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Expanded redox accessibility via ligand substitution in an octahedral Fe$_6$Br$_6$ cluster†

T. David Harris, Qinliang Zhao, Raúl Hernández Sánchez and Theodore A. Betley*

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Oxidation of the nominally all-ferrous hexanuclear cluster ($^4$L)$_2$Fe$_6$ with six equivalents of ferrocenium in the presence of bromide ions results in a six-electron oxidation of the Fe$_6$ core to afford the nominally all-ferric cluster ($^4$L)$_2$Fe$_6$Br$_6$. The hexabromide cluster is also structurally characterized in a 4+ core oxidation state. A structural comparison of these two clusters provides an insight into the Fe$_6$ core electronic structure. Multielectron redox processes are mediated in nature through polynuclear transition metal clusters that comprise the active sites of proteins. Importantly, these clusters self-assemble and function according to the template provided by the protein superstructure. In view of these principles, we have set out to design modular ligand scaffolds that bind metal ions in a proximal arrangement, such that the metal—metal interactions result in a common delocalized electron reservoir shared by the close metal centers. Ultimately, this delocalized polynuclear core can potentially be exploited to drive multielectron reaction chemistry. Toward this end, we recently reported the synthesis of a hexamine ligand, $^4$HL$_6$, that, upon deprotonation, readily binds three metal ions in a vicinal trigonal planar arrangement. Subsequently, we demonstrated that, in the absence of phosphine ancillary ligands, two ($^4$L)$_2$Fe$_3$ units can dimerize to generate the all-ferrous octahedral cluster ($^4$L)$_2$Fe$_6$. Remarkably, this cluster can readily be oxidized and reduced, enabling clean isolation of the electron-transfer series [(H L)$_2$Fe$_6$(NCMe)$_6$]$^{n+}$ ($n = -1, 0, 1, 2, 3, 4$). Structural analysis of this series, in conjunction with Mössbauer spectroscopy and magnetic susceptibility measurements, indicate a delocalized electronic structure. Finally, NMR and Mössbauer spectroscopy suggest that a hexacationic cluster can be generated for short periods of time using strong oxidants, such as NO$^+$. However, this unstable species rapidly decomposes to the tetracationic cluster, [(H L)$_2$Fe$_6$(NCMe)$_6$]$^{4+}$, along with a mixture of other multinuclear iron complexes and the free $^4$HL$_6$ ligand.

In order to extend the redox chemistry of the ($^4$L)$_2$Fe$_6$ platform, with a particular emphasis on accessing higher oxidation states, we have begun to explore the coordination chemistry of these clusters. As a first approach, simple substitution reactions, where the bound NCMe ligands are replaced with monoanionic ligands, are being explored. Here, the presence of up to six monoaionic ligands will dramatically lower the overall cluster charge of the molecule, thereby giving rise to a cathodically shifted redox window and potentially granting access to novel reactivity. Herein, we report the preparation of the nominally all-ferric cluster ([($^4$L)$_2$Fe$_6$Br$_6$] (I), which is cleanly isolated via a six-electron oxidation of the all-ferrous ($^4$L)$_2$Fe$_6$ by the mild oxidant ferrocenium ion, in the presence of bromide ions. In addition, the reaction of bromide with [($^4$L)$_2$Fe$_6$(NCMe)$_6$]$^{4+}$ affords the cluster [($^4$L)$_2$Fe$_6$Br$_6$]$^{2+}$, which features a tetra-cationic [($^4$L)$_2$Fe$_6$]$^{4+}$ core.

Treatment of ($^4$L)$_2$Fe$_6$ with six equivalents each of [Cp$_2$Fe](PF$_6$) and (Bu$_4$N)Br in acetonitrile results in the rapid precipitation of I from solution as a black amorphous solid in high yield (see Scheme 1). The zero-field $^{57}$Fe Mössbauer spectrum of I (see Fig. S1†), obtained for a powder sample at 100 K, displays a single, symmetric quadrupole doublet with an isomer shift of $\delta = 0.37$ mm s$^{-1}$ and a quadrupole splitting of $|\Delta E_Q| = 2.78$ mm s$^{-1}$. These values are in close agreement with those obtained for the related short-lived cluster [($^4$L)$_2$Fe$_6$(NCMe)$_6$]$^{6+}$, which also features an [($^4$L)$_2$Fe$_6$]$^{6+}$ core ($\delta = 0.37$ mm s$^{-1}$, $|\Delta E_Q| = 2.60$ mm s$^{-1}$).

