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Synthesis, Identification, and Reactivity Properties of Symmetrical $MoFe_3S_4$ Double Cubanes with Fe−S−Fe and Fe−O−Fe Bridges

Jiesheng Huang and R. H. Holm*

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138

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Singly bridged double cubane clusters containing Fe_4S_4 and/or $MoFe_3S_4$ cores and linked by an Fe−S−Fe unit bear an interesting compositional similarity to the cofactor of nitrogenase and constitute a nearly unexplored class of clusters. We have expanded recently our investigation of the prototypic cluster $\{[(\mathrm{Meida})MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$ (**6**) (Huang et al.; *J. Am. Chem. Soc.* **1997**, *119*, 8662) to other types $\{[(\mathrm{Meida})MoFe_3S_4L_2]_2(\mu_2\text{-}S)\}^{4-}$ (L = EtS^-, ArO^- (**8**−**10**)) (Meida = *N*-methylimidodiacetate(2-)). Clusters are formed by coupling reactions of the single cubanes $[(\mathrm{Meida})MoFe_3S_4L_3]^{2-}$ (L = Cl^- (**1**), ArO^- (**3**−**5**)) at their substitutionally labile iron sites with primarily Li_2S. Using 2 NaOEt/H_2O as an oxide source in Me_2SO, the oxo-bridged clusters $\{[(\mathrm{Meida})MoFe_3S_4L_2]_2(\mu_2\text{-}O)\}^{4-}$ (L = Cl^- (**13**), ArO^- (**14**, **15**)) have been prepared. All double cubanes were obtained as a mixture of as many as four diastereomers. Double cubane structures were established by NMR and electrochemical criteria. Both the sulfido- and oxo-bridged clusters undergo terminal ligand substitution reactions with bridge retention. Oxo bridges are much more susceptible than sulfido bridges to protic cleavage with water, $(Et_3NH)Cl$, ArOH, and HS^-. Reaction of **13** with hydrosulfide affords a second route to **6**. These and other results define a set of reactions that are regiospecific at either the terminal ligand or bridge sites and provide a basis for future reactivity manipulation of symmetrical and unsymmetrical bridged double cubanes.

Introduction

We have recently observed that the core composition $M_2Fe_6S_9$ of a singly sulfido-bridged double cubane cluster is close to (M = Mo), or identical with (M = Mo, Fe), the MFe_7S_9 core of the FeMo cofactor (FeMoco) of nitrogenase.[1] While the two cores are different in topology, $[MFe_3(\mu_3\text{-}S)_4]_2(\mu_2\text{-}S)$ for a double cubane vs $[MoFe_3(\mu_3\text{-}S)_3](\mu_2\text{-}S)_3[Fe_4(\mu_3\text{-}S)_3]$ for FeMoco,[2] the former is a potential precursor of the latter by rearrangement reactions and/or redox processes.[1] Core rearrangement reactions of iron−sulfur clusters are well established and have been summarized.[3] To proceed with a study of the possible rearrangements of double cubanes, it is first necessary to develop a synthesis and certain fundamental spectroscopic and reactivity features of this virtually unexplored class of clusters. Members of this class that are of interest in the cofactor context are those having only Fe−S−Fe bridging interactions between individual cubanes, in contrast to the great majority of double cubanes in which the bridges include the heteroatom M = Mo or W in individual MFe_3S_4 cubanes.[4] Bridges involving these atoms will be less labile than Fe−S−Fe bridges and, in any case, are not involved in conjoining the two cuboidal fragments of FeMoco. The first double cubane cluster containing an Fe−S−Fe bridge was $\{[Fe_4S_4(LS_3)]_2S\}^{4-}$, prepared by linking two [1:3] iron site-differentiated clusters with sulfide.[5] This was followed shortly thereafter by the synthesis of $[(Fe_4S_4Cl_3)_2S]^{4-}$ and crystallographic proof of an Fe−S−Fe bridge with an angle of 102°.[6]

