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Homodinuclear Iron Thiolate Nitrosyl Compounds $[(ON)Fe(S,S\text{-}C_6H_4)_2Fe(NO)_2]^-$ and $[(ON)Fe(SO_2,S\text{-}C_6H_4)(S,S\text{-}C_6H_4)Fe(NO)_2]^-$ with $\{Fe(NO)\}^7$–$\{Fe(NO)_2\}^9$ Electronic Coupling: New Members of a Class of Dinitrosyl Iron Complexes

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Reaction of $Fe(CO)_2(NO)_2$ and $[(ON)Fe(S,S\text{-}C_6H_3R)_2]^-$ (R = H (**1**), CH_3 (**1-Me**))/$[(ON)Fe(SO_2,S\text{-}C_6H_4)(S,S\text{-}C_6H_4)]^-$ (**4**) in THF afforded the diiron thiolate/sulfinate nitrosyl complexes $[(ON)Fe(S,S\text{-}C_6H_3R)_2Fe(NO)_2]^-$ (R = H (**2**), CH_3 (**2-Me**)) and $[(ON)Fe(S,SO_2\text{-}C_6H_4)(S,S\text{-}C_6H_4)Fe(NO)_2]^-$ (**3**), respectively. The average N–O bond lengths ([Fe-$(NO)_2$] unit) of 1.167(3) and 1.162(4) Å in complexes **2** and **3** are consistent with the average N–O bond length of 1.165 Å observed in the other structurally characterized dinitrosyl iron complexes with an $\{Fe(NO)_2\}^9$ core. The lower $\nu(^{15}NO)$ value (1682 cm^{-1} (KBr)) of the $[(^{15}NO)FeS_4]$ fragment of $[(^{15}NO)Fe(S,S\text{-}C_6H_3CH_3)_2Fe(NO)_2]^-$ (**2-Me-*15N***), compared to that of $[(^{15}NO)Fe(S,S\text{-}C_6H_3CH_3)_2]^-$ (**1-Me-*15N***) (1727 cm^{-1} (KBr)), implicates the electron transfer from $\{Fe(NO)_2\}^{10}$ $Fe(CO)_2(NO)_2$ to complex **1-Me**/**1** may occur in the process of formation of complex **2-Me**/**2**. Then, the electronic structures of the $[(NO)FeS_4]$ and $[S_2Fe(NO)_2]$ cores of complexes **2**, **2-Me**, and **3** were best assigned according to the Feltham–Enemark notation as the $\{Fe(NO)\}^7$–$\{Fe(NO)_2\}^9$ coupling (antiferromagnetic interaction with a *J* value of –182 cm^{-1} for complex **2**) to account for the absence of paramagnetism (SQUID) and the EPR signal. On the basis of Fe–N(O) and N–O bond distances, the dinitrosyliron $\{L_2Fe(NO)_2\}$ derivatives having an Fe–N(O) distance of ∼1.670 Å and a N–O distance of ∼1.165 Å are best assigned as $\{Fe(NO)_2\}^9$ electronic structures, whereas the Fe–N(O) distance of ∼1.650 Å and N–O distance of ∼1.190 Å probably imply an $\{Fe(NO)_2\}^{10}$ electronic structure.

Introduction

Iron sulfur nitrosyl complexes, in particular the dinitrosyliron compounds (DNICs), have attracted considerable interest stimulated by their structures, functions, and biological activities; e.g. (i) the formation of protein-bound dinitrosyliron complexes was reported in the anaerobic reaction of high-potential iron protein with nitric oxide,[1,2] (ii) DNICs have been suggested as storage and transporters of NO *in vivo* as well as intermediates of iron-catalyzed degradation and formation of *S*-nitrosothiols,[3,4] (iii) activation of SoxR protein, a redox-sensitive transcription activator, in *Escherichia coli* on exposure to macrophage-generated NO has been suggested to occur through nitrosylation of the [2Fe−2S] clusters to form protein-bound dinitrosyliron dithiol adducts,[5] and (iv) DNICs have been identified as endogenous NO carriers.[4]

Existence of the paramagnetic $\{Fe(NO)_2\}^9$ DNICs $[(RS)_2Fe(NO)_2]^-$ is generally characterized by an isotopic EPR

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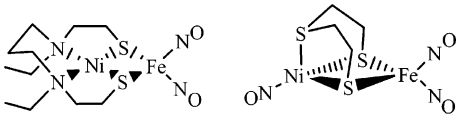
signal of $g = 2.03$.[1−5] The oxidation level of the $\{Fe(NO)_2\}$ unit in the paramagnetic $\{Fe(NO)_2\}^9$ DNICs was verified, recently, in a study of the photochemistry of the dinitrosyliron complex $[S_5Fe(NO)_2]^-$ leading to reversible formation of $[S_5Fe(\mu\text{-}S)_2FeS_5]^{2-}$.[6] DFT calculations, magnetic susceptibility measurements, EPR, and Fe K/L-edge XAS suggest the electronic structure of the $\{Fe(NO)_2\}$ core of the complex $[S_5Fe(NO)_2]^-$ is better described as $\{Fe^+(^\bullet NO)_2\}^9$ than as $\{Fe^-(NO^+)_2\}$.[9] Rhombic EPR signals ($g_z = 2.0148$, $g_x = 2.0270$, and $g_y = 2.0485$) at 77 K confirmed the existence of the unpaired electron in $[S_5Fe(NO)_2]^-$.[6] In contrast, the neutral diamagnetic $\{Fe(NO)_2\}^{10}$ DNICs $[L_2Fe(NO)_2]$ are stabilized by neutral donor ligands such as L = PPh_3, CO, and N-containing ligands.[4]

