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# Synthesis and Redox Properties of Triiron Complexes Featuring Strong Fe–Fe Interactions**

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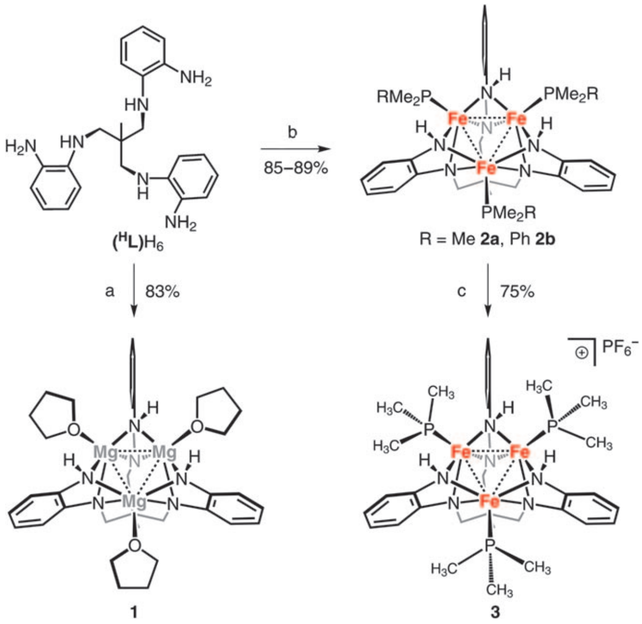
Polynuclear metalloenzymes mediate multielectron redox processes extensively in biology. For example, polymetallic assemblies are utilized in the cofactors of nitrogenases (FeMo, VFe, Fe-only, P-cluster),[1] Mn−O clusters in the oxygen-evolving complex of photosystem II,[2] and the $Cu_Z$ site in $N_2O$ reductase.[3] The cluster nature of these assemblies aids enzymatic function by mediating multielectron redox processes,[2b,4] providing multiple metal sites and coordination modes for cooperative substrate binding,[5] and facilitating electron transport between proteins.[6] The protein superstructure provides the organizational template within which the polynuclear core self-assembles and functions. In the absence of a protein, we sought to generate a modular ligand scaffold that could accommodate multiple transition metal ions in the same proximal space, allowing us to explore the reaction chemistry of clusters as molecular units.

Several factors limit the design and synthesis of multinuclear assemblies, including nonselective reactivity, redox instability, and ligand lability.[7] Cluster synthesis is largely a self-assembly process where few means of control exist to dictate the immediate coordination environments of each metal center. An ideal ligand platform would permit control over the coordination environments of the individual metal sites within a multimetallic assembly, while directing the open coordination sites to allow the transition metal ions to interact cooperatively. We report herein our progress in synthesizing trinuclear molecular units utilizing multidentate amine ligands.[8]

To this end, the tris-amine 1,1,1-tris(aminomethyl)ethane hydrochloric acid (tame·3 HCl)[9] was derivatized with *o*-fluoronitrobenzene by nucleophilic aromatic substitution (8 equiv $K_2CO_3$, acetonitrile, 120 °C, 48 h). Subsequent reduction of the bright orange trinitro species using $H_2$ (50 psi) over 5 % Pd/C afforded the hexamine $MeC(CH_2NHPh\text{-}o\text{-}NH_2)_3$ ($(^{H}L)H_6$) in good overall yield (84 %). Within $(^{H}L)H_6$ each binding site consists of an *o*-phenylenediamine subunit which when doubly deprotonated can potentially bind a divalent metal ion, providing an overall hexa-anionic core to stabilize multiple metal ions. After screening of a number of divalent metallic precursors, iron(II) provided easy entry into our efforts at understanding the coordination modes of these ligands.

The ligand $(^{H}L)H_6$ can be fully deprotonated with 3 equivalents of $n\mathrm{Bu}_2\mathrm{Mg}$ in tetrahydrofuran to furnish the trimagnesium complex $[(^{H}L)Mg_3(THF)_3]$ (**1**, Scheme 1).



**Scheme 1.** Conditions: a) 3 equiv $n\mathrm{Bu}_2\mathrm{Mg}$; b) 1.5 equiv $[Fe_2\{N(SiMe_3)_2\}_4]$, 3 equiv $PMe_2R$; c) $Fc^+PF_6^-$.