Owing to the propensity of I to rapidly precipitate from solution, along with its general insolubility in organic solvents, a layering technique was employed to grow single crystals of I. The layering, composed of an acetonitrile solution containing [($^4$L)$_2$Fe$_6$(NCMe)$_6$]$^{4+}$ and [Cp$_2$Fe]$^{2+}$ on top of an aqueous layer containing Br$^-$ ion, produced black, plate-shaped crystals of I (see Scheme 1).

Scheme 1 Oxidation of the all-ferrous cluster ($^4$L)$_2$Fe$_6$ in the presence of bromide to give the all-ferric cluster ($^4$L)$_2$Fe$_6$Br$_6$. 

† Electronic supplementary information (ESI) available: Experimental details, crystal packing diagram of I, X-ray crystal structure of 2, Mössbauer spectrum of I, tables of crystallographic data for I and 2, and X-ray crystallographic files (CIF) for I and 2. CCDC 818032 and 818033. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11561h

Department of Chemistry and Chemical Biology, Harvard University, CambridgeMassachusetts 02138, USA.
E-mail: betley@chemistry.harvard.edu

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crystals of I over the course of two weeks. Notably, omitting [Cp2Fe]"+ from the layering still produces crystals of I, suggesting that ambient oxygen also facilitates the two-electron oxidation. The structure of I, depicted in Fig. 1, consists of an edge-bridged octahedral Fe6 core supported by two trinucleating [H(L)]6" ligands and six Fe-bound bromide ions (see also Fig. S2†). Each Fe center resides in a square pyramidal coordination environment, with four amide nitrogen atoms forming the base of the plane and a bromide ligand occupying the apical position. The mean Fe–Fe distance within the Fe6 core is 2.713(3) Å, longer than those observed in [(H(L))2Fe6(NCMe)]4+ (n = 0–4, blue diamonds) and [(H(L))2Fe6Br6]2− (n = 0, 2, red triangles).

The variable-temperature dc magnetic susceptibility data for I, collected on a powder sample under an applied field of 1 T, is depicted in Fig. 2 as a plot of χw(T) vs. T. As the temperature is decreased from 300 K, the data undergo a slight, near-linear decrease down to ca. 100 K, with an average value of χw(T) = 1.36 cm³ K mol⁻¹, followed by a precipitous decline below 100 K. Previous work with the [(H(L))2Fe6(NCMe)]4+ series demonstrated that the Fe6 cluster core can best be described by a delocalized electronic structure, where a spin ground state remains isolated from the excited states up to at least 300 K. Accordingly, the average value of χw(T) = 1.36 cm³ K mol⁻¹ obtained for I in the range 100–300 K is consistent with the exclusive thermal population of an S = 1 spin ground state, with a value of g slightly larger than 2.00 and a small temperature-independent paramagnetic contribution to the susceptibility. The precipitous decline below 100 K likely results from significant zero-field splitting, Zeeman splitting, and/or weak intermolecular antiferromagnetic exchange interactions.

Attempts to cleanly isolate compounds containing the hexabromide cluster in other oxidation states have thus far produced mixtures of insoluble products, possibly containing a distribution of redox isomers bearing a range of ligand combinations. Nevertheless, treatment of the cationic cluster [(H(L))2Fe6(NCMe)]4+ with a saturated DMF solution of (Ph4P)Br can stabilize the cluster [(H(L))2Fe6Br6]2− in solution for periods of several hours. Indeed, one such reaction resulted in a mixture of amorphous solid and black, block-shaped crystals of (Ph4P)[(H(L))2Fe6Br6]·2DMF (2), suitable for single-crystal X-ray diffraction. The structure of 2 closely resembles that of I, with an octahedral Fe6 core ligated by two [H(L)]6" ligands and six bromide ions (see Fig. S3†). The most notable difference is that the core is significantly expanded compared to that of I, with a mean Fe–Fe distance of 2.758(2) Å and a volume of 9.885(3) Å³ (see Tables S3 and S4†). This volumetric increase represents a core expansion of 5% in moving from 1 to 2. In addition, the structure of 2 features a mean Fe–Br distance of 2.504(1), which is considerably longer than that observed in I. This elongated distance is reflective of the lower positive charge (4+ vs. 6+ for I) that is delocalized about the [(H(L))2Fe6]4+ core.