Our latest and most extensive investigation of bridged double cubanes has resulted in the synthesis of species containing the core units $[(MFe_3S_4)_2(\mu_2\text{-}S)]^{4+}$ and $[(MFe_3S_4)(\mu_2\text{-}S)(Fe_4S_4)]^{3+}$.[1] These and $[(Fe_4S_4)_2(\mu_2\text{-}S)]^{2+}$ double cubanes are prepared by coupling individual single cubanes with sulfide in ligand substitution reactions,[1,5−8] as in the illustrative core coupling reaction 1.[1] The preparation of heterometal double cubanes

$$2[(\mathrm{Meida})MoFe_3S_4Cl_3]^{2-} + Li_2S \rightleftarrows \{[(\mathrm{Meida})MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-} + 2LiCl \quad (1)$$

requires protection of the M sites by a tight tridentate ligand such as *N*-methylimidodiacetate(2−) (Meida) so as to direct substitution to the labile iron sites. That investigation provided a general route to sulfido-bridged double cubanes and led to spectroscopic and electrochemical criteria of their formation. The emphasis in that work was placed on clusters with terminal chloride ligands owing to their ease of displacement in reactions such as (1). The present study addresses previously uninvestigated aspects of the reactivity of single and double $[MoFe_3S_4]^{3+}$ cubanes that contribute to the development of this class of cluster compounds and are in substantial part relevant to subsequent core rearrangement experiments. (i) Can single cubanes with terminal ligands other than chloride be coupled to form stable sulfido-bridged double cubanes? (ii) Can chloride-ligated double cubanes undergo substitution at the iron sites with retention of the bridge? (iii) Are *oxo*-bridged double cubanes

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[1] Huang, J.; Mukerjee, S.; Segal, B. M.; Akashi, H.; Zhou, J.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 8662.

[2] (a) Chan, M. K.; Kim, J.; Rees, D. C. *Science* **1993**, *260*, 792. (b) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965.

[3] Beinert, H.; Holm, R. H.; Münck, E. *Science* **1997**, *277*, 653.

[4] Huang, J.; Goh, C.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 356 and references therein.

[5] Stack, T. D. P.; Carney, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1670. LS_3 = 1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(*p*-tolylthio)benzenate(3−).

[6] Challen, P. R.; Koo, S.-M.; Dunham, W. R.; Coucouvanis, D. *J. Am. Chem. Soc.* **1990**, *112*, 2455.

[7] Weigel, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 4184.

[8] Zhou, C.; Holm, R. H. *Inorg. Chem.* **1997**, *35*, 4066.