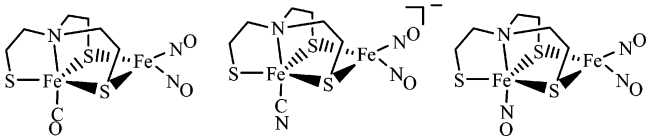
Two heterobimetallic nickel−iron thiolate nitrosyl complexes containing a dinitrosyliron $\{Fe(NO)_2\}^{10}/\{Fe(NO)_2\}^9$ motif, $[Ni^{II}(\mu\text{-}S(CH_2)_2N(Et)(CH_2)_3N(Et)(CH_2)_2S)Fe(NO)_2]$ (**A**)[7] and $[(NO)Ni^0(\mu\text{-}S(CH_2)_2S(CH_2)_2S)Fe(NO)_2]$ (**B**),[8] were



(A) (B)

reported. Complexes **A** and **B** with Ni−Fe distances of 2.797(1) and 2.8001(6) Å, respectively, may be viewed as mononuclear $Fe(NO)_2$ units with thiolate ligands modified by distal metal interactions. The distal Ni^{II} metal of complex **A** creates neutral sulfur donor sites and stabilizes the electron-rich or -reduced form $\{Fe(NO)_2\}^{10}$, as does CO or PR_3 in the neutral DNICs $[L_2Fe(NO)_2]$.[9] The $\{Ni^0NO^+\}$ unit of complex **B** effectively generates a monoanionic dithiolate ligand donor set, which stabilizes the oxidized form $\{Fe(NO)_2\}^9$. The different oxidation levels of the $\{Fe(NO)_2\}^n$ unit in **A** and **B** also reflect the distinctly different hinge angles of the $Ni(\mu\text{-}SR)_2Fe$ unit, 104.6° for complex **A** and 162.8° for complex **B**.[7,8]

Additionally, diiron thiolate nitrosyl complexes $[Fe(NO)_2\{Fe(NS_3)(CO)\}]$ (**C**), $[Fe(NO)_2\{Fe(NS_3)(CN)\}]^-$ (**D**), and $[Fe(NO)_2\{Fe(NS_3)(NO)\}]$ (**E**) ($NS_3 = [N(CH_2CH_2S)_3]^{3-}$),



(C) (D) (E)

containing an $Fe(NO)_2$ motif and a CO/CN/NO ligand occupying the axial position of a trigonal bipyramidal Fe center, were also reported.[10] It is proposed that the oxidation state of the iron of the $Fe(NS_3)$ motif in complexes **C**, **D**, and **E** is essentially unchanged upon its ligation to the $Fe(NO)_2$ motif, and the oxidation state of the iron of the $Fe(NS_3)$ motif is Fe(II) in complexes **C** and **D** and Fe(III) in complex **E**.[10] Here the metal nitrosyl unit is generally designated as $\{M(NO)_x\}^n$ (M = transition metal).[11] This formalism $\{M(NO)_x\}^n$ invokes the Enemark−Feltham notation, which stresses the well-known covalency and delocalization in the electronically amorphous $M(NO)_x$ unit,[11] without committing to a formal oxidation state on M, that is, assignments to $M^{II}(NO^-)_2$, $M^0(^\bullet NO)_2$, $M^{II-}(NO^+)_2$, or some mixture thereof.

Despite a large number of mononuclear/tetranuclear iron thiolate nitrosyl complexes,[10,12,13] examples of dinuclear iron thiolate complexes containing an $\{Fe(NO)_2\}$ motif are limited.[10,13] To gain understanding of the physical and chemical properties of dinitrosyliron complexes and mimic the metalloprotein-bound DNICs,[1a] we have prepared complexes $[(ON)Fe(\mu\text{-}S,S\text{-}C_6H_3R)_2Fe(NO)_2]^-$ (R = H (**2**), CH_3 (**2-Me**)) and $[(ON)Fe(S,SO_2\text{-}C_6H_4)(S,S\text{-}C_6H_4)Fe(NO)_2]^-$ (**3**). The isolated crystals of complexes **2**, **2-Me**, and **3** were characterized by IR, NMR, UV/vis, X-ray diffraction, EPR, and magnetic susceptibility measurements.

Results and Discussion

In contrast to NO binding to the $[(C_4H_8O)Fe(S,S\text{-}C_6H_4)_2]^-$, leading to the formation of $[Fe(NO)(S,S\text{-}C_6H_4)_2]^-$,[14] the dark red-brown $[Fe(NO)(S,S\text{-}C_6H_3R)_2]^-$ (R = H (**1**), CH_3 (**1-Me**)) were prepared, alternatively, by reaction of 1,2-benzenedithiol (or toluene-3,4-dithiol, 0.8 mmol) and $[Fe(CO)_3(NO)]^-$ (0.4 mmol) in THF. Complexes **1** and **1-Me** are thermally stable and soluble in CH_2Cl_2, THF, and CH_3CN. Diamagnetism of the magnetic measurements of complex **1**/**1-Me** is in accord with the ^1H NMR spectrum, which displays the expected signals (δ 6.87 (m), 7.65 (m) ppm ($CDCl_3$) for complex **1**) for the $[S,S\text{-}C_6H_4]^{2-}$ ligands. The reversibility of the NO ligand lability of complex **1-Me** was demonstrated by exposing the THF solution of $[(^{15}NO)Fe(S,S\text{-}C_6H_3CH_3)_2]^-$ to a NO atmosphere. The IR ν_{NO} peak at 1727 cm^{-1} shifted to a single absorbance at 1763 cm^{-1} (KBr).

