

Precursors to Clusters with the Topology of the P^N Cluster of Nitrogenase: Edge-Bridged Double Cubane Clusters [(Tp)₂Mo₂Fe₆S₈L₄]^{z-}: Synthesis, Structures, and Electron Transfer Series

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Received October 12, 2005

Members of the cluster set [(Tp)₂Mo₂Fe₆S₈L₄]^{z-} contain the core unit M₂Fe₆(μ₃-S)₆(μ₄-S)₂ in which two MoFe₃S₄ cubanes are coupled by two Fe–(μ₄-S) interactions to form a centrosymmetric edge-bridged double cubane cluster. Some of these clusters are synthetic precursors to [(Tp)₂Mo₂Fe₆S₉L₂]³⁻, which possess the same core topology as the P^N cluster of nitrogenase. In this work, the existence of a three-member electron-transfer series of single cubanes [(Tp)MoFe₃S₄L₃]^{z-} (z = 3–, 2–, 1–) and a four-member series of double cubanes [(Tp)₂Mo₂Fe₆S₈L₄]^{z-} (z = 4–, 3–, 2–, 1–) with L = F⁻, Cl⁻, N₃, PhS⁻ is demonstrated by electrochemical methods, cluster synthesis, and X-ray structure determinations. The potential of the [4–/3–] couple is extremely low (<–1.5 V vs SCE in acetonitrile) such that the 4– state cannot be maintained in solution under normal anaerobic conditions. The chloride double cubane redox series was examined in detail. The members [(Tp)₂Mo₂Fe₆S₈Cl₄]^{4–,3–,2–} were isolated and structurally characterized. The redox series includes the reversible steps [4–/3–] and [3–/2–]. Under oxidizing conditions, [(Tp)₂Mo₂Fe₆S₈Cl₄]²⁻ cleaves with the formation of single cubane [(Tp)MoFe₃S₄Cl₃]¹⁻. The quasireversible [2–/1–] couple is observed at more positive potentials than those of the single cubane redox step. Structure comparison of nine double cubanes suggests that significant dimensional changes pursuant to redox reactions are mainly confined to the Fe₂(μ₄-S)₂ bridge rhomb. The synthesis and structure of [(Tp)₂Mo₂Fe₆S₉F₂·H₂O]³⁻, a new topological analogue of the P^N cluster of nitrogenase, is described. (Tp = hydrotris(pyrazolyl)borate(1-)).

Introduction

The edge-bridged double cubane (EBDC) core unit M₂Fe₆S₈ = M₂Fe₆(μ₃-S)₆(μ₄-S)₂ is now a familiar structural motif in weak-field iron–sulfur and heterometal–iron–sulfur clusters.¹ Examples with M = Fe,^{2–4} V,^{5–7} Mo,^{6,8–17} and W¹⁸ have been prepared and structurally characterized. We have

utilized clusters of this type as precursors in reactions with sulfide to form M₂Fe₆S₉ = M₂Fe₆(μ₂-S)₂(μ₃-S)₆(μ₆-S) clusters with M = V^{6,7} and Mo.^{6,11,14,15} These are the first synthetic molecules shown to possess the core structural topology of the P^N cluster of nitrogenase.^{19,20} As such, they constitute part of our biomimetic approach to the clusters of this enzyme. Of the various clusters employed for this purpose,

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Table 1. Crystallographic Data for Compounds Containing the Clusters [(Tp)₂Mo₂Fe₆S₈(PEt₃)₄]¹⁺ (**7**), [(Tp)₂Mo₂Fe₆S₈F₄]⁴⁻ (**8**), [(Tp)₂Mo₂Fe₆S₈(N₃)₄]⁴⁻ (**10**), [(Tp)₂Mo₂Fe₆S₈F₄]³⁻ (**11**), [(Tp)₂Mo₂Fe₆S₈Cl₄]³⁻ (**12**), and [(Tp)₂Mo₂Fe₆S₉F₂·H₂O]³⁻ (**18**)^a

	[7](CF ₃ SO ₃)	(Bu ₄ N) ₄ [8]·7MeCN·2H ₂ O	(Et ₄ N) ₄ [8]·7MeCN·3H ₂ O	(Bu ₄ N) ₄ [10]
formula	C ₄₃ H ₈₀ B ₂ F ₃ Fe ₆ Mo ₂ N ₁₂ O ₃ P ₄ S ₉	C ₉₆ H ₁₈₉ B ₂ F ₄ Fe ₆ Mo ₂ N ₂₃ O ₂ S ₈	C ₆₄ H ₁₂₇ B ₂ F ₄ Fe ₆ Mo ₂ N ₂₃ O ₃ S ₈	C ₈₂ H ₁₆₄ B ₂ Fe ₆ Mo ₂ N ₂₈ S ₈
fw	1831.23	2578.78	2147.94	2347.47
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁	<i>P</i> <i>nnm</i>	<i>C</i> 2/ <i>c</i>
Z	1	2	2	4
<i>a</i> (Å)	11.690(4)	16.08(1)	14.678(9)	17.38(4)
<i>b</i> (Å)	12.858(4)	15.94(1)	29.26(2)	19.10(6)
<i>c</i> (Å)	14.298(5)	25.45(2)	11.092(2)	33.68(8)
α (deg)	72.16(2)	90	90	90
β (deg)	79.29(2)	95.53(1)	90	101.7(2)
γ (deg)	65.66(2)	90	90	90
<i>V</i> (Å ³)	1859(1)	6491(3)	4764(5)	10950(50)
GOF (<i>F</i> ²)	1.06	1.008	1.036	1.072
<i>R</i> ₁ , ^b <i>wR</i> ₂ ^c	0.042, 0.13	0.069, 0.15	0.082, 0.17	0.076, 0.16

	(Bu ₄ N) ₃ [11]·2MeCN	(Bu ₄ N) ₃ [12]·2DMF	(Et ₄ N) ₃ [18]·0.5MeCN
formula	C ₇₀ H ₁₃₄ B ₂ F ₄ Fe ₆ Mo ₂ N ₁₇ S ₈	C ₇₂ H ₁₄₂ B ₂ Cl ₄ Fe ₆ Mo ₂ N ₁₇ O ₂ S ₈	C ₄₃ H _{83.5} B ₂ F ₂ Fe ₆ Mo ₂ N _{15.5} OS ₉
fw	2095.02	2224.92	1708.89
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>m</i>
Z	1	2	2
<i>a</i> (Å)	13.305(3)	15.078(6)	13.902(2)
<i>b</i> (Å)	13.884(3)	17.873(8)	17.331(3)
<i>c</i> (Å)	15.835(3)	21.30(1)	16.724(3)
α (deg)	65.041(3)	72.33(2)	90
β (deg)	67.339(4)	72.61(2)	109.696(3)
γ (deg)	81.031(4)	72.47(1)	90
<i>V</i> (Å ³)	2447.2(8)	5077.8(3)	3793(1)
GOF (<i>F</i> ²)	1.06	1.019	1.086
<i>R</i> ₁ , ^b <i>wR</i> ₂ ^c	0.045, 0.12	0.037, 0.099	0.055, 0.20

^a Collected using Mo K α radiation ($\lambda = 0.71073$ Å) at *T* = 213 K. ^b $R(F_o) = \sum[(F_o - F_c)]/\sum(F_o)$. ^c $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

those with hydrotris(pyrazolyl)borate(1-) (Tp) terminal ligands at the M site have proven to be particularly advantageous. The generic centrosymmetric structure of the Tp-ligated double cubane cluster [(Tp)₂M₂Fe₆S₈L₄]^z is illustrated in Figure 1 for M = Mo. Clusters with L = PR₃, Cl⁻, Br⁻, N₃⁻, PhS⁻, and [NC(Me)(CH₂CN)]⁻ have been isolated and structurally characterized. Trigonally symmetric Tp coordination eliminates isomers originating at the M site, protects that site from further reaction, and promotes crystallinity of tetraalkylammonium salts. These clusters are to be distinguished from another type of Mo₂Fe₆S₈ cluster in which two cubane units are connected by a single Fe-(μ_4 -S) bridge.²¹ They are related to certain M₂Fe₆S₉ species in which the additional sulfur is present in a single Fe-(μ_2 -S)-Fe bridge between individual MFe₃S₄ cubane units.^{22,23} These sulfide-bridged double cubanes lack μ_4 -S bridging atoms. Elsewhere we have shown that the P^N ↔ EBDC core transformation in either direction can be affected.¹⁵

Despite our rather extensive use of edge-bridged double cubane clusters in synthesis, their physicochemical properties other than crystal structures and several Mössbauer spectra have been incompletely examined. In particular, there has been no information on solution behavior and the range of accessible oxidation levels, a key property in understanding M-Fe-S clusters. The recent finding that clusters can be isolated in two different oxidation states (*z* = 4-, 2-)¹⁵ has

led to an examination of their redox behavior and other solution aspects and Mössbauer properties and structures in different oxidation states. The leading results of this investigation, which bear on the reactivity behavior of these clusters, are reported here.

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. Because of the small scale of most of the preparations, one representative compound was analyzed. The fluorine content of three clusters was obtained by the NMR method described below. The seven compounds in Table 1 were characterized by X-ray structure determinations. In addition, all clusters display distinctive isotropically shifted ¹H NMR spectra leading to the establishment of the identity and satisfactory purity of isolated compounds. (As in previous work, not all pyrazolyl proton signals were located because of paramagnetic broadening.) When crystallized for structure determination, five of the compounds were obtained as solvates. In the preparations that follow, yields are based on unsolvated formula weights unless indicated otherwise. Chemical shifts given in the preparations of compounds containing 4- EBDCs refer to spectra of 3- clusters, as explained in a subsequent section. In addition to the compounds used in the following preparations, (Bu₄N)₂[(Tp)MoFe₃S₄Cl₃],¹³ (Et₄N)[(Tp)MoFe₃S₄Cl₃],¹³ (Et₄N)₂[(Tp)MoFe₃S₄(N₃)₃],¹⁵ (Et₄N)₄[(Tp)₂Mo₂Fe₆S₈(N₃)₄],¹⁵ and (Bu₄N)₃[(Tp)₂Mo₂Fe₆S₈(SPh)₄]¹⁵ were prepared as previously described.