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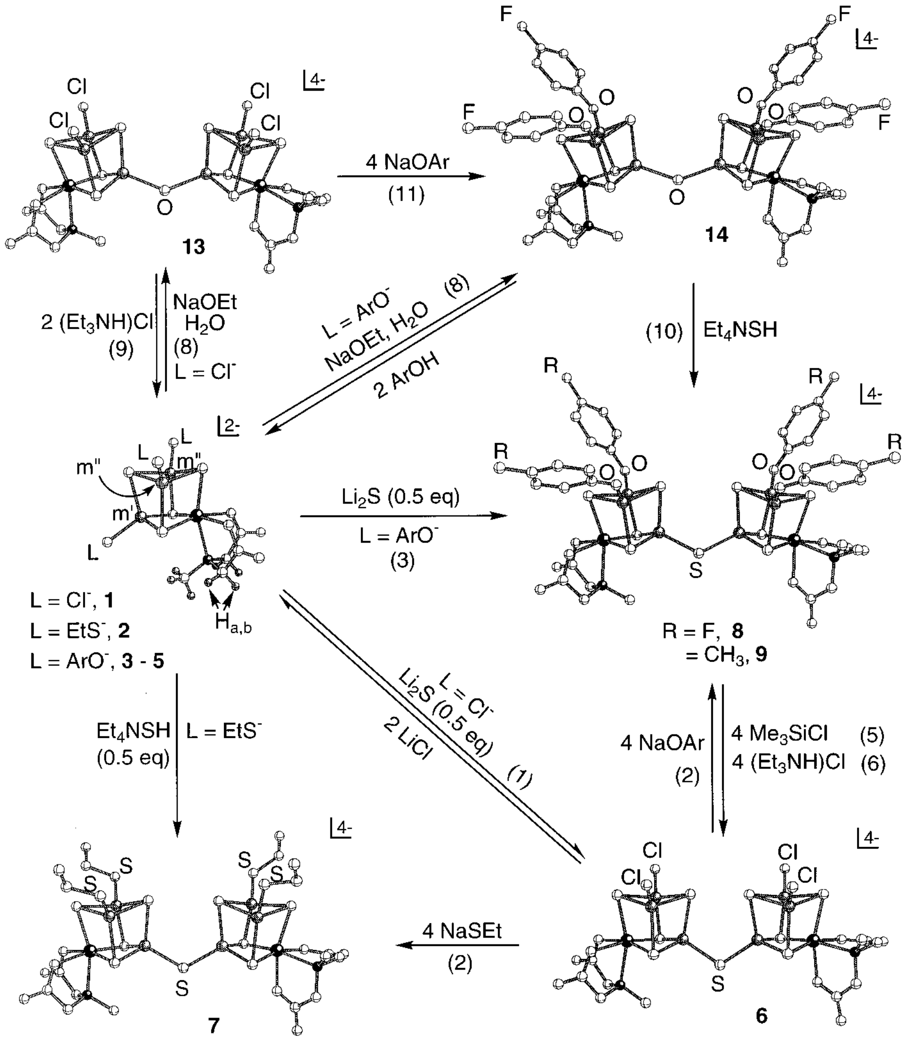

Figure 1. Reaction scheme showing the formation and interconversion of sulfido-bridged and oxo-bridged double cubanes. For the single cubane clusters $[(\mathrm{Meida})\mathrm{MoFe_3S_4L_3}]^{2-}$, different Fe sites (m′ and m″) and the diastereotopic methylene protons ($H_{a,b}$) of the Meida ligand are indicated.

accessible and, if so, what are the reactivity properties of the terminal and bridge atoms?

Experimental Section

Preparation of Compounds. All operations and manipulations were carried out under a pure dinitrogen atmosphere. Solvents were purified as appropriate and degassed prior to use. The cluster compounds $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4Cl_3}]$, $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4(SEt)_3}]$, $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4(O\text{-}\mathit{p}\text{-}C_6H_4CH_3)_3}]$, and $(\mathrm{Et_4N})_4\{[(\mathrm{Meida})\mathrm{MoFe_3S_4Cl_2}]_2(\mu_2\text{-S})\}$ were prepared as previously described.[1] $\mathrm{NaOC_6D_5}$ was obtained by reaction of $\mathrm{C_6D_5OD}$ (Aldrich) with 1 equiv of sodium methoxide in methanol. The cluster sites m′ and m″ and diastereotopic protons $H_{a,b}$ used in NMR signal assignments are illustrated in Figure 1. The bridged double cubanes were obtained as isomeric mixtures[1] (see text) which give rise to multiple NMR signals. All compounds were substantially pure by ^{1}H and ^{19}F NMR criteria.

