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Dinitrosyl Iron Complexes Relevant to Rieske Cluster Nitrosylation

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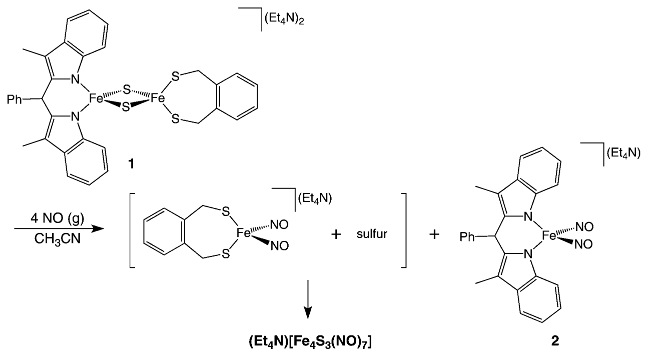
Iron-sulfur clusters are among the most ubiquitous cofactors in biology. The diversity of structures encountered in iron-sulfur proteins reflects the many functions nature employs for these versatile units, from electron transfer to substrate binding and activation.[1] Of the many variations of iron-sulfur clusters, only a select few have ligands other than cysteine. Among these, the best-documented examples are Rieske-type Fe_2S_2 clusters[2] that contain a pair of histidine residues ligating one iron atom.[3,4] Recently, the first synthetic analogue of a Rieske cluster was reported (**1**, Scheme 1).[5] We were interested to explore the nitric oxide reactivity of such a compound as part of ongoing investigations into the reactivity of non-heme iron with NO. Moreover, there is very little information about the interaction of Rieske proteins with NO,[6] which contrasts with the large body of literature regarding nitric oxide reactivity with purely cysteine-bound iron-sulfur clusters.[7] Herein we report the results of our studies of NO reactions with **1** (Scheme 1) and introduce related N-bound dinitrosyl iron complexes (DNICs) containing β-diketiminate ligands.

Scheme 1. Reaction of the Rieske-Type Cluster with NO



Reaction of Rieske model complex **1** with 4 equiv of nitric oxide in acetonitrile solution results in the appearance of two new nitrosyliron species after workup as judged by IR spectroscopy. The first displays ν_{NO} bands at 1795, 1743, and 1705 cm^{-1} (THF solution) consistent with formation of Roussin's black salt (RBS), $[Fe_4S_3(NO)_7]^-$.[8] We demonstrated previously that RBS can arise from reaction of NO with an Fe_2S_2 cluster containing $(S_2\text{-}o\text{-xyl})^{2-}$ ligands via the intermediacy of the thiolate-bound DNIC.[9] This DNIC can be observed by IR spectroscopy in reactions of **1** with Ph_3CSNO in benzonitrile. After addition of 1−2 equiv of nitrosothiol, ν_{NO} bands at 1739 and 1679 cm^{-1} appear, consistent with formation of $[Fe(S_2\text{-}o\text{-xyl})(NO)_2]^-$. Upon addition of further equivalents of Ph_3CSNO, these IR bands diminish, giving rise to those of RBS.

The second iron nitrosyl species obtained from the reaction shown in Scheme 1 displays ν_{NO} peaks at 1761 and 1692 cm^{-1} (IR, KBr). Recrystallization from DMF/Et_2O and subsequent spectroscopic characterization identified a new DNIC, **2** (Scheme 1). The N-bound DNIC displays a rhombic EPR signal centered at 2.03 (Supporting Information, SI), consistent with its formulation as an $S = {}^1/_2$ paramagnetic complex and a $\{Fe(NO)_2\}^9$ species in the Enemark-Feltham notation.[10] Compound **2** also contains a quadrupole doublet with an isomer shift of 0.16(2) mm/s in the ^{57}Fe Mössbauer spectrum (SI), which corresponds well with the value of 0.18(2) mm/s determined previously for $(Et_4N)[Fe(PhS)_2(NO)_2]$.[9] The quadrupole splitting is 0.85(2) mm/s. Notably, several examples of DNICs containing nitrogen donor ligands have been published previously as potential models for histidine-ligated DNICs.[11] The synthesis of compound **2** represents the first verification that such a DNIC can be prepared directly from reaction of an iron-sulfur cluster with nitric oxide. Compound **2** was also independently synthesized by salt metathesis of $(Et_4N)[FeCl_2(NO)_2]$ with the lithium salt of the nitrogen ligand displayed in Scheme 1. Spectroscopic features of the DNIC prepared in this fashion are identical in all respects to those observed for that prepared from **1**.

