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Synthesis of well-defined bicapped-octahedral iron clusters

$[(\text{trenL})_2\text{Fe}_8(\text{PMe}_2\text{Ph})_2]^n$ ($n = 0, -1$)

Raúl Hernández Sánchez[§], Alexander M. Willis[§], Shao-Liang Zheng, and Theodore A. Betley^{*}

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St. Cambridge, MA, 02138 USA

Abstract

The synthesis of polynuclear clusters with control over size and cluster geometry remains an unsolved challenge. Herein, we report the synthesis and characterization of open-shell octairon clusters subtended by two heptaamine ligands, ^{tren}LH₉. The molecular crystal structure of the all-ferrous species $(\text{trenL})_2\text{Fe}_8(\text{PMe}_2\text{Ph})_2$ (**1**) displays a bicapped-octahedral geometry with Fe–Fe distances ranging from 2.4071(6) to 2.8236(5) Å, where the ligand amine units are formally in amine, amide, and imide oxidation states. Several redox states of the octairon cluster are accessible as ascertained via cyclic voltammetry. The one-electron reduced clusters $[\text{M}]^+[(\text{trenL})_2\text{Fe}_8(\text{PMe}_2\text{Ph})_2]^-$ ($\text{M} = \text{Bu}_4\text{N}$ **2a**, (15-crown-5)Na(THF) **2b**) were isolated and fully characterized. Variable-temperature magnetic susceptibility data indicates that the overall interaction within the $[\text{Fe}_8]$ core is antiferromagnetic (AF) and magnetometry reveals an $S = 2$ spin ground state and a Curie constant (θ) of -204.3 . The intracore AF coupling decreases substantially in the mixed valence compound **2a** ($\theta = -61.7$). The synthetic methodology reported here could be employed to build even larger clusters.

Keywords

Polynuclear clusters; Bicapped-octahedral; Octairon

Polynuclear metal clusters have significant utility in nature to perform transformations of high complexity (e.g., small molecule activation catalysis).^[1] Nature's polynuclear catalysts possess multiple metal centres at the reaction site that facilitate substrate binding and activation^[2] as well as multielectron delivery.^[3] The cluster catalysts are hosted within a protein framework that maintains the metallocofactor structural integrity.^[4] In the absence of the protein superstructure the synthetic chemist must rely on ligands to serve as the cluster template. Synthesis of polynuclear clusters in a predictable manner has been an active research area over the last four decades.^[5] Cluster synthesis remains far from programmatic,^[6] as most successful cluster syntheses rely heavily on the principles of self-assembly and are, thus, highly dependent on metal precursor, solvent, and temperature,

^{*}betley@chemistry.harvard.edu.

[§]These authors contributed equally to this work.

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where small alterations can result in drastically different products.^[5h, 5l, 7] To address this challenge, we present herein our efforts to synthesize well-defined, high nuclearity clusters.

Previous work from our lab demonstrates the feasibility of synthesizing tri^[8] and hexanuclear^[9] clusters embedded within multidentate ligand scaffolds featuring multiple metal binding sites. The parent ^HLH₆ ligand [(*o*-NH₂C₆H₄NHCH₂)₃CMe] contains three *ortho*-phenylenediamine (OPDA) units connected via a C₃-symmetric backbone. Upon double deprotonation of each of the OPDA subunits, ^HL⁶⁻ can bind three divalent metal ions. We envisioned that incorporation of an additional metal binding site would potentially afford clusters of higher nuclearity. To this end tris(2-aminoethyl)amine (tren), was functionalized at the primary amine positions via a nucleophilic aromatic substitution with *o*-fluoronitrobenzene (4 equiv. K₂CO₃, MeCN, 120°C). The bright orange product {*o*-NO₂C₆H₄NH(CH₂)₂}₃N was then reduced to the corresponding heptaamine {*o*-H₂NC₆H₄NH(CH₂)₂}₃N (^{tren}LH₉) under 90 psi of H₂ at 60 °C over 5% Pd/C in THF in good yield (9.7 g, 79%).