Attempts to use **1** as a transmetalating reagent with metal halide starting materials (e.g. $FeCl_2$) yielded inconsistent results (likely due to metal reduction), prompting us to pursue other metal installation routes. Reaction of ligand $(^{H}L)H_6$ with 1.5 equivalents of $[Fe_2\{N(SiMe_3)_2\}_4]$ and 3 equivalents of a tertiary phosphine ligand in THF affords the stable triiron complexes $[(^{H}L)Fe_3(PMe_2R)_3]$ (R = Me **2a**, Ph **2b**) as dark brown solids in good yields (85–89 %).

Storage of **2a** and **2b** at −35 °C in ether/hexanes and saturated hexanes, respectively, afforded crystals suitable for X-ray diffraction analysis. Solid-state structure determination for both **2a** and **2b** verified three irons are bound within the ligand platform, giving nearly isostructural complexes (Figure 1a and Figure S3 in the Supporting Information).[10] Each of the ligand $\eta^2$-amide residues bridge adjacent metal ions oriented around a vertical axis of $C_3$ symmetry. Each iron has a local square pyramidal geometry, bound to four amides forming an equatorial plane with the apical tertiary phosphine

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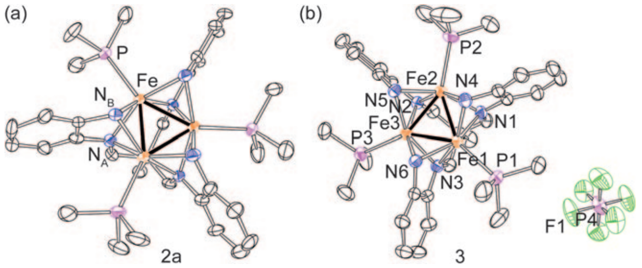

***Figure 1.*** Solid-state molecular structures for a) **2a** and b) **3** with the thermal ellipsoids set at the 50% probability level (hydrogen atoms omitted for clarity; Fe orange, C black, N blue, P magenta, F green). Average bond lengths [Å] for **2a** (from 4 molecules in asymmetric unit): Fe–Fe 2.2995(19), Fe–$N_A$ 1.984(8), Fe–$N_B$ 2.024(8), Fe–P 2.324(4), N–$C_{Ar}$ 1.411(12), $C_{Ar}$–$C_{Ar}$ 1.392(14). Bond lengths [Å] for **3**: Fe1–Fe2 2.2499(4), Fe1–Fe3 2.2868(4), Fe2–Fe3 2.2863(5); average bond lengths: Fe–N1,2,3 2.001(2), Fe–N4,5,6 1.986(2), Fe–P 2.363(1), N–$C_{Ar}$ 1.415(3), $C_{Ar}$–$C_{Ar}$ 1.392(4).

*trans* to a diiron unit. The average Fe–Fe distances of 2.299(2) Å for **2a** and **2b** are shorter than the Fe–Fe distance found in metallic iron (2.48 Å),[11] and consistently on the short end for clusters featuring two or more irons (for $Fe_n$ $d_{\text{Fe-Fe}}$ [Å]: $n=2$[12,13] 2.198–3.619; $n\geq 3$[14] 2.380–3.619). The close Fe–Fe distances suggest metal–metal bonding[15] and are not solely due to ligand-enforced interactions. The $Mg^{2+}$ in **1** share the same local coordination environment as the Fe ions in **2a** or **2b**, but the Mg ions are on average separated by 2.847(1) Å,[16] indicating the ligand can accommodate much larger intermetallic spacing.

The cyclic voltammograms for both the free ligand $(^{H}L)H_6$ and the tris-magnesium complex $[(^{H}L)Mg_3(THF)_3]$ (**1**) feature an irreversible oxidation wave with the peak anodic current shifting from −22 mV for $(^{H}L)H_6$ to −530 mV for **1** versus $[(C_5H_5)_2Fe^+]/[(C_5H_5)_2Fe]$ (Figure S6). The cyclic voltammogram of **2a** exhibits two quasi-reversible one-electron oxidation processes at $E_{1/2}=-1.59$ and −1.04 V, followed by a quasi-reversible two-electron oxidation process at −0.61 V, with the open-circuit potential for **2a** was consistently measured to be −1.8 V. The last redox process is nearly coincident with the irreversible oxidation event observed for **1** where the peak anodic current occurs at −530 mV for both species.