Single Cubanes. (Et₄N)₂[(Tp)MoFe₃S₄F₃]. To a solution of 0.21 g (0.16 mmol) of [(Tp)MoFe₃S₄(PEt₃)₃](BPh₄)¹⁴ in 10 mL of

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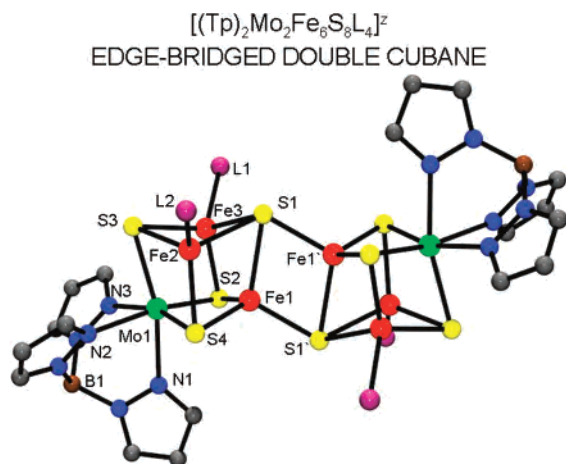


Figure 1. Generic centrosymmetric structure of edge-bridged double cubane [(Tp)₂Mo₂Fe₆S₈L₄]^z.

acetonitrile was added a solution of 0.091 g (0.49 mmol) of (Et₄N)F·2H₂O (Fluka) in 4 mL of acetonitrile. The mixture was stirred for 4 h; volatile materials were removed in vacuo, and the residue was washed with ether. The black solid was dissolved in 1.5 mL of acetonitrile, and the solution was filtered. THF (18 mL) was slowly added to the filtrate, and the mixture was allowed to stand for 2 days. The solid was collected, washed with ether, and dried in vacuo to afford the product as 0.11 g (75%) of black solid. ¹H NMR (CD₃CN, anion): δ 3.64 (1), 18.3 (v br, -1), 20.5 (1).

(Et₄N)₂[(Tp)MoFe₃S₄(SPh)₃]. To a solution of 0.040 g (0.041 mmol) of (Et₄N)₂[(Tp)MoFe₃S₄Cl₃] in 3 mL of acetonitrile was added a suspension of 0.017 g (0.13 mmol) of NaSPh. The mixture was stirred for 15 h and filtered through a Celite pod. Ether (12 mL) was layered on the filtrate, causing precipitation of the product as 0.032 g (65%) of a black needlelike crystalline solid. ¹H NMR (CD₃CN, anion): δ -4.36 (1), -3.24 (br, 2), 5.95 (1), 14.83 (1), 16.49 (2).

Double Cubanes. (Bu₄N)₄[(Tp)₂Mo₂Fe₆S₈F₄]. A suspension of 0.11 g (0.062 mmol) of [(Tp)₂Mo₂Fe₆S₈(PEt₃)₄] in 8 mL of THF was stirred for 5 h. To the brown solution was added a solution of 0.084 g (0.27 mmol) of (Bu₄N)F·3H₂O (Acros) in 2 mL of THF. The mixture was stirred for 20 min and filtered through Celite. Vapor diffusion of ether into the filtrate gave the product as 0.104 g (74%) of black platelike crystals. ¹H NMR (CD₃CN, anion): δ 4.39 (2), 13.9 (br, 1), 16.5 (v br), 20.0 (2), 25.4 (1). Anal. Calcd. for C₈₂H₁₆₄B₂F₄Fe₆Mo₂N₁₆S₈: C, 43.67; H, 7.33; N, 9.94; F, 3.37; S, 11.37; Fe, 14.86; Mo, 8.51. Found: C, 43.08; H, 6.84; N, 10.02; F, 2.70; S, 11.49; Fe, 15.39; Mo, 8.56.

(Bu₄N)₄[(Tp)₂Mo₂Fe₆S₈(N₃)₄]. To a suspension of 0.16 g (0.095 mmol) of [(Tp)₂Mo₂Fe₆S₈(PEt₃)₄] in 5 mL of DMF was added 0.11 g (0.38 mmol) of (Bu₄N)(N₃) in 3 mL of acetonitrile. The mixture was stirred for 3 h and filtered through Celite. Vapor diffusion of ether into the filtrate yielded the product as 0.80 g (36%) of black blocklike crystals. ¹H NMR (CD₃CN, anion): δ 5.4 (2), 13.5 (br, 1), 17.1 (v br, -2), 19.2 (2), 26.1 (1).

(Bu₄N)₃[(Tp)₂Mo₂Fe₆S₈Cl₄]. To a suspension of 0.088 g (0.052 mmol) of [(Tp)₂Mo₂Fe₆S₈(PEt₃)₄] in 5 mL of DMF was added 0.058 g (0.21 mmol) of Bu₄NCl. The black solution that formed within 1 min was stirred for 1 h and filtered through Celite. Vapor diffusion of ether into the filtrate yielded the product as 0.093 g (86%) of black blocklike crystals. ¹H NMR (CD₃CN, anion): δ 5.40 (2), 13.9 (br, 1), 18.2 (v br), 19.0 (2), 26.4(1).

(Et₄N)₂[(Tp)₂Mo₂Fe₆S₈Cl₄]. Method A. To a suspension of 0.16 g (0.085 mmol) of (Et₄N)₄[(Tp)₂Mo₂Fe₆S₈Cl₄] in 5 mL of aceto-

nitrile was added 0.34 g (0.085 mmol) of [(C₅Me₅)₂Fe](BF₄) in 1 mL of acetonitrile. The mixture was stirred for 30 min and filtered through Celite. Vapor diffusion of ether into the filtrate afforded the product as 0.084 g (61%) of black blocklike crystals. ¹H NMR (CD₃CN, anion): δ 7.40(2), 10.2(2), 22.8 (br, 1), 35.3(1). **Method B.** A green solution of 0.042 g (0.097 mmol) of [(C₅Me₅)₂Fe](BF₄) in 5 mL of acetonitrile was added to 0.096 g (0.051 mmol) of solid (Et₄N)₄[(Tp)₂Mo₂Fe₆S₈Cl₄]. The reaction mixture was stirred for 30 min and filtered through Celite. The product was isolated as in the previous preparation as 0.068 g (82%) of black crystals. The ¹H NMR spectrum is identical to the product of Method A.

[(Tp)₂Mo₂Fe₆S₈(PET₃)₄](OTf). To a suspension of 0.10 g (0.059 mmol) of [(Tp)₂Mo₂Fe₆S₈(PET₃)₄] in 9 mL of acetonitrile was added a solution of 0.011 mL (0.061 mmol) of Me₃SiOTf in 3 mL of acetonitrile. The mixture was stirred for 4 h and filtered through a Celite pod. Diffusion of ether into the filtrate gave the product as 0.074 g (68%) of black blocklike crystals. ¹H NMR (CD₃CN): δ 1.36 (18), 5.96 (1), 7.21 (2), 13.05 (br, 2), 13.97 (2), 15.11 (br, 1), 16.01 (6), 17.76 (6), 21.32 (1). E_{1/2} = -0.83 V (acetonitrile).

[(Tp)₂Mo₂Fe₆S₈(PET₃)₄](BF₄). A suspension of 0.020 g (0.012 mmol) of [(Tp)₂Mo₂Fe₆S₈(PET₃)₄] in 2 mL of THF was stirred for 3 h and treated with a solution of 5.0 mg (0.012 mmol) of [(C₅-Me₅)₂Fe](BF₄) in 0.5 mL of acetonitrile. The mixture was stirred for 1 h and filtered through a Celite pod. Diffusion of ether into the filtrate caused separation of the product as 0.013 g (61%) of a black crystalline product, whose ¹H NMR spectrum is identical to that of the triflate salt.

(Et₄N)₃[(Tp)₂Mo₂Fe₆S₉F₂·H₂O]. To a suspension of 0.10 g (0.060 mmol) of [(Tp)₂Mo₂Fe₆S₈(PET₃)₄] in 5 mL of acetonitrile was added (Et₄N)F·2H₂O (0.045 g, 0.24 mmol), and the mixture was stirred for 6 h. After filtration of the mixture through Celite, ether was diffused into the filtrate. The black solid that separated was a mixture of (Et₄N)₃[(Tp)₂Mo₂Fe₆S₈F₄] and (Et₄N)_{3/4}-[(Tp)₂Mo₂Fe₆S₉F₂] (2:1 mol ratio on the basis of NMR). This material was redissolved in 4 mL of acetonitrile and a solution of 1.0 mL of 0.040 M (Me₃Si)₂S (0.040 mmol) was added dropwise over 15 min. The reaction mixture was stirred for 8 h and filtered through Celite. Vapor diffusion of ether into the filtrate caused separation of the product as 0.045 g (44%) of black crystalline solid. ¹H NMR (CD₃CN, anion): δ 4.83 (2), 6.39 (1), 11.4 (2), 12.6 (1), 15.4 (2).