A. Single Cubane Clusters. $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4(O\text{-}\mathit{p}\text{-}C_6H_4F)_3}]$. To a solution of $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4Cl_3}]$ (100 mg, 0.11 mmol) in 2 mL of acetonitrile was added dropwise a solution of $\mathrm{Na(O\text{-}\mathit{p}\text{-}C_6H_4F)}$ (44.5 mg, 0.33 mmol) in 1 mL of acetonitrile. The mixture was stirred for 2 h and then filtered through Celite. Addition of 20 mL of ether to the dark red brown filtrate caused separation of a dark brown crystalline solid, which was collected by filtration. The solid was washed with ether and dried in vacuo, affording 116 mg (93%) of product. ^{1}H NMR ($\mathrm{CD_3CN}$, anion): δ 19.5 (*m*-H′), 14.8 (*m*-H″), 13.5 (H_a), 5.2 (H_b), −3.3 (*o*-H″), −9.8 (*o*-H′). The *N*-methyl signal was not located. ^{19}F NMR ($\mathrm{Me_2SO}$-d_6): δ −89.3 (*m*′-Fe), −100.1 (*m*″-Fe).

$(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4(OC_6H_5)_3}]$. This cluster was similarly prepared by reaction of $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4Cl_3}]$ (100 mg, 0.11 mmol) with $\mathrm{NaOC_6H_5}$ (38.5 mg, 0.33 mmol) in 90% yield as a dark brown solid. ^{1}H NMR ($\mathrm{CD_3CN}$, anion): δ 19.9 (*m*-H′), 15.3 (*m*-H″), 13.6 (H_a), 5.3 (H_b), −3.49 (*p*-H″), −8.81 (*p*-H′). The *o*-H″ and *o*-H′ proton resonances were obscured by the *p*-H″ and *p*-H′ signals, respectively. The *N*-methyl signal was not located.

B. Sulfido-Bridged Double Cubane Clusters. $(\mathrm{Et_4N})_4\{[(\mathrm{Meida})\mathrm{MoFe_3S_4(O\text{-}\mathit{p}\text{-}C_6H_4F)_2}]_2(\mu_2\text{-S})\}$. A mixture of $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4(O\text{-}\mathit{p}\text{-}C_6H_4F)_3}]$ (100 mg, 0.088 mmol) and $\mathrm{Li_2S}$ (2.0 mg, 0.044 mmol) solids was treated with 2 mL of $\mathrm{Me_2SO}$. After the mixture was shaken for 10 min, a homogeneous dark brown solution was obtained. Addition of 10 mL of THF/ether (1:1 v/v) precipitated a dark brown solid, which was collected by filtration and washed with the same solvent mixture. Recrystallization of the crude material from DMF/ether afforded 65 mg (71%) of product as a dark brown solid. ^{1}H NMR ($\mathrm{Me_2SO}$-d_6, anion): δ 23.1, 22.7, 22.5, 21.9, 21.6, 21.0, 20.7 (*m*-H, H_a); δ 17.7, 17.1, 16.9 (H_a); δ 6.27 (H_b); δ −4.3 (N-Me); δ −14.3 (*o*-H). ^{19}F NMR ($\mathrm{Me_2SO}$-d_6): δ −79.0, −79.7, −81.0, −81.7, −83.0, −83.4, −84.3.

$(\mathrm{Et_4N})_4\{[(\mathrm{Meida})\mathrm{MoFe_3S_4(O\text{-}\mathit{p}\text{-}C_6H_4CH_3)_2}]_2(\mu_2\text{-S})\}$. This compound was prepared in a similar manner by reaction of $(\mathrm{Et_4N})_2[(\mathrm{Meida})\mathrm{MoFe_3S_4(O\text{-}\mathit{p}\text{-}C_6H_4CH_3)_3}]$ (90 mg, 0.080 mmol) with $\mathrm{Li_2S}$ (1.9 mg, 0.04 mmol) and was obtained in 67% yield as a dark brown solid. ^{1}H NMR ($\mathrm{Me_2SO}$-d_6, anion): δ 24.1, 23.6, 23.5, 23.1, 22.7, 22.5, 22.1, 21.5, 21.4 (*m*-H, *p*-Me, H_a); δ 17.5, 16.8 (H_a); δ 6.23 (H_b); −4.3 (N-Me); δ −14.1 (*o*-H).