Comparing the Fe–Fe distances and core volumes in 1 and 2 to those observed in the [(H(L))2Fe6(NCMe)]4+ series provides some insight into the Fe6 core electronic structure and how it is
perturbed by bromide versus acetonitrile ligands. In the \( [H(L)_{2}Fe_{6}(NCMe)]^{+} \) series, the mean Fe–Fe distance increases linearly with increasing charge from the all-ferrous cluster to the tricationic cluster, which is likely to be a result of the increasing electronic population of antibonding orbitals. However, oxidation of the tricationic to the tetracationic species results in a decrease in the number of electrons that reside in antibonding orbitals and, consequently, a decrease in the mean Fe–Fe distance.\(^{6}\) Accordingly, one would expect the mean Fe–Fe distance to decrease further upon moving from \( [H(L)_{2}Fe_{6}(NCMe)]^{+} \) to \( [H(L)_{2}Fe_{6}(NCMe)]^{3+} \). Unfortunately, the absence of a crystal structure of the hexacationic species has precluded validation of this hypothesis. Nevertheless, comparison of structural data for \( 1 \) and \( 2 \) reveals that an analogous contraction does indeed occur in moving from a tetra- to a hexacationic \( [H(L)_{2}Fe_{6}]^{3+} \) core. This observation suggests that the increase in oxidation state removes electrons from antibonding orbitals. Additionally, the increased mean Fe–Fe distance in \( 2 \) relative to \( [H(L)_{2}Fe_{6}(NCMe)]^{+} \) likely stems from the negative charges of the weaker ligand field bromide ions, which lead to an increase in the energies of the antibonding frontier orbitals.

The foregoing results demonstrate the ability of bromide ligands to enable facile six-electron oxidation of the all-ferrous cluster \( (H L)_{2}Fe_{6} \) to the all-ferric cluster \( (H L)_{2}Fe_{6}Br_{6} \), requiring only the mild oxidant \( [Cp_{2}Fe]^{+} \). This compound introduces an avenue through which to extend the redox accessibility in \( (H L)_{2}Fe_{6} \) clusters, which could previously only be cleanly isolated with up to tetracationic \( ([H(L)_{2}Fe_{6}]^{3+}) \) cores. Additionally, single crystals containing the electron-transfer isomer \( ([H(L)_{2}Fe_{6}]Br)_{2} \) were obtained through reaction of \( [H(L)_{2}Fe_{6}(NCMe)]^{+} \) with bromide. Work is underway to explore the coordination chemistry of the Fe\(_6\) platform by preparing related clusters featuring other mono-anionic ligands. Comparing data from physical measurements, such as Mössbauer spectroscopy and magnetic susceptibility, across a series of these clusters will enable a systematic examination of the effects of ligand strength and bonding interactions on the Fe\(_6\) core electronic structure.

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Notes and references

1 X-ray analysis for \( 1 \) (C\(_{46}\)H\(_{48}\)Br\(_{6}\)Fe\(_{6}\)N\(_{12}\), \( \text{fw} = 1583.45 \)) at \( T = 100 \text{ K} \): space group \( R3 \), \( a = b = 12.475(4) \text{\AA}, c = 26.820(7) \text{\AA}, V = 3614.9(18) \text{\AA}^3, Z = 3, \Delta_{\text{calc}} = 2.182 \text{g cm}^{-1}, R_{I} = 0.0485, wR_{2} = 0.1469\).

2 X-ray analysis of \( 2 \) (C\(_{29}\)H\(_{28}\)Br\(_{6}\)Fe\(_{6}\)PO\(_{3}\), \( \text{fw} = 2408.41 \)) at \( T = 100 \text{ K} \): space group \( P1 \), \( a = 12.8566(13) \text{\AA}, b = 13.5153(14) \text{\AA}, c = 15.7219(16) \text{\AA}, \alpha = 91.218(2) \text{\degree}, \beta = 110.219(2) \text{\degree}, \gamma = 113.491(2) \text{\degree}, V = 2310.6(4) \text{\AA}^3, Z = 1, \Delta_{\text{calc}} = 1.731 \text{g cm}^{-1}, R_{I} = 0.0369, wR_{2} = 0.0854\).