Fluorine Analysis. Because the fluoride reagents used in cluster synthesis are hydrated and because of the possibility of mistaking fluoride for hydroxide in X-ray structures,²⁴ we analyzed the preceding three cluster compounds for fluorine using a ¹⁹F NMR method based on the reaction Fe-F + Bu^mMe₂SiCl → Fe-Cl + Bu^mMe₂SiF. The following is a representative procedure. A solution of 21.7 mg (0.00962 mmol) of (Bu₄N)₄[(Tp)₂Mo₂Fe₆S₈F₄] and 24.3 mg (0.161 mmol) of Bu^mMe₂SiCl in 1.5 mL of CD₃CN was stirred at room temperature for 24 h. To the solution was added 17.5 mg (0.0629 mmol) of Ph₃SiF. Stirring was continued for 5 min, and the solution was analyzed by ¹⁹F NMR by integration of the signals of Bu^mMe₂SiF (sept, δ -169.4) and the internal standard Ph₃SiF (δ -168.9). The response ratio [Bu^mMe₂SiF]/[Ph₃SiF] was 1.31 from control measurements, the relaxation time was 10 s, and the chemical shifts were based on C₆F₆ (δ -163.0). From the relative intensities, the percent of cluster fluorine liberated was calculated. Each compound was measured in two separate experiments, with the following average values obtained: (Et₄N)₂[(Tp)MoFe₃S₄F₃], 97%; (Bu₄N)₄[(Tp)₂Mo₂Fe₆S₈F₄], 98%; (Et₄N)₃[(Tp)₂Mo₂Fe₆S₉F₂], 92%.

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Chart 1. Designation of Clusters

$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{L}_3]^{2-}$	$\text{L} = \text{F}^- \mathbf{1}, \text{Cl}^- \mathbf{2}^{14}, \text{N}_3^- \mathbf{3}^{15}, \text{PhS}^- \mathbf{4}$
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-}$	$\mathbf{5}^{13}$
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]^z$	$z = 0 \mathbf{6}^{14}, 1+ \mathbf{7}$
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{4-}$	$\text{L} = \text{F}^- \mathbf{8}, \text{Cl}^- \mathbf{9},^{14} \text{N}_3^- \mathbf{10}^{15}$
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{3-}$	$\text{L} = \text{F}^- \mathbf{11}, \text{Cl}^- \mathbf{12}, \text{N}_3^- \mathbf{13}, \text{PhS}^- \mathbf{14}^{15}$
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{2-}$	$\text{L} = \text{Cl}^- \mathbf{15},^{15} \text{Br}^- \mathbf{16}^{15}$
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{1-}$	$\mathbf{17}$
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9\text{F}_2\cdot\text{H}_2\text{O}]^{3-}$	$\mathbf{18}$

EBDC, edge-bridged double cubane; SC, single cubane; solv, solvate molecule; TfO, trifluoromethanesulfonate(1-); Tp, hydrotris(pyrazolyl)borate(1-); Tp*, hydrotris(3,5-dimethyl-pyrazolyl)borate(1-)

X-ray Structure Determinations. The structures of the seven compounds in Table 1 were determined. Diffraction-quality crystals were obtained by vapor diffusion of ether into acetonitrile or DMF solutions. Crystals were mounted in Inifinium oil on a fiber on a goniometer head that was placed in a dinitrogen cold stream on a Siemens (Bruker) SMART CCD-based diffractometer at 193 K. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data were collected in 0.3° intervals in N and T for 30 s/frame such that a hemisphere of data was collected. A total of 1270 frames was collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of the data collection to monitor intensity decay; none was detected. The highly redundant data sets were reduced with the use of SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied with SADABS supplied by Bruker. Structures were solved by direct methods using SHELX-97. The position of the metal atoms and their first coordination sphere atoms were located from *E* maps. Other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso} . Crystallographic parameters are collected in Table 1.²⁵

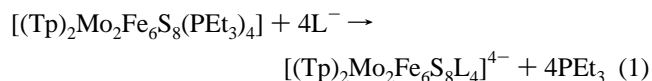
Other Physical Measurements. All measurements were performed under anaerobic conditions. ^1H NMR spectra were obtained with a Varian AM-400 spectrometer. Electrochemical measurements were made with a Princeton Applied Research model 263 potentiostat/galvanostat using a glassy carbon working electrode and 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ supporting electrolyte. Potentials are referenced to a standard calomel electrode (SCE). 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.

In the sections that follow, clusters are designated **1–18** according to Chart 1.

Results and Discussion

Cluster Synthesis. Both single and double cubane clusters are essential to this investigation. Single cubane (SC) clusters are accessible by ligand-substitution reactions of $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{PEt}_3)_3]^{1+}$ or **2** in acetonitrile. Treatment of the former with $(\text{Et}_4\text{N})\text{F}\cdot 2\text{H}_2\text{O}$ affords fluoride cluster **1**, whereas reaction of **2** with NaSPh leads to thiolate cluster **4**, which is a member of the set $[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{SR})_3]^{2-}$ whose single cubane structures have been demonstrated.¹⁴

The principal precursor compound of this investigation is the phosphine-ligated EBDC **6**, which has been shown to undergo complete phosphine substitution with 4 equiv of halide, azide, or benzenethiolate in reaction 1.^{14,15}



This reaction is depicted in Figure 2 for the preparation of chloride cluster **9**. Clusters **1**, **8**, **11**, and **18** (see below) are the only fluoride-ligated M–Fe–S clusters of any type to have been prepared. The vanadium cluster $[(\text{Tp})_2\text{V}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]$ supports analogous reactions yielding $[(\text{Tp})_2\text{V}_2\text{Fe}_6\text{S}_8\text{L}_4]^{4-}$ ($\text{L} = \text{Cl}^-, \text{PhS}^-$).^{5,7} Under strictly anaerobic conditions, clusters **8–10** are isolable as tetraanion salts; thiolate cluster **14** has thus far been obtained only as a trianion salt.¹⁵ The previous structures of the Et_4N^+ salts of **9**¹⁴ and **14**¹⁵ and those of two salts of fluoride cluster **8** and $(\text{Bu}_4\text{N})_4[\mathbf{10}]$ determined in this work establish the EBDC stereochemistry, which is illustrated by the X-ray structure of **8** in Figure 3. These observations, together with crystallographic establishment of the oxidized compounds $(\text{Et}_4\text{N})_2[\mathbf{15}]$ and $(\text{Et}_4\text{N})_2[\mathbf{16}]$,¹⁵ provide sufficient evidence that the EBDC motif is capable of supporting at least three total oxidation states and have led to an investigation of the redox properties of this family of clusters.

Redox Reactions of EBDC Clusters. (a) Halide and Azide Clusters. As is evident from the voltammograms in Figure 4, SCs **1–4** sustain the three-member electron-transfer series 2 set out in Table 2. Core oxidation states are indicated. Redox potentials, collected in Table 2, establish the oxidizability order $\text{L} = \text{F}^- > \text{PhS}^- > \text{Cl}^- > \text{N}_3^-$. The ^{57}Fe isomer shift data in Table 3 reveal a difference of 0.13 mm/s between clusters **2** and **5**, consistent with a more oxidized core in **5**, and the shifts themselves support the probable oxidation state descriptions $[\text{MoFe}_3\text{S}_4]^{3+} \approx [\text{Mo}^{3+}\text{Fe}^{2+}\text{Fe}^{3+}_2\text{S}_4]^{3+}$ and $[\text{MoFe}_3\text{S}_4]^{2+} \approx [\text{Mo}^{3+}\text{Fe}^{2+}_2\text{Fe}^{3+}\text{S}_4]^{2+}$.¹³ In solution, the two chloride clusters are distinguishable by their isotropically shifted ^1H NMR spectra, presented in panels a and b of Figure 5, which arise from the paramagnetic cores $[\text{MoFe}_3\text{S}_4]^{3+}$ ($S = 3/2$) and $[\text{MoFe}_3\text{S}_4]^{2+}$ ($S = 2$).¹ The terminal reduced member of series 2 (Table 2) would be an all-ferrous cluster. However, isolation of such a species is highly problematic because of the large negative redox potentials for the [3–/2–] couples (–1.5 to –1.9 V).

The mean isomer shifts of all EBDC tetraanions occur in the range 0.68–0.71 mm/s (Table 3), fully consistent with the presence of two all-ferrous cubane subcores $[\text{MoFe}_3\text{S}_4]^{1+}$ of the cluster core $[\text{Mo}_2\text{Fe}_6\text{S}_8]^{2+}$. The empirical correlation of isomer shift and oxidation state for iron–sulfur clusters predicts $\delta = 0.69$ mm/s for tetrahedral $\text{Fe}^{\text{II}}\text{S}_4$.²⁶ When $(\text{Et}_4\text{N})_4[\mathbf{9}]$ was dissolved in acetonitrile under anaerobic conditions, the ^1H NMR spectrum of the resulting solution (Figure 5d) showed similarities to that of thiolate cluster trianion **14**.¹⁵ Coinciding observations were made for **8** and **10**, whose spectra (panels b and d, respectively, of Figure

(25) See paragraph at the end of this article for Supporting Information available.

(26) Rao, P. V.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527–559.

