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Dinuclear $[\{Fe(NO)_2\}^{10}{-}\{Fe(NO)_2\}^{10}]$ Dinitrosyl Iron Complex with Thiolate−CO-Bridged Ligands

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Air-sensitive complexes $\{Fe(NO)_2\}^9{-}\{Fe(NO)_2\}^9$ $[Fe(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(NO)_2]_2$ (**1**), $\{Fe(NO)_2\}^9{-}\{Fe(NO)_2\}^{10}$ $[Fe(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(NO)_2]_2^-$ (**2**), the anionic $\{Fe(NO)_2\}^{10}$ $[(SC_6H_4\text{-}o\text{-}N(CH_3)_2)Fe(NO)_2]^-$ (**3**), and the anionic $\{Fe(NO)_2\}^{10}{-}\{Fe(NO)_2\}^{10}$ $[Fe(NO)_2(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(\mu\text{-}CO)Fe(NO)_2]^-$ (**4**) with mixed CO−thiolate-bridged ligands were synthesized. All complexes were characterized by IR, UV−vis, electron paramagnetic resonance, and single-crystal X-ray diffraction. The interconversions among these complexes were demonstrated. The interconversion between complexes **1** and **2** is accomplished by reduction and oxidation. Complex **3** adapts a $\{Fe(NO)_2\}^{10}$ electronic structure with a N/S ligation mode and serves as a donor reagent of the $\{Fe(NO)_2\}^{10}$ moiety. $\{Fe(NO)_2\}^{10}{-}\{Fe(NO)_2\}^{10}$ complex **4** possesses the butterfly-like $[Fe(\mu\text{-}S)(\mu\text{-}C)Fe]$ core with a shorter Fe$\cdots$Fe distance of 2.5907(5) Å attributed to the shorter Fe−S and Fe−C bond distances.

Nitric oxide (NO) is one of the most important small molecules in physiology.[1] Dinitrosyl iron complexes (DNICs), endogenous NO-containing compounds, are known as one of two possible naturally occurring forms for the storage and delivery of NO in a biological system.[2] DNICs are classified into protein-bound and low-molecular-weight (LMW) DNICs serving as the storage and donor of the NO or $\{Fe(NO)_2\}$ moiety. In vitro/vivo, both protein-bound and LMW DNICs are possibly identified and characterized by their distinctive electron paramagnetic resonance (EPR) signals at $g = 2.03$.[3] Roussin's red esters (RREs), the dimeric form of DNICs, are interconvertible to DNICs and considered to perform the same role as DNICs.[4] Like $\{Fe{-}NO\}^n$ ($n = 6{-}8$), well studied by Wieghardt et al.,[5] on the basis of the oxidation levels of the $\{Fe(NO)_2\}$ core of DNICs, DNICs can be divided into three major types: monomeric EPR-active $\{Fe(NO)_2\}^9$, EPR-silent $\{Fe(NO)_2\}^{10}$, and dimeric EPR-silent/active $[\{Fe(NO)_2\}^9{-}\{Fe(NO)_2\}^9]/[\{Fe(NO)_2\}^9{-}\{Fe(NO)_2\}^{10}]$.[6] Ford et al. have reported the X-ray structures of $\{Fe(NO)_2\}^{10}$ $[Fe(NO)_2(\text{imidazolate})]_4$ and $[Fe(NO)_2(1\text{-MeIm})_2]$ DNICs with the N,N-ligation mode.[7] In addition to the varieties of $\{Fe(NO)_2\}^9$ DNICs containing various ligation modes [S,S]/[S,O]/[S,N]/[N,N],[8] Liaw et al. demonstrated interconversion among $[(RS)_2Fe(NO)_2]^-$, dimeric DNICs $[Fe(\mu\text{-}SR)(NO)_2]_2$, and anionic dimeric DNICs $[Fe(\mu\text{-}SR)(NO)_2]_2^-$ ($R = {}^tBu$).[9] Also, Liaw et al. elucidated the anionic mixed thiolate−sulfide-bridged RRE as a key intermediate in the transformation of DNICs/anionic RREs into [2Fe−2S]

