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Multi-Site Reactivity: Reduction of Six Equivalents of Nitrite To Give an $Fe_6(NO)_6$ Cluster with a Dramatically Expanded Octahedral Core

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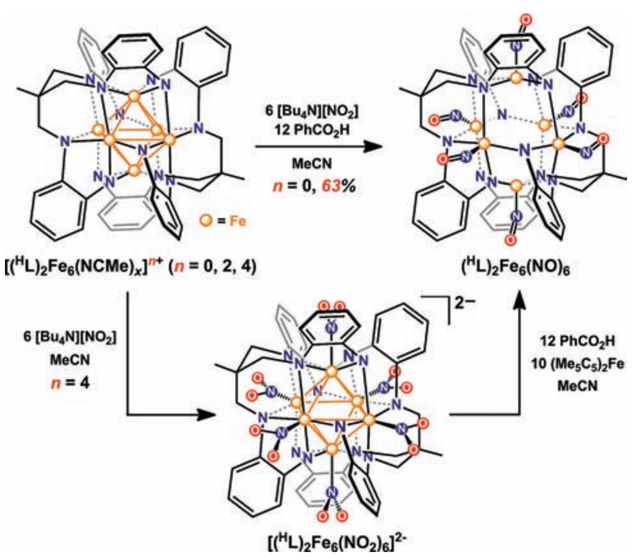
S *Supporting Information*

ABSTRACT: Reaction of NO_2^- with the octahedral cluster $(^{H}L)_2Fe_6$ in the presence of a proton source affords the hexanitrosyl cluster $(^{H}L)_2Fe_6(NO)_6$. This species forms via a proton-induced reduction of six nitrite molecules per cluster, utilizing each site available on the polynuclear core. Formation of the hexanitrosyl cluster is accompanied by a near 2-fold expansion of the $(^{H}L)_2Fe_6$ core volume, where intracore Fe—Fe interactions are overcome by strong π-bonding between Fe centers and NO ligands. A core volume of this magnitude is rare in octahedral metal clusters not supported by interstitial atoms. Moreover, the structural flexibility afforded by the $(^{H}L)_2Fe_6$ platform highlights the potential for other reaction chemistry involving species with metal—ligand multiple bonds. Carrying out the reaction of the cluster $[(^{H}L)_2Fe_6(NCMe)_6]^{4+}$ with nitrite in the absence of a proton source serves to forestall the nitrite reduction and enables clean isolation of the intermediate hexanitro cluster $[(^{H}L)_2Fe_6(NO_2)_6]^{2-}$.

In nature, the activation of small molecules, such as N_2,[1] H_2O,[2] and NO_2,[3] are often carried out by multinuclear transition metal clusters housed within the protein superstructures of enzymes. These clusters are composed of metal centers situated within close proximity to one another, such that the metal centers can act in concert to engage in substrate binding and to effect multielectron redox processes.[4] In the laboratory, one can envision use of a flexible, multinucleating ligand as a protein scaffold surrogate, in order to direct the formation of predesigned multinuclear architectures capable of mimicking the functions of protein active sites. Toward this end, we recently reported the trinucleating ligand platform, $^{H}LH_6$,[5] and its ability to direct the formation of trigonal planar Fe_3 clusters.[5,6] The close proximity of iron centers in these clusters enables cooperative substrate binding and small-molecule activation, as evidenced by the ability of $(^{tbs}L)Fe_3(thf)$ to reduce inorganic azide to afford a corresponding μ^3-nitride complex.[6]

As an alternative to clusters where metal centers are proximally situated to promote cooperative substrate binding, one can envision utilizing metal centers situated at the faces or vertices of polyhedral clusters in order to activate multiple equivalents of substrate on each cluster molecule. A promising candidate to effect multi-site reactivity is the octahedral cluster $(^{H}L)_2Fe_6$, which features a delocalized electronic structure that permits facile isolation of a seven-member electron-transfer series.[7] Importantly, the ancillary solvent ligands in these clusters can be readily replaced by other ligands,[8] highlighting the capacity for reaction chemistry at each site within the cluster. Herein, we present the observed reactivity of $(^{H}L)_2Fe_6$ to mediate a proton-induced reduction of nitrite to give the hexanitrosyl cluster $(^{H}L)_2Fe_6(NO)_6$.

