Published in final edited form as:

Inorg Chem. 2007 January 22; 46(2): 510–516. doi:10.1021/ic061704y.

Stabilization of Reduced Molybdenum-Iron-Sulfur Single and Double Cubane Clusters by Cyanide Ligation

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Abstract

Recent work has shown that cyanide ligation increases the redox potentials of Fe_4S_4 clusters, enabling the isolation of $[\text{Fe}_4\text{S}_4(\text{CN})_4]^{4-}$, the first synthetic Fe_4S_4 cluster obtained in the all-ferrous oxidation state (Scott, T. A.; Berlinguette, C. P.; Holm, R. H.; Zhou, H.-C., *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 9741). The generality of reduced cluster stabilization has been examined with MoFe_3S_4 clusters. Reaction of single cubane $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{PET}_3)_3]^{1+}$ and edge-bridged double cubane $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_4]$ with cyanide in acetonitrile affords $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$ (**2**) and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$ (**5**), respectively. Reduction of **2** with $\text{KC}_{14}\text{H}_{10}$ yields $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{3-}$ (**3**). Clusters were isolated in ca. 70–90% yields as Et_4N^+ or Bu_4N^+ salts; Clusters **3** and **5** contain all-ferrous cores; **3** is the first $[\text{MoFe}_3\text{S}_4]^{1+}$ cluster isolated in substance. The structures of **2** and **3** are very similar; the volume of the reduced cluster core is slightly larger (2.5%), a usual effect upon reduction of cubane-type Fe_4S_4 and MFe_3S_4 clusters. Redox potentials and ^{57}Fe isomer shifts of $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{L}_3]^{2-,3-}$ and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{4-,3-}$ clusters with $\text{L} = \text{CN}$, PhS , halide, and PET_3 are compared. Clusters with π -donor ligands ($\text{L} = \text{halide}$, PhS) exhibit larger isomer shifts and lower (more negative) redox potentials while π -acceptor ligands ($\text{L} = \text{CN}$, PET_3) induce smaller isomer shifts and higher (less negative) redox potentials. When potentials of **3/2** and $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{SPh})_3]^{3-/2-}$ are compared, cyanide stabilizes **3** by 270 mV vs. the reduced thiolate cluster, commensurate with the 310 mV stabilization of $[\text{Fe}_4\text{S}_4(\text{CN})_4]^{4-}$ vs. $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{4-}$ where four ligands differ. These results demonstrate the efficacy of cyanide stabilization of lower cluster oxidation states. ($\text{Tp} = \text{hydrotris}(\text{pyrazolyl})\text{borate}(1-)$).

Introduction

The most significant feature of heterometallic cubane-type clusters $[\text{L}'\text{L}''\text{MoFe}_3\text{S}_4\text{L}_3]^z$ is an extensive redox capacity, encompassing the core oxidation states $[\text{MoFe}_3\text{S}_4]^{4+,3+,2+,1+}$. Their relative stability is highly dependent upon the terminal ligands L' , L'' and L at the six-coordinate molybdenum and tetrahedral iron sites, respectively. Very few clusters exhibit the full four-member electron transfer series,¹ and the most oxidized member, produced at very positive potentials, has only been observed electrochemically. Stability is biased toward the other three members, such that redox series 1 is of practical synthetic and electrochemical importance.² However, the all-ferrous state $[\text{MoFe}_3\text{S}_4]^{1+}$, containing $\text{Mo}^{\text{III}} + 3\text{Fe}^{\text{II}}$, has never been isolated. Reductive coupling of single cubane (SC) clusters affords the edge-bridged double cubane (EBDC) clusters $[\text{L}'_2\text{L}''_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^z$,^{1,3,4} which contain the $\text{Mo}_2\text{Fe}_6\text{S}_8 = \text{Mo}_2\text{Fe}_6(\mu_3\text{-S})_6(\mu_4\text{-S})_2$ centrosymmetric core. In many clusters, $\text{L}' = \text{Cl}_4\text{cat}^5$ and $\text{L}'' = \text{PR}_3$, solvate, or other unidentate ligand, or $\text{L}' = \text{Tp}$ (L'' absent). Examples of SC and EBDC clusters are present in Figure 1. Combinations of the SC oxidation states $[\text{MoFe}_3\text{S}_4]^{2+,1+}$ have been stabilized in the EBDC geometry and are linked in redox series 2. Clusters in the $4+, 2, 3, 6-9, 3+, 2, 9, 10$, and $2 + 2, 4, 9$ states have been isolated. A fourth oxidation state, $[\text{Mo}_2\text{Fe}_6\text{S}_8]^{5+}$, has been noticed electrochemically but is too unstable to isolate.²

