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A Dinitrosyliron Complex within the Homoleptic $Fe(NO)_4$ Anion: NO as Nitroxyl and Nitrosyl Ligands within a Single Structure

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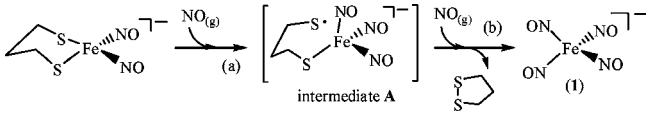
Supporting Information

ABSTRACT: Nitrosylation of the chelate−thiolate-containing dinitrosyliron complex (DNIC) $[(S(CH_2)_3S)Fe(NO)_2]^-$ triggers nitric oxide (NO) activation to generate the homoleptic nitrosyl $\{Fe(NO)_2\}^9$ DNIC $[Fe(NO)_4]^-$ (**1**) made up of two nitroxyls (or two NO anions) attached to a delocalized $\{Fe(NO)_2\}^9$ motif. The significantly longer N3−O3/N4−O4 [1.380(12) and 1.280(12) Å] and Fe1−N3/Fe1−N4 [2.008(11) and 2.045(10) Å] bond distances reflect that N3−O3 and N4−O4 of complex **1** may act as the nitroxyl-coordinated ligands. That is, the electronic structure of the DNIC **1** is best described as a $\{Fe(NO)_2\}^9$ motif coordinated by two nitroxyl (NO^-) ligands.

Nitric oxide (NO), a small molecule exhibiting multiple physiological functions such as vasodilation, neuronal transmission, inflammation, immune system response, and cancer remedy, is produced by NO synthases.[1] The dinitrosyliron complex (DNIC), the intrinsic NO-derived species existing in various NO-overproducing tissues, is known as one of two possible forms for the storage and transport of NO in a biological system.[2] Nitrosylation of [Fe−S] proteins and iron-containing proteins yielding protein-bound DNICs and Roussin's red esters (RREs) has been intensely studied.[3] A nitroxyl anion (HNO/NO^-), the one-electron-reduced state of NO claimed to modulate contraction and relaxation in normal/cardiac hearts in vivo, was proposed to be produced by NO synthases in vitro.[4,5] Also, nitroxyl was suggested to be an attractive candidate for the treatment of heart failure.[5] In aqueous solution, HNO rapidly converting into N_2O and H_2O was characterized.[6] In chemistry, syntheses of the metal-bound HNO including (i) the selective oxidation of coordinated hydroxylamine of $[Re(CO)_3(NH_2OH)(PPh_3)_2][SO_3CF_3]$ producing $([Re(CO)_3(NH{=}O)(PPh_3)_2][SO_3CF_3])$ at low temperature,[7] (ii) protonation of the reduced species of $\{Fe(NO)\}$,[7] in the Enemark−Feltham electronic notation, [Fe(tpp)NO] (tpp = tetraphenylporphyrinato dianion) by phenol, yielding the proposed [Fe(tpp)(HNO)],[8] (iii) hydride reduction of the nitrosyl ligand of the $\{Ru(NO)\}^6$ $[Ru(tpp)(NO)(1\text{-MeIm})]^+$, yielding the Ru-bound HNO,[9] and (iv) NO conversion to HNO by means of a proton-coupled electron-transfer reaction upon nitrosylation of $[HCr(CO)_3C_5Me_5]$ were reported.[10] In addition, HNO was proposed to be generated via the conversion of $[Fe(LH)(NO)_2]$ to $[Fe(L)(NO)]$ [L = $S(CH_2)_2NMe(CH_2)_3NMe(CH_2)_3S$] triggered by the proton−electron-transfer reaction.[11] Recently, the release of the distinct NO redox-interrelated forms (NO^+, NO, and HNO) derived from the DNIC $[(C_{12}H_8N)_2Fe(NO)_2]^-$ ($C_{12}H_8N$ = carbazolate) modulated by the incoming substitution ligands was demonstrated.[12] Investigation of the transformation among chelate- and monodentate-peptide-bound RREs and DNICs demonstrates the importance of the chelating effect.[13] We are aware that the treatment of $[Fe(CO)_5]$ with NO under high pressure (100 atm) for 3 days yielding $[(Fe(NO)_3)^+(NO)^-]$ characterized by IR and complex $[RuCl(NO)_2(PPh_3)_2]^+$ having linear and bent nitrosyl ligands (coordinated $[NO^-]$ and $[NO^+]$ ligands) characterized by IR and single-crystal X-ray structure determination were reported.[14] In this contribution, the synthesis and characterization of a $\{Fe(NO)_2\}^9$ DNIC within the homoleptic $Fe(NO)_4$ anion, with NO as nitroxyl and nitrosyl ligands within a single structure, were uncovered $\{[PPN][Fe(NO)_4]$ (**1**)$\}$.