Scheme 1



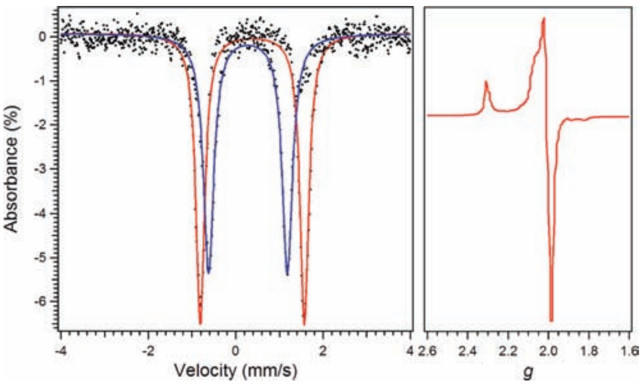


Figure 1. (Left) Zero-field ^{57}Fe Mössbauer spectra for **1** and **2**, collected at 100 K; (●) experimental data; (—) fits of the data for **1** (blue) and **2** (red). (Right) Solid-state EPR spectrum for **1**, obtained at 3 K (X-band, 9.393 GHz).

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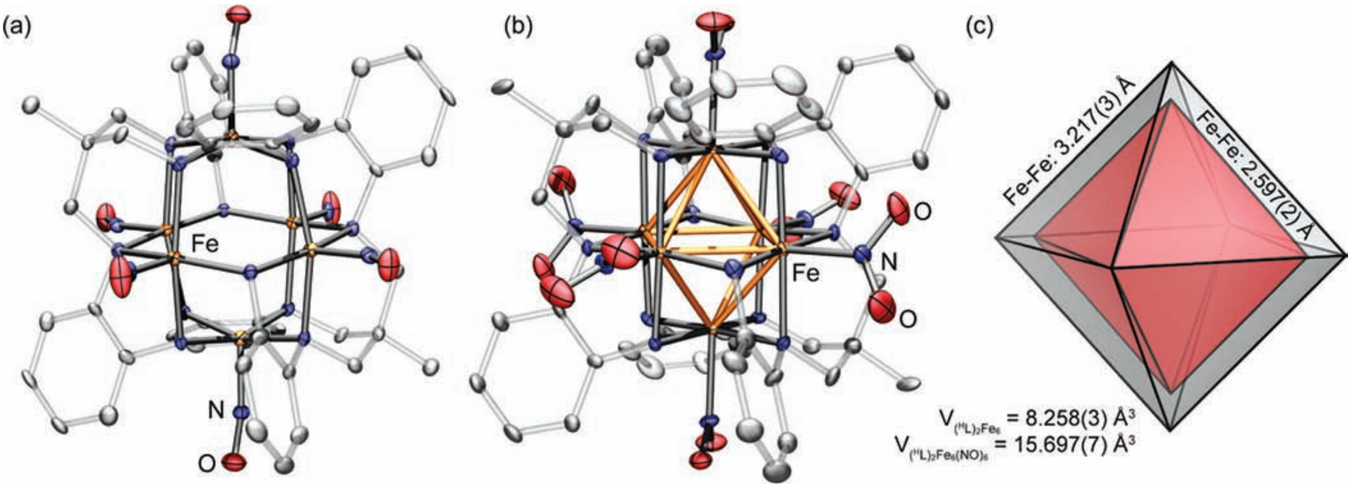