The reactivity of SC and EBDC clusters as precursors to other cluster species is dependent on core oxidation state. For example, SCs condense to EBDCs only when reduced below the $[\text{MoFe}_3\text{S}_4]^{3+}$ state,^{3,4} and EBDCs in oxidation states below $[\text{Mo}_2\text{Fe}_6\text{S}_8]^{4+}$ and preferably $[\text{Mo}_2\text{Fe}_6\text{S}_8]^{2+}$ react with sulfide or selenide nucleophiles to form P^N-type clusters.^{2,4,9,11} Consequently, we have continued our investigation of ligand-modulated redox stability of both types of clusters with the goal of finding other species useful as precursors in the construction of weak-field clusters, with emphasis on those related to the P-cluster and the MoFe-cofactor cluster of nitrogenase.¹² Recently, it has been established that the redox potentials of cubane-type Fe_4S_4 clusters are increased by means of cyanide ligation, facilitating the isolation of $[\text{Fe}_4\text{S}_4(\text{CN})_4]^{4-}$, the first synthetic cluster obtained in substance in the all-ferrous $[\text{Fe}_4\text{S}_4]^0$ oxidation state.^{13,14} In this work, we have examined the consequences of cyanide ligation on the stability of SC and EBDC clusters with $\text{L}' = \text{Tp}$, thereby extending the scope of our recent study of SC and EBDC redox stabilities as dependent on terminal ligands L .²

Experimental Section

Preparation of Compounds

All reactions and manipulations were performed under a pure dinitrogen atmosphere using either Schlenk techniques or an inert atmosphere box. Solvents were passed through an Innovative Technology solvent purification system prior to use. Volume reduction and drying steps were carried out in vacuo. The compounds $(\text{Et}_4\text{N})[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]$,¹⁵ $(\text{Tp})\text{MoFe}_3\text{S}_4(\text{PEt}_3)_3(\text{BPh}_4)$, $(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4$, and $(\text{Et}_4\text{N})_3[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SH})_2]$,⁴ and $(\text{Et}_4\text{N})_3[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{CN})_2]$ ¹¹ were prepared as described. Because of the small scale of the preparations, isolated compounds were not analyzed. They were characterized by three physical methods. Structures of the three compounds in Table 1 were determined by X-ray diffraction. Like other SC and EBDC MoFe_3S_4 clusters,^{2,4,9,11} those obtained in this work display distinctive isotropically shifted ¹H NMR spectra, fully consistent with solid state structures and satisfactory purity of isolated compounds. Parent ions with isotope distributions consistent with the formulations given were observed in electrospray mass spectra (M = cluster). In the following preparations, yields are based on the unsolvated formula weights of the cluster compounds.

$(\text{Bu}_4\text{N})_2[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]$

Method A. To 150 mg of $(\text{Tp})\text{MoFe}_3\text{S}_4(\text{PEt}_3)_3(\text{BPh}_4)$ (0.117 mmol) in 4 mL of acetonitrile was added 94 mg of $(\text{Bu}_4\text{N})(\text{CN})$ (0.35 mmol) dissolved in 2 mL of acetonitrile. The black-brown solution was stirred for 1 h and reduced to one-half the original volume. Careful addition of a layer of ether (85 mL) caused separation of the product as 128 mg (93%) of a black microcrystalline solid. ¹H NMR (CD_3CN , anion): δ 14.8 (br, 1), 14.04(1), 6.33(1). IR (KBr): 2038 cm^{-1} (ν_{CN}). ESMS: m/z 927.2 (calcd for $\{\text{M} + \text{Bu}_4\text{N}\}^-$ 927.0), 684.9 (calcd for $\{\text{M}\}^-$, 684.8), 658.9 (calcd for $\{\text{M}-\text{CN}\}^-$, 658.7), 342.6 (calcd for $\{\text{M}\}^{2-}$, 342.4). **Method B.** The title compound can also be generated in situ by the addition of excess cyanide (5 equiv) to 1 equiv of $(\text{Et}_4\text{N})[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]$ in an acetonitrile solution and stirring for 2–3 h. The yield is 70–80% based on ¹H NMR spectra.

$(\text{Et}_4\text{N})_3[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]$ (3)

To a solution of 100 mg (0.118 mmol) of $(\text{Et}_4\text{N})[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]$ in 3 mL of acetonitrile was added a solution of 83 mg (0.54 mmol) of $(\text{Et}_4\text{N})(\text{CN})$ in 2 mL of acetonitrile to generate

a black-brown solution. The reaction mixture was stirred for 2.5 h, a freshly prepared solution of 0.023 g (0.207 mmol) of potassium anthracenide in THF was added to produce an initial deep blue solution that quickly converted to a black color. This solution was stirred for 15–20 min, filtered through Celite, and layered with 10 mL of ether. After 24 h, the product was collected as 92 mg (72%) of a black crystalline solid. ^1H NMR (CD_3CN , anion): 12.95(1), 11.7 (br, 1), 5.14(1). IR (KBr, cm^{-1}): 2059 (ν_{CN}). ESMS: m/z 1205.5 (calcd for $\{\text{M} + 4\text{Et}_4\text{N}\}^+$ 1205.4), 1075.3 (calcd for $\{\text{M} + 3\text{Et}_4\text{N}\}^+$, 1075.2).