As shown in Scheme 1a, diiron thiolate nitrosyl complexes $[PPN][(NO)Fe(S,S\text{-}C_6H_3R)_2Fe(NO)_2]$ (R = H (**2**), CH_3 (**2-Me**)) were synthesized in a single step by treating $Fe(CO)_2(NO)_2$ with complex **1**/**1-Me** in THF under a N_2 atmosphere at 10 °C. Complex **2**, soluble in THF, CH_2Cl_2, and CH_3CN, was isolated as a dark green solid. The IR spectrum of complex **2** in the aprotic solvent THF reveals three ν(NO) absorption bands at 1766 sh, 1746 vs, and 1719 s cm^{-1}.

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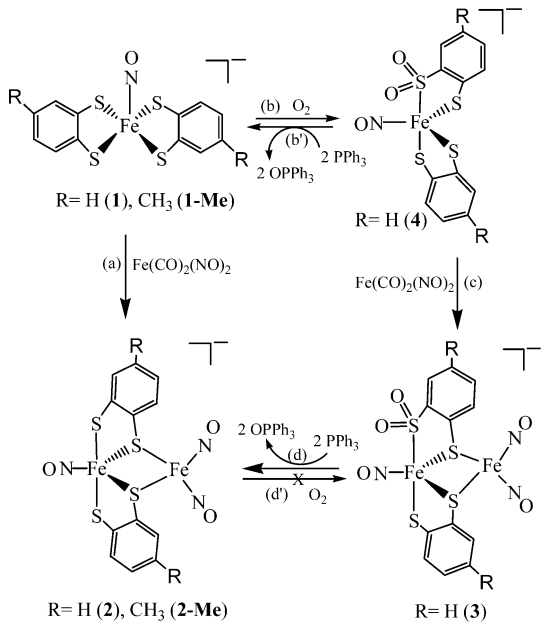
Scheme 1



Complex **2** exhibits a diagnostic ^{1}H NMR spectrum with resonances at δ 6.72−6.75 (m) and 7.44−7.62 (m) ppm ($CDCl_3$). On the basis of ^{1}H NMR, EPR, and magnetic measurements, complex **2** is characterized as a diamagnetic species.

Figure 1 displays a thermal ellipsoid plot of the anionic complex **2**, and selected bond distances and angles are given in Table 1. The geometry of Fe(1) of complex **2** is trigonal bipyramidal ([Fe(NO)$(S)_4$] core) with a NO ligand occupying the equatorial position (N(1)−Fe(1)−S(4) = 121.67(8)°, N(1)−Fe(1)−S(2) = 128.58(8)°, and S(4)−Fe(1)−S(2) = 109.75(3)°), while N(3)−Fe(2)−N(2) = 119.80(13)°, N(2)−Fe(2)−S(2) = 107.69(10)°, and S(4)−Fe(2)−S(2) = 106.06(3)° are consistent with the nearly regular tetrahedral coordination environment about Fe(2). In contrast to the distorted square pyramidal complex **1** with a S_4 base and an apical NO group,[14] the geometry of Fe(1) in complex **2** is disturbed by the coordination of an additional [Fe$(NO)_2$] unit

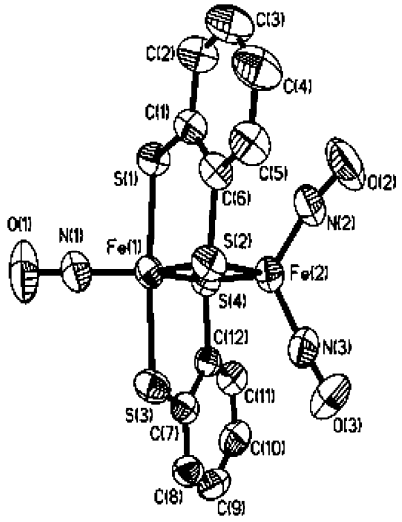


Figure 1. ORTEP drawing and labeling scheme of [(NO)Fe(S,S-$C_6H_4)_2$-Fe$(NO)_2]^-$.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes **2** and **3**

Complex **2**			
Fe(1)−N(1)	1.632(3)	Fe(1)−S(2)	2.2466(7)
Fe(1)−S(3)	2.3001(8)	Fe(1)−S(4)	2.2352(7)
Fe(1)−S(1)	2.2935(7)	Fe(1)−Fe(2)	2.6688(5)
Fe(2)N(3)	1.660(3)	Fe(2)−N(2)	1.661(3)
Fe(2)−S(4)	2.2860(7)	Fe(2)−S(2)	2.3019(8)
N(1)−O(1)	1.167(3)	N(2)−O(2)	1.168(3)
N(3)−O(3)	1.167(3)		
N(1)−Fe(1)−S(4)	121.67(8)	S(4)−Fe(1)−S(2)	109.75(3)
S(4)−Fe(1)−S(1)	89.39(3)	S(4)−Fe(1)−S(3)	88.64(3)
S(1)−Fe(1)−S(3)	175.72(3)	N(1)−Fe(1)−Fe(2)	176.38(8)
N(2)−Fe(2)−N(3)	119.80(13)	N(2)−Fe(2)−S(4)	108.97(9)
N(2)−Fe(2)−S(2)	107.69(10)	N(1)−Fe(1)−S(2)	128.58(8)
S(4)−Fe(2)−S(2)	106.06(3)	O(1)−N(1)−Fe(1)	178.2(3)
O(3)−N(3)−Fe(2)	172.2(3)	O(2)−N(2)−Fe(2)	169.2(3)
Fe(1)−S(2)−Fe(2)	71.84(2)		
Complex **3**			
Fe(1)−N(1)	1.641(3)	Fe(1)−S(2)	2.2272(9)
Fe(1)−S(3)	2.2929(11)	Fe(1)−S(4)	2.2318(9)
Fe(1)−S(1)	2.2630(10)	Fe(1)−Fe(2)	2.6482(7)
Fe(2)−N(3)	1.672(3)	Fe(2)−N(2)	1.671(3)
Fe(2)−S(4)	2.3005(10)	Fe(2)−S(2)	2.2728(10)
N(1)−O(1)	1.169(4)	N(2)−O(2)	1.160(4)
N(3)−O(3)	1.164(4)	S(1)−O(4)	1.459(3)
S(1)−O(5)	1.463(3)		
N(1)−Fe(1)−S(4)	130.49(11)	N(1)−Fe(1)−S(2)	119.30(11)
S(4)−Fe(1)−S(2)	110.20(4)	S(4)−Fe(1)−S(1)	89.97(3)
S(4)−Fe(1)−S(3)	88.80(3)	S(1)−Fe(1)−S(3)	177.81(4)
N(1)−Fe(1)−Fe(2)	174.05(11)	N(2)−Fe(2)−N(3)	121.12(16)
N(2)−Fe(2)−S(4)	108.41(12)	N(2)−Fe(2)−S(2)	103.28(11)
S(4)−Fe(2)−S(2)	106.19(4)	O(1)−N(1)−Fe(1)	178.4(3)
O(3)−N(3)−Fe(2)	169.7(4)	O(2)−N(2)−Fe(2)	173.4(3)
Fe(1)−S(2)−Fe(2)	72.09(3)		