Figure 2. Solid-state molecular structures of $(^{H}L)_2Fe_6(NO)_6$ (a) and $[(^{H}L)_2Fe_6(NO_2)_6]^{2-}$ (b), with ellipsoids shown at the 35 and 25% probability level, respectively. Orange, red, blue, and gray ellipsoids represent Fe, O, N, and C atoms, respectively; H atoms are omitted for clarity. Selected mean interatomic distances (Å) and angles (deg) for **1**: *cis*-Fe−Fe 3.217(3), *trans*-Fe−Fe 4.550(2), $Fe-N_{NO}$ 1.708(9), N−O 1.18(8), Fe−N−Fe 105.9(5), Fe−N−O 149(4); for **2**: *cis*-Fe−Fe 2.727(4), *trans*-Fe−Fe 3.856(3), $Fe-N_{NO_2}$ 2.01(2), N−O 1.21(3), Fe−N−Fe 88.1(7), Fe−N−O 124(2), O−N−O 111(2). (c) Overlay of the octahedra subtended by the $[Fe_6]$ cores in **1** (gray) and $(^{H}L)_2Fe_6$ (red), illustrating the volume expansion upon conversion to **1**.

Reaction of the formally all-ferrous cluster $(^{H}L)_2Fe_6$ with 6 equiv of $[Bu_4N][NO_2]$ and 12 equiv of benzoic acid ($pK_a = 20.7$ in MeCN)[9] in acetonitrile leads to the precipitation of $(^{H}L)_2Fe_6(NO)_6$ (**1**) as a black solid over the course of 24 h in 63% yield (see Scheme 1). The solid is insoluble in water and organic solvents, similar to previously reported neutral $(^{H}L)_2Fe_6$ clusters.[7,8] Note that **1** can also be obtained from the clusters $[(^{H}L)_2Fe_6(NCMe)_x]^{n+}$ ($n = 2, 4$). These reactions require the addition of the external reductant $(Me_5C_5)_2Fe$ (see below) to drive conversion to **1** (see Figures S1−S2 in the Supporting Information [SI]).

The infrared spectrum of **1** features a prominent peak at 1658 cm^{-1} that is assigned as the nitrosyl stretch arising from the reduced nitrite (see Figure S4 in SI).[10] The zero-field ^{57}Fe Mössbauer spectrum of **1** at 100 K exhibits a single, symmetric quadrupole doublet, with an isomer shift of $\delta = 0.28$ mm s^{-1} and a quadrupole splitting of $\Delta E_Q = 1.80$ mm s^{-1} (see left panel of Figure 1). The presence of a single quadrupole doublet is indicative of a single iron electronic environment in **1**. Moreover, these spectroscopic parameters are consistent with an Enemark−Feltham description[11] of $\{Fe(NO)\}^7$, where the iron−nitrosyl linkage can be described by the resonance forms $[Fe^{II}NO^{\bullet}] \leftrightarrow [Fe^{III}NO^{-}]$.[10] Finally, solid-state EPR spectra collected for **1** at 3, 77, and 300 K show a rhombic signal ($g = 2.00, 2.06, 2.30$) that is consistent with an $S = {}^{1}/_{2}$ spin state (see right panel of Figures 1 and S5 [SI]). This result suggests that each [FeNO] fragment behaves as an $S = {}^{1}/_{2}$ center, in agreement with spin states previously observed for $\{Fe(NO)\}^7$ systems exhibiting similar spectroscopic parameters.[10]