$(\text{Et}_4\text{N})_4[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]$ (5)

To a solution of 115 mg (0.068 mmol) of $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_4]$ in 3 mL of acetonitrile was added a solution of 44 mg (0.28 mmol) of $(\text{Et}_4\text{N})(\text{CN})$ in 3 mL of acetonitrile. The black solution was stirred for 10 min, diluted with 0.2 mL of ether and left to stand under an ether atmosphere overnight. The solid that separated was washed with 3×10 mL of acetonitrile to afford the product as 106 mg (85%) of a black microcrystalline solid. ^1H NMR (CD_3CN , anion): δ 15.48(1), 14.15(2), 10.15 (vbr, 1), 7.54 (vbr, 2), 4.74(2), 4.43(1). IR (KBr, cm^{-1}): 2086, 2059 (ν_{CN}). ESMS: m/z 1965.3 (calcd for $\{\text{M} + 5\text{Et}_4\text{N}\}^+$ 1965.3), 1836.1 (calcd for $\{\text{M} + 4\text{Et}_4\text{N}\}^+$ 1836.1), 1075.2 (calcd for $\{\frac{1}{2}\text{M} + \text{CN} + 3\text{Et}_4\text{N}\}^+$ 1075.2).

In the sections that follow, clusters are numerically designated according to the Chart.

X-ray Structure Determinations

Suitable crystals of $(\text{Bu}_4\text{N})_2[\mathbf{2}]$, $(\text{Et}_4\text{N})_3[\mathbf{3}]\text{-MeCN}$ and $(\text{Et}_4\text{N})_3[\mathbf{5}]\text{-6MeCN}$ were acquired by ether diffusion into an acetonitrile solution for at least 24 h. Crystals were coated with paratone-N oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an LT-2 low temperature apparatus operating at 213 K. Data were collected with scans of $0.3^\circ/\text{frame}$ for 30 s, so that 1271–1850 frames were collected for a hemisphere of data. The first 50 frames were recollected at the end of the data collection to monitor for decay; no significant decay was detected for any compound. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorenz polarization and decay. Absorption corrections were applied using SADABS. Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP.

The asymmetric unit of $(\text{Bu}_4\text{N})_2[\mathbf{2}]$ consists of the cluster anion and two cations refined to full occupancy; that of $(\text{Et}_4\text{N})_3[\mathbf{3}]\text{-MeCN}$ contains the cluster anion, two cations at full occupancy and two at one-half occupancy, and one acetonitrile solvate molecule. In $(\text{Et}_4\text{N})_4[\mathbf{5}]\text{-6MeCN}$, the asymmetric unit includes one-half of the centrosymmetric cluster anion, two cations at full occupancy and acetonitrile solvate molecules. Structures were solved by direct methods and refined against all data by full-matrix least-squares techniques on F^2 using the SHELXTL-97 package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions on carbon atoms. Crystal parameters and agreement factors are reported in Table I.¹⁶

Other Physical Measurements

All measurements were performed under anaerobic conditions. ^1H NMR spectra were obtained with a Varian AM-400 spectrometer. Electrochemical measurements were made with a Princeton Applied Research model 263 potentiostat/galvanostat using acetonitrile and solutions, a glassy carbon working electrode, and 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ supporting electrolyte. Potentials are referenced to a standard calomel electrode (SCE). Electrospray mass spectra were recorded on acetonitrile and DMF solutions (~ 1 mM) directly infused into a LCT mass spectrometer at a flow rate of 5 $\mu\text{L}/\text{min}$; experimental parameters are given elsewhere.¹¹ Infrared spectra were measured with a Nexus 470 FT-IR instrument. ^{57}Fe Mössbauer spectra

were collected with a constant acceleration spectrometer. Data were analyzed using WMOSS software (WEB Research Corp., Edina, MN); isomer shifts are referenced to iron metal at room temperature.

Results and Discussion

Cluster Synthesis and Characterization

An established entry point to diversely substituted single and double cubane clusters is ligand substitution of the phosphine clusters **1** and **4**.^{2,4,9} Application of this procedure with cyanide in acetonitrile affords SC **2** (93%) and EBDC **5** (85%) in the indicated yields as black air-sensitive Bu_4N^+ and Et_4N^+ salts, respectively. Reduction of **2** generated in situ with excess potassium anthracenide afforded the Et_4N^+ salt of **3** (72%). All compounds were isolated as black air-sensitive solids. Clusters **2**, **3**, **5** and recently reported **6**,¹¹ a topological analogue of the P^{N} cluster of nitrogenase, comprise the current set of Tp- and cyanide-ligated MoFe_3S_4 clusters. Cluster **3** is the first SC isolated in the $[\text{MoFe}_3\text{S}_4]^{1+}$ oxidation state.