REDOX REACTIONS OF EDGE-BRIDGED DOUBLE CUBANES

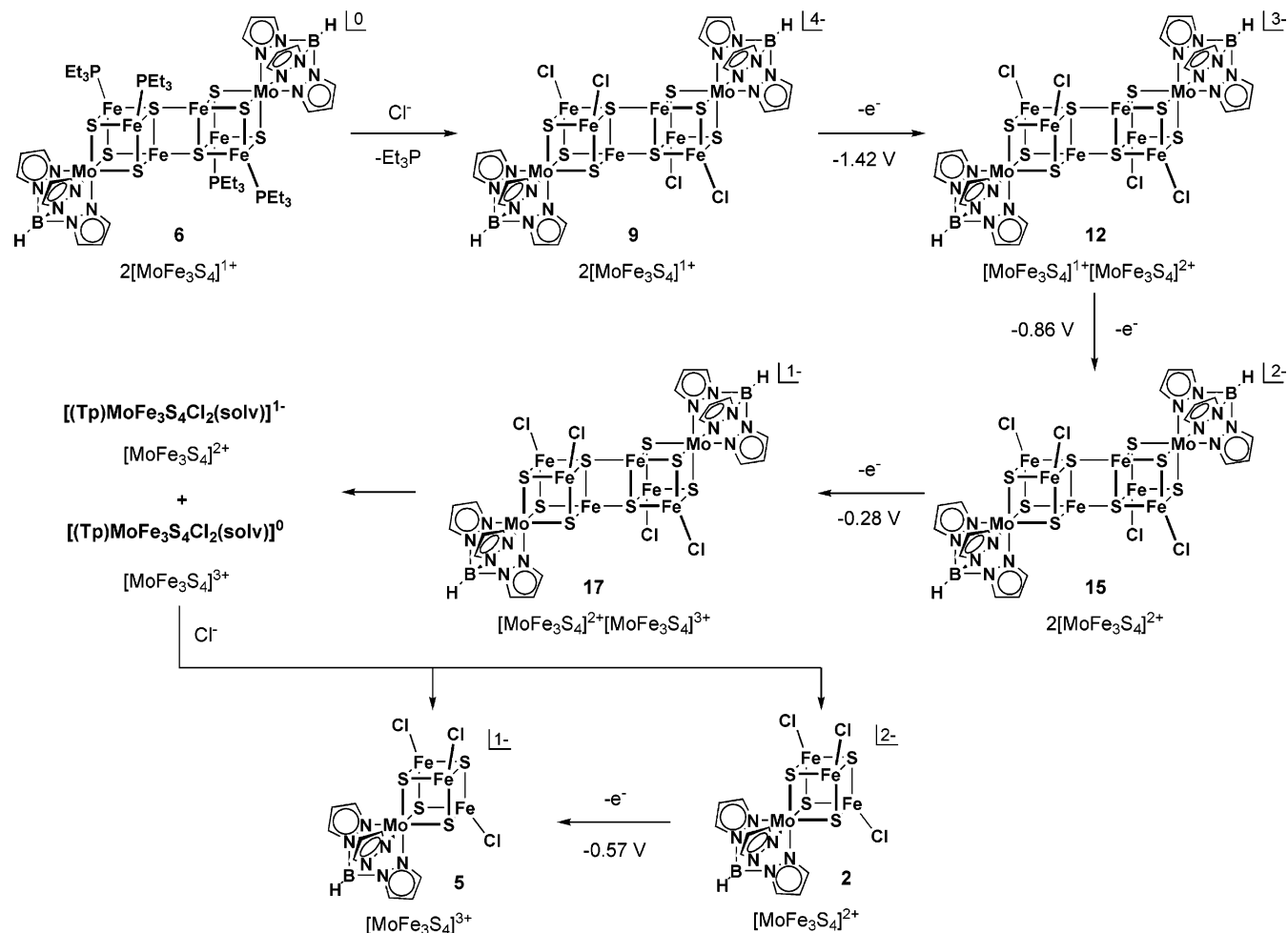


Figure 2. Scheme depicting the preparation of EBDC $[(Tp)_2Mo_2Fe_6S_8Cl_4]^{4-}$ (**9**) from phosphine cluster **6** and the oxidation reactions of **9**, affording **12** and **15**, and the oxidation of **15** to **17** (not isolated). Clusters **15** and **17** cleave to presumed monosolvated SCs that are converted to **2** and **5** with chloride. Oxidation states of individual cubane units within double cubanes are indicated. Similar schemes apply to the clusters $[(Tp)_2Mo_2Fe_6S_8L_4]^z$ ($L = F^-, N_3^-$, and PhS^-).

Table 2. Electron-Transfer Series and Redox Potentials^a of $MoFe_3S_4$ Single Cubanes and Edge-Bridged Double Cubanes

	$[(Tp)MoFe_3S_4L_3]^{3-}$ $[MoFe_3S_4]^{1+}$	\rightleftharpoons	$[(Tp)MoFe_3S_4L_3]^{2-}$ $[MoFe_3S_4]^{2+}$	\rightleftharpoons	$[(Tp)MoFe_3S_4L_3]^{1-}$ $[MoFe_3S_4]^{3+}$	(2)	
$L = F^-$		-1.87^b		-0.73 V			
$L = Cl^-$		-1.64^b		-0.57 V			
$L = N_3^-$		-1.54^b		-0.53 V			
$L = PhS^-$		-1.76^b		-0.69 V			
$[(Tp)_2Mo_2Fe_6S_8L_4]^{4-}$ $2[MoFe_3S_4]^{1+}$	\rightleftharpoons	$[(Tp)_2Mo_2Fe_6S_8L_4]^{3-}$ $[MoFe_3S_4]^{1+}[MoFe_3S_4]^{2+}$	\rightleftharpoons	$[(Tp)_2Mo_2Fe_6S_8L_4]^{2-}$ $2[MoFe_3S_4]^{2+}$	\rightleftharpoons	$[(Tp)_2Mo_2Fe_6S_8L_4]^{1-}$ $[MoFe_3S_4]^{2+}[MoFe_3S_4]^{3+}$	(3)
$L = F^-$	-1.65		-1.04		-0.38 V ^b		
$L = Cl^-$	-1.42		-0.88		-0.28 V ^b		
$L = N_3^-$	-1.29		-0.75		-0.23 V ^{b,c}		
$L = PhS^-$	-1.57		-0.98		-0.38 V ^b		

^a Versus SCE at 298 K in acetonitrile. ^b Quasireversible. ^c Poorly defined.

6) resemble each other and that of **9**. Further, recrystallization of structurally authenticated $(Bu_4N)_4[8]$ from acetonitrile afforded a crystalline product with a spectrum (Figure 6b) very similar to that of the solution prepared from $(Et_4N)_4[9]$, yet the crystal structure of this material was that of 3:1 EDBC salt containing trianion cluster **11**. These observations were explicated by an electrochemical investigation.

Cyclic voltammograms of solutions prepared from salts of EBDCs **8** and **9** are provided in Figure 7. Rest potentials are ca. -1.2 to -1.3 V. At more negative potentials, the clusters show chemically reversible ($i_{pc}/i_{pa} = 1$) steps at $E_{1/2} = -1.65$ V (**8**) and -1.42 V (**9**). At more positive potentials, three additional processes are observed. The results are interpreted in terms of the four-member electron-transfer series 3 in Table 2; redox steps are indicated in brackets in

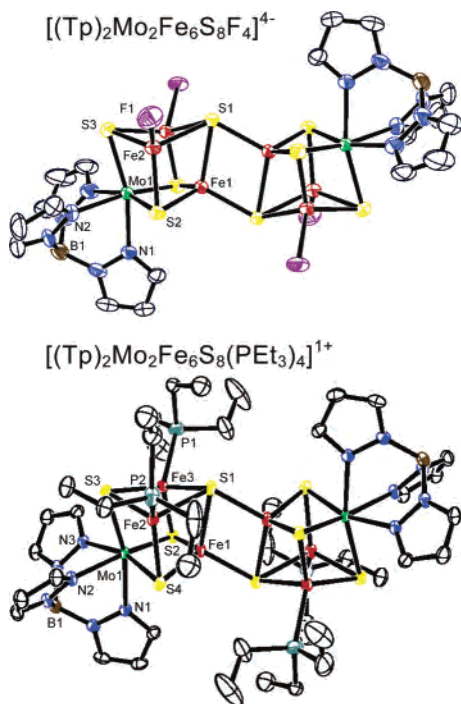
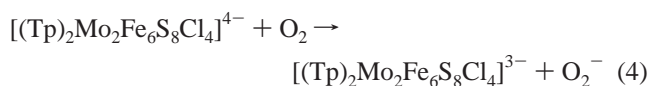


Figure 3. Structures of EBDCs $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{F}_4]^{4-}$ (top) and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]^{1+}$ (bottom) showing 50% probability level ellipsoids and atom-labeling schemes for the asymmetric unit. Both clusters have a crystallographically imposed inversion center.

Figure 7. The preceding two potentials are associated with the $[4-/3-]$ couple. The oxidizability order is the same as for the SCs. Although $4-$ clusters can be isolated as moderately to sparingly soluble salts in acetonitrile, attempts to maintain this oxidation state in solution have not been successful; conversion to the $3-$ state by adventitious oxidation occurs in all cases. Extreme sensitivity to oxidation follows from the markedly low $[4-/3-]$ potentials, all of which are < -1.5 V.²⁷ Using the chloride clusters as an example and $E_{1/2} = -0.87$ V for the couple $\text{O}_2 + e^- \rightarrow \text{O}_2^-$ in acetonitrile,²⁸ oxidation reaction 4 is strongly favored ($K_{\text{eq}} = 2.0 \times 10^9$, 298 K). Similar results apply to clusters **8** and **10**.



Singly oxidized cluster **12** has been reproducibly isolated under standard workup conditions as the Bu_4N^+ salt (86%). A reproducible preparation of a salt of fluoride cluster **11** was not sought; however, its structure was determined (see below). Other observations using acetonitrile solutions prepared with $(\text{Et}_4\text{N})_4[\mathbf{9}]$ and reactions monitored by ^1H NMR substantiate spontaneous one-electron oxidation of $4-$

(27) In our experience under anaerobic conditions, reduced clusters with potentials < -1.5 V vs SCE are formidable to isolate as pure (non-oxidized) solids and are exceptionally difficult to handle in solution without oxidation by trace dioxygen. We note, for example, the successful isolation of such compounds as $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SBU}^t)_4]$ ($E_{1/2} = -1.42$ V, DMF)³² and, more recently, $(\text{Bu}_4\text{N})_4[\text{Fe}_4\text{S}_4(\text{CN})_4]$ ($E_{1/2} = -1.42$ V, CH_2Cl_2).³³ However, their clusters are extraordinarily sensitive to oxidation in solution.