Metallation of ^{tren}LH₉ in the presence of 2 equivalents of Fe₂(Mes)₄ and 1 equivalent of dimethylphenylphosphine (PMe₂Ph) afforded in 59% yield the octanuclear (^{tren}L)₂Fe₈(PMe₂Ph)₂ (**1**) cluster that has a bicapped-octahedral metal core geometry (Scheme 1). Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated solution of **1** in THF:Et₂O at room temperature. The molecular crystal structure of (^{tren}L)₂Fe₈(PMe₂Ph)₂ shown in Figure 1a has a C₂ axis that runs through Fe1 (phosphine-bound iron site) and the *trans*-disposed Fe6 site. Thus, crystallographically **1** contains five different iron sites: the phosphine-bound iron centre, Fe1; the *trans*-disposed iron site with respect to Fe1, Fe6; any two adjacent iron centres in the equatorial positions of the bicapped-octahedron, e.g. Fe2 and Fe3; and the iron centre capping the central octahedron, Fe7. The molecular structure of **1** reveals four 4-coordinate iron sites: the phosphine-bound site Fe1, Fe6, and the iron sites bound to the *tren* moiety's tertiary central amine Fe7 (and Fe7'). The remaining four equatorial iron sites (Fe2/Fe2' and Fe3/Fe3') are bound to three anilido residues making up the equatorial sites on the central octahedron. The Fe–Fe distances in **1** range from 2.4071(6) to 2.8236(5) Å.^[10]

Examination of the cluster **1** reveals that two ligands support an all-ferrous (via charge-balance to deprotonated anilide groups) octa-iron core. Full deprotonation of ^{tren}LH₉ would afford a nona-anionic ligand; nonetheless only eight ligand deprotonations occur during formation of **1**, corresponding to the stabilization of four equivalents of Fe^{II}. This ligand deprotonation state requires two primary anilido positions to be doubly deprotonated, formally creating two imido units per ligand, which has not been observed with these ligand types before.^[8b, 9, 11] A total of four ligand imido functionalities cap a tri-iron face in a μ³-fashion of the Fe₈ cluster. For the remaining two primary anilido groups, their hydrogens were located in the electron density map, see Figure 1a. In contrast to the previously reported hexanuclear clusters where two ligands forming the polynuclear species were *transdisposed*, **1** is formed by two C₂-symmetry related ^{tren}L⁸⁻ ligands sitting at the base of the iron-based bicapped-octahedron. The apical iron site is bound only to two anilido groups, thus requiring the additional phosphine co-ligand to complete its coordination sphere.

Chemical reduction of **1** was accomplished with one equivalent of sodium naphthalenide in THF followed either by salt metathesis with [Bu₄N]Cl to afford a black powder from which we were able to grow crystals of [Bu₄N][(^{tren}L)₂Fe₈(PMe₂Ph)₂] (**2a**), or Na⁺ encapsulation with 15-crown-5 to afford [(15-crown-5)Na(THF)][(^{tren}L)₂Fe₈(PMe₂Ph)₂] (**2b**). Crystals of **2a** and **2b** were grown in a standing solution of THE:Et₂O at –35 °C to verify their composition. The molecular crystal structures of **2a** and **2b** are isostructural to **1** with the exception of containing the counter cation to charge balance the one-electron reduced cluster, as shown in Figure 1c and S5, respectively.^[12] The local symmetry of the [Fe₈][–] cluster in **2a** has lost the crystallographic C₂ axis presumably due to a crystal packing effect as the symmetry decrease appears to be due to a slight rotation of the phosphine co-ligands. There is no marked correlation on the Fe–Fe distances upon reduction which vary from 2.386(2) to 2.864(1) Å in **2a** (Figure S6).

Both neutral **1** and its reduced congener **2a** were investigated by zero-field ⁵⁷Fe Mössbauer spectroscopy. Polycrystalline samples were immobilized in Paratone-N oil and their spectrum recorded at 90 K. The spectrum for **1** displays three distinct Fe-environments, Figure 1b (top); although five distinct geometry environments are expected from the single crystal molecular structure. Modeling the spectrum as such yields the following component metrical parameters [δ, |E_Q| (mm/s): 0.35, 0.94 (60%, blue fit); 0.55, 1.64 (20%, brown trace); and 0.61, 2.37 (20%, green trace)]. Based on the composition of **1** and the similarities of the local coordination environments of the iron centres therein, we propose positions Fe2–Fe7 comprise the lower isomer shift doublets, whereas the phosphine bound Fe1 site likely represents the higher isomer shift site. The metrical parameters are consistent with the ferrous clusters,^[8–9] as well amide based ferric clusters,^[13] previously reported, specifically the high spin ferrous clusters bearing a similar *N*-rich ligand environment supported by tertiary phosphine ancillary ligation.^[14] The Mössbauer spectrum of **2a** is almost identical to that of **1** with only one major difference: the intermediate isomer shift iron environment has merged with the main component (blue trace). Thus, the fitting of the spectrum of **2a** displays two components [δ, |E_Q| (mm/s): (1) 0.40, 1.02 (67%) and (2) 0.73, 1.95 (33%)], Figure 1b (bottom). The increase in isomer shift is consistent with overall reduction of the iron valency states, suggesting delocalization of the added electron (vide infra).¹⁴