Clusters were characterized by mass spectra, ^1H NMR, and X-ray structure determinations. The structural integrity of the cyanide clusters in solution was verified by low-resolution electrospray mass spectroscopy; selected spectra are depicted in Figure 2. In all cases, a parent ion species was observed in either positive or negative collection mode. For cluster **2**, the anions $\{(\text{Bu}_4\text{N})[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]\}^-$ (m/z 927.2) and $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$ (m/z 342.6) were observed, along with the monoanion $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^-$ (m/z 684.9). For cluster **3**, the species $\{(\text{Et}_4\text{N})_4[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]\}^+$ (m/z 1205.5) and $\{(\text{Et}_4\text{N})_3[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]\}^+$ (m/z 1075.3) were detected. The parent cation $\{(\text{Et}_4\text{N})_5[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]\}^+$ was observed at 1965.3 m/z for **5**, as well as an oxidation product containing **2**, corresponding to $\{(\text{Et}_4\text{N})_3[\text{TpMoFe}_3\text{S}_4(\text{CN})_3]\}^+$ (m/z 1075.2).

^1H NMR spectra of the set of four cyanide clusters are presented in Figure 3. Previous work has shown that the chemical shifts of pyrazolyl ring protons in SCs and EBDCs, isotropically shifted because of cluster paramagnetism, are quite sensitive to terminal ligands L.² Spectra of **2** and **3** evidence three equivalent pyrazolyl rings, consistent with C_{3v} symmetry. Reduced cluster **3** is converted to **2** upon standing or upon treatment with one equivalent of $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+$. Cluster **5**, generated in situ, shows four well-resolved signals in a 2:1 intensity ratio, consistent with two inequivalent rings in the EBDC structure. The remaining two signals are apparently broadened beyond clear detection by cluster paramagnetism. In comparison, all signals of the two inequivalent equivalent rings of P^{N} -type cluster **6** are well-resolved. The spectra of **3** and **5** are the first recorded for all-ferrous SC and EBDC clusters with anionic ligands. Although several $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{4-}$ clusters with L = halide or azide have been crystallized,^{2,4,9} they are extremely easily oxidized in solution and the spectra of $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{3-}$ were obtained.² All spectra are consistent with the solid state structures described below.

Cluster Structures

The structures of clusters **2**, **5**, and **6** are presented in Figure 4; metric data in the form of mean bond distances and core volumes are listed in Table 2. In all cases, cyanide functions as a terminal ligand and Fe-CN groups are nearly linear. Because the structures of numerous MoFe_3S_4 SCs,^{12,17,18} including those with Tp ligation at the molybdenum site,^{2,4,9,15} have been reported and metric features of the clusters reported here are normal, no extensive discussion of these structures is required. The results in Figure 4 are provided as structure proofs. The structures of **2** and **3** (not shown) are practically identical and in this sense resemble the structures of another cluster pair, $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-,2-,15}$ that differ by one electron. A slight increase (*ca.* 3.8%) in the volume of MoFe_3S_4 portion of the core as calculated from

atomic coordinates¹⁹ is noted. A small increase in core total volume upon reduction is normally observed, as with **2/3** (2.5%), [(Tp)MoFe₃S₄Cl₃]^{1-,2-} (1.1%), and [Fe₄S₄(CN)₄]^{3-,4-} (*ca.* 1%),¹⁴ and presumably arises from increased population of antibonding MOs with metal-sulfur character. Centre symmetric cluster **5** is isostructural and essentially isodimensional with species such as [(Tp)₂Mo₂Fe₆S₈L₄]⁴⁻ (L = F⁻, Cl⁻, N₃⁻).

A prior X-ray study of the Et₄N⁺ salt of **6** established atom connectivity but because of disorder problems refined only to *R*₁ = 13%.¹¹ Here we provide a structural depiction demonstrating that the cluster is a structural analogue of the P^N cluster of nitrogenase,^{20,21} with the μ₆-S atom and a large external Fe-(μ₆-S)-Fe angle (143.0(3)°) being the most conspicuous features. Lastly, we note that terminal Fe-CN binding has been previously established in Fe₄S₄^{13,14,22,24} and terminal Mo-CN binding in MoFe₃S₄^{25,29} clusters, although only in the [MoFe₃S₄]²⁺ oxidation state. In solution reactions, it was found that with labile ligands initially present at both iron and molybdenum sites, cyanide is bound first at the latter site.²⁶ The protective aspect of Tp-Mo ligation directs substitution to the iron sites, a feature necessary to the synthesis of EBDC and P^N-type clusters.

