Expanded redox accessibility via ligand substitution in an octahedral Fe₆Br₆ cluster†

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

Received 17th March 2011, Accepted 15th April 2011
DOI: 10.1039/c1cc11561h

Oxidation of the nominally all-ferrous hexanuclear cluster (HL)₂Fe₆ with six equivalents of ferrocenium in the presence of bromide ions results in a six-electron oxidation of the Fe₆ core to afford the nominally all-ferric cluster (HL)₂Fe₆Br₆. 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 Fe₆ 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, HL₆, 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 (HL)₂Fe₃ units can dimerize to generate the all-ferrous octahedral cluster (HL)₂Fe₆. Remarkably, this cluster can readily be oxidized and reduced, enabling clean isolation of the electron-transfer series [(HL)₂Fe₆(NCMe)₆]₄⁺, [(HL)₂Fe₆(NCMe)₄Br]⁺, [(HL)₂Fe₆Br₆]⁺ and [(HL)₂Fe₆Br₆]²⁻, which features a tetra-cationic [(HL)₂Fe₆]⁺⁺ core.

In order to extend the redox chemistry of the (HL)₂Fe₆ 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 monoanionic 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 (HL)₂Fe₆Br₆ (I), which is cleanly isolated via a six-electron oxidation of the all-ferrous (HL)₂Fe₆ by the mild oxidant ferrocenium ion, in the presence of bromide ions. In addition, the reaction of bromide with [(HL)₂Fe₆(NCMe)₆]²⁻ affords the cluster [(HL)₂Fe₆Br₆]²⁻, which features a tetra-cationic [(HL)₂Fe₆]⁺⁺ core.

Treatment of (HL)₂Fe₆ with six equivalents each of [CP₂Fe](PF₆) and (Bu₄N)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 ⁵⁷Fe 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 δ = 0.37 mm s⁻¹ and a quadrupole splitting of |ΔE_Q| = 2.78 mm s⁻¹. These values are in close agreement with those obtained for the related short-lived cluster [(HL)₂Fe₆(NCMe)₆]⁴⁺, which also features an [(HL)₂Fe₆]⁺⁺ core (δ = 0.37 mm s⁻¹, |ΔE_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 [(HL)₂Fe₆(NCMe)₆]⁴⁺ and [CP₂Fe]⁺ on top of an aqueous layer containing Br⁻ ion, produced black, plate-shaped

Scheme 1 Oxidation of the all-ferrous cluster (HL)₂Fe₆ in the presence of bromide to give the all-ferric cluster (HL)₂Fe₆Br₆.

† Electronic supplementary information (ESI) available: Experimental details, crystal packing diagram of I, X-ray crystal structure of 2, Mössbauer spectrum of 1, 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
edge-bridged octahedral Fe₆ core supported by two trinucleating oxygen atom.¹⁴,¹⁵

The single Fe center in the periphery of the [H L]₆ core for clarity. The periphery of the octahedral Fe₆ core. The single Fe center in the asymmetric unit resides on a site of S₆ symmetry. Selected mean interatomic distances (Å) and angles (deg): Fe–N 1.97(1), Fe–Br 2.445(2), Fe–Fe 2.713(3), trans-Fe–Fe 3.837(2), Fe–N–Fe 87.1(3).

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)₆]⁺ (n = −1–4; 2.5804(11)–2.7040(13) Å) (see Tables S1 and S2†). In addition, the Fe₆ core subtends an approximate Fe₆ octahedron of volume 9.413(4) Å³. Finally, the cluster features an Fe–Br distance of 2.445(2) Å. We note that while a number of octahedral M₆X₆ (M = Cu,⁷ Zr,⁸ Nb,⁹ Mo,¹⁰ Ta,¹¹ W,¹² Re¹³) clusters have been previously isolated, to the best of our knowledge, compound I represents the first example of a structurally characterized octahedral MₓX₆ cluster comprised of a Group VIII metal core not supported by an interstitial oxygen atom.¹⁴,¹⁵

Fig. 1 The crystal structure of (H L)₂Fe₆Br₆, with ellipsoids shown at the 50% probability level. Orange, maroon, gray and blue ellipsoids represent Fe, Br, C, and N atoms, respectively; H atoms are omitted for clarity. The periphery of the [H L]₆⁺ ligand is transparent to aid visualization of the octahedral Fe₆ core. The single Fe center in the asymmetric unit resides on a site of S₆ symmetry. Selected mean interatomic distances (Å) and angles (deg): Fe–N 1.97(1), Fe–Br 2.445(2), Fe–Fe 2.713(3), trans-Fe–Fe 3.837(2), Fe–N–Fe 87.1(3).

