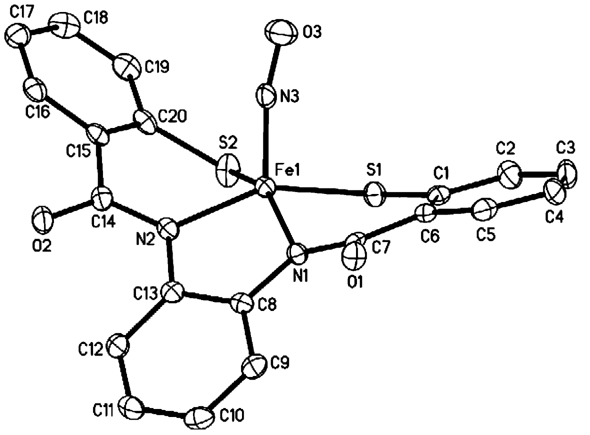

Figure 1. ORTEP diagram of $[Fe(PhPepS)(NO)]^{2-}$, the anion of **2**, showing the atom labeling scheme. H atoms are omitted for the sake of clarity. Selected bond lengths [Å] and bond angles [deg]: Fe−S1, 2.2164(9); Fe−S2, 2.2437(9); Fe−N1, 1.989(2); Fe−N2, 1.990(2); Fe−N3, 1.700(2); N3−O3, 1.191(3); C7−O1, 1.246(3); Fe−N3−O3, 149.3(2).

MeCN (see the Supporting Information). When purified NO gas was purged through a solution of **1** in MeOH at room temperature, the original brick red color changed to an olive green. Storage of this solution under a NO atmosphere for 12 h afforded dark green microcrystalline **2** in 70% yield. The IR spectrum of **2** exhibits a strong ν_{NO} band at 1626 cm^{-1}, a value consistent with the $\{Fe-NO\}^7$ notation.[8] Both the magnetic susceptibility value ($\mu_{eff} = 1.87\ \mu_B$ at 298 K) and the isotropic EPR spectrum ($g = 2.026$, MeCN/MeOH glass, 100 K) confirm the $S = {}^1/_2$ ground state of **2** (see the Supporting Information).[8,9] As shown in Figure 1, the Fe center in **2** resides in a distorted square-pyramidal geometry. The Fe−N(O) bond distance (1.700(2) Å) and the Fe−N−O bond angle (149.3(2)°) of **2** are similar to those noted for other $\{Fe-NO\}^7$ complexes.[6,8-10] The N−O distance in **2** (1.191(3) Å) is close to the distance in free NO (1.15 Å) but appreciably shorter than the N−O distance of NO^- (1.26 Å).

The reaction of NO with **1** took a very different course in an aprotic solvent like MeCN. Passage of NO through a solution of **1** in MeCN resulted in a rapid change of color to deep violet, and **3** precipitated out as a violet microcrystalline solid within minutes. The IR spectrum of **3** displays a strong ν_{NO} at 1827 cm^{-1}, which is within the range expected for $\{Fe-NO\}^6$ complexes.[5-8,11-13] The ^1H NMR spectrum of **3** in CD_3CN exhibits sharp well-resolved peaks arising from the $PhPepS^{4-}$ ligand frame and confirms its $S = 0$ ground state. As shown in Figure 2, the coordination geometry around the Fe centers in the dimeric anion of **3** is distorted octahedral. The most noticeable feature is the different mode of coordination of the $PhPepS^{4-}$ ligand frame. Instead of the typical coordination of the N_2S_2 ligand in the basal plane of the metal ion (as seen in **1** and **2**), the ligand serves as a bridging one in **3**, with one thiolato sulfur of each $PhPepS^{4-}$ unit acting as the sixth donor to the neighboring Fe center. Such rearrangement of the N_2S_2 ligand frame has been observed by Sellmann and Ruf.[14] Each Fe center in the centrosymmetric anion of **3** is coordinated to one carboxamido nitrogen and three thiolato sulfurs in the equatorial plane, while one carboxamido nitrogen and one NO molecule occupy the axial positions. The average $Fe-N_{amido}$ and $Fe-S_{terminal}$ bond lengths of **3** (1.973(3) and 2.2755(9) Å, respectively) are similar to those of other Fe(III) complexes in a similar coordination environment.[5,15] As is expected for $\{Fe-NO\}^6$ type complexes, the Fe−N−O bond angle is almost linear (176.1(3)°), with Fe−N(O) and N−O bond lengths of 1.656(3) and 1.145(3) Å, respectively. These values are comparable to other structurally characterized $\{Fe-NO\}^6$ complexes.[5-8,11-13]

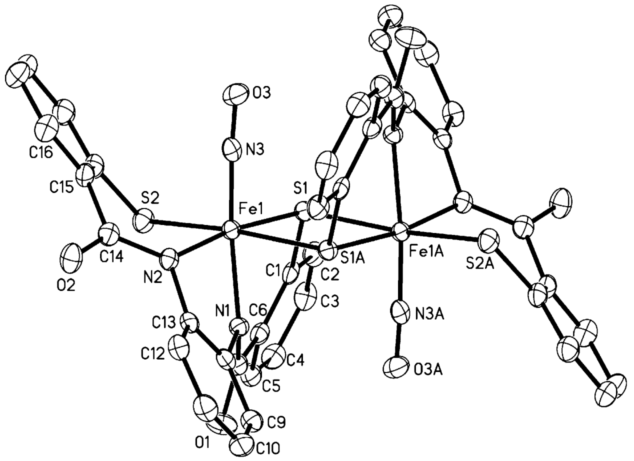

Figure 2. ORTEP diagram of $[\{Fe(PhPepS)(NO)\}_2]^{2-}$, the anion of **3**, showing the atom labeling scheme. H atoms are omitted for the sake of clarity. Selected bond lengths [Å] and bond angles [deg]: Fe1−S1, 2.2592(9); Fe1−S2, 2.2918(9); Fe1−S1A, 2.3824(9); Fe1−N1, 1.972(2); Fe1−N2, 1.973(3); Fe1−N3, 1.656(3); N3−O3, 1.145(3),; C7−O1, 1.240(4); Fe1−N3−O3, 176.1(3).