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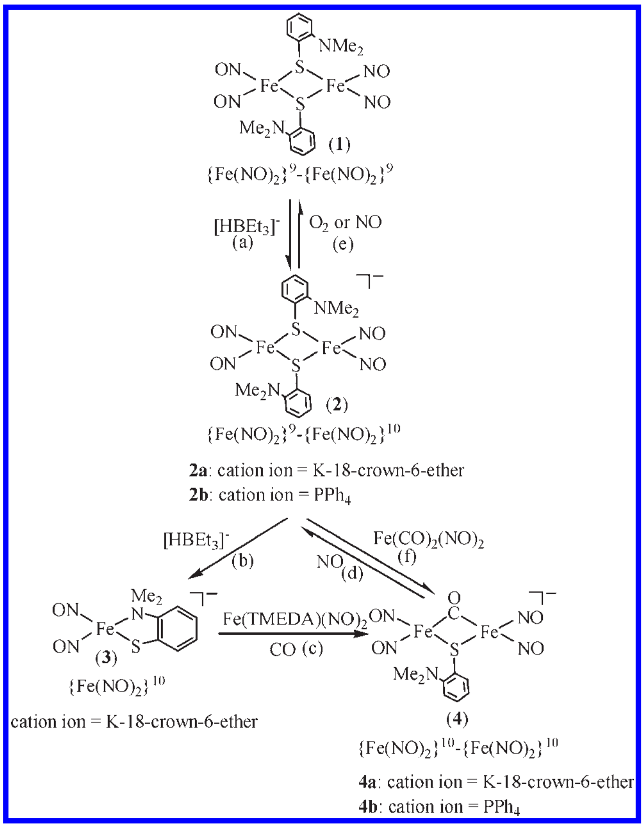
Scheme 1



clusters facilitated by $HSCPh_3$ via the reassembling process.[10] Recently, we have reported the synthesis of the neutral five-coordinate $\{Fe(NO)_2\}^9$ DNICs $[(TMEDA)Fe(NO)_2I]$.[11] In this contribution, the anionic dimeric DNIC $[Fe(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(NO)_2]_2^-$ (**2**) and the reduction product $\{Fe(NO)_2\}^{10}$ $[(SC_6H_4\text{-}o\text{-}N(CH_3)_2)Fe\text{-}(NO)_2]^-$ (**3**) were isolated. Further, the reaction of complex **3** with $Fe(TMEDA)(NO)_2$ under a carbon monoxide (CO) atmosphere yielded the first anionic, dimeric $\{Fe(NO)_2\}^{10}$−$\{Fe(NO)_2\}^{10}$ $[Fe(NO)_2(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(\mu\text{-}CO)Fe(N\ O)_2]^-$ (**4**) DNIC containing the mixed thiolate−CO-bridged ligands.

The tetrahydrofuran (THF) solution of complex **1** and $KHBEt_3$ was stirred at 0 °C for 10 min (Scheme 1a); reduction occurred to yield complex **2**. The IR spectrum of complex **2** in a [K-18-crown-6 ether]$^+$ salt (**2a**) exhibits diagnostic ν_{NO} stretching frequencies at 1684 s and 1664 s cm $^{-1}$ (THF) with $\Delta\nu_{NO}$ = 20 cm^{-1}. The IR spectra for complexes **1** and **2a** have different patterns/positions [1808 vw, 1778 s, and 1752 s cm^{-1} for **1** versus 1684 s and 1664 s cm $^{-1}$ (THF) for **2a**] and $\Delta\nu_{NO}$ ($\Delta\nu_{NO}$ = 26 cm^{-1} for **1** versus $\Delta\nu_{NO}$ = 20 cm^{-1} for **2a**).[12] In contrast to complex **1**, exhibiting four absorption bands at 314, 370, 586, and 806 nm (THF) and complex $[Fe(\mu\text{-}SEt)_2)(NO)_2]_2^-$,[13] complex **2a** displays three absorption bands at 309, 371, and 509 nm (THF). The EPR spectrum of complex **2b** displays an isotropic signal at g = 2.002 at 298 K (Figure S1 in the Supporting Information). The reaction of complex **2a** and $KHBEt_3$ led to the formation of complex **3** in a THF solution at 0 °C (Scheme 1b). Complex **3** displays an EPR-silent $\{Fe(NO)_2\}^{10}$ electronic structure with N/S-ligation mode.