The redox reversibility of **1** was investigated by electrochemical methods. Towards this end cyclic voltammetry on a THF solution of **1** revealed an open circuit potential of –1.30 V and a reversible reduction at E_{1/2} = –1.52 V (all potentials reported vs. Ag/Ag⁺, Figure S12). Given the improved solubility of **2b** in THF, we surmised that better electrochemical kinetics could be obtained with the monoanionic cluster [Fe₈][–]. Cyclic voltammetry analysis of **2b** displayed an open circuit potential of –1.80 V confirming thus the assignment of a one-electron event at E_{1/2} = –1.52 V as a reduction event. As expected the cyclic voltammogram of **2b** displays the same redox events as **1** with the exception that the couple [Fe₈][–]/[Fe₈]^{2–} becomes rigorously reversible (Figure 2a). From **2b** the first reduction occurs at –2.11 V followed by a poorly defined second reduction at ca. –2.8 V. In the anodic scan three oxidations are observed. The first one is reversible at –1.49 V followed by two irreversible oxidations at E_{pa} = –0.75 and –0.52 V. The irreversible electrochemical oxidation behavior provides a potential reason why attempted chemical oxidations of **1** were

unsuccessful. The redox events between -1.10 and -2.50 V were confirmed to be fully reversible by scanning at various rates (10 and 150 mV/s) and fitting the resulting peak current density (j_p) to the Randles-Sevcik equation (Figure 2a, right).^[15] The diffusion coefficient (D_s) of a molecule in solution is well known to give an indirect measure of its size.^[16] From the above data the extracted D_s is $4.5(5) \times 10^{-6}$ cm²/s; which lies between small molecules like ferrocene (2×10^{-5} cm²/s)^[17] and large macromolecules like dendrimers (1×10^{-7} cm²/s).^[18]

The determination of the electronic structure of metal cofactors in biological systems has provided insight into the nature of intermediates and their potential mechanism of action.^[19] In synthetic cluster systems a wider range of spectroscopic and magnetic techniques are available for electronic structure determination that are otherwise inaccessible to biological cofactors. We thus explored the magnetic properties of **1** and **2a** by acquiring variable-temperature magnetic susceptibility data collected on heating from 5 to 300 K in 5 K increments (1 T dc field, Figure 2b). The purity of the complexes was ascertained by checking the linearity of the magnetization data at 100 K (to rule out ferromagnetic impurities, see Figure S13-14); and from the superimposable $\chi_M T$ data at two different applied dc fields (Figure S15). At 300 K the all-ferrous species **1** and the one-electron reduced **2a** have $\chi_M T$ values of 12.7 and 18.4 cm³K/mol, respectively. These values are significantly smaller than the expected for eight non-interacting Fe^{II} high-spin $S = 2$ centres (24 cm³K/mol, $g = 2.0$) in the case of **1**; or seven $S = 2$ and one $S = 3/2$ iron centres (22.875 cm³K/mol, $g = 2.0$) in **2a**. The magnetic behavior across the temperature range investigated displays a monotonic decrease of $\chi_M T$ for both **1** and **2a** as temperature is lowered. At 5 K **1** and **2a** have $\chi_M T$ values of 2.68 and 3.55 cm³K/mol, respectively. This behaviour indicates antiferromagnetic coupling within the [Fe₈] cluster core. Unfortunately, the VT magnetic susceptibility data could not be modeled employing the Kambe method^[20] as pointed out by Belorizky and Fries^[21] for an octahedral bicapped geometry. Instead the reciprocal molar magnetic susceptibility ($1/\chi_M$) was fit to the Curie-Weiss law, $1/\chi_M = (T - \theta)/C$ (Figure 2b). Data in the range 150–300 K was fit in this manner. The Curie constants obtained were $C = 21.3$ and 22.1 cm³K/mol with Weiss constants θ of -204.3 and -61.7 for **1** and **2a**, respectively. Although the actual magnitude of the magnetic interactions within the octanuclear cluster could not be obtained, the Weiss constants clearly point towards strong antiferromagnetic interactions in **1**. It is interesting to note that θ in **2a** is significantly smaller; in addition to the overall geometry and metal-metal distances not changing from that of the neutral species **1**, this indicates that the itinerant electron within the octanuclear core attenuates the antiferromagnetic exchange interaction due to electron delocalization via double exchange.^[22]