C. Oxo-Bridged Double Cubane Clusters. $(\mathrm{Et_4N})_4\{[(\mathrm{Meida})\mathrm{MoFe_3S_4Cl_2}]_2(\mu_2\text{-O})\}\cdot\mathrm{DMF}\cdot2\mathrm{NaCl}$. To a mixture of $(\mathrm{Et_4N})_2[(\mathrm{Meida})$-

$MoFe_3S_4Cl_3$] (100 mg, 0.11 mmol) and NaOEt (7.5 mg, 0.11 mmol) solids was added a mixture of Me_2SO (2 mL) and water (1.0 μL, 0.055 mmol). After the mixture was shaken for 15 min, a dark brown solution was obtained. Addition of 2 mL of DMF and 15 mL of ether caused separation of a dark brown solid, which was collected by filtration, washed by ether, and dried in vacuo to give 71 mg (66%) of product. ^{1}H NMR (Me_2SO-d_6, anion): δ 19.1, 18.6, 15.5, 15.4 (H_a); δ 7.24, 6.73 (H_b), −2.3 (N-Me). Anal. Calcd for $C_{45}H_{101}N_7O_{10}Cl_6Fe_6S_8Mo_2Na_2$: C, 27.82; H, 5.24; N, 5.05; Cl, 10.95; S, 13.21; Fe, 17.25; Mo, 9.88. Found: C, 27.66; H, 5.22; N, 5.04; Cl, 10.99; S, 13.22; Fe, 17.18; Mo, 9,71.

$(Et_4N)_4\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}$. This compound was prepared in a similar manner by reaction of $(Et_4N)_2[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_3]$ (100 mg, 0.088 mmol) with NaOEt (6.0 mg, 0.088 mmol) and water (0.8 μL, 0.044 mmol) in Me_2SO in 76% yield as a dark brown solid. ^{1}H NMR (Me_2SO-d_6, anion): δ 21.3, 20.8, 20.6, 20.3 (*m*-H, H_a); δ 16.7, 16.4, 16.3 (H_a); δ 6.76, 6.12 (H_b); δ −3.4 (N-Me); δ −12.0 (*o*-H). ^{19}F NMR (Me_2SO-d_6): δ −84.8, −85.3, −86.2, −86.4, −86.6.

Reactivity of Sulfido- or Oxo-Bridged Double Cubanes. Reactions were carried out on an NMR scale unless otherwise specified, and the products were determined by NMR. A typical example is given as follows. To a solution of $(Et_4N)_4\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}$(10 mg, 4.8 μmol) in 0.5 mL of Me_2SO-d_6 was added $(Et_3NH)Cl$ (2.6 mg, 19 μmol). The mixture was shaken for 15 min and then examined by NMR. The products were identified as $p\text{-}FC_6H_4OH$, Et_3N, and $(Et_4N)_4\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}$.

Physical Measurements. All measurements were made under anaerobic conditions. ^{1}H and ^{19}F NMR spectra were obtained using a Bruker AM-400 spectrometer. Chemical shifts are referenced to Me_4Si and $CFCl_3$, respectively. Electrochemical measurements were performed with a PAR model 263 potentiostat/galvanostat using a glassy carbon working electrode and 0.1 M $(Bu_4N)PF_6$ supporting electrolyte. Potentials are referenced to the SCE.

Results and Discussion

Clusters **1**−**15** are of principal interest in this work; **4**, **5**, **7**−**10**, and **12**−**15** have been obtained for the first time. Certain