Chemical oxidation of **2a** with $[(C_5H_5)_2Fe]PF_6$ proceeds in nearly quantitative yield (integration of ferrocene produced versus internal standard) and the cationic triiron complex $[(^{H}L)Fe_3(PMe_3)_3]PF_6$ (**3**) could be isolated in 75% yield following crystallization from THF at −35 °C (Scheme 1). The solid-state molecular structure for **3** is shown in Figure 1 b and is very close to the structures of the neutral phosphine complexes **2a** and **2b**. Like its neutral congeners, the bond metrics within each of the *o*-phenylenediamide ligand branches of **3** are characteristic of being aromatic, closed-shell dianions (N–$C_{Ar}$ 1.415(2); $C_{Ar}$–$C_{Ar}$ 1.392(2) Å; Table S3), unchanged from **2a** within the error of the measured bond lengths.[17] The most significant structural change from **2a** to **3** is the contraction of the triiron core: Fe1–Fe2 2.2499(4); Fe1–Fe3 2.2868(4); Fe2–Fe3 2.2863(5) Å (Table S2).

The origin of the observed redox reaction was of special interest and we thus probed the complexes by a variety of spectroscopic means. Complexes **2a**, **2b**, and **3** share a common set of intense absorptions in the UV range with shoulders near 250 and 290 nm (Figure S7). One major visible absorption observed at 705 nm in the spectra for **2a** and **2b** ($\varepsilon=900$–$1000\,\text{M}^{-1}\text{cm}^{-1}$) intensifies substantially in the spectrum of triiron complex **3** ($\varepsilon=4800\,\text{M}^{-1}\text{cm}^{-1}$). This shift is a hallmark absorption attributed to ligand oxidation by Wieghardt and co-workers, indicating some extent of ligand participation in the oxidation of **2a**.[17d,e]

Magnetic susceptibility data (Figure S8) for **2a** and **2b** affords $\mu_{\text{eff}}=3.0$ and 3.2 $\mu_B$, respectively (consistent with solution magnetic moments obtained by Evans' method), while **3** shows a larger magnetic moment ($\mu_{\text{eff}}=4.1\,\mu_B$ at 300 K). The observed magnetic moments ($\mu_{\text{eff}}$) for all the iron complexes **2**–**3** gradually increase with increasing temperature regardless of the applied magnetic field (0.5, 1, and 2 T). The zero-field $^{57}$Fe Mössbauer spectra of the triiron complexes (Figure 2) reveal a single symmetric quadrupole doublet for each triiron complex, including the cationic complex **3** which has a lower isomer shift ($\delta$, $|\Delta E_Q|$ [mm s$^{-1}$]): **2a** 0.38, *1.03*; **2b** 0.39, *0.96*; **3** 0.28, *0.78*).[18] The magnitude of the change in the isomer shift from **2a** to **3** is consistent with molecular oxidation distributed over multiple Fe ions in iron–sulfur clusters.[19]

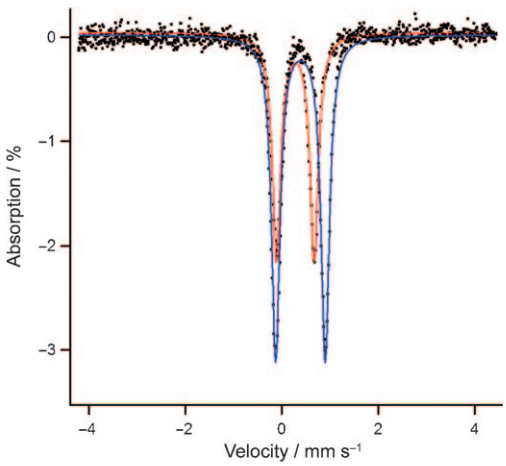

***Figure 2.*** Zero-field $^{57}$Fe Mössbauer spectra obtained at 77 K for **2a** represented by black dots and spectral fit as solid blue line ($\delta$, $|\Delta E_Q|$ [mm s$^{-1}$]): 0.38, *1.03*; and for **3** represented by black dots and spectral fit as solid red line ($\delta$, $|\Delta E_Q|$ [mm s$^{-1}$]): 0.28, *0.78*.