The formation of **1** proceeds through a proton-induced reduction of nitrite. Similar transformations have been previously observed in iron complexes.[12] In fact, the heptanitrosyl cluster $[Fe_4S_3(NO)_7]^-$, commonly known as Roussin's black anion, was prepared from a mixture of $FeSO_4$, $NaNO_2$, and KSH more than a century ago.[13] Additionally, the formation of an $\{FeNO\}^7$ species is thought to occur during the reduction of nitrite to ammonia by the enzyme nitrite reductase.[14] Previous work has shown that nitrite reduction is often facilitated by the addition of two protons to an oxygen atom of an iron-bound nitro unit to generate $\{Fe(NO)\}^6$ with concomitant expulsion of water.[12g] Subsequent reduction of $\{Fe(NO)\}^6$ to $\{Fe(NO)\}^7$ requires an additional electron. For example, the thiolate-ligated complex $[Fe(S^{Me2}N_4(tren)(NO)]^+$ requires a sacrificial reductant to cleanly generate the $\{FeNO\}^7$ species.[12g] Analogously, the formation of **1** likely requires 12 equiv of H^+ per cluster molecule to release water and generate a cluster containing $\{FeNO\}^6$ fragments. The resulting species likely then undergoes a disproportionation to afford a mixture of **1** and a second oxidized species, reflected in the modest yield of **1** (63%). Note that carrying out the reaction with excess nitrite does not lead to an increased isolated yield, suggesting that nitrite does not facilitate the cluster reduction. Attempts to minimize the proposed disproportionation during the synthesis of **1** from $(^{H}L)_2Fe_6$ by incorporating sacrificial reductants have thus far not resulted in increased isolated yields of **1**. Nevertheless, addition of $(Me_5C_5)_2Fe$ is indeed necessary to drive formation of **1** from $[(^{H}L)_2Fe_6(NCMe)_x]^{n+}$ ($n = 2, 4$). Finally, note that the transformation from $(^{H}L)_2Fe_6$ to **1** proceeds through a net six-electron reduction of the combined Fe_6 core and nitrite molecules.

Owing to the insolubility of **1**, crystals were grown by allowing a solution of the tetracationic cluster compound $[(^{H}L)_2Fe_6(NCMe)_6][PF_6]_4$ in acetonitrile to slowly combine with an aqueous solution of $NaNO_2$ via a layering technique. Over the course of two weeks, black plate-like crystals, suitable for single-crystal X-ray diffraction, formed at the layer interface (see Table S1[SI]). Here, water serves as the most probable proton source, and the reduction from $\{FeNO\}^6$ to $\{FeNO\}^7$ linkages is likely facilitated by the disproportionation described above. The structure of **1**, depicted in Figure 2a, is markedly different than those observed for other Fe_6 clusters supported by the $[^{H}L]^{6-}$ ligand.[7,8] Each Fe center resides in a square pyramidal coordination environment, comprised of four amide nitrogen atoms at the base and an *N*-bound nitrosyl at the apex. The Fe centers are considerably bowed out of the N_4 cavity, with a mean separation between Fe and N_4 plane of 0.284(2) Å. The short mean Fe−N bond distance 1.708(9) Å and the mean Fe−N−O angle of 149(4)° are in good agreement with other compounds featuring $\{Fe(NO)\}^7$ linkages.[10,15] To our knowledge, **2** represents the first example of a molecule featuring an octahedral arrangement of NO ligands.[16] While the structure consists of a general edge-bridged octahedral arrangement of Fe centers, the core is drastically expanded. For instance, **1** features an average Fe···Fe separation of 3.217(3) Å and Fe−N−Fe angle of 105.9(5)°, corresponding to a Fe_6 core volume of 15.697(7) $Å^3$. Remarkably, the core volume represents an 190% increase over that of the starting cluster $(^{H}L)_2Fe_6$ (V = 8.258(3)$Å^3$), illustrated by the octahedra overlay in Figure 2c. Moreover, the presence of such a large core volume in an octahedral transition metal cluster not supported by an interstitial atom is rare. Examples of larger core volumes among other edge-bridged octahedral clusters include the compound Pd_6Cl_{12},[17] the dithiolene complex $Pd_6[S_2C_2(COOMe)_2]_6$,[18] and an orthophenylenediamine-supported Mg_6 cluster.[19] Considering face-capped octahedral complexes, Co_6Te_8 clusters with slightly larger volumes have been characterized.[20]