(28) Sawyer, D. T. In *Oxygen Chemistry*; Oxford University Press: New York, 1991.

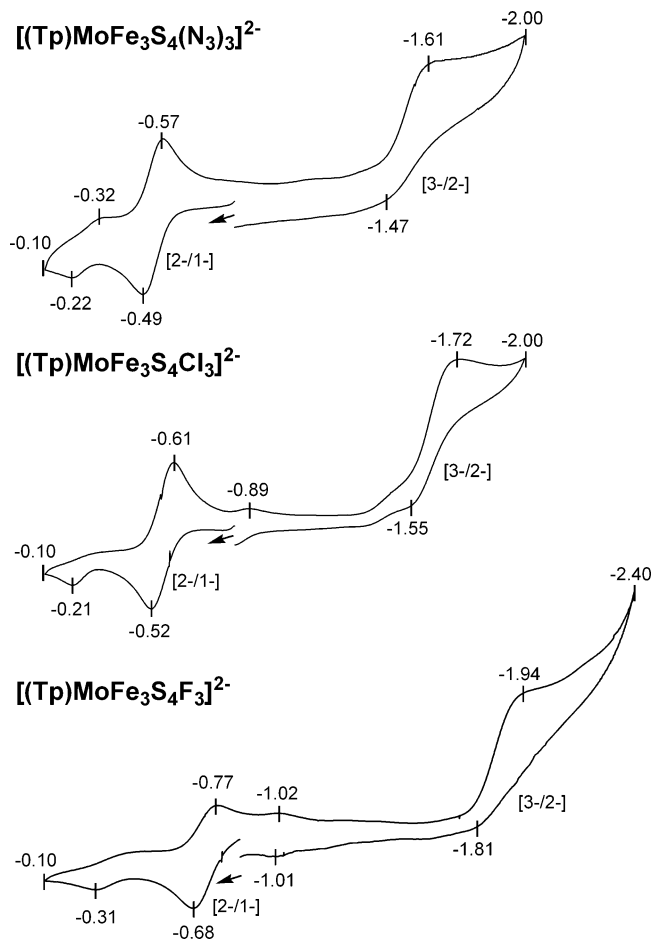


Figure 4. Cyclic voltammograms (100 mV/s) of the SCs $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{L}_3]^{2-}$ ($\text{L} = \text{N}_3^-, \text{Cl}^-, \text{F}^-$) in acetonitrile at 298 K. Peak potentials and the redox couples $[2^-/1^-]$ and $[3^-/2^-]$ are indicated.

Table 3. Mössbauer Parameters^a for Clusters $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{L}_3]^{2-}$ and $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{2-}$ at 4.2 K

cluster	cluster no.	δ (mm/s) ^{a,b}	ΔE_Q (mm/s) ^{a,c}
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{F}_3]^{2-d}$	1	0.58(1), 0.65(2)	0.53(1), 1.15(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{2-e,f}$	2	0.60(1), 0.61(2)	0.51(1), 1.11(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4(\text{N}_3)_3]^{2-d}$	3	0.58	0.52(1), 1.23(2)
$[(\text{Tp}^*)\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-g}$		0.32(1), 0.59(2)	0.87(1), 1.01(2)
$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-d,h}$	5	0.46(1), 0.51(2)	0.61(1), 1.09(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{F}_4]^{4-e}$	8	0.71	0.86
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{4-d}$	9	0.65(1), 0.74(2)	0.65(1), 0.94(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{N}_3)_4]^{4-d}$	10	0.65(1), 0.70(2)	0.67(1), 1.00(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{F}_4]^{3-j}$	11	0.53(1), 0.59(2)	0.59(1), 1.19(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-e,h}$	12	0.58(1), 0.64(2)	0.45(1), 0.83(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{N}_3)_4]^{3-j}$	13	0.58(1), 0.65(2)	0.49(1), 0.95(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-d}$	15	0.53(1), 0.58(2)	0.95(1), 0.65(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]^i$	6	0.58(1), 0.56(2)	0.54(1), 1.05(2)
$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]^{1+l}$	7	0.48	1.05

^a Relative areas in parentheses. ^b ± 0.02 mm/s. ^c ± 0.03 mm/s. ^d Et_4N^+ salt. ^e Bu_4N^+ salt. ^f Improved fit from the data in ref 13. ^g See ref 18. ^h At 77 K. ⁱ See ref 14. ^j Acetonitrile solution. ^k See ref 13. ^l TfO^- salt.

clusters upon dissolution. Chemical and electrochemical redox and related reactions 5–17 of chloride-ligated SC and EBDC clusters are collected in Table 4. Chemical reactions utilized $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{1+}$ ($E_{1/2} = -0.11$ V vs SCE).

Reaction 5 requires 1 molar equiv of oxidant; EBDC **15** was identified by its ^1H NMR spectrum (Figure 5c). When the reaction was carried out on a preparative basis, $(\text{Et}_4\text{N})_2[\mathbf{15}]$ was isolated (61%, Method A). In a variation of this

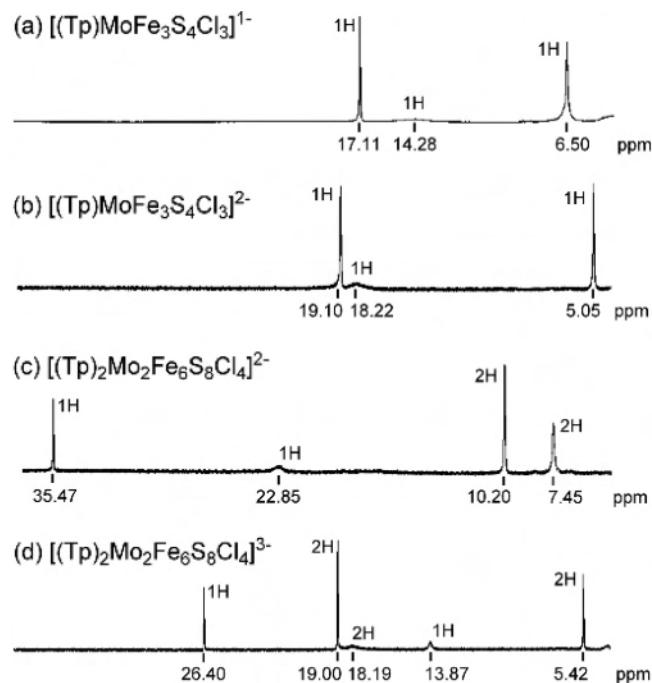


Figure 5. 1H NMR spectra of the complete set of isolated chloride-ligated SC and EBDC clusters in different oxidation states in acetonitrile solutions; relative signal intensities are indicated.

procedure, 2 equiv of the oxidant in an acetonitrile solution was added to solid $(Et_4N)_4[9]$. Immediately, a dark-colored solution developed; standard workup afforded the product (82%, Method B). In this method, the oxidation reaction proceeds with the stoichiometry of reaction 6. The addition of excess Et_4NCl to the reaction 5 mixture led to reaction 7 causing cleavage of **15** with formation of 2 equiv of SC **2** (Figure 5b). Reaction 8 requires 3 molar equiv of oxidant and also involves cleavage of dianion **15** in the presence of excess Et_4NCl (10 equiv) to generate oxidized SC **5** (Figure 5a). Cluster trianion **12** is not cleaved by excess chloride in the absence of an oxidant. In each reaction, the only detectable cluster final product is that indicated. The stoichiometry of these reactions necessitates that the reactant cluster has the 3 $-$ oxidation state. In recent work, the Et_4N^+ salt of bromide-ligated cluster dianion **16** was isolated by a different procedure.¹⁵

In the chloride series, the potential of the [3 $-$ /2 $-$] step is -0.88 V (reaction 11). Correspondingly, both trianion **12** and dianion **15** can be maintained in solution without oxidation under normal anaerobic conditions. However, **12** is subject to the comproportionation reaction 9 for which $K_{com} = \exp[(E_{2-/3-} - E_{3-/4-})F/RT] = 2.9 \times 10^9$ (298 K). Values for the fluoride and azide clusters are 2.0×10^{10} and 1.3×10^9 , respectively. This equilibrium accounts for the observation that attempted crystallization of $(Et_4N)_3[12]$ from oxidized solutions prepared with $(Et_4N)_4[9]$ resulted, after ether diffusion, in the isolation of the latter compound, which is only sparingly soluble in acetonitrile. When reaction 1 ($L = Cl^-$) was carried out in DMF in the presence of Bu_4NCl , $(Bu_4N)_3[12]$ was isolated and identified crystallographically. The use of Bu_4N^+ evidently diminishes the solubility

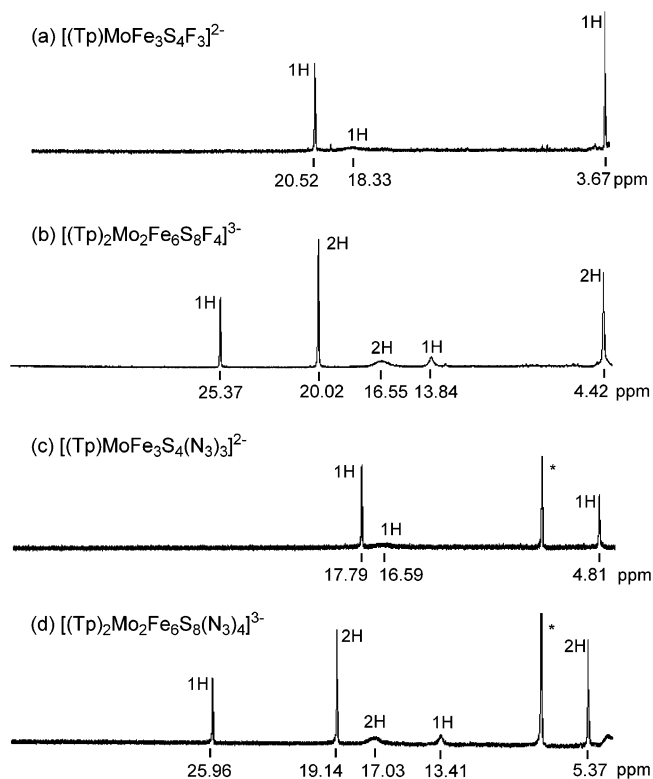


Figure 6. 1H NMR spectra of fluoride- and azide-ligated SC and EBDC cubane clusters in acetonitrile solutions; relative signal intensities are indicated. (* = solvent).

differences among the components of reaction 9 such that the desired cluster can be isolated.