In contrast to the facile conversion of monodentate−thiolate-containing $[(SEt)_2Fe(NO)_2]^-$ into $[(SEt)Fe(NO)_2]_2$ under the presence of NO(g),[15] the transformation of chelate−thiolate-containing $[(S(CH_2)_3S)Fe(NO)_2]^-$ into the dark red-brown $\{Fe(NO)_2\}^9$ DNIC $[Fe(NO)_4]^-$ (**1**) (yield 53%) was demonstrated when a tetrahydrofuran (THF) solution of $[(S(CH_2)_3S)Fe(NO)_2]^-$ was treated with NO(g) at ambient temperature for 30 min (Scheme 1a,b). Complex **1**, characterized by IR, UV−vis, electron paramagnetic resonance (EPR), SQUID, X-ray absorption spectroscopy (XAS), and single-crystal X-ray diffraction, is air-sensitive in the solid state and the THF solution. Complex **1** exhibits the diagnostic IR ν_{NO} spectrum 1776 s, 1708 s, 1345 w cm^{-1} in KBr [Supporting Information (SI), Figure S1], in which the stretching frequency

Scheme 1



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1345 w cm^{-1} is assigned to the bent N−O vibration.[8b,16] The slightly lower-energy NO bands of complex **1** shifted by ∼4 cm^{-1} from those of $[(NO_2)_2Fe(NO)_2]^-$ [1782 s, 1712 s cm^{-1} (KBr)] reflect the similar electron-donating ability and binding affinity of ligands [NO^-] and [NO_2^-] toward the $\{Fe(NO)_2\}^9$ motif (SI, Experimental Section).[17a] Compared with $[(S(CH_2)_3S)Fe(NO)_2]^-$, which is dominated by intense absorption bands at 366, 430, 578, and 807 nm (THF),[17] complex **1** displays three absorption bands at 385, 473, and 744 nm (THF). Consistent with the characteristic g value of $\{Fe(NO)_2\}^9$ DNICs,[17] complex **1** displays an isotropic EPR spectrum with a principal g value of 2.031 at 298 K and a rhombic spectrum with $g_1 = 2.063$, $g_2 = 2.033$, and $g_3 = 2.003$ at 4 K ($g_1 = 2.053$, $g_2 = 2.030$, $g_3 = 2.013$ at 77 K; SI, Figure S2). Magnetic susceptibility data of a powdered sample of complex **1** were collected in the temperature range of 2−300 K in a 1 T applied field. The effective magnetic moment (μ_{eff}) decreases from 1.75 at 300 K to 1.49 at 2 K (SI, Figure S3). The temperature-dependent magnetic moment in complex **1** may be attributed to the dipolar coupling of the iron center and nitroxyl ligands,[18] consistent with the observed half-field signal of the EPR spectrum at 4 K (SI, Figure S2). The Fe K-edge preedge energy ($Fe_{1S} \rightarrow Fe_{3d}$ transition) of 7113.6 eV for complex **1** lies within the range of 7113.4−7113.8 eV (SI, Figure S4), the characteristic preedge energy of mononuclear/dinuclear $\{Fe(NO)_2\}^9$ DNICs.[19] From the CV study, the electrochemistry of complex **1** displays an irreversible oxidation process at room temperature.

The reaction sequences given in Scheme 1a,b reasonably account for the transformation of $[(S(CH_2)_3S)Fe(NO)_2]^-$ into complex **1** along with byproduct 1,2-dithiolane triggered by nitrosylation. The reaction proceeds via nitrosylation to yield intermediate **A** containing the proposed $\{Fe(NO)_3\}^{11}$ core and a thiyl radical ligand.[20] That is, nitrosylation of the $\{Fe(NO)_2\}^9$ DNIC $[(S(CH_2)_3S)Fe(NO)_2]^-$ undergoes thiolate-based oxidation because density functional theory computations of DNICs $[(SR)_2Fe(NO)_2]^-$ (R = Ph, Et) indicate that the highest occupied molecular orbital (HOMO) is dominated by the thiolates' contribution (87% and 77% of ligands [SPh^-] and [SEt^-] for B3LYP, respectively; 62% and 56% of ligands [SPh^-] and [SEt^-] for BP86, respectively), obtained in the previous study.[19a] The subsequent reduction of the incoming NO(g) by intermediate **A** and the concomitant coordination of nitroxyl lead to the formation of complex **1** accompanied by the release of byproduct 1,2-dithiolane ($[S(CH_2)_3S]$) identified by ^1H NMR [δ 2.53 (s), 1.91 (s) ppm ($CDCl_3$)].