Isomer Shifts and Oxidation States

The ability to vary terminal ligands L in a large set of clusters of essentially constant structure provides an opportunity to examine the effects of these ligands on electron distribution as sensed the ⁵⁷Fe isomer shifts and on redox potentials. While in mononuclear iron chemistry numerous homoleptic [FeL₄]²⁻ and a smaller number of [FeL₄]¹⁻ complexes are known, reversible redox reactions are limited. Further, complexes of the type [FeL'₃L]²⁻ with variable L are largely unknown, presumably because of unfavorable kinetic labilities. Collected in Table 3 are redox potentials and Mossbauer spectroscopic parameters for cyanide clusters **2**, **3**, and **5** and other SC and EBDC clusters with different anionic terminal ligands for comparison purposes. Additional data for Tp-coordinated clusters of these types are available elsewhere.^{2,4,15} Isomer shifts of a large number of single cubanes and double cubanes of different structural types have led to the conclusion that redox reactions effect changes in electron population largely localized in the three iron atoms of a MFe₃S₄ unit and that the probable oxidation state of the heteroatom (Mo,V) is M^{3+1,12,15,30,31}

The Mössbauer spectra for **2**, **3**, and **5** are set out in Figure 5. Those of **2** and **5** are particularly well resolved for these structure types and oxidation levels. These spectra, as those for nearly all other SCs and EBDCs, can be analyzed in terms of two (usually overlapping) quadrupole doublets. In the following considerations, weighted average isomer shifts are used. The difference of 0.08 mm/s between the isomer shifts of **2** and **3** is consistent with the latter being more reduced. This value is very similar to the *ca.* 0.1 mm/s observed for [Fe₄S₄]^{2+,1+} clusters with thiolate ligands.³² Isomer shifts respond to changes in *one* ligand at tetrahedral iron sites. The series 3 is observed for tetrahedral FeS₃L sites in SCs with the [MoFe₃S₄]²⁺ (3Fe²³³⁺) oxidation level, and also applies to EBDCs with the [Mo₂Fe₆S₈]²⁺ (6Fe²⁺) core in which the isomer shifts are 0.08–0.14 mm/s higher. On a relative basis in this series, ir-donor ligands increase (larger isomer shifts) while it-acceptor ligands diminish (smaller chemical shifts) electron density at the iron nuclei. Crudely, the larger isomer shifts are associated with higher Fe²⁺ character. The order Cl⁻ > RS > PR₃ has also been observed for VFe₃S₄ clusters.³⁰

$$\begin{array}{ccccccc} \text{L} = & \text{F}^- & \gtrsim & \text{Cl}^- & \gtrsim & \text{N}_3^- & > & \text{PhS}^- & > & \text{CN}^- & > & \text{PEt}_3 \\ \delta_{\text{av}} = & 0.63 & & 0.61 & & 0.58 & & 0.52 & & 0.47 & & 0.34 \text{ mm/s} \end{array} \quad (3)$$

In acetonitrile, all SCs show chemically reversible 3-/2- redox couples (*i*_{pc}/*i*_{pa} ~1, series 1) and EBDCs display similarly reversible 4-/3- and 3-/2- couples (series 2). Further, most SCs support a well-defined 2-/1- couple. Clusters **2/3** show the 3-/2- couple at -1.49 V but the 2-/1- step is irreversible. Cluster **5** shows the 4-/3- couple at -1.46 V; other redox steps are

not reversible. By use of the 3⁻/2⁻ potentials of SCs, stability order 4 emerges in which the range

$$L = F^- < PhS^- < Cl^- < N_3^- < CN^- \quad (4)$$

is 380 mV (i.e., the ease of oxidation increases from fluoride to cyanide). The 4⁻/3⁻ potentials of EBDCs generate a similar series except for the position of cyanide which occurs between PhS and Cl⁻. In order 4, cyanide produces a 270 mV stabilization of 3 vs. [(Tp)MoFe₃S₄(SPh)₃]³⁻, comparable to 310 mV for [Fe₄S₄(CN)₄]⁴⁻ (*E*_{1/2}^{4-/3-} = -1.42 V) vs. [Fe₄S₄(SPh)₄]⁴⁻ (*E*_{1/2}^{4-/3-} = -1.73 V) in acetonitrile.¹⁴ The efficacy of cyanide ligation in stabilizing all-ferrous cores toward oxidation is evident. The first indication of the influence of cyanide binding on potentials was obtained from the site-specific substitution reactions 5 in which a single ligand is displaced.^{23,24}

The observed redox stability order *L'* = PhS < CF < CN⁻, consistent with series 4, spans a range of 90 mV in acetonitrile.²⁴ It may be noted that the more negative redox potentials for any reaction are associated with the presence of ir-donor ligands, with fluoride effecting both the largest isomer shifts and lowest redox potentials. The correlation is uneven but for single cubanes it does place cyanide near the end of series 3 and at the end position in series 4. Phosphine clusters **1** and **4** possess the highest isomer shifts and highest potentials. Because of different cluster charges, PET₃ is not placed in ligand stability order 4. Previously, we had observed that the double cubanes [M₂Fe₆(n3-SEt)₃(SEt)₆]³⁻ with variable M exhibited a trend in isomer shift paralleling that in redox potential.³³ Increasing ferrous character of the core led to more negative redox potentials.