to become trigonal bipyramidal. Such a geometrical change of the Fe(1) center from complex **1** to **2** may be accompanied by an electronic rearrangement resulting from a short Fe(1)···Fe(2) distance character (Fe(1)···Fe(2) distance of 2.6688(5) Å) and two bridging thiolate ligands.[15] Ligand displacement resulting in the formation of complex **1** and {Fe$(NO)_2$}^{10} $(PPh_3)_2$Fe$(NO)_2$ was not observed when complex **2** was stirred with 2 equiv of PPh_3 in THF at room temperature for two weeks.[9] In contrast, reaction of complex **2** and 2 equiv of [PPN][SPh] in THF solution at room temperature yielded the known {Fe$(NO)_2$}^{9} [$(PhS)_2$Fe$(NO)_2]^-$[8] and {Fe(NO)}^{7} [(NO)Fe(S,S-$C_6H_4)_2]^{2-}$,[16] which were characterized by IR, UV−vis, and X-ray single-crystal diffraction. On the basis of a recent study on the electronic structure of the {Fe$(NO)_2$}^{9} core of dinitrosyliron complex [S_5Fe$(NO)_2]^-$,[6] and the reported qualitative MO energy level orderings for the five-coordinate {Fe(NO)}^{7} metal nitrosyl structure types (square pyramidal with bent apical NO, trigonal bipyramidal with linear equatorial NO, and trigonal bipyramidal with linear axial NO),[15] the oxidation levels of the [S_2Fe$(NO)_2$] and [(NO)FeS_4] motifs of complex **2** may be assigned. For a five-coordinate metal nitrosyl complex, computational studies have suggested that a geometrical change from square pyramidal to trigonal bipyramidal with linear equatorial NO may occur upon changing from an {Fe(NO)}^{6} to an {Fe(NO)}^{7} electronic structure.[15] Assignment to the oxidation

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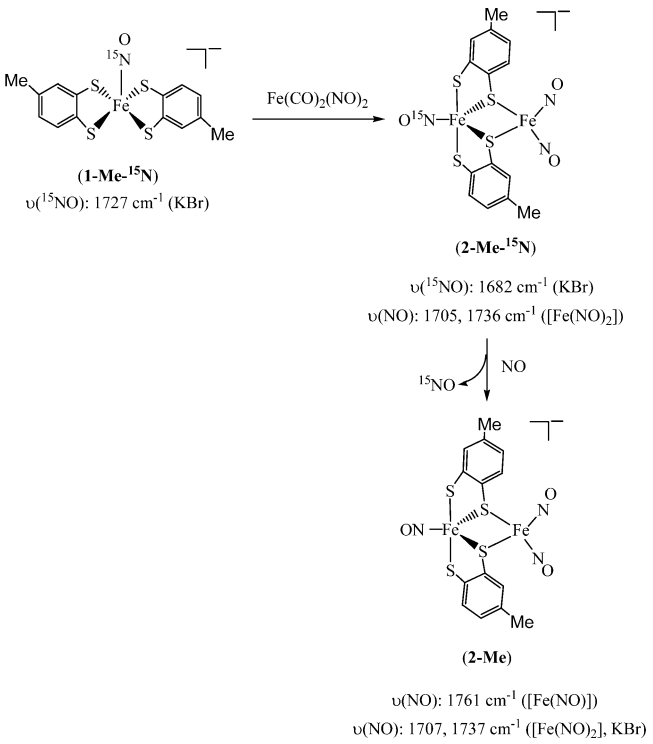
levels of two Fe atoms of complex **2**/**2-Me** would, then, have to invoke electronic coupling of the $\{Fe(NO)_2\}^9$ $[S_2Fe(NO)_2]$ and the $\{Fe(NO)\}^7$ $[(NO)FeS_4]$ centers to account for the diamagnetism and the EPR silence in complex **2**/**2-Me**, although we cannot unambiguously rule out the possibility that the dimer formation (complexes **2** and **2-Me**) may simply involve partial charge delocalization around the diamond-shaped, planar $[FeS_2Fe]$ core in complex **2**/**2-Me**. The electronic configurations of the $\{Fe(NO)\}^7$ and $\{Fe(NO)_2\}^9$ centers are, therefore, best assigned as $\{Fe^+(NO^+)\}^7$ and $\{Fe^+(^{\bullet}NO)_2\}$,[9] respectively. Both centers have $S = 1/2$ spins that magnetically couple to each other possibly via the pathway of direct d−d orbital overlap (Fe···Fe = 2.6688(5) Å) and the bridging sulfurs.[17] The relatively strong magnetic interaction ($J = -182$ cm^{-1}) leads to the ground state $S_T = 0$.[17]