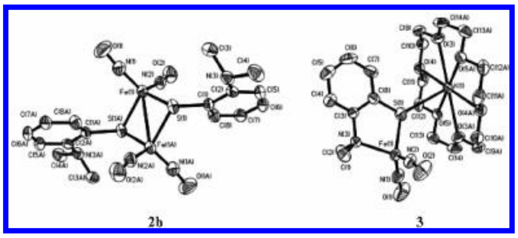


Figure 1. X-ray diffraction structures of complexes **2b** and **3**.

The IR spectrum of complex **3** also exhibits diagnostic ν_{NO} stretching frequencies at 1660 s and 1610 s cm^{-1} (THF) with $\Delta\nu_{NO}$ = 50 cm^{-1}. The single-crystal X-ray structures of complexes **2b** and **3** are depicted in Figure 1.

Upon the addition of 1 equiv of $Fe(TMEDA)(NO)_2$ into complex **3** under a CO atmosphere in THF (Scheme 1c), a pronounced color change from brown to dark blue occurred at ambient temperature. The formation of EPR-silent complex **4** was confirmed by IR, UV−vis, and single-crystal X-ray diffraction. The electronic structure of complex **4** is best described as the anionic dinuclear $\{Fe(NO)_2\}^{10}$−$\{Fe(NO)_2\}^{10}$ DNIC. Obviously, the strong π-accepting bridging CO plays a key role in stabilizing the $\{Fe(NO)_2\}^{10}$−$\{Fe(NO)_2\}^{10}$ complex **4** via relieving the electronic richness of the $[\{Fe(NO)_2\}^{10}$−$\{Fe(NO)_2\}^{10}]$ centers. As presented in Scheme 1f, upon the addition of $Fe(CO)_2(NO)_2$ into the THF solution of complex **2b** in a 1:1 stoichiometry, a reaction ensued over the course of 3 h to yield the anionic complex **4b** along with complex **1** in the yield of a 1:2 molar ratio. Presumably, $Fe(CO)_2(NO)_2$ acts as $\{Fe(NO)_2\}^{10}$ as well as a CO-donor reagent in this reaction. One of the labile CO donors derived from $Fe(CO)_2(NO)_2$ bound to the Fe atom of the $\{Fe(NO)_2\}^{10}$ part of complex **2b** accompanied by the bridged-thiolate cleavage may rationalize the formation of complex **1** derived from the dimerization of $[Fe(NO)_2(SC_6H_4\text{-}o\text{-}N(CH_3)_2)]$ motifs. The subsequent combination of $[Fe(NO)_2(SC_6H_4\text{-}o\text{-}N(CH_3)_2)(CO)]$ and the $[Fe(NO)_2]$ motif led to the formation of complex **4b**. The IR spectrum of complex **4b** shows ν_{NO} stretching frequencies at 1705 s and 1691s cm^{-1} and the ν_{CO} stretching frequency at 1843 w cm^{-1} (THF). The absorbance bands of complex **4b** are at 314, 381, 606, and 975 nm.

The single-crystal X-ray structure of the $[Fe(NO)_2(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(\mu\text{-}CO)Fe(NO)_2]^-$ unit in a PPh_4 salt (**4b**) is depicted in Figure 2. Two nitrosyl groups and bridging thiolate and carbonyl define the distorted tetrahedral geometry of each Fe atom, leading to acute angles Fe(1)−S(1)−Fe(2) 82.31(10° and S(1)−Fe(1)−C(1) 103.86(8)°. The $[Fe(\mu\text{-}S)(\mu\text{-}C)Fe]$ core geometry of complex **4b** is best described as a butterfly-like structure with a dihedral angle of 170.95° (the intersection of the Fe_2S and Fe_2C planes). As observed in this study, reduction of the $[\{Fe(NO)_2\}^9$−$\{Fe(NO)_2\}^9]$ complex **1** to the $[\{Fe(NO)_2\}^9$−$\{Fe(NO)_2\}^{10}]$ complex **2** results in elongation of the Fe−S and Fe(1)···Fe(1A) bond distances to relieve the richness of the electron density surrounding the $[\{Fe(NO)_2\}^9$−$\{Fe(NO)_2\}^{10}]$ $[Fe(\mu\text{-}S)_2Fe]$ centers.[8c] In contrast, the shorter Fe···Fe distance [2.5907 (5) Å] found in the electron-rich complex **4b** may be ascribed to the shorter bridging Fe−S [2.2805(7) and