The volumetric expansion in **1** results from considerable π-bonding between each iron and nitrosyl at the expense of Fe−Fe intracore interactions. The short average $Fe-N_{NO}$ distance of 1.708(9) Å is well within the bonding range invoked for metal−ligand multiple bonding present in a tetragonal field.[21] The electronically populated frontier orbitals of $(^{H}L)_2Fe_6$ that stabilize the intracore Fe−Fe interactions present orbitals of both σ- and π-symmetry outward from the Fe_6 core at each of the iron centers.[7] During the reduction of nitrite to **1**, electron density originating in the intracore interactions is transferred into the π^* orbitals of each nitrosyl ligand. As such, the stabilization provided to the overall electronic structure of the cluster by the delocalized Fe_6 core is compensated by the π-backbonding stabilization.

Given the dependence of the nitrite reduction on protonation of the nitro ligands, we sought to forestall the reduction by omitting a proton donor from the reaction and thus isolate a reaction intermediate. Toward this end, $[Bu_4N][NO_2]$ was added to $[(^{H}L)_2Fe_6(NCMe)_6][PF_6]_4$ in neat acetonitrile. Diffusion of diethyl ether vapor into the resulting dark solution yielded dark red, plate-like crystals of the hexanitro cluster compound $[Bu_4N]_2[(^{H}L)_2Fe_6(NO_2)_6]\cdot 0.5MeCN$ (**2**·0.5MeCN, see Table S1in SI). The structure of $[(^{H}L)_2Fe_6(NO_2)_6]^{2-}$, depicted in Figure 2b, exhibits the same ligand coordination mode found in **1**, where each iron center is apically bound by a single nitro ligand. The cluster features an average Fe−Fe distance of 2.727(4) Å, corresponding to an Fe_6 core volume of 9.558(8) $Å^3$, and an average $Fe-N_{amide}-Fe$ angle of 88.1(7)°. Additionally, each Fe center is slightly bowed in from the N_4 cavity composed of four amide nitrogen atoms, toward the center of the octahedron, with an average distance between the Fe ion and N_4 plane of 0.038(2) Å. These values are comparable to those observed in the related clusters $[(^{H}L)_2Fe_6(NCMe)_x]^{n+}$ ($n = -1$ -4)[7] and $[(^{H}L)_2Fe_6Br_6]^{n-}$ (n = 0, 2),[8] and are in stark contrast to those observed in compound **1**. The zero-field Mössbauer spectrum of **2**, obtained at 100 K, shows a single, symmetric quadrupole doublet with an isomer shift of $\delta = 0.38$ mm s^{-1} and a quadrupole splitting of $\Delta E_Q = 2.38$ mm s^{-1} (see left panel of Figure 1). These values are reflective of a single iron coordination environment and delocalized Fe_6 core electronic structure, consistent with the related formally mixed-valence clusters $[(^{H}L)_2Fe_6(NCMe)_x]^{n+}$ (n = −1, 3, 4).[7]

The foregoing results demonstrate the ability of $(^{H}L)_2Fe_6$ clusters to readily engage in multi-site reactivity, illustrated by the reduction of 6 equiv of nitrite in the presence of proton donors to afford the hexanitrosyl cluster $(^{H}L)_2Fe_6(NO)_6$. The ligation of six nitrosyl ligands on the cluster is enabled by considerable flexibility of the $(^{H}L)_2Fe_6$ core, which nearly doubles in volume during the reaction. This dramatic core expansion highlights the stabilization associated with a shift from intracore interactions between Fe centers to substantial π-interactions between Fe and the terminal NO ligands. Finally, omitting the proton source from the reaction leads to the isolation of the intermediate hexanitro dianion $[(^{H}L)_2Fe_6(NO_2)_6]^{2-}$. Work is currently underway to comprehensively examine the mechanistic elements of the conversion of **2** to **1**. In addition, the reaction chemistry of compound **1**, with an emphasis of further activation of the N−O bond, is being explored.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, infrared spectra for **1** and **2**, Mössbauer spectra, EPR spectra for **1**, crystallographic tables for **1** and **2**, and crystallographic information files (CIF) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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