The redox behavior of EBDC clusters over the entire region of electroactivity (0 to -2.0 V), deduced from the voltammograms of Figure 7 recorded at 50 mV/s and related observations, is schematically depicted in Figure 2 using chloride clusters as an example. The electrochemical behavior is best described in terms of a traversal of the cyclic voltammogram starting at the rest potential. A cathodic scan to -2.0 V followed by reversal of the scan to ca. -0.7 V encompasses the reversible [4 $-$ /3 $-$] and [3 $-$ /2 $-$] couples, reactions 10 and 11, respectively. Reaction 11 has been accomplished in the form of chemical oxidation reaction 5. At less negative potentials, the electrochemical behavior becomes more complicated. The next feature encountered has $E_{pa} = -0.52$ V. In scans at 300 mV/s and terminating at -0.35 V in the positive direction, this peak and that at $E_{pc} = -0.60$ V are essentially eliminated (not shown), indicating that they are coupled. These features must be assigned to reversible SC reaction 14 whose potentials are identical with the authentic couple (Figure 4, Table 2). To account for the appearance of this couple, we proposed solvent-assisted cleavage reaction 12 followed by ligand redistribution reaction 13 between cores of the same oxidation level to produce the required cluster **2**, which is oxidized to **5**. Although we have been unable to observe reaction 12 separately at NMR concentrations (Figure 5c), oxidation reaction 14, imposed by the electrode potential, would tend to displace reactions 12 and 13 toward the formation of **2**. The final redox event is a quasireversible process with E_{pa}

ELECTRON TRANSFER REACTIONS OF DOUBLE CUBANES

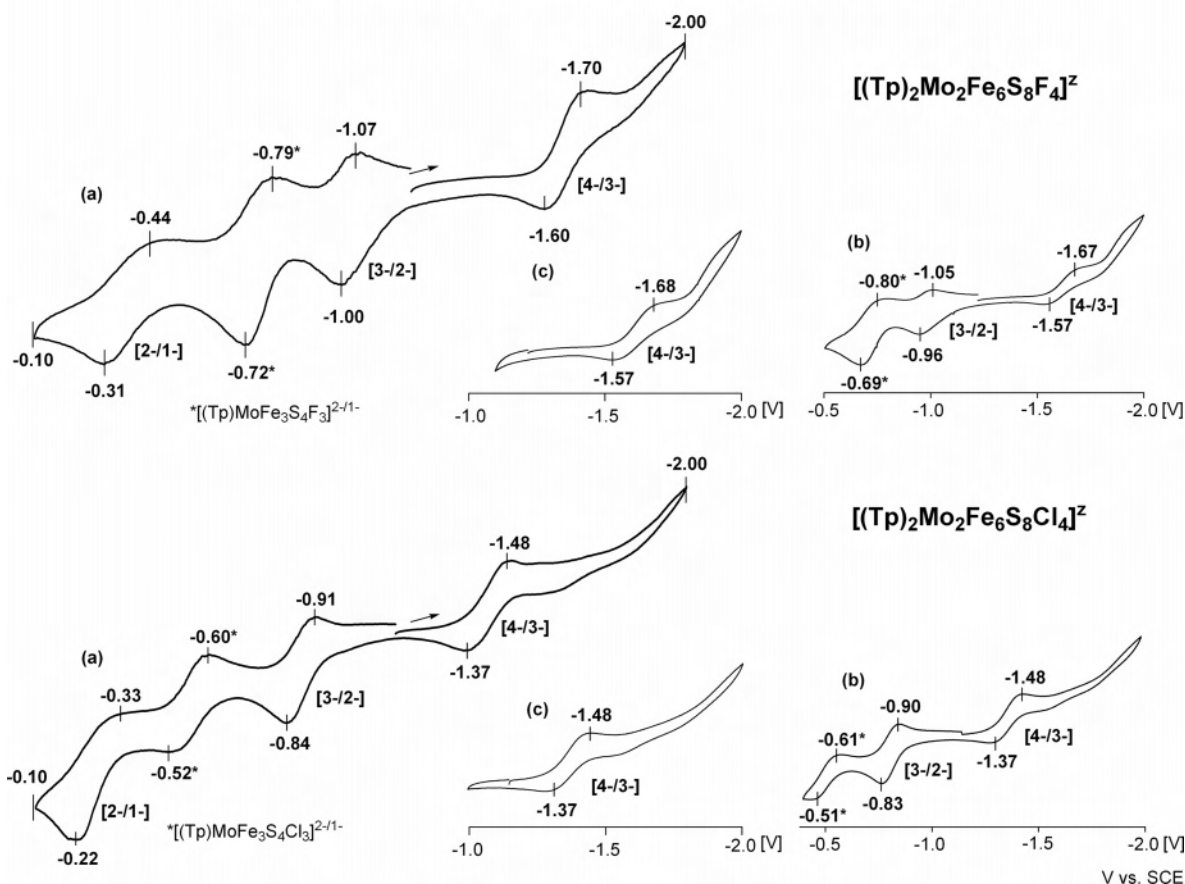


Figure 7. Cyclic voltammograms (50 mV/s) of EBDCs $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{3-}$ ($\text{L} = \text{F}^-, \text{Cl}^-$) in acetonitrile at 298 K. Peak potentials arising from the double cubane redox couples $[2-/1-]$, $[3-/2-]$, and $[4-/3-]$ and the single cubane $[2-/1-]^*$ redox couples are indicated. (a) Complete voltammograms from -0.1 to -2.0 V. (b) Voltammograms covering the redox steps of single and double cubanes that (excluding $1-$) have been isolated with $\text{L} = \text{Cl}^-$. (c) Voltammograms restricted to the $[4-/3-]$ double cubane couple. Solutions were prepared from salts of $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{L}_4]^{4-}$.

Table 4. Redox and Related Reactions of Chloride- and Phosphine-Ligated Single and Edge-Bridged Double Cubanans

reaction no.	reaction	E_{pa} (V)	E_{pc} (V)
5	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-} + [(\text{C}_5\text{Me}_5)_2\text{Fe}]^{1+} \rightarrow [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-} + [(\text{C}_5\text{Me}_5)_2\text{Fe}]$		
6	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{4-} + 2 [(\text{C}_5\text{Me}_5)_2\text{Fe}]^{1+} \rightarrow [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-} + 2 [(\text{C}_5\text{Me}_5)_2\text{Fe}]$		
7	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-} + [(\text{C}_5\text{Me}_5)_2\text{Fe}]^{1+} + 2\text{Cl}^- \rightarrow 2[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{2-} + [(\text{C}_5\text{Me}_5)_2\text{Fe}]$		
8	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-} + 3[(\text{C}_5\text{Me}_5)_2\text{Fe}]^{1+} + 2\text{Cl}^- \rightarrow 2[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-} + 3[(\text{C}_5\text{Me}_5)_2\text{Fe}]$		
9	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-} + [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{4-} \rightleftharpoons 2[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-}$		
10	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-} + \text{e}^- \rightleftharpoons [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{4-}$	-1.37	-1.48
11	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{3-} \rightleftharpoons [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-} + \text{e}^-$	-0.84	-0.91
12 ^a	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-} + 2\text{solv} \rightleftharpoons 2[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{sol})]^{1-}$		
13	$2[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{sol})]^{1-} \rightleftharpoons [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{2-} + [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}(\text{sol})_2]^{0}$		
14	$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{2-} \rightleftharpoons [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-} + \text{e}^-$	-0.52	-0.60
15	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{2-} \rightleftharpoons [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{1-} + \text{e}^-$	-0.22	-0.33
16 ^a	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{Cl}_4]^{1-} + 2\text{solv} \rightleftharpoons [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{sol})]^{0} + [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{sol})]^{1-}$		
17	$[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{sol})]^{0} + [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{sol})]^{1-} \rightleftharpoons [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-} + [(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}(\text{sol})_2]^{0}$		
18	$[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_4] + [(\text{C}_5\text{Me}_5)_2\text{Fe}]^{1+} \rightleftharpoons [(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_4]^{1+} + [(\text{C}_5\text{Me}_5)_2\text{Fe}]$		

^a Solvate stoichiometry and number bound are arbitrary.

= -0.22 V with a counterpart feature at $E_{\text{pc}} = -0.33$ V. Because the peak at -0.22 V appears in 300 mV/s scans in the positive direction to 0 V when the SC feature at -0.52 V is barely observable, it does not arise from a SC. Further, the authentic SC does not exhibit a reaction in this potential range. The process is assigned to the $[2-/1-]$ couple 15 of the EBDC remaining from reaction 11 and producing cluster monoanion 17. As noted above, this species has not been isolated.