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 ÑₐT 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 ÑₐT = 1.36 cm³ K mol⁻¹, followed by a precipitous decline below 100 K. Previous work with the [(H L)₂Fe₆(NCMe)₆]⁺ series demonstrated that the Fe₆ cluster core can best be described by a delocalized electronic structure, where a spin ground state results from significant zero-field splitting, Zeeman splitting, and/or weak intermolecular antiferromagnetic exchange interactions.

Attempts to cleanly isolate compounds containing the hexa-bromide 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)₆]⁺ 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)₂[(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 I 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]⁺ core.

Comparing the Fe–Fe distances and core volumes in I and 2 to those observed in the [(H L)₂Fe₆(NCMe)₆]⁺ series provides some insight into the Fe₆ core electronic structure and how it is

Fig. 2 Variable-temperature dc magnetic susceptibility data for I, collected under an applied field of 1 T.
perturbed by bromide versus actetinolate ligands. In the \([\text{HL}]_2 \text{Fe}_4(\text{NCMe})_6\)\(^{2+}\) 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 remain 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 \([\text{HL}]_2 \text{Fe}_4(\text{NCMe})_6\)\(^{3+}\) to \([\text{HL}]_2 \text{Fe}_4(\text{NCMe})_6\)\(^{4+}\). 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 \([\text{HL}]_2 \text{Fe}_6\)\(^{4+}\) 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 \([\text{HL}]_2 \text{Fe}_4(\text{NCMe})_6\)\(^{3+}\) 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 \((\text{HL})_2 \text{Fe}_6\) to the all-ferric cluster \((\text{HL})_2 \text{Fe}_6\text{Br}_6\), requiring only the mild oxidant \([\text{CP}_2 \text{Fe}]^+\). This compound introduces an avenue through which to extend the redox accessibility in \((\text{HL})_2 \text{Fe}_6\) clusters, which could previously only be cleanly isolated with up to \(2\) 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 \(\text{Fe}_6\) core electronic structure.

This work was supported by Harvard University. We thank Prof. R. H. Holm for generous use of his Mössbauer spectrometer.

Notes and references

\(^1\) X-ray analysis for \(1\) \((\text{C}_{46} \text{H}_{48} \text{Br}_6 \text{Fe}_6 \text{N}_{12}, \text{fw} = 1583.45)\) at \(T = 100\,\text{K}\); space group \(\text{R}3\), \(a = b = 12.475(4)\,\text{Å}\), \(c = 26.820(7)\,\text{Å}\), \(V = 3614.9(18)\,\text{Å}^3\), \(Z = 3\), \(d_{\text{calc}} = 2.182\,\text{g}\,\text{cm}^{-3}\), \(R_1 = 0.0485\), \(wR_2 = 0.1469\).

\(^2\) X-ray analysis for \(2\) \((\text{C}_{86} \text{H}_{72} \text{Br}_6 \text{Fe}_6 \text{O}_{12} \text{P}_6, \text{fw} = 2408.41)\) at \(T = 100\,\text{K}\); space group \(\text{P}1\), \(a = 12.8566(13)\,\text{Å}\), \(b = 13.5153(14)\,\text{Å}\), \(c = 15.7219(16)\,\text{Å}\), \(\alpha = 91.218(2)\,\text{°}\), \(\beta = 110.219(2)\,\text{°}\), \(\gamma = 113.491(2)\,\text{°}\), \(V = 2310.6(4)\,\text{Å}^3\), \(Z = 1\), \(d_{\text{calc}} = 1.731\,\text{g}\,\text{cm}^{-3}\), \(R_1 = 0.0369\), \(wR_2 = 0.0854\).