Presumably, complex **2** was produced upon substitution of two carbonyls of $Fe(CO)_2(NO)_2$ by thiolate ligands of complex **1** accompanied by electron transfer from the $\{Fe(NO)_2\}^{10}$ $[Fe(NO)_2]$ unit of $[Fe(CO)_2(NO)_2]$ to $\{Fe(NO)\}^6$ complex **1**. The proposed electron-donating/accepting process between $[Fe(2)(NO)_2]$ and $[(NO)Fe(1)S_4]$ units in the formation of complex **2** is also reflected in the ν_{NO} values. On treatment of $[(^{15}NO)Fe(S,S\text{-}C_6H_3CH_3)_2]^-$ (**1-Me-^{15}*N***) with 1 equiv of $Fe(CO)_2(NO)_2$ in THF, the reaction mixture led to the formation of the dinuclear $[(^{15}NO)Fe(S,S\text{-}C_6H_3CH_3)_2\text{-}Fe(NO)_2]^-$ (**2-Me-^{15}*N***) showing three ν_{NO} infrared bands (1682 m, 1705 s, 1736 vs cm^{-1} (KBr)). Known to serve as a reporter of electron density at iron similarly to CO,[18a] the lower $\nu(^{15}NO)$ value (1682 cm^{-1} (KBr)) of the $[(^{15}NO)FeS_4]$ fragment of **2-Me-^{15}*N***, compared to that of **1-Me-^{15}*N*** (1727 cm^{-1} (KBr)), would then imply that the $[(^{15}NO)FeS_4]$ unit of **2-Me-^{15}*N*** is substantially reduced. That is, the $\{Fe(NO)_2\}^{10}$ $[Fe(NO)_2]$ unit of $Fe(CO)_2(NO)_2$ acts as a donor motif of −1 charge to **1-Me-^{15}*N*** in the process of formation of complex **2-Me-^{15}*N***. When a THF solution of complex **2-Me-^{15}*N*** is purged with NO, the IR ν_{NO} peaks (1682 m, 1705 s, 1736 vs cm^{-1}) shift to 1707 s, 1737 vs, and 1761 m cm^{-1} (KBr), consistent with the formation of complex **2-Me** (Scheme 2). The magnitude ∼55 cm^{-1} of the isotopic shift ($\Delta\nu_{NO}$) is consistent with the calculated position, on the basis only of the difference in masses between ^{14}NO and ^{15}NO.

The Fe−N(1) distance of 1.599(2) Å in complex **1** is significantly shorter than those of $\{Fe(NO)\}^7$ $[Fe(NO)(S_2CNMe_2)_2]$ (Fe−N = 1.705(16) Å)[18b] and $\{Fe(NO)\}^8$ $[Fe(NO)(S_2C_2O_2)_2]^{2-}$ (Fe−N = 1.690(2) Å).[19] The shorter Fe−S bond distances of 2.226(11) Å (average) in complex **1**, compared with the reported Fe−S bond length of 2.294(2) Å in $[Fe(NO)(S_2CNMe_2)_2]$,[18b] are attributed to the strong π-donating ability of the bidentate $[S,S\text{-}C_6H_4]^{2-}$ ligands.[20]

Scheme 2



Comparable to the shorter Fe−S (average 2.226(1) Å) and Fe−N(O) (1.599(2) Å) bond distances of complex **1**, the Fe(1)−S (average 2.2689(8) Å) and Fe(1)−N(1) (1.632(3) Å) bond distances of complex **2** are disturbed by the coordination of an additional $[Fe(NO)_2]$ unit. The Fe(1)−$S_{bridging}$ bond length (average 2.2409(7) Å, Fe(1)−S(2) = 2.2466(7) Å and Fe(1)−S(4) = 2.2352(7) Å) is shorter than that of Fe(1)−$S_{terminal}$ (average 2.2968(8) Å, Fe(1)−S(3) = 2.3001(8) Å and Fe(1)−S(1) = 2.2935(7) Å). The average Fe(2)−NO bond distance ($[Fe(NO)_2]$ unit) of 1.661(3) Å (Fe(2)−N(3) = 1.660(3) Å and Fe(2)−N(2) = 1.661(3) Å) in complex **2** is within the ranges observed for other structurally characterized $\{Fe(NO)_2\}^9$ complexes **B** (average Fe−N(O) = 1.672(3) Å),[7] $[(NO)_2Fe(SePh)_2]^-$ (average Fe−N(O) = 1.669(4) Å),[8] and $[(NO)_2FeS_5]^-$ (average Fe−N(O) = 1.678(3) Å),[6] but significantly longer than the Fe−N(O) bond distances of 1.652(3) and 1.650(7) Å found in $\{Fe(NO)_2\}^{10}$ complexes **A** and $(PPh_3)_2Fe(NO)_2$, respectively.[7,9] The Fe(1)−N(1) bond length of 1.632(3) Å in complex **2** is shorter than the Fe−NO bond distance (1.670(4) Å) found in [(NO)Fe(TC-5,5)].[21]

The ligand-modified analogue $[(ON)Fe(S,SO_2\text{-}C_6H_4)(S,S\text{-}C_6H_4)]^-$ (**4**) is also expected to promote the formation of the diiron sulfinate nitrosyl complex (Scheme 1b). To corroborate this interpretation, we treated a THF solution of complex **4** with 1 equiv of $Fe(CO)_2(NO)_2$ at 10 °C (Scheme 1c).[14] The IR ν_{NO} stretching frequencies (1726 s, 1762 s, 1783 m cm^{-1} (KBr)), UV−vis data, and X-ray structural study are consistent with the formation of $[(ON)Fe(S,SO_2\text{-}C_6H_4)(S,S\text{-}C_6H_4)Fe(NO)_2]^-$ (**3**). The higher ν_{NO} values of **3** versus **2** would then imply that the S-bonded monosulfinate substantially "neutralizes" the thiolate negative charge of