The structure of the $[Fe(NO)_4]^-$ unit for complex **1** in $[PPN]^+$ salt is shown in Figure 1. It is noticed that the Fe1−N3−O3 and Fe1−N4−O4 bond angles of 106.8(7)° and 113.2(7)° are distinct from those [163.0(7)° and 160.9(8)°] of Fe1−N1−O1 and Fe1−N2−O2. In the linear Fe1−N1−O1 and Fe1−N2−O2 bonds, the average Fe−N [Fe1−N1 1.696(7) Å and Fe1−N2 1.719(8) Å] and N−O [N1−O1 1.174(8) Å and N2−O2 1.154(9) Å] bond lengths of 1.707(7) and 1.164(9) Å fall within the ranges of 1.661(4)−1.695(3) and 1.160(6)−1.178(3) Å, respectively, observed in the $\{Fe(NO)_2\}^9$ DNICs.[19a] Compared to the N−O bond distances of 0.95, 1.15, and 1.26 Å in NO^+, the NO radical, and NO^-, respectively, the significantly longer N3−O3/N4−O4 [1.380(12) and 1.280(12) Å] and Fe1−N3/Fe1−N4 [2.008(11) and 2.045(10) Å] bond distances reflect that N3−O3 and N4−O4 of complex **1** may act as the nitroxyl-coordinated ligands.[16c] That is, the electronic structure of the

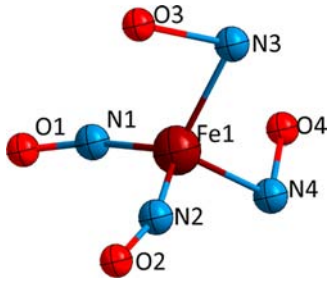

Figure 1. ORTEP drawing and labeling scheme of the $[Fe(NO)_4]^-$ unit in $[PPN]^+$ salt with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (deg): Fe1−N1 1.696(7), Fe1−N2 1.719(8), Fe1−N3 2.008(11), Fe1−N4 2.045(10), N1−O1 1.174(8), N2−O2 1.154(9), N3−O3 1.380(12), N4−O4 1.280(12); Fe1−N1−O1 163.0(7), Fe1−N2−O2 160.9(8), Fe1−N3−O3 106.8(7), Fe1−N4−O4 113.2(7), N1−Fe1−N2 111.7(4), N1−Fe1−N3 121.3(6), N1−Fe1−N4 112.6(5) (SI, Table S4).

DNIC **1** is best described as a $\{Fe(NO)_2\}^9$ motif coordinated by two nitroxyl (NO^-) ligands (or described as $\{Fe(NO)_4\}^{13}$ based on the Enemark−Feltham electronic notation).[19b] Presumably, the two groups of NO-coordinated ligands ($[(NO^-)_2Fe(NO)_2]^-$) should rapidly interconvert between linear and bent coordination modes in a THF solution.

The geometry of the $[Fe(NO)_4]^-$ anion is optimized in the C_s point group by high-level ab initio theory at the level of SAC-CI using a direct algorithm (computational details were described in the SI).[21] The optimized structure agrees very well with the experimental X-ray structure (SI, Table S1). The spin density and charge distributions over each atom are analyzed at this optimized structure and summarized in the SI, Table S2; the results confirm that the electronic structure of this converged geometry is an anion with the charge of 1− distributed at each of the two bent NO sites, while the sum of the charge distributed at a $[Fe(NO)_2]$ motif is close to 1+. The frontier orbitals show that SOMO−1 (HOMO) is a π bond mainly contributed from all nitrogen atoms (minor contribution from an iron atom; Figure 2 and SI, Figure S5). Compared

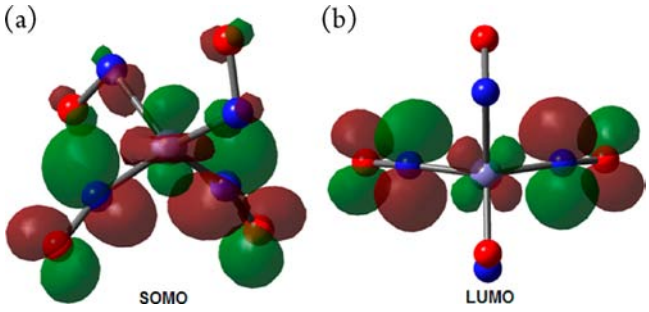

Figure 2. Frontier molecular orbitals of **1**: (a) SOMO; (b) lowest unoccupied molecular orbital (LUMO).

with the nonbonding singly occupied molecular orbital (SOMO), the character of SOMO−2 (HOMO−1) is the σ bonds between the iron atom and two nitroxyl ligands, while that of SOMO−3 (HOMO−2) is the π bonds between the iron atom and two NO^- perpendicular to the π bond of SOMO−1 (SI, Figure S5). The atomic contribution of each molecular orbital is shown in the SI, Table S3.

In summary, nitrosylation of the chelate−thiolate-containing $\{Fe(NO)_2\}^9$ DNIC $[(S(CH_2)_3S)Fe(NO)_2]^-$ yields the tetrani-

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trosyliron complex **1** with NO as nitroxyl and nitrosyl ligands within a single structure. The bent Fe1−N3−O3 and Fe1−N4−O4 bonds [bond angles 106.8(7)° and 113.2(7)°, respectively] and the significantly longer N3−O3/N4−O4 [1.380(12) and 1.280(12) Å] and Fe1−N3/Fe1−N4 [2.008(11) and 2.045(10) Å] bond distances reflect that the electronic structure of **1** is best described as a $\{Fe(NO)_2\}^9$ motif coordinated by two nitroxyl (NO^-) ligands.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details concerning the synthesis, characterization, and protonation of complex **1**, EPR and SQUID experiments, and crystallographic and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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