In order to prepare more soluble versions of Rieske cluster-derived DNICs such as **2** for more extensive studies, we turned our attention to sterically demanding β-diketiminate ligands. We reasoned that β-diketiminates would chelate the $\{Fe(NO)_2\}^9$ unit, giving rise to stable DNICs, thereby avoiding many of the common shortcomings of thiolate ligands such as tendency toward oxidation and kinetic lability. Furthermore, β-diketiminate ligands have been employed previously to stabilize low-valent iron.[12] As an entry into this chemistry, the iodide precursor $[FeI_2(NO)_2]^-$ was selected as a source of the $\{Fe(NO)_2\}^9$ unit.[13] Reaction of the lithium salt of $[(2,6\text{-diisopropylphenyl})NC(Me)]_2CH$ (Ar-nacnac) with $(PPN)[FeI_2(NO)_2]$ ($PPN^+ = \mu$-nitridobis(triphenylphosphine) cation) affords the new compound, $[(\text{Ar-nacnac})Fe(NO)_2]$ (**3**), after workup. Unlike typical anionic DNICs such as **2**, neutral **3** is soluble in alkane and arene solvents and can be conveniently freed from salt impurities by recrystallization from pentane. The spectroscopic features of **3** ($\nu_{NO} = 1761$, 1709 cm^{-1}, benzene-d_6) are similar to those of **2**, consistent with an $\{Fe(NO)_2\}^9$ formulation (SI). The solid-state structure of **3** (Figure 1) displays pseudo-tetrahedral geometry at iron, with the dinitrosyl iron unit residing in a steric pocket created by the β-diketiminate ligand. It is interesting to contrast the pseudo-tetrahedral structure of **3** with the square-planar geometry of a related Fe(I) dicarbonyl complex.[14] The Fe−N−O metrics in **3** are similar to those observed in previously characterized DNICs.[15]

The $\{Fe(NO)_2\}^9$ unit of most DNICs can be reduced by one electron to give the diamagnetic $\{Fe(NO)_2\}^{10}$ configuration. Typically this reduction process is quasi-reversible electrochemically. Only in rare instances can the reduced DNIC be isolated.[16] With DNICs containing thiolate ligands, reduction is followed by dissociation of RS^-, leading to formation of the reduced Roussin red ester derivatives.[17] The cyclic voltammogram of **3** (SI) displays a quasi-reversible ($i_{pr}/i_{pf} = 0.95$) one-electron reduction at −1.34 V (vs ferrocene/ferrocenium) in THF. Chemical reduction of **3** with

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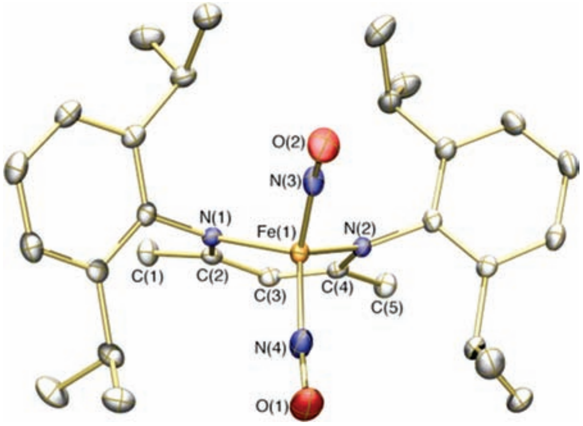

Figure 1. Structure of **3** displaying 50% thermal ellipsoids with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−N(3), 1.6964(18); Fe(1)−N(4), 1.6882(18); N(3)−O(2), 1.177(2); N(4)−O(1), 1.174(2); N(3)−Fe(1)−N(4), 114.27(9); Fe(1)−N(3)−O(2), 162.7(2); Fe(1)−N(4)−O(1), 170.1(2).