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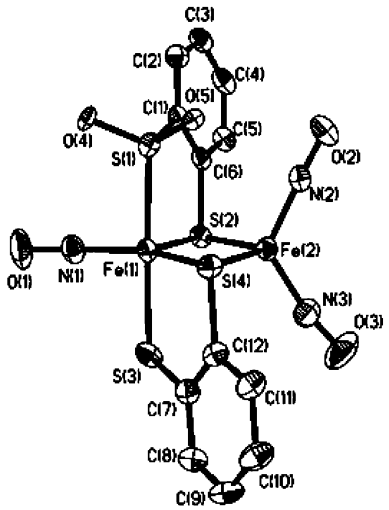

Figure 2. ORTEP drawing and labeling scheme of $[(ON)Fe(S,SO_2\text{-}C_6H_4)\text{-}(S,S\text{-}C_6H_4)Fe(NO)_2]^-$.

complex **4**, and donates slightly less electron density to the $\{Fe(NO)_2\}^9$ unit as compared to the two dithiolate donors of complex **2**. The ^{1}H NMR spectrum of complex **3** shows the expected signals for the 1,2-benzenedithiolate and -sulfinate groups involved and displays characteristics of diamagnetic species. As observed in complex **2**, the EPR and magnetic measurements of complex **3** also suggest the diamagnetism. Instead of formation of complex **4** and $\{Fe(NO)_2\}^{10}$ $(PPh_3)_2Fe(NO)_2$,[9] the S-bonded monosulfinate complex **3** undergoes oxygen-transfer reaction in THF solution with 2 equiv of PPh_3 (expected to be an O atom abstracting agent) over the course of 90 min at 50 °C to yield complex **2** and triphenylphosphine oxide identified by ^{31}P NMR spectroscopy (Scheme 1d).[22] This study also shows that complex **2** does not initiate O_2 activation to yield iron sulfinate complex **3** identified by IR spectra; complexes **1** and **4** and an insoluble solid were isolated instead.

The structure of complex **3** is presented in Figure 2. Analysis of the bond angles of complex **3** reveals that Fe(1) is best described as existing in a distorted trigonal bipyramidal coordination environment with NO and sulfinate groups occupying equatorial and axial positions, respectively. Distorted tetrahedral geometry is adopted in Fe(2). Consistent with other published transition-metal sulfinate complexes,[23] the S−O bond lengths average ca. 1.461(3) Å. The relief of the antibonding character from the Fe dπ/S pπ overlap overwhelming the S-donating ability from thiolate to sulfinate may rationalize the observed shortening (Δ(Fe−S) = 0.03 Å) of the Fe−S(O_2) bond length in complex **3**.[23] Presumably, the change in Fe(1)−Fe(2) distance (2.6625(2) Å for **2** and 2.6482(7) Å for **3**) is undoubtedly caused by electronic perturbations from the sulfur oxygenation. The shorter Fe(1)−Fe(2) distance of 2.6482(7) Å in complex **3** further implies an electronic interaction between the two metal centers, and an assignment of $\{Fe(NO)\}^7$−$\{Fe(NO)_2\}^9$ coupling would be realistic. The average N−O bond lengths ($[Fe(NO)_2]$ unit) of 1.167(3) and 1.162(4) Å in complexes **2** and **3**, respectively, are comparable to those of the other structurally characterized $\{Fe(NO)_2\}^9$ complexes **B** (average N−O = 1.161(3) Å),[7] $[(NO)_2Fe(SePh)_2]^-$ (average N−O = 1.162(5) Å),[8] and $[(NO)_2FeS_5]^-$ (average N−O = 1.177(3) Å),[6] but significantly shorter than the N−O bond lengths of 1.190(7) and 1.190(10) Å (average) observed in $\{Fe(NO)_2\}^{10}$ complexes **A** and $(PPh_3)_2Fe(NO)_2$, respectively.[7,9] Consistent with the observation in complex **B**, the hinge angle of the Fe(μ-SR)$_2$Fe unit, 178.9° for **2** and 178° for **3**, also supports a $[(NO)FeS_4]^-/[(NO)FeS_3(SO_2)]^-$ moiety bound by an $\{Fe(NO)_2\}^9$ unit.[8]

Conclusion and Comments

Studies on the dinuclear iron thiolate nitrosyl complexes **2**/**2-Me** and **3** have led to the following results.

(1) Dinuclear iron thiolate/sulfinate nitrosyl complexes **2**/**2-Me** and **3** stabilized by $\{Fe(1)(NO)\}^7$−$\{Fe(2)(NO)_2\}^9$ coupling were synthesized and characterized by IR, UV−vis, ^{1}H NMR, and X-ray single-crystal diffraction. The magnetic coupling between the $\{Fe(NO)\}^7$ and $\{Fe(NO)_2\}^9$ centers (J value of -182 cm^{-1} in complex **2**) is responsible for the absence of paramagnetism (SQUID) and the EPR signal in complexes **2**/**2-Me** and **3**.

(2) The roughly planar structure in the $[FeS_2Fe]$ core of complexes **2** and **3** (hinge angles 178.9° and 178°, respectively) also supports that complex **2**/**3** is best described as a $[(NO)FeS_4]/[(NO)FeS_3(SO_2)]$ moiety bound by an interacting $\{Fe(NO)_2\}^9$ unit, respectively.