Formation of P^N-Type Clusters

In addition to scrutinizing the effect of cyanide ligation on redox stability, there was an additional issue that led to the present investigation. The cores of P^N-type clusters, exemplified by **6** (Figures 1 and 4), are of current interest as structural analogues of the P^N cluster of nitrogenase and possible progenitors of similar analogues of the MoFe₇S₉X core (X = C, N, or O) of the FeMo-cofactor cluster.³⁴ The means and scope of the formation of P^N-type clusters, including the types of bridging atoms that can be incorporated, remain to be elucidated.

The most effective method at present for the preparation of clusters with this topology is by the reaction of an EBDC with a strong anionic nucleophile.^{4,9,35} Reaction of phosphine cluster **1** with hydrosulfide or hydroselenide affords [(Tp)₂Mo₂Fe₆S₈Q(QH)₂]³⁻, which upon treatment with cyanide results in terminal ligand substitution to yield [(Tp)₂Mo₂Fe₆S₈Q(CN)₂]³⁻ (Q = S (**6**), Se).¹¹ The reaction pathway is undefined, but present evidence indicates that the attacking nucleophile is incorporated within the core as a μ₂-Q atom. When this nucleophile is EtS or MeO, these species are assimilated in μ₂ positions.⁹ Given that RS⁻, RO⁻, and CN⁻ are among the strongest nucleophiles (kinetics definition), an investigation of the reaction with cyanide under comparable conditions resulted in ligand substitution to give **5** in high yield. Formation of a P^N-type structure with cyanide would most likely implicate a symmetrical (C_{2v}) Fe-C(N)-Fe μ₂-η²-C interaction. This is a recognized but infrequent cyanide bridging mode; linear or slightly bent M-ON-M and nonlinear M-(CN)-M μ₂-η²-C²N¹ bridging are much more commonly encountered.³⁶ The first of these is incompatible with the P^N core and the second, while structurally documented with second and third row metals,³⁷⁻³⁹ has never been observed with iron and may also be unsuitable. Formation of P^N-type cores with non-sulfur nucleophiles as a means of introducing atom X in structural analogues of biological clusters is under investigation in this laboratory.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This research was supported by NIH Grant GM 28856

References and Notes

1. Osterloh F, Segal BM, Achim C, Holm RH. *Inorg Chem* 2000;39:980–989. [PubMed: 12526378]
2. Berlinguette CP, Miyaji T, Zhang Y, Holm RH. *Inorg Chem* 2006;45:1997–2007. [PubMed: 16499360]
3. Demadis KD, Campana CF, Coucouvanis D. *J Am Chem Soc* 1995;777:7832–7833.
4. Zhang Y, Holm RH. *J Am Chem Soc* 2003;725:3910–3920. [PubMed: 12656626]
5. Abbreviations are given in the Chart.
6. Han J, Koutmos M, Al-Ahmad S, Coucouvanis D. *Inorg Chem* 2001;40:5985–5999. [PubMed: 11681915]
7. Koutmos M, Coucouvanis D. *Inorg Chem* 2004;43:6508–6510. [PubMed: 15476337]
8. Koutmos M, Georgakaki IP, Coucouvanis D. *Inorg Chem* 2006;45:3648–3656. [PubMed: 16634597]
9. Zhang Y, Holm RH. *Inorg Chem* 2004;43:674–682. [PubMed: 14731029]
10. Osterloh F, Achim C, Holm RH. *Inorg Chem* 2001;40:224–232. [PubMed: 11170527]
11. Berlinguette CP, Holm RH. *J Am Chem Soc* 2006;728:11993–12000. [PubMed: 16953641]
12. Lee SC, Holm RH. *Chem Rev* 2004;104:1135–1157. [PubMed: 14871151]
13. Scott TA, Zhou HC. *Angew Chem Int Ed* 2004;43:5628–5631.
14. Scott TA, Berlinguette CP, Holm RH, Zhou HC. *Proc Natl Acad Sci USA* 2005;702:9741–9744. [PubMed: 15985547]
15. Fomitchev DV, McLauchlan CC, Holm RH. *Inorg Chem* 2002;41:958–966. [PubMed: 11849099]
16. See paragraph at the end of this article for Supporting Information available.
17. Holm, RH.; Simhon, ED. *Molybdenum Enzymes*. Spiro, TG., editor. Wiley; New York: 1985. p. 1-87.
18. Malinak SM, Coucouvanis D. *Prog Inorg Chem* 2001;49:599–662.
19. Kasper, JS.; Lonsdale, K. *International Tables for X-Ray Crystallography*. Kynoch; Birmingham, U.K: 1967. p. 36-49.
20. Peters JW, Stowell MHB, Soltis SM, Finnegan MG, Johnson MK, Rees DC. *Biochemistry* 1997;3d: 1181–1187. [PubMed: 9063865]
21. Mayer SM, Lawson DM, Gormal CA, Roe SM, Smith BE. *J Mol Biol* 1999;292:871–891. [PubMed: 10525412]
22. Weigel JA, Srivastava KKP, Day EP, Miinck E, Holm RH. *J Am Chem Soc* 1990;772:8015–8023.
23. Weigel JA, Holm RH. *J Am Chem Soc* 1991;773:4184–4191.
24. Zhou C, Holm RH. *Inorg Chem* 1997;36:4066–4077.
25. Mascharak PK, Armstrong WH, Mizobe Y, Holm RH. *J Am Chem Soc* 1983;705:475–483.
26. Palermo RE, Holm RH. *J Am Chem Soc* 1983;705:4310–4318.
27. Palermo RE, Singh R, Bashkin JK, Holm RH. *J Am Chem Soc* 1984;106:2600–2612.
28. Demadis KD, Chen SJ, Coucouvanis D. *Polyhedron* 1994;73:3147–3151.
29. Demadis KD, Coucouvanis D. *Inorg Chem* 1995;34:436–448.
30. Hauser C, Bill E, Holm RH. *Inorg Chem* 2002;41:1615–1624. [PubMed: 11896732]
31. Christou G, Mascharak PK, Armstrong WH, Papaefthymiou GC, Frankel RB, Holm RH. *J Am Chem Soc* 1982;104:2820–2831.
32. Rao PV, Holm RH. *Chem Rev* 2004;104:527–559. [PubMed: 14871134]
33. Cen W, Lee SC, Li J, MacDonnell FM, Holm RH. *J Am Chem Soc* 1993;775:9515–9523.