In negative potential scans from ca. 0 V, the -0.60 V peak is encountered. Whereas at slow scan rates SC 5 may be generated for reduction at this potential via reactions 12–14, there is clearly another source of this cluster. Fast positive scans to 0 V at 300 mV/s show a very weak peak at -0.52 V but a strong response at -0.60 V in the reverse direction and also the $[2-/3-]$ SC couple at $E_{\text{pc}} \approx -1.7$ V (Figure 4). If the voltammetry is carried out in a potential range in which oxidized cluster 17 does not form, peaks of the SC

redox processes are barely observable. Consequently, we propose the occurrence of EBDC cleavage reaction 16 followed by ligand redistribution reaction 17, furnishing **5** for the observed reduction step. In the latter reaction, chloride is transferred to the more oxidized cluster, as might be expected. The remainder of the negative scan to -2.0 V reverses reaction 11 and affects reaction 10. Under this interpretation, the formation of **2** for oxidation by reactions 12 and 13 is much slower than the formation of **5** for reduction by reactions 16 and 17. A reaction scheme analogous to that in Figure 2 applies to the fluoride and azide clusters.

When the voltammetry was repeated in the presence of 0.5–12 equiv of added Et_4NCl , the peaks associated with reaction 14 intensified relative to other features. With 12 equiv at 100 mV/s, features due to reaction 15 were not detectable, indicating complete cleavage of the oxidized EBDCs. All electrochemical observations with added chloride are consistent with chemical oxidation reactions 7 and 8, which subsume cleavage of both oxidized clusters **15** and **17**.

(b) Phosphine and Thiolate Clusters. Neutral phosphine cluster **6** can be maintained as a suspension in acetonitrile or as a solution in THF under anaerobic conditions. It is subject to controlled chemical oxidation in reaction 18 to afford monocation **7**, isolated as the BF_4^- salt (61%). Cluster **6** can also be oxidized with Me_3SiOTf to afford the triflate salt (68%). This $[0/1+]$ couple is isoelectronic with the $[4-/3-]$ couple in series 3 (Table 2) and proceeds with $E_{1/2} = -0.83$ V in acetonitrile. A structure determination has verified retention of the EBDC construction upon oxidation to **7** (Figure 3).

Thiolate cluster trianion **14** was isolated directly from reaction 1 ($L = PhS^-$) under anaerobic conditions.¹⁵ Its voltammetry was examined to ascertain consistency with the behavior of halide and azide clusters. The voltammogram of Figure 8 confirms analogous behavior; redox steps are assigned on the same basis as in Figure 7. In particular, steps with $E_{1/2} = -1.75$ V and -0.68 V are readily assigned upon comparison with the voltammetry of SC **4**. Potentials of the three-member series 2 and the four-member electron-transfer series 3 are given in Table 2. Again, it is evident that the very low potential of the $[4-/3-]$ couple is responsible for the destabilization of the cluster tetraanion.

Structural Systematics. The overall structural features of the EBDC motif (Figure 1) have been described in some detail previously,^{2,5,10,12,16} rendering unnecessary a similar discussion here. We simply note that these double cubanes have idealized or actual centrosymmetry with the heterometal M atoms necessarily transoid, trigonally distorted octahedral MN_3S_3 sites, distorted tetrahedral FeS_4 and FeS_3L sites, and intercube Fe–S1' bonds that are shorter than intracubane Fe1–S1 bonds.

With the availability of some nine EBDC structures $[(Tp)_2Mo_2Fe_6S_8L_4]^z$ (Figure 1), there are now sufficient results to examine features at (i) constant oxidation state z and variable terminal ligands L and at (ii) variable z and constant L. Because of the large number of structural

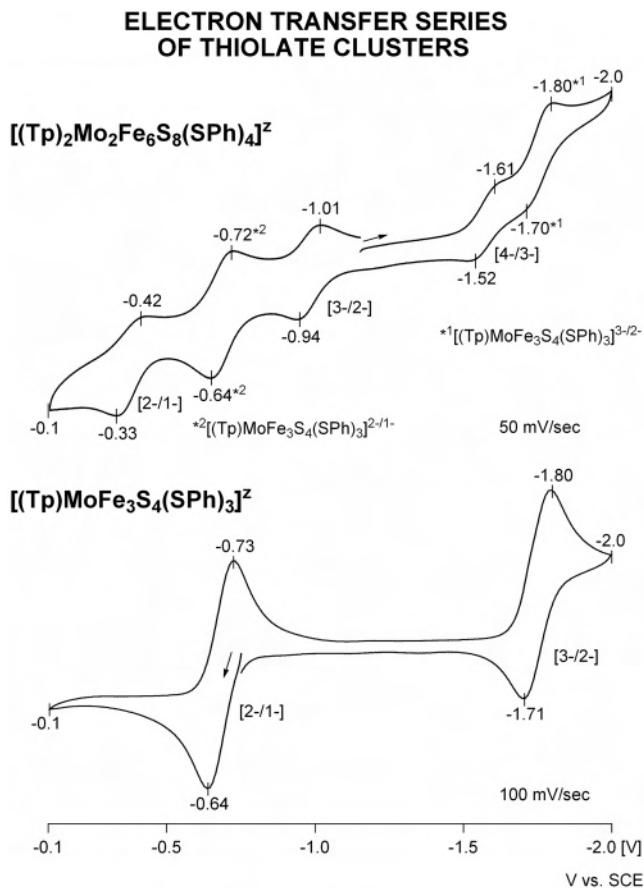


Figure 8. Cyclic voltammograms of the EBDC $[(Tp)_2Mo_2Fe_6S_8(SPh)_4]^{3-}$ (50 mV/s) and the SC $[(Tp)MoFe_3S_4(SPh)_3]^{2-}$ (100 mV/s) in acetonitrile at 298 K. Peak potentials are indicated.

parameters involved, mean values of interatomic distances are used to describe intracubane features except for Fe1–S1 bond lengths, which are individual values. Intercubane dimensions involving distances and angles of the Fe1–S1–Fe1'–S1' bridge rhombs are individual values. Data are summarized in Table 5. Comparisons are made between corresponding intracubane distances and intercube distances and angles.

Case (i) with $z = 4-$ involves clusters **8** (two compounds), **9**, and **10**. Intracubane distances differ by ≤ 0.06 Å and in all but two distances by ≤ 0.04 Å. The largest differences in intercube dimensions are 0.16 Å for **8/10** and 0.13 Å for **9/10** in Fe1–Fe1' and 4.1–4.8° for **8,9/10** in both S1–Fe1–S1' and Fe1–S1–Fe1'. If this case is extended to include isoelectronic **6**, intracubane distances differ by ≤ 0.09 Å and intercube dimensions differ by 0.02–0.11 Å and 0.5–3.4°. Case (ii) with $z = 4-, 3-, 2-$ involves fluoride clusters **8** and **11** and chloride clusters **9**, **12**, and **15**, and with $z = 0, 1+$ phosphine clusters **6** and **7**. The following distance parameters respond in fairly clear trends to increasing oxidation in the chloride series and are described by the span of values over the three clusters: Fe–Cl 0.09 Å, Fe–Fe 0.07 Å, Fe1–S1 0.12 Å, Fe1–S1' 0.06 Å, Fe1–Fe1' 0.14 Å. The decrease in terminal bond lengths is a result of the decreased size of the iron atom, a behavior found in cubane-type Fe_4S_4 clusters.²⁶ (Radii for tetrahedral Fe^{II} and

Table 5. Selected Mean Values of Bond Distances (Å) and Angles (deg) for [(Tp)₂Mo₂Fe₆S₈L₄]^z Clusters (L = F⁻, Cl⁻, N₃⁻, PEt₃)

cluster	intracubane						intercubane				
	Mo–N	Mo–S	Fe–L ^a	Fe–S ^b	Fe(1)–S(1)	Mo–Fe	Fe–Fe	Fe(1)–Fe(1')	Fe(1)–S(1')	S(1)–Fe(1)–S(1')	Fe(1)–S(1)–Fe(1')
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ F ₄] ^{4–c} (8)	2.226[5]	2.366[6]	1.879(7)	2.31[5]	2.407(5)	2.73[1]	2.662[4]	2.709(5)	2.262(5)	109.1(2)	70.9(2)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ F ₄] ^{4–d} (8)	2.23[2]	2.39[1]	1.90[2]	2.32[6]	2.444[5]	2.76[3]	2.64[3]	2.784(5)	2.281[1]	107.85(2)	72.22(3)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ F ₄] ^{3–d} (11)	2.238[6]	2.367[7]	1.863[2]	2.31[6]	2.421(1)	2.726[3]	2.74[4]	2.695(1)	2.269(1)	109.76(5)	70.64(4)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ Cl ₄] ^{4–c,e} (9)	2.246[2]	2.384[2]	2.32[1]	2.32[6]	2.426(1)	2.74[1]	2.63[3]	2.737(1)	2.286(6)	109.07(4)	70.93(4)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ Cl ₄] ^{3–d} (12)	2.233[4]	2.36[1]	2.261[6]	2.30[5]	2.372[6]	2.72[3]	2.69[2]	2.690(1)	2.26[2]	109.40(4)	70.60(4)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ Cl ₄] ^{2–c,e} (15)	2.228[2]	2.362[6]	2.225(2)	2.28[5]	2.312(2)	2.69[2]	2.70[3]	2.603(2)	2.226(2)	110.04(6)	69.96(6)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ (N ₃) ₄] ^{4–d} (10)	2.244[7]	2.37[1]	2.019[8]	2.32[6]	2.422(1)	2.72[3]	2.60[1]	2.868(1)	2.284(1)	104.96(3)	75.04(3)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ (PEt ₃) ₄] ^f (6)	2.242[6]	2.38[1]	2.358[2]	2.29[5]	2.455(2)	2.67[2]	2.574[6]	2.757(2)	2.248(2)	108.38(7)	71.62(7)
[(Tp) ₂ Mo ₂ Fe ₆ S ₈ (PEt ₃) ₄] ^{1+f} (7)	2.23[1]	2.37[2]	2.342[3]	2.26[4]	2.375(1)	2.673[6]	2.61[1]	2.651(1)	2.220(1)	111.17(5)	70.40(4)

^a L = terminal ligand. ^b Mean value excludes Fe(1)–S(1). ^c Et₄N⁺ salt. ^d Bu₄N⁺ salt. ^e See ref 14. ^f (CF₃SO₃)⁻ salt.