either decamethylcobaltocene or sodium amalgam affords the reduced $\{Fe(NO)_2\}^{10}$ DNIC. Metathesis of the cobaltocenium cation for Bu_4N^+ produces $(Bu_4N)[(Ar\text{-}nacnac)Fe(NO)_2]$ (**4a**) after crystallization from Et_2O. Compound **4a** is a stable (mp = 198−200 °C) diamagnetic solid as judged by sharp features in its ^1H NMR spectrum (SI). Exposure of **4a** to air immediately results in regeneration of **3** as judged by IR and UV−vis spectroscopy. The ν_{NO} bands in a benzene-d_6 solution of **4a** appear at 1627 and 1567 cm^{-1}, a shift of >130 cm^{-1} from those observed for **3**. Crystals of **4a** proved unsuitable for X-ray determination so the PPN^+ salt, **4b**, was prepared.

The solid-state structure of the anion of **4b** (Figure 2) resembles closely that of **3**. One considerable difference is the elongated Fe−N(nacnac) bonds in **4b** and the smaller displacement of the Fe atom out of the nacnac plane compared with that in **3** (0.24 vs 0.62 Å). The Fe−N(NO) bonds for **4b** are also ~0.03−0.04 Å shorter than those of **3**, consistent with a greater degree of π-backbonding in the reduced $\{Fe(NO)_2\}^{10}$ core. This phenomenon is also manifest by the longer N−O bonds of **4b** (Figures 1 and 2).

In conclusion, reaction of the cluster analogue **1** with NO leads to formation of a new nitrogen-containing $\{Fe(NO)_2\}^9$ DNIC. This reaction demonstrates that naturally occurring Rieske clusters may be susceptible to disassembly by NO, similar to the findings for cysteine-bound Fe_2S_2 clusters. The reaction of **1** with NO(g) to form two $\{Fe(NO)_2\}^9$ units follows directly from previous work with synthetic clusters of the type $[Fe_2S_2(SR)_4]^{2-}$ and suggests an intrinsic reactivity of the $\{Fe_2S_2\}^{2+}$ core toward NO.[9,18] β-Diketiminates are excellent ligands for dinitrosyl iron complexes, allowing for isolation of a rare set of homologous DNIC redox partners. Preliminary studies (data not shown) using [Fe(TPP)Cl] (TPP = *meso*-tetraphenylporphine dianion) as an NO receptor demonstrate that these DNICs display different NO transfer properties, suggesting that control of NO transfer in biology might be redox triggered. This hypothesis is currently under investigation in our laboratory.

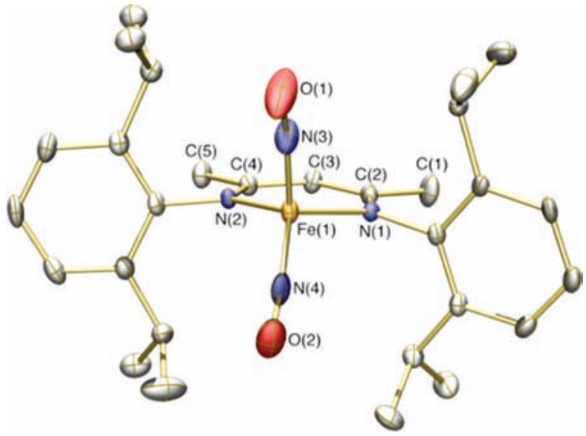

Figure 2. Structure of the anion of **4b** displaying 50% thermal ellipsoids with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−N(3), 1.668(5); Fe(1)−N(4), 1.649(4); N(3)−O(1), 1.191(6); N(4)−O(2), 1.218(6); N(3)−Fe(1)−N(4), 109.2(2); Fe(1)−N(3)−O(1), 163.2(5); Fe(1)−N(4)−O(2), 165.1(5).

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Supporting Information Available: Experimental details, additional reaction schemes, spectroscopic data, crystallographic data, refinement details, and fully labeled thermal ellipsoid diagrams for **3** and **4b**, as well as the corresponding CIF files. This information is available free of charge via the Internet at http://pubs.acs.org.

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