Complexes **2**–**3** are interesting because the overall molecule has a non-zero magnetic moment, comprised of three irons with individual moments to consider, in addition to the potential for ligand-based redox activity to add further complexity to the overall electronic structure. The ligand bond metrics are consistent with aromatic, closed-shell dianions, and the extremely short Fe–Fe separations indicate the molecular spin state must be considered, where the 18 valence electrons populate molecular orbitals comprised of the 15 Fe 3d orbitals akin to the orbital interactions described by Cotton for the bonding in $[Re_3Cl_9(\mu^2\text{-}Cl)_3]^{3-}$.[20] Mixing the frontier orbitals of the three iron centers produces four bonding, three non-bonding, and five anti-bonding molecular orbital combinations (illustrated in Figure S12). Populating the 18 Fe d electrons $[(1a_1)_\sigma^{2}(2a_1)_\sigma^{2}(1e)_\pi^{4}(3a_1)_{nb}^{2}(2e)_{nb}^{4}\text{-})_\sigma^{2}(2a_1)_\sigma^{2}(1e)_\pi^{4}(3a_1)_{nb}^{2}(2e)_{nb}^{4}(1a_2)_{\sigma*}^{2}(3e)_{\pi*}^{2}]$ suggests a net bond order of 2 within the triiron core, consistent with the short Fe–Fe bonds in **2a** and **2b**, and predicts triplet ground state for the low-spin molecule. Furthermore, oxidation of **2a** would remove an electron from an Fe–Fe antibonding orbital (removing an electron from the $(1a_2)_{\sigma*}$ orbital to give the $S = {}^3/_2$ formulation $[(1a_1)_\sigma^{2}(2a_1)_\sigma^{2}(1e)_\pi^{4}(3a_1)_{nb}^{2}(2e)_{nb}^{4}\text{-}(1a_2)_{\sigma*}^{1}(3e)_{\pi*}^{2}]$), consistent with the observed contraction in the triiron core observed in **3** and maintaining the electronic equivalence of the iron ions within the molecule for both neutral **2** and cationic **3**.

The new hexadentate ligand permits the isolation and full characterization of all-ferrous triiron complexes. The trimetallic complexes feature very short Fe–Fe distances, consistent with strong bonding between the metal sites. The surprisingly low chemical potential observed for the triiron complex is attributed to the strong M–M interactions present. The bonding within the triiron core can be described by mixing of the frontier metal 3d orbitals, which predicts a triplet ground-state for the low-spin complex and allows the observed spectral data to be described in terms of the molecular electronic structure. Work is currently underway to investigate how the electronic structure can be varied by ligand steric modification and ancillary ligand substitution.

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**Keywords:** iron complexes · metal cluster · polyamide ligand · polynuclear complexes · redox reactions

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[10] **1**: $C_{39}H_{56}Mg_3N_6O_4$, $M_r = 745.83$, triclinic, $P\bar{1}$, $a = 12.546(1)$, $b = 12.834(2)$, $c = 14.047(2)$ Å, $\alpha = 95.038(2)°$, $\beta = 101.484(2)°$, $\gamma = 118.428(2)°$, $V = 1904.8(4)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.300$ Mg m$^{-3}$, $\mu = 0.129$ mm$^{-1}$, $R1 = 0.0467$, $wR2 = 0.1163$, GOF = 1.024. **2a**: $C_{32}H_{51}Fe_3N_6P_3$, $M_r = 780.25$, triclinic, P1, $a = 12.6339(5)$, $b = 17.0101(7)$, $c = 17.4540(7)$ Å, $\alpha = 91.360(3)°$, $\beta = 91.290(3)°$, $\gamma = 108.680(2)°$, $V = 3550.3(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.460$ Mg m$^{-3}$, $\mu = 1.377$ mm$^{-1}$, $R1 = 0.1029$, $wR2 = 0.1461$, GOF = 1.002. **2b**: $C_{47}H_{57}Fe_3N_6P_3$, $M_r = 966.45$, triclinic, $P\bar{1}$, $a = 12.7214(5)$, $b = 12.7230(4)$, $c = 31.643(1)$ Å, $\alpha = 82.402(2)°$, $\beta = 79.382(2)°$, $\gamma = 60.162(2)°$, $V = 4361.6(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.472$ Mg m$^{-3}$, $\mu = 1.137$ mm$^{-1}$, $R1 = 0.0804$, $wR2 = 0.0948$, GOF = 1.006. **3**: $C_{36}H_{59}F_6Fe_3N_6OP_4$, $M_r = 997.32$, monoclinic, $P21/n$, $a = 12.542(1)$, $b = 20.036(2)$, $c = 18.663(2)$ Å, $\beta = 107.673(1)°$, $V = 4468.7(9)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.482$ Mg m$^{-3}$, $\mu = 1.165$ mm$^{-1}$, $R1 = 0.0371$, $wR2 = 0.0914$, GOF = 1.027. CCDC 765960 (**1**), 765961 (**2a**), 765962 (**2b**), 772302 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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