(3) In contrast to the distorted square pyramidal complex **1**/**1-Me** with a S_4 base and an apical NO group,[14] the geometry of Fe(1) in complex **2** becomes trigonal bipyramidal upon complex **1** being coordinated by an additional $[Fe(NO)_2]$ unit.

(4) For the formation mechanism of complex **2**/**3**, the isotopic experiments imply that the $\{Fe(NO)_2\}^{10}$ $[Fe(NO)_2]$ unit of $Fe(CO)_2(NO)_2$ acts as a donor motif of -1 charge to complex **1**/**4** to yield the stable diiron thiolate/sulfinate nitrosyl complex **2**/**3** containing an $\{Fe(NO)_2\}^9$ motif, respectively.

(5) From the viewpoint of the Fe−N(O) and N−O bond distances, the dinitrosyliron $\{Fe(NO)_2\}$ derivatives having an Fe−N(O) distance of ∼1.670 Å and a N−O distance of ∼1.165 Å are best assigned as $\{Fe(NO)_2\}^9$ electronic structures. The much shorter Fe−N(O) distance of ∼1.650 Å and longer N−O distance of ∼1.190 Å probably imply an $\{Fe(NO)_2\}^{10}$ electronic structure.

Isolation and characterization of the dinuclear iron thiolate nitrosyl complexes **2**/**2-Me** and **3** containing a dinitrosyl iron motif may be useful for taking into consideration the formation/existence of the metalloprotein-bound dinitrosyliron complexes in the anaerobic reaction of iron−sulfur protein and nitric oxide.[1−5] Also, the findings in this study imply that the dinitrosyl nonheme iron complexes may exist after biosynthetic evolution of NO *in vitro* and from the

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addition of NO to iron-centered proteins, even without the characteristic isotropic EPR signal of $g = 2.03$.[24]

Experimental Section

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (hexane and tetrahydrofuran (THF) from sodium/benzophenone, diethyl ether and methylene chloride from CaH_2, and acetonitrile from $CaH_2-P_2O_5$) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. Nitrogen was purged through these solvents before use. Solvent was transferred to a reaction vessel via a stainless steel cannula under a positive pressure of N_2. The reagents iron pentacarbonyl, sodium nitrite, toluene-3,4-dithiol, and 1,2-benzenedithiol (Lancaster/Aldrich) were used as received. Compounds [PPN][$Fe(CO)_3(NO)$], $Fe(CO)_2(NO)_2$, and [PPN][(ON)Fe(S,S-C_6H_4)$_2$] were synthesized and characterized by published procedures.[9,14] Infrared spectra of the ν_{NO}/ν_{CO} stretching frequencies were recorded on a Perkin-Elmer model Spectrum One B spectrometer with sealed solution cells (0.1 mm) and KBr windows. ^{1}H NMR spectra were recorded on a Varian Unity-500 spectrometer. GBC Cintra 10e spectrophotometers were used to record the UV−vis spectra of each complex. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of [PPN][(ON)Fe(S,S-$C_6H_3CH_3$)$_2$] (1-Me). Toluene-3,4-dithiol (0.8 mmol, 100 μL) was added to a THF solution (5 mL) of [PPN][$Fe(CO)_3(NO)$] (0.4 mmol, 0.283 g), and the resulting solution was stirred overnight at room temperature in contact with air. The reaction was monitored with FTIR. The IR spectrum (IR (THF): 1785 s (ν_{NO}) cm^{-1}) was assigned to the formation of **1-Me**.[14] The solution was then filtered through Celite, and hexane (15 mL) was added to precipitate the dark red-brown solid **1-Me** (yield 0.3356 g, 90%). Diffusion of hexane into a THF solution of complex **1-Me** at −15 °C for 2 weeks gave dark red-brown crystals suitable for X-ray crystallography. IR (ν_{NO}): 1785 s (THF); 1763 s (KBr) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.20 (s) (CH_3); 6.693 (d), 7.51−7.55 (m) (C_6H_3) ppm. Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 321 (37700), 500 (4200). Anal. Calcd for $C_{50}H_{42}OFeN_2S_4P_2$: C, 64.37; H, 4.54; N, 3.00. Found: C, 64.25; H, 4.19; N, 3.51.

Preparation of [PPN][(ON)Fe(μ-S,S-C_6H_3R)$_2$Fe(NO)$_2$] (R = H (2), CH_3 (2-Me)). Compound **1** (0.5 mmol, 0.452 g) was dissolved in 2 mL of dry THF, and 5 mL of a THF solution of $Fe(CO)_2(NO)_2$ (0.5 mmol) prepared freshly (obtained from reaction of [NO][PF_6] and [PPN][$Fe(CO)_3(NO)$] in THF in a 1:1 ratio)[9] was added to it by cannula under a positive pressure of N_2. The reaction mixture was stirred at 10 °C for 1 h. The solution was then filtered through Celite, and hexane was added to precipitate a green solid. The solid was washed twice with THF−hexane and dried under vacuum. The yield of complex **2** was 0.418 g (80%). X-ray-quality crystals were obtained by diffusion of hexane into a saturated THF solution of complex **2** at −15 °C. The following are data for **2**. IR (ν_{NO}): 1766 sh, 1746 vs, 1719 s (THF); 1768 sh, 1748 s, 1720 s (CH_2Cl_2); 1759 m, 1735 vs, 1715 s (KBr) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.72−6.75 (m), 7.44−7.62 (m) ppm (C_6H_4). Absorption spectrum (CH_2Cl_2) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 313 (46619), 363 (15936), 417 (7557), 623 (3059), 790 (1367). Anal. Calcd for $C_{48}H_{38}O_3N_4P_2S_4Fe_2$: C, 56.48; H, 3.75; N, 5.49. Found: C, 56.29; H, 3.66; N, 5.55. The following are data for **2-Me**. IR (ν_{NO}): 1764 sh, 1745 vs, 1717 s (THF); 1761 m, 1737 vs, 1707 s (KBr) cm^{-1}.