Fe^{III} differ by ~0.14 Å.²⁹) This trend is not reflected by the fluoride or phosphine clusters. Decreases in the two types of Fe–S distances likely have a similar origin, and a shortening of the Fe1–Fe1' separation is a consequence of changes in these distances. Similar trends are observed in the phosphine series. The fluoride set does not manifest these trends, primarily because of dimensional differences in the two compounds containing **8**. Because we are seeking trends, we have arbitrarily not included esd's in the foregoing limits and differences, as they would both increase and decrease these values. From the data of Table 5, we conclude that all clusters are essentially isostructural, isoelectronic cores approach an isometric condition, and that, overall, significant dimensional differences accompanying oxidation or reduction are largely confined to the bridge rhombs. The cleavage of oxidized double cubanes to SCs by excess chloride is a probable consequence of increased electrophilicity of the oxidized cluster instead of a weaker intercubane Fe–S bond. Consistent with the behavior of all weak-field mixed-valence Fe–S or M–Fe–S clusters of nuclearity four or higher, there is no clear crystallographic evidence of localized iron oxidation states. Nor are there structurally distinct subcores in **7**, **11**, and **12**, formally described as containing [MoFe₃S₄]¹⁺–[MoFe₃S₄]²⁺.

⁵⁷Fe Isomer Shifts. Isomer shifts (δ) and quadrupole splittings (ΔE_Q) for five SCs and nine EBDCs are collected in Table 3. Selected spectra are shown in Figure 9. The majority of spectra were fit satisfactorily with two overlapping quadrupole doublets in a 2:1 intensity ratio taken from the EBDC structure. However, such unresolved spectra resist unique fits; no conclusions are made concerning the relative shifts of the two populations of iron atoms. The isomer shifts do reflect the different oxidation states of the clusters and follow the well-established trend of decreasing isomer shift with increasing oxidation state. With the halide and azide clusters, isomer shifts show no clear dependence on terminal ligand. For EBDCs, mean isomer shifts of 4– (0.68–0.71 mm/s), 3– (0.57–0.63 mm/s), and 2– (0.56 mm/s, one example) clusters fall into the indicated ranges. The mean shift difference between chloride clusters **9** and **15** is 0.14 mm/s, which is comparable to the value of ca. –0.1 mm found between adjacent oxidation states of Fe₃S₄ clusters at the parity of terminal ligands.²⁶ For reasons unclear, the 3–

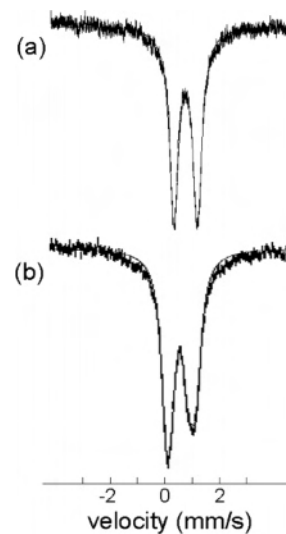


Figure 9. Mössbauer spectra at 4.2 K of (a) polycrystalline (Bu₄N)₄[(Tp)₂Mo₂Fe₆S₈F₄] and (b) an acetonitrile solution prepared from (Bu₄N)₄[(Tp)₂Mo₂Fe₆S₈F₄] and containing [(Tp)₂Mo₂Fe₆S₈F₄]³⁻. Spectra were fitted with the parameters in Table 3.

shifts are biased toward the 2– clusters. The spectra do not even partially resolve the two subcores of the 3– state.

When the fully reduced clusters **8** and **10** were examined in solution (Figure 9a), it was observed that the isomer shifts decreased compared to those of the solid state and were consistent with the formation of the 3– clusters **11** and **13**, respectively. These observations further support spontaneous oxidation in solution, as deduced from voltammetry and ¹H NMR spectra. For phosphine clusters **6** and **7**, isomer shifts also decrease upon oxidation but are not directly comparable with the halide and azide clusters. Previous work has established that for isoelectronic cubane-type clusters, shifts decrease in the order L = Cl⁻ > RS⁻ > R₃P.⁵ The isomer shifts of the pairs **6/9** and **7/12** adhere to this trend.

Structural Analogues of P^N Clusters. All methods for preparing these clusters utilize EBDC precursors.^{14,15} One of two initial routes employed a reaction mixture prepared from (Et₄N)₄[**9**] and 3 equiv of NaSH in acetonitrile. The product cluster was one electron more oxidized than expected, a matter that is now explained by reaction 19 in which the actual reactant is the 3– cluster. The other route involves the reaction of **6** with hydrosulfide; to accommodate the product oxidation state 0.5 equiv of dihydrogen was invoked as a product. Reaction 1 with L = F⁻ proceeds in THF to

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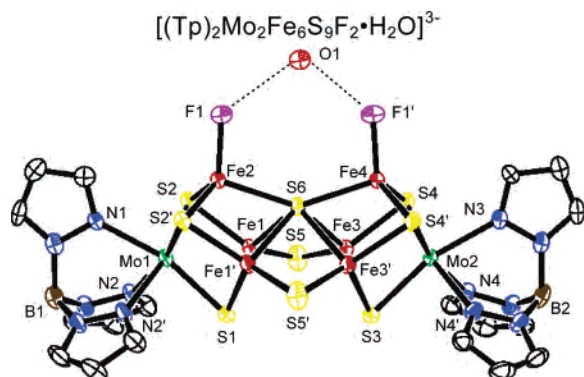
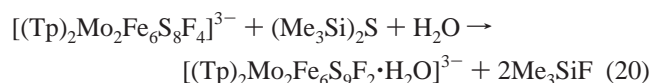
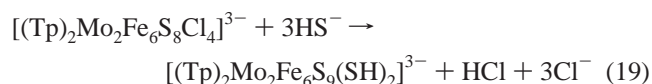


Figure 10. Structure of $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9\text{F}_2\cdot\text{H}_2\text{O}]^{3-}$ showing 50% probability level ellipsoids and the atom-labeling scheme; primed and unprimed atoms are related by a crystallographically imposed symmetry plane. Selected metric parameters (Å, deg) for $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9\text{F}_2\cdot\text{H}_2\text{O}]^{3-}$: Mo–N 2.247[9] (4), Mo–S 2.380[8] (4), Mo–Fe 2.73[2] (4), Fe–(μ_2 -S) 2.226[9] (2), Fe–(μ_3 -S) 2.269[3] (6), Fe–(μ_6 -S) 2.40[2] (4), Fe1–Fe3 2.792(2), other Fe–Fe 2.69[2] (4), Fe–F 1.88[1] (2), F1–O 2.70(2), F1'–O 2.57(2), Fe–(μ_2 -S)–Fe 77.70(8), Fe(2)–S(6)–Fe(4) 143.1(1), F1–O–F1' 108.2(6).

afford fully reduced cluster **8**, isolated as the Bu_4N^+ salt (74%). When the reaction was conducted in acetonitrile with hydrated $(\text{Et}_4\text{N})\text{F}$, the solid product was found by ^1H NMR to be a 2:1 mixture of $(\text{Et}_4\text{N})_4[\mathbf{11}]$ and the Et_4N^+ salt of a new cluster subsequently identified as **18**. Treatment of the mixture with $(\text{Me}_3\text{Si})_2\text{S}$ resulted in the conversion of **11** to **18** by proposed reaction 20 and the isolation of $(\text{Et}_4\text{N})_3[\mathbf{18}]$ (43%).



The structure of cluster **18**, displayed in Figure 10, reveals it to be a structural analogue of the P^{N} cluster of nitrogenase. The core consists of two MoFe_3S_4 cubane units bridged by sulfide atoms S5 and $\text{S5}'$ and the μ_6 - S6 atom, resulting in an Fe2–S6–Fe4 angle of $143.1(1)^\circ$. The sextuply bridging sulfide atom and the markedly obtuse bridge angle are the most distinctive features of the structure. Cluster **18** is isostructural and nearly isometric with $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SH})_2]^{3-}$ (141.0°) and $^{14}[(\text{Tp})_2\text{V}_2\text{Fe}_6\text{S}_9(\text{SH})_2]^{4-}$ (140.8°)⁷ and is similar to $[(\text{Tp}^*)_2\text{W}_2\text{Fe}_5\text{NaS}_9(\text{SH})(\text{MeCN})]^{3-}$ (138.8°).¹⁸ The structural description of $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SH})_2]^{3-}$ largely applies to **18**. The structure of the latter differs by having two terminal fluoride ligands in place of two hydrosulfide ligands on two of the iron atoms bridged by μ_6 -S. A water molecule is hydrogen bonded between the fluoride atoms. Reaction 20 is presumably assisted by the ≤ 60 kcal/mol difference between Si–S and Si–F bond energies^{30,31} and may imply a synthetic method for the possible introduction into the core of atom/group X from a $(\text{Me}_3\text{Si})_2\text{X}$ reagent.

Acknowledgment. This research was supported by NIH Grant GM 28856. We thank Dr. J. Jiang for a contribution to the X-ray structure determinations.

Supporting Information Available: X-ray crystallographic files in CIF format for the seven compounds in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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