

New Members of the $\{\text{Fe}(\text{NO})_2\}^{10}$ Dinitrosyliron Complexes Bound with [Thiolate, Thiolate] and [Amide, Amide] Ligations

Jheng-Hong Wang[†] and Chien-Hong Chen^{*,†,‡}

[†]School of Applied Chemistry, Chung Shan Medical University, Taichung City 40201, Taiwan, and

[‡]Department of Medical Research, Chung Shan Medical University Hospital, Taichung City, Taiwan

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The first dianionic $\{\text{Fe}(\text{NO})_2\}^{10}$ dinitrosyliron complexes (DNICs) $[\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^{2-}$ (**1**) and $[\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^{2-}$ (**2**), coordinated with thiolates and amides, were prepared by the reaction of $\text{Fe}(\text{TMEDA})(\text{NO})_2$ with 2 equiv of ligands $[\text{SC}_7\text{H}_4\text{SN}]^-$ and $[\text{OC}_7\text{H}_4\text{SN}]^-$, respectively. The reversible interconversion between the dianionic $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs **1/2** and the anionic $\{\text{Fe}(\text{NO})_2\}^9[\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^-$ (**3**)/ $[\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^-$ (**4**), respectively, was demonstrated. The transformation of DNICs **2** and **3** into the thermally stable DNICs **1** and **4**, respectively, via the ligand-exchange reaction reveals that $[\text{OC}_7\text{H}_4\text{SN}]^-$ shows a high binding affinity toward the $\{\text{Fe}(\text{NO})_2\}^9$ motif and $[\text{SC}_7\text{H}_4\text{SN}]^-$ prefers the $\{\text{Fe}(\text{NO})_2\}^{10}$ motif. This result rationalizes that the intermolecular electron transfer from DNIC **2** to DNIC **3** occurs to lead to the formation of the more thermally stable DNICs **1** and **4** upon the reaction of DNICs **2** and **3** in tetrahydrofuran.

Interest in nitric oxide (NO) derives from its physiological and biological functions in living organisms.¹ In vivo, NO can be stabilized and stored in the two forms protein-bound thionitrosyls ($\text{R}_{\text{protein}}\text{SNO}$) and protein-bound dinitrosyliron complexes (protein-bound DNICs).² The displacement of protein-bound DNICs with free thiols/thiolates yielding low-molecular-weight DNICs (LMW-DNICs) has been suggested.³ In vitro/in vivo, both protein-bound DNICs and LMW-DNICs are possibly identified and characterized by their distinctive electron paramagnetic resonance (EPR) signals at

$g = 2.03$.⁴ In spite of the major thiol components of cellular DNICs composed of cysteine and glutathione in vivo,⁵ DNICs ligated by phenoxide, thiolate, imidazole, and deprotonated imidazole were proposed in enzymology based on EPR spectra.^{3a,6} Recently, the protein-bound DNIC with [S, O] ligation has been well characterized by an X-ray diffraction study via the addition of a dinitrosyldiglutathionyliron complex into human glutathione transferase P1-1 in vitro/in vivo.^{6c} In biomimetic complexes, varieties of DNICs containing S/O/N-donor ligands were synthesized to serve as spectroscopic references.^{7,8} On the basis of the Enemark–Fetham

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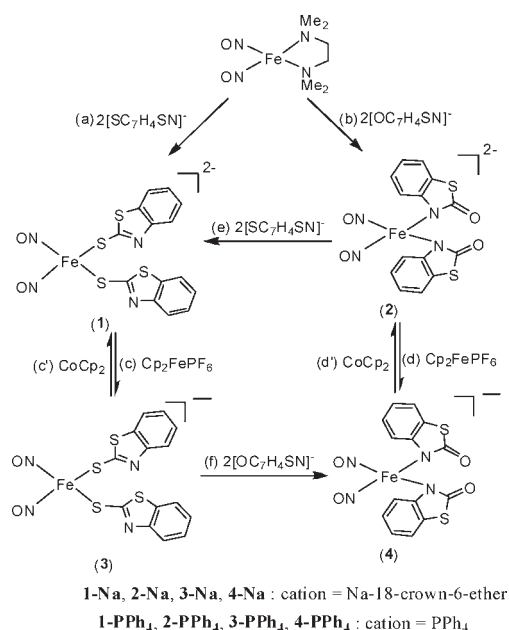
*To whom correspondence should be addressed. E-mail: cchwind@csmu.edu.tw.