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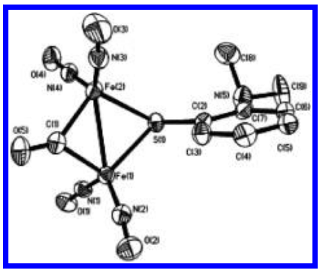

Figure 2. ORETP drawing and labeling scheme of the $[Fe(NO)_2(\mu\text{-}SC_6H_4\text{-}o\text{-}N(CH_3)_2)(\mu\text{-}CO)Fe(NO)_2]^-$ unit in a PPh_4 salt (**4b**) with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (deg): Fe(1)···Fe(2) 2.5907(5); Fe(1)−N(1) 1.664(2); Fe(1)−N(2) 1.658(2); Fe(2)−N(3) 1.653(2); Fe(2)−N(4) 1.660(2); Fe(1)−S(1) 2.2805(7); Fe(2)−S(1) 2.2737(7); Fe(1)−C(1) 1.960(3); Fe(2)−C(1) 1.976(3); O(1)−N(1) 1.186(3); O(2)−N(2) 1.177(3); O(3)−N(3) 1.177(3); O(4)−N(4) 1.180(3); C(1)−O(5) 1.156(3); N(1)−Fe(1)−N(2) 120.65(11); N(1)−Fe(1)−S(1) 109.17(7); N(2)−Fe(1)−S(1) 115.87(8); N(1)−Fe(1)−C(1) 103.07(10); N(2)−Fe(1)−C(1) 101.51(11); S(1)−Fe(1)−C(1) 103.86(8); O(1)−N(1)−Fe(1) 172.1(2); O(2)−N(2)−Fe(1) 172.2(2).

2.2737(7) Å] and Fe−C [1.960(3) and 1.976(3) Å] bond distances. The mean N−O bond length of 1.180(3) Å in complex **4b**, slightly shorter than the average N−O bond distance of 1.187(6) Å observed in complex **2b**, is nearly at the lower end of 1.214(6)−1.189(4) Å for the neutral $\{Fe(NO)_2\}^{10}$ DNICs.[8c] Meanwhile, the mean Fe−N(O) distances of 1.659(2) Å in complex **4b** also approach the upper end of 1.650(7) −1.638(3) Å for the neural neutral $\{Fe(NO)_2\}^{10}$ DNICs.[8c] The Fe−C bond distances [1.960(3) and 1.976(3) Å] of complex **4** are slightly longer than those found in $[(\mu\text{-SR})(\mu\text{-CO})Fe_2(CO)_6]^{-1}$ (R = $C_6H_2Me_3$) [1.927(7) and 1.925 Å], and the C═O bond distance of 1.156(3) Å for the bridged carbonyl of **4b** is shorter than that of $[(\mu\text{-SR})(\mu\text{-CO})Fe_2(CO)_6]^{-1}$ (R = $C_6H_2Me_3$) [1.208(7) Å].[14] The re-formation of complex **2** upon the addition of NO gas into complex **4b** demonstrated that the CO-bridging ligand of complex **4b** is labile (Scheme 1d).

Here, we demonstrate the interconversion of $[\{Fe(NO)_2\}^9\text{-}\{Fe(NO)_2\}^9]$, $[\{Fe(NO)_2\}^9\text{-}\{Fe(NO)_2\}^{10}]$, $[\{Fe(NO)_2\}^{10}\text{-}\{Fe(NO)_2\}^{10}]$, and $[\{Fe(NO)_2\}^{10}]$ DNICs. The first anionic dinuclear $[\{Fe(NO)_2\}^{10}\text{-}\{Fe(NO)_2\}^{10}]$ complex **4** adapts CO, a π acceptor, as a bridging ligand. The chemical properties as well as potential pharmaceutical applications of these complexes are currently being investigated in our laboratory.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structural determination of **2**−**4**, experimental details, UV−vis, IR, and ^1H NMR spectra, crystallographic data and refinement parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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