Efforts to elucidate the ground state of these clusters were carried out by collecting variable-temperature (VT), variable-field (VH) magnetization studies as well as VT electron paramagnetic resonance spectra. The reduced magnetization data of **1** could be fit well to $S = 2$ with fit parameters: $g = 2.16 \pm 0.01$, $|D| = 6.3 \pm 0.1$ cm⁻¹ and $|E/D| = 0.30 \pm 0.03$ (Figure S16). In the case of **2a** magnetization saturation occurs at $4.79 \mu_B$ at 1.8 K and 7 T; close to the expected value of $5.0 \mu_B$ for an ideal $S = 5/2$ ($g = 2.0$) in the absence of zero-field splitting. Despite several fitting strategies, we were not able to find a satisfactory model to

reproduce the VTVH magnetization data of **2a** (Figure S17). Similarly, the X-band VT EPR display complex spectra with multiple transitions between 200 and 1700 Gauss for which we currently do not have an interpretation (Figure S18).

From our previous research on the synthesis of polynuclear complexes we have learned that well-defined octahedral hexanuclear clusters can be prepared by dimerization of two trinuclear units supported by hexamine ligands.^[9] In the present report we expanded the ligand backbone into a tetraamine moiety by use of tren to accommodate a fourth metal per ligand, affording bicapped-octahedral octanuclear clusters. Prediction of polynuclear cluster geometry can be made by use of Wade's rules,^[23] later expanded by Lewis et al.^[24] to polycarbonyl clusters. Wade's rules predictions are applicable to many cluster types and nuclearities.^[25] The reported species **1** and **2a-b** do not strictly follow these rules as the calculated number of skeletal electron pairs (Sk) is 6 or 8 (expected = 7).^[26] This discrepancy may be in part to the geometry restriction imposed by the trenL^{8-} ligand in contrast to the self-assembled polycarbonyl clusters, which relax to the respective thermodynamically stable configuration. In fact, there are no reported^[27] bicapped-octahedral molecular clusters for first-row transition metal (TM) homonuclear clusters; though examples with second-row TM^[7b, 28] and third-row TM,^[24b, 29] as well as one heterobimetallic $[\text{Os}_6\text{Pt}_2]$ cluster are known.^[30] Thus, the ligand framework reported here allowed us to synthesize octairon clusters with a rare cluster configuration and redox tunability.

In conclusion, octairon clusters **1** and **2a-b** display open-shell configurations with metal-metal interactions that feature antiferromagnetic coupling. The coupling is significantly attenuated in the mixed-valence species **2a**, potentially due to delocalization of the itinerant electron. The synthetic strategy adopted here to increase cluster nuclearity may be employed to synthesize even larger assemblies with some control on geometry and size.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Molecular crystal structures of $(\text{tren}^{\text{L}})_2\text{Fe}_8(\text{PMe}_2\text{Ph})_2$ (**1**, a) and $[\text{Bu}_4\text{N}][(\text{tren}^{\text{L}})_2\text{Fe}_8(\text{PMe}_2\text{Ph})_2]$ (**2a**, c) with thermal ellipsoids set at 50% probability level (Fe orange, C gray, N blue, H white and P magenta); b) zero-field ^{57}Fe Mössbauer Spectra for **1** (top) and **2a** (bottom) with fit parameters as described in the text.

Figure 2.

(a) Cyclic voltammetry (left) starting with species [(15-crown-5)Na(THF)] [(^HTren)₂Fe₈(PMe₂Ph)₂] (**2b**). The black and red traces were both collected at 20 mV/s and with 0.1 M [Bu₄N]PF₆ as supporting electrolyte in THF. (Right) Cathodic (open symbols) and anodic (filled symbols) current density vs. square root of the scan rate for E_{1/2}s at -1.49 and -2.11 V vs. Ag/AgNO₃. Blue and red symbols correspond to the latter redox couples, respectively. B) Variable-temperature dc magnetic susceptibility of (^HTren)₂Fe₈(PMe₂Ph)₂ (**1**, green symbols); and [Bu₄N][(^HTren)₂Fe₈(PMe₂Ph)₂] (**2a**, blue symbols). Both datasets were collected at 0.5 T. χ_MT and the reciprocal molar magnetic susceptibility (1/χ_M) vs. temperature are shown on the left and right vertical axis, respectively.

Scheme 1.

Synthesis of $(\text{trenL})_2\text{Fe}_8(\text{PMe}_2\text{Ph})_2$ and its anion.