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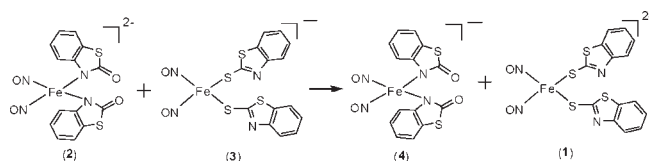
Scheme 1



notation,⁹ these synthesized LMW-DNICs can be classified as the EPR-active $\{\text{Fe}(\text{NO})_2\}^9$ DNICs and the EPR-silent $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs. In spite of a large number of neutral $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs with nitrogen or phosphorus ligands, the dianionic $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs are limited.⁸ Recently, we report the monoanionic sulfur-containing $\{\text{Fe}(\text{NO})_2\}^{10}$ DNIC $[\text{K}-18\text{-crown-6-ether}][\text{Fe}(\text{SC}_6\text{H}_4\text{-}o\text{-NMe}_2)(\text{NO})_2]^-$.¹⁰ In addition to the classical four-coordinate DNICs, the nonclassical DNICs, including the five-coordinate DNICs $[(6\text{-Me}_3\text{-TPA})\text{Fe}(\text{NO})_2]^+$ and $[(\text{TMEDA})\text{Fe}(\text{NO})_2]^+$,^{11,12} and the six-coordinate DNIC $[(1\text{-Melm})_2(\eta^2\text{-ONO})\text{Fe}(\text{NO})_2]^{13} are also structurally characterized. In this contribution, the dianionic $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs with [thiolate, thiolate] and [amide, amide] ligation, $[\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^{2-}$ (1) and $[\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^{2-}$ (2) [cation = Na-18-crown-6-ether (1-Na/2-Na), PPh₄ (1-PPh₄/2-PPh₄)], were delineated. The reversible interconversion among the dianionic $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs 1/2 and the anionic $\{\text{Fe}(\text{NO})_2\}^9$ DNICs $[\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^-$ (3)/ $[\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^-$ (4) [cation = Na-18-crown-6-ether (3-Na/4-Na), PPh₄⁺ (3-PPh₄/4-PPh₄)] was demonstrated. In particular, the different binding affinities of $[\text{OC}_7\text{H}_4\text{SN}]^-$ versus $[\text{SC}_7\text{H}_4\text{SN}]^-$ toward the $\{\text{Fe}(\text{NO})_2\}^9/\{\text{Fe}(\text{NO})_2\}^{10}$ motif were studied.$

The reaction of $\text{Fe}(\text{TMEDA})(\text{NO})_2$ with 2 equiv of $[\text{SC}_7\text{H}_4\text{SN}]^-$ and $[\text{OC}_7\text{H}_4\text{SN}]^-$ yielded DNICs 1 and 2 characterized by single-crystal X-ray diffraction, IR, and UV/vis spectra, respectively (Scheme 1a,b). DNICs 1 and 2 display the EPR-silent $\{\text{Fe}(\text{NO})_2\}^{10}$ electronic structures with [thiolate, thiolate]/[amide, amide] ligation mode. Compared to the other $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs, 1-PPh₄ is the first example of the dianionic mononuclear $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs coordinated with two thiolate ligands.

Scheme 2



Upon the addition of Cp_2FePF_6 into the CH_3CN solution of DNICs 1 and 2 in a 1:1 stoichiometry, respectively (Scheme 1c,d), oxidation ensued over the course of 5 h to yield the $\{\text{Fe}(\text{NO})_2\}^9$ DNICs 3 and 4, respectively, identified by EPR and IR spectra. In contrast to ligand-centered oxidation of the thiolate-containing $\{\text{Fe}(\text{NO})_2\}^9$ DNICs resulting in dimeric $\{\text{Fe}(\text{NO})_2\}^9-\{\text{Fe}(\text{NO})_2\}^9$ Roussin's red esters (RREs),^{7c,f} the isolation of DNIC 3 may reveal that oxidation of the thiolate-containing $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs is a metal-centered process.

In cyclic voltammograms of 3-PPh₄ and 4-PPh₄, the quasi-reversible one-electron reductions at -0.94 and -1.17 V ($E_{1/2}$ vs Fc^+/Fc), respectively, in CH_3CN are observed and assigned to the $\{\text{Fe}(\text{NO})_2\}^9-\{\text{Fe}(\text{NO})_2\}^{10}$ couple (Figure S1 in the Supporting Information). The slightly negative reduction potential of 4-PPh₄ versus that of 3-PPh₄ indicates that $[\text{OC}_7\text{H}_4\text{SN}]^-$ has a stronger electron-donating ability than $[\text{SC}_7\text{H}_4\text{SN}]^-$. The chemical reduction of 3-PPh₄ and 4-PPh₄ with CoCp_2 (Scheme 1c',d') afforded $[\text{PPh}_4][\text{CoCp}_2][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^-$ and $[\text{PPh}_4][\text{CoCp}_2][\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^-$, respectively, characterized by Fourier transform IR. The reduction process is also consistent with the $\{\text{Fe}(\text{NO})_2\}^9-\{\text{Fe}(\text{NO})_2\}^{10}$ couple in the cyclic voltammogram of 3-PPh₄/4-PPh₄. In contrast to the reduction of the thiolate-containing $\{\text{Fe}(\text{NO})_2\}^9$ DNICs leading to the dissociation of thiolate of DNICs reported previously,^{7b} the redox reaction of DNICs 3 and 1 displays the reversible interconversion between the thiolate-containing $\{\text{Fe}(\text{NO})_2\}^9$ and $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs.