The $\{Fe-NO\}^7$ nitrosyl **2** is sensitive to oxygen; in MeCN or DMF, **2** is slowly oxidized to **3** upon exposure to air. The rate of the aerobic oxidation is *much* slower in MeOH. It is evident that MeOH provides extra stabilization to the $\{Fe-NO\}^7$ species.[16] Indeed, simple storage of solutions of

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(16) The few $\{Fe-NO\}^7$ species reported so far have been synthesized in protic media such as MeOH[6,9a] and water.[10a]

3 in protic solvents such as MeOH and EtOH under dinitrogen leads to conversion into **2**. Successful isolations of **2** and **3** therefore depend critically on the solvent.

The cyclic voltammogram (CV) of **3** in MeCN contains a reversible wave with $E_{1/2} = -0.165$ V (vs SCE) (see the Supporting Information). No additional redox process is observed up to -1.0 V vs SCE. Since the parent Fe(III) complex **1** does not show any reduction up to -1.0 V vs SCE, it is evident that the redox process with $E_{1/2} = -0.165$ V in the case of **3** is NO-centered. In the initial cathodic scan, the coordinated NO molecule in the $\{Fe-NO\}^6$ complex **3** is reduced to yield the $\{Fe-NO\}^7$ species **2**. Wieghardt and co-workers have assigned redox processes related to $NO^+ \rightarrow NO^•$ and $NO^• \rightarrow NO^-$ reductions in [Fe(NO)(cyclam-ac)]$^{2+/1+/0}$ complexes.[13a,17] The $E_{1/2}$ value of **3** suggests that the observed redox process is most possibly related to $NO^+ \leftrightarrow NO^•$ transformation. Because the CV of **2** in MeCN exhibits a reversible wave with $E_{1/2} = -0.130$ V (vs SCE) (see the Supporting Information), it appears that the initial oxidized $\{Fe-NO\}^6$ product remains monomeric in the CV time scale in this case and hence the $E_{1/2}$ value is slightly different from that of **3** (dimeric $\{Fe-NO\}^6$ complex). The monomeric $\{Fe-NO\}^6$ species is eventually converted into the final dimeric $\{Fe-NO\}^6$ complex **3**; this is proven by the fact that bulk electrolysis of **2** at a holding potential of $+0.20$ V (vs SCE in MeCN) for ~10 min results in the formation of **3** in MeCN.[18] The **2** → **3** conversion presumably proceeds via the transient five-coordinate $\{Fe-NO\}^6$ intermediate, which rearranges to the more stable six-coordinate dimeric complex **3** via rotation along the C14−C15 axis. Such a twist brings down S2 from an axial position to an equatorial position (Figure 2). A similar twist has been noted in metal complexes with ligands of this kind.[14,19] Complex **3** can also be synthesized via chemical oxidation of **2** with $(Fc^+)(PF_6^-)$. The chemical oxidation is clean, and no other side product(s) is observed in the **2** → **3** conversion. The CV of **2** in MeOH has also been run to examine the effect(s) of a protic solvent on the oxidation of the bound NO molecule. In the anodic scan, **2** exhibits a process with E_p at -0.03 V (vs SCE), but no cathodic wave is observed in the reverse scan. This shows that the transient five-coordinate $\{Fe-NO\}^6$ intermediate is not stable in a protic medium. As stated above, **3** is also converted into **2** in MeOH.

Much like the $\{Fe-NO\}^6$ complexes containing thiolato-S donors by Artaud,[5] Kovacs,[12] and Grapperhaus,[13b] **3** does not exhibit any photolability of the bound NO. This behavior is in stark contrast to the $\{Fe-NO\}^6$ complexes of the polypyridine ligands containing one[7,8,11] or two carboxamide group(s)[6] that exhibit excellent photolability under mild illumination. Interestingly, in aprotic solvents such as MeCN and DMF, the $\{Fe-NO\}^7$ species **2** is photooxidized to **3** when exposed to visible light. At this time, we are studying this unusual photooxidation process. The results will be reported in due time.

Acknowledgment. T.C.H. received support from NIH IMSD Grant GM58903.

Supporting Information Available: Spectroscopic data for all of the complexes; ORTEP diagram of **1** (Figure S1); X-band EPR spectrum of **2** (Figure S2); CVs of **2** and **3** (Figure S3); FTIR spectra of **2** and **3** (Figure S4); and ^1H NMR spectra of the monomeric $\{Fe-NO\}^6$ intermediate and **3** in CD_3CN (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The $E_{1/2}$ value for the $NO^+ \rightarrow NO^•$ reduction ($\{Fe-NO\}^6 \rightarrow \{Fe-NO\}^7$ conversion) in the case of Wieghardt's complex (0.40 V vs SCE in MeCN) is more positive compared to the $E_{1/2}$ value of **3**. This difference arises from the substantial electron density provided to the Fe center in **3** by the strong in-plane carboxamido nitrogens and thiolato sulfurs (all negatively charged).

(18) Indeed, the ^1H NMR spectrum of the electrolyzed product in CD_3CN first showed six resonances in the aromatic region consistent with the five-coordinate monomeric structure of the intermediate $\{Fe-NO\}^6$ species. This spectrum changes to a complex one within 15 min that matches with the spectrum of authentic **3** (see the Supporting Information).

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