34. Einsle O, Tezcan FA, Andrade SLA, Schmid B, Yoshida M, Howard JB, Rees DC. *Science* 2002;297:1696–1700. [PubMed: 12215645]
35. Zuo JL, Zhou HC, Holm RH. *Inorg Chem* 2003;46:4624–4631. [PubMed: 12870953]
36. Dunbar KR, Heintz RA. *Prog Inorg Chem* 1997;45:283–391.
37. Deraniyagala SP, Grundy KR. *Inorg Chim Acta* 1984;84:205–211.
38. Bartley SL, Bernstein SN, Dunbar KR. *Inorg Chim Acta* 1993;273:213–231.
39. Bera JK, Szalay PS, Dunbar KR. *Inorg Chem* 2002;41:3429–3436. [PubMed: 12079461]

Figure 1. Scheme showing the synthesis of cyanide single cubane (**2**, **3**), edge-bridged double cubane (**5**), and P^N-type (**6**) clusters from phosphine clusters **1** and **4**.

Figure 2.

Experimental and calculated electrospray mass spectra of species containing the intact clusters $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$ and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$.

Figure 3. ^1H NMR spectra of cyanide clusters $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-,3-}$, $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$, and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{CN})_2]^{3-}$ in CD_3CN solutions at room temperature. The EBDC was generated in solution because of the insolubility of the Et_4N^+ salt in acetonitrile.

Figure 4.

X-ray structures of $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$, $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$, and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{CN})_2]^{3-}$ showing partial atom labeling schemes. Primed and unprimed atoms in the middle and lower structures are related by a crystallographically imposed inversion center and mirror.

Figure 5.

^{57}Fe Mossbauer spectra of polycrystalline salts of the clusters $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$, $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{3-}$, and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$ at 4.2 K in zero field. Solid lines are fits to the data using the parameters of Table 3.

$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{PEt}_3)_4]^{1+}$	1 ⁴
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$	2
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{3-}$	3
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]$	4 ⁴
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$	5
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{CN})_2]^{3-}$	6 ¹¹

Cl₄cat = tetrachlorocatecholate(2-), EBDC = edge-bridged double cubane,

LS₃ = 1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(*p*-tolylthio)benzene(3-),

SC = single cubane, Tp = hydrotris(pyrazolyl)borate(1-)

Chart.

Designation of Clusters and Abbreviations

Table 1

Crystallographic Data for Compounds Containing the Clusters $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$, $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{3-}$, and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-}$.