The relative affinity of the different ligands toward the $\{\text{Fe}(\text{NO})_2\}^9$ motif has been studied by Liaw et al. via the ligand-exchange experiments.^{7b,g,j} Similarly, the coordinated ligands $[\text{SC}_7\text{H}_4\text{SN}]^-$ of $\{\text{Fe}(\text{NO})_2\}^9$ 3-PPh₄ could be replaced by the stronger donor $[\text{OC}_7\text{H}_4\text{SN}]^-$ to yield the more stable 4-PPh₄ (Scheme 1f). Interestingly, the addition of 2 equiv of $[\text{SC}_7\text{H}_4\text{SN}]^-$ to the tetrahydrofuran (THF) solution of $\{\text{Fe}(\text{NO})_2\}^{10}$ 2-Na led to the light-green precipitates of the more stable 1-Na, characterized by IR spectra (Scheme 1e). The different binding affinities of $[\text{OC}_7\text{H}_4\text{SN}]^-$ and $[\text{SC}_7\text{H}_4\text{SN}]^-$ toward the $\{\text{Fe}(\text{NO})_2\}$ core of DNICs reveal that the electron-rich $\{\text{Fe}(\text{NO})_2\}^{10}$ motif prefers the binding of the less electron-donating ligand $[\text{SC}_7\text{H}_4\text{SN}]^-$. In contrast, the stronger electron-donating ligand $[\text{OC}_7\text{H}_4\text{SN}]^-$ favors coordination to the electron-deficient $\{\text{Fe}(\text{NO})_2\}^9$ motif. This rationalization may support the fact that the reaction of $\{\text{Fe}(\text{NO})_2\}^9$ 2-PPh₄ and $\{\text{Fe}(\text{NO})_2\}^9$ 3-PPh₄ afforded the relatively stable $\{\text{Fe}(\text{NO})_2\}^9$ 4-PPh₄ and $\{\text{Fe}(\text{NO})_2\}^{10}$ 1-PPh₄ via intermolecular electron transfer in THF (Scheme 2).

Figures 1 and 2 display the thermal ellipsoid plots of the dianionic 1-PPh₄ and 2-PPh₄, respectively, and the selected bond angles and bond lengths are given in the figure captions, respectively. The structures of 1-PPh₄ and 2-PPh₄ contain a four-coordinate iron center in a distorted tetrahedral geometry. Comparisons of the mean Fe–S bond distances [2.2941(18) Å in $[\text{PPN}][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]^{7b}$ vs 2.3460(13) Å in 1-PPh₄] and Fe–N bond distances [1.993(2) Å in 4-PPh₄ (Figure S2 in the Supporting Information) vs 2.094(2) Å in 2-PPh₄] reveal

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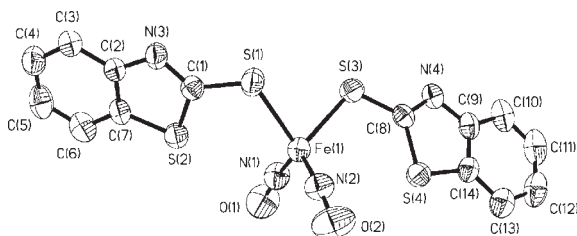


Figure 1. Structure of the anion of **1-PPh₄** displaying 50% thermal ellipsoids for all non-hydrogen atoms. Selected bond distances (Å) and angles (deg): Fe(1)–N(1), 1.645(4); Fe(1)–N(2), 1.642(4); Fe(1)–S(1), 2.3679(13); Fe(1)–S(3), 2.3240(13); N(1)–O(1), 1.193(4); N(2)–O(2), 1.205(4); Fe(1)–N(1)–O(1), 168.3(4); Fe(1)–N(2)–O(2), 167.6(4); N(1)–Fe(1)–N(2), 115.34(19); S(1)–Fe(1)–S(3), 84.48(5).