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Table 2. Crystallographic Data of Complexes **2** and **3**

	2	**3**
empirical formula	$C_{48}H_{38}Fe_2N_4O_3P_2S_4$	$C_{48}H_{38}Fe_2N_4O_5P_2S_4$
fw	1020.70	1052.70
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
λ, Å (Mo Kα)	0.71073	0.71073
a, Å	10.3579(4)	10.2033(4)
b, Å	24.8932(11)	25.0154(9)
c, Å	18.2655(8)	18.2842(6)
α, deg	90	90
β, deg	93.8840(10)	91.941(1)
γ, deg	90	90
V, Å^3	4698.8(3)	4664.2(3)
Z	4	4
d_{calcd}, g cm^{-3}	1.443	1.499
μ, mm^{-1}	0.909	0.921
T, K	150(2)	150(1)
R	0.0369[a]	0.0615[a]
R_w	0.1015[b]	0.1334[b]
GOF	0.749	1.276

[a] $R = \sum|(F_o - F_c)|/\sum F_o$. [b] $R_w = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$.

^{1}H NMR ($CDCl_3$): δ 2.088 (s), 2.117 (s) (CH_3); 6.518−6.543 (m), 7.579−7.635 (m) (C_6H_3) ppm. Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 370 (10465), 427 (5266), 590 (2038), 650 (2129), 793 (1160). Anal. Calcd for $C_{50}H_{42}O_3N_4P_2S_4Fe_2$: C, 57.26; H, 4.04; N, 5.34. Found: C, 57.66; H, 4.38; N, 4.85.

The analogous [^{15}N]nitrosyl complexes **1-Me-^{15}N** and **2-Me-^{15}N** were prepared as above using enriched [PPN][$^{15}NO_2$] to prepare the starting material [PPN][$Fe(CO)_3(^{15}NO)$].

Preparation of [PPN][(ON)Fe(S,SO_2-C_6H_4)(S,S-C_6H_4)Fe(NO)$_2$] (3). Compound [PPN][(ON)Fe(S,SO_2-C_6H_4)(S,S-C_6H_4)] (0.2 mmol, 0.187 g) was dissolved in 2 mL of dry THF in a 25 mL Schlenk tube, 5 mL of a THF solution of $Fe(CO)_2(NO)_2$ (0.2 mmol) prepared freshly was added to it by cannula under a positive pressure of N_2, and the resulting solution was stirred at 10 °C for 1 h.[14] The solution was then filtered through Celite, and hexane was added to precipitate a green solid. The solid was washed twice with THF−hexane, and the yield of **3** was 0.150 g (71%). X-ray-quality crystals were obtained by diffusion of hexane−diethyl ether into a saturated CH_2Cl_2 solution of complex **3** at −15 °C. IR: 1783 m, 1762 s, 1726 s (ν_{NO}); 1192 m, 1055 m (ν_{SO}) (KBr); 1790 sh, 1771 s, 1733 m (ν_{NO}) (CH_2Cl_2); 1787 sh, 1768 s, 1733 m (ν_{NO}) (THF) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 6.832 (t), 7.174 (t), 7.252 (t), 7.260 (d), 7.332 (d), 7.722 (d), 7.772 (d) ppm (C_6H_4). Absorption spectrum (CH_2Cl_2) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 305 (33836), 363 (14272), 595 (2113), 717 (1468). Anal. Calcd for $C_{48}H_{38}O_5N_4P_2S_4Fe_2$: C, 54.765; H, 3.64; N, 5.32. Found: C, 54.96; H, 3.49; N, 5.28.

Magnetic Measurements. The magnetic data were recorded on a SQUID magnetometer (MPMS5, Quantum Design) under a 1 T external magnetic field in the temperature range of 2−300 K. The magnetic susceptibility data were corrected with temperature-independent paramagnetism (TIP; 2×10^{-4} cm^3 mol^{-1}) and the ligand diamagnetism by the tabulated Pascal constants. The equation for one J spin-coupled system is derived from the Hamiltonian and Van Vleck's equation. The magnetic coupling constant J of **2** is obtained from the least-squares fit of the magnetic susceptibility data.

Crystallography. Crystallographic data of complexes **2** and **3** are summarized in Table 2. The crystals of **2** and **3** chosen for X-ray single-crystal diffraction studies were measured $0.50 \times 0.50 \times 0.50$ and $0.30 \times 0.25 \times 0.25$ mm, respectively. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. Unit cell parameters were obtained by least-squares refinement. Diffraction measurements for complexes **2** and **3** were carried out at 150(1) K on a SMART CCD diffractometer with graphite-

monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) and θ between 1.38° and 28.31° for complex **2** and between 1.38° and 27.50° for complex **3**. Least-squares refinement of the positional and anisotropic thermal parameters of all non-hydrogen atoms and fixed hydrogen atoms was based on F^2. A SADABS[25] absorption correction was made. The SHELXTL[26] structure refinement program was employed. In the case of complex **3**, the $S(1)O_2$ group (shown in Figure 2) is found at disordered positions (O(4)O(5): O(4′)O(5′) = 1/2:1/2) and was refined by partial occupancies.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of [PPN][(NO)Fe-(S,S-C_6H_4)$_2$Fe(NO)$_2$] and [PPN][(ON)Fe(S,SO_2-C_6H_4)(S,S-C_6H_4)-Fe(NO)$_2$]. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC reference numbers are 235829 and 235830.

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