	$(\text{Bu}_4\text{N})_2[2]$	$(\text{Et}_4\text{N})_3[3]\cdot\text{MeCN}$	$(\text{Et}_4\text{N})_4[5]\cdot 6\text{MeCN}$
formula	$\text{C}_{44}\text{H}_{82}\text{BF}_3\text{MoN}_{11}\text{S}_4$	$\text{C}_{38}\text{H}_{73}\text{BFe}_3\text{MoN}_{13}\text{S}_4$	$\text{C}_{66}\text{H}_{118}\text{B}_2\text{Fe}_6\text{Mo}_2\text{N}_{26}\text{S}_8$
fw	1167.75	1116.22	2080.94
cryst system	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P-1$	$P-1$
Z	4	2	1
a , Å	11.189(2)	12.790(5)	12.022(5)
b , Å	40.210(5)	13.476(7)	14.269(7)
c , Å	12.596(3)	17.120(6)	15.744(8)
α , deg	90	89.51(4)	112.40(4)
β , deg	97.934(8)	75.03(3)	96.86(5)
γ , deg	90	66.86(3)	107.08(4)
V , Å ³	5613(2)	2607(2)	2304(2)
GOF (F^2)	1.045	1.051	1.090
R_p^b , wR_2^c	0.054, 0.14	0.055, 0.15	0.058, 0.13

^a Collected using Mo K α radiation ($\lambda = 0.71073$ Å) radiation at $T = 213$ K.

^b $R(F_o) = \Sigma[(F_o - F_c)]/\Sigma(F_o)$.

^c $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected Mean Bond Lengths (Å) and Volumes (Å³) of Cyanide-Ligated Clusters

	[(Tp)MoFe ₃ S ₃ (CN) ₃] ²⁻	[(Tp)MoFe ₃ S ₃ (CN) ₃] ³⁻	[(Tp) ₂ Mo ₂ Fe ₆ S ₈ (CN) ₄] ⁴⁻
Mo-S ^a	2.36[1]	2.37[1]	2.379[9]
Fe-S	2.26(4) ^b	2.27[3] ^f	2.28[1], 2.40[2], <i>cade</i>
Mo-Fe ^a	2.697[1]	2.72[2]	2.718[9]
Fe-Fe ^a	2.64[1]	2.686[6]	2.61[1], 2.827(3) ^f
Fe-C ^a	2.02[1]	2.00[3]	2.049[1]
V(MoFe ₃) ^g	2.24	2.32	2.22
V(S ₄) ^g	5.66	5.66	6.22
V(MoFe ₃ S ₄) ^g	9.15	9.38	9.39

^aMean of 3.

^bMean of 9.

^cMean of 6.

^dFe(1-3)-S1,

^eFe1-S1',

^fFe1-Fe1'.

^gAdditional volume data in the order listed: [(Tp)MoFe₃S₄Cl₃]¹⁻ -- 2.38, 5.54, 9.50 Å³; [(Tp)MoFe₃S₄Cl₃]²⁻ -- 2.39, 5.73, 9.60 Å³.

Table 3

Redox Potentials and ^{57}Fe Mossbauer Parameters for the Clusters $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{L}_3]^{1-2-}$ and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{4-0}$

cluster	4-/3-	$E_{1/2}^a$ (V)	2-/1-	δ (mm/s) ^b	ΔE_Q (mm/s)
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-}$	---	-1.64	-0.57 ^c	0.51(2), 0.46(1) ^d	0.61(1), 1.09(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{SEt})_3]^{1-}$	---	---	-0.96 ^d	0.39 ^d	1.02
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{F}_3]^{2-}$	---	-1.87	-0.73 ^c	0.58(1), 0.65(2) ^c	0.53(1), 1.15(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{2-}$	---	^e	---	0.60(1), 0.61(2) ^c	0.51(1), 1.11(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{SPh})_3]^{2-}$	---	-1.76	-0.69 ^c	0.52(2), 0.51(1)	0.84(2), 2.16(1)
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{2-}$	---	-1.49	(-0.23) ^g	0.45(1), 0.48(2)	2.47(1), 0.96(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{PEt}_3)_3]^{1+}$	---	-0.79 ⁱ	---	0.33(1), 0.35(2)	2.17(1), 1.46(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{CN})_3]^{3-}$	---	^f	---	0.47(1), 0.59(2)	2.63(1), 2.15(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{F}_4]^{4-}$	-1.65	-1.04	-0.38 ^c	0.71 ^c	0.86
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{4-}$	-1.42	-0.88	-0.28 ^c	0.65(1), 0.74(2) ^c	0.45(1), 0.83(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_4]^{3-}$	-1.57	-0.98	-0.38 ^c	---	---
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{CN})_4]^{4-h}$	-1.46	(-0.66) ^g	---	0.60(1), 0.61(2)	0.48(1), 1.30(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]^j$	-0.83, ^{ci}	---	---	0.37(1), 0.44(2)	0.46(1), 1.16(2)

^a V_s. SCE in acetonitrile at 298K unless otherwise noted.^b 4.2 K, ± 0.02 mm/s, relative intensities of quadrupole doublets indicated in parenthesis.^c Ref. 2.^d Ref. 15.^e Same as 1-cluster.^f Same as 2-cluster 0/1 + couple.^g Irreversible; $E_{p,a}$.^h Potentials in DMF.ⁱ 0/1+ couple.^j The isomer shifts for this compound are given incorrectly in ref. ⁴.