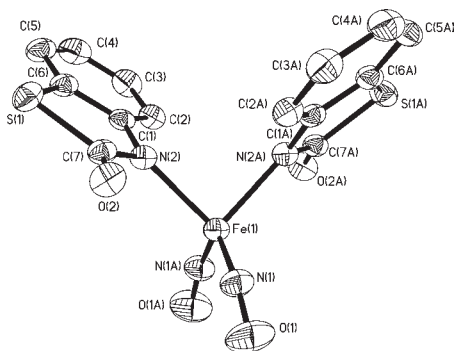


Figure 2. Structure of the anion of **2-PPh₄** displaying 50% thermal ellipsoids for all non-hydrogen atoms. Selected bond distances (Å) and angles (deg): Fe(1)–N(1), 1.638(3); Fe(1)–N(2), 2.094(2); N(1)–O(1), 1.203(3); N(1)–Fe(1)–N(1A), 110.45(19); N(2)–Fe(1)–N(2A), 88.80(13); Fe(1)–N(1)–O(1), 164.6(3).

that reduction of the $\{\text{Fe}(\text{NO})_2\}^9$ core to the $\{\text{Fe}(\text{NO})_2\}^{10}$ core leads to elongation of the Fe–N and Fe–S distances. Meanwhile, the shorter Fe–N(O) bond distances of 1.644(4) and 1.638(3) Å and the longer N–O bond distances of 1.199(4) and 1.203(3) Å found in **1-PPh₄** and **2-PPh₄**, respectively, compared to the Fe–N(O) bond distances of 1.684(6) and 1.687(2) Å and the N–O bond distances of 1.174(6) and 1.175(3) Å found in $[\text{PPN}][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$ and **4-PPh₄**, respectively, are consistent with a relatively considerable degree of π -back-bonding in the $\{\text{Fe}(\text{NO})_2\}^{10}$ core. In contrast to the distinct bond distances in $[\text{PPN}][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$ and **1-PPh₄**/**4-PPh₄** and **2-PPh₄**, the comparable Fe–N–O bond angles [169.9(5)° in $[\text{PPN}][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$ vs 168.0(4)° in **1-PPh₄** and 163.6(2)° in **4-PPh₄** vs 164.6(3)° in **2-PPh₄**] are observed when the $\{\text{Fe}(\text{NO})_2\}^9$ DNICs are reduced to the structurally analogous $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs.

In summary, the dianionic $\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs containing [thiolate, thiolate]/[amide, amide] ligation were isolated and structurally characterized. The synthetic methodology reveals that $\text{Fe}(\text{TMEDA})(\text{NO})_2$ acts as an $\{\text{Fe}(\text{NO})_2\}^{10}$ motif donor reagent in the presence of thiolates and amides. The redox reaction between DNICs **1/2** and **3/4** successfully demonstrates the reversible interconversion with no dissociation of the coordinated ligands of the structurally analogous $\{\text{Fe}(\text{NO})_2\}^9/\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs. The ligand substitution reactions of DNICs **2** and **3** to form the relatively stable DNICs **1** and **4**, respectively, have demonstrated that the $\{\text{Fe}(\text{NO})_2\}^9$ motif shows a strong preference for the stronger electron-donating ligands over the weaker electron-donating ligands; however, the $\{\text{Fe}(\text{NO})_2\}^{10}$ motif shows a stronger binding affinity toward the weaker electron-donating ligands. In addition to the ligand-exchange reactions yielding the more stable DNICs,^{7b,g,j} the reaction of $\{\text{Fe}(\text{NO})_2\}^{10}$ **2-PPh₄** and $\{\text{Fe}(\text{NO})_2\}^9$ **3-PPh₄** yielding the relatively stable $\{\text{Fe}(\text{NO})_2\}^9$ **4-PPh₄** and $\{\text{Fe}(\text{NO})_2\}^{10}$ **1-PPh₄** may signify that the intermolecular electron transfer between $\{\text{Fe}(\text{NO})_2\}^{10}$ and $\{\text{Fe}(\text{NO})_2\}^9$ DNICs is the alternative mechanism to afford the more stable DNICs for transport and storage of NO in biology. Studies on the electronic structure (NO/Fe oxidation states) of the series of $\{\text{Fe}(\text{NO})_2\}^9/\{\text{Fe}(\text{NO})_2\}^{10}$ DNICs by X-ray absorption spectroscopy and density functional theory calculations are ongoing. Also, the binding preference of a series of ligands toward $\{\text{Fe}(\text{NO})_2\}^9/\{\text{Fe}(\text{NO})_2\}^{10}$ motifs is currently being investigated in our laboratory.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structural determinations of complexes **1-PPh₄**, **2-PPh₄**, and **4-PPh₄**, experimental details, 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>.