$[(Meida)MoFe_3S_4Cl_3]^{2-}$	**1**[1,9]
$[(Meida)MoFe_3S_4(SEt)_3]^{2-}$	**2**[1]
$[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4CH_3)_3]^{2-}$	**3**[1]
$[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_3]^{2-}$	**4**
$[(Meida)MoFe_3S_4(OC_6H_5)_3]^{2-}$	**5**
$[(Meida)MoFe_3S_4(OC_6D_5)_3]^{2-}$	**5**-d_5
$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$	**6**[1]
$\{[(Meida)MoFe_3S_4(SEt)_2]_2(\mu_2\text{-}S)\}^{4-}$	**7**
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-}$	**8**
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4CH_3)_2]_2(\mu_2\text{-}S)\}^{4-}$	**9**
$\{[(Meida)MoFe_3S_4(OC_6D_5)_2]_2(\mu_2\text{-}S)\}^{4-}$	**10**-d_{10}
$\{[(Meida)MoFe_3S_4Cl](\mu_2\text{-}S)\}_n^{2n-}$	**11**[1]
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)](\mu_2\text{-}S)\}_n^{2n-}$	**12**
$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-}$	**13**
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}^{4-}$	**14**
$\{[(Meida)MoFe_3S_4(OC_6D_5)_2]_2(\mu_2\text{-}O)\}^{4-}$	**15**-d_{10}

clusters are depicted schematically in Figure 1, which also introduces notations for iron sites and diastereotopic methylene protons of the *fac*-Meida ligand and summarizes much of the cluster reactivity established in this study. Site m′ lies in the mirror plane of an individual cubane, and the sites m″ are related by the mirror plane. Double cubanes have four isomers. Bridging of single cubanes through m′/m′, m″/m″, and m′/m″ sites gives rise to three isomers. However, the m″/m″ linkage actually generates two isomers in which the Meida nitrogen atoms are transoid or cisoid around the Fe−S−Fe bridge. Isomers are depicted elsewhere.[10] Note that four isomers of the generalized double cubane $\{[(Meida)MoFe_3S_4L_2]_2(\mu_2\text{-}S)\}^{z-}$ can produce a total of nine NMR signals of H_a and of H_b and each type of terminal ligand L resonance. Because the $[MoFe_3S_4]^{3+}$ core is paramagnetic (ground-state S = $^3/_2$),[11] resonances of single cubanes are fully resolved and those of isomeric double cubanes (except for H_b) are usually largely resolved because of the substantial isotropic components of the chemical shifts. All reactions described below were monitored by NMR under strictly anaerobic conditions.

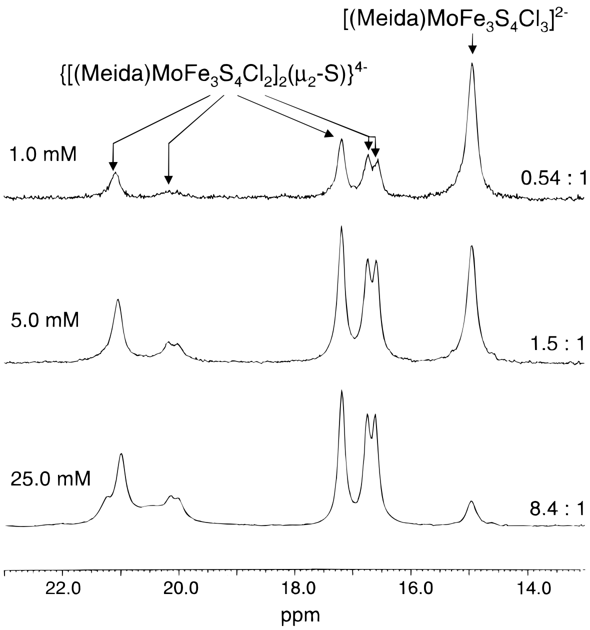

Figure 2. ^{1}H NMR spectra of $\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$ in Me_2SO-d_6 at various concentrations at 297 K. Only the H_a signals are shown. The mole ratio of $\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$ and $[(Meida)MoFe_3S_4Cl_3]^{2-}$ at each concentration is indicated.

Sulfido-Bridged Double Cubanes. A. $\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$. (1) Equilibrium in Solution. We begin consideration of cluster reactivity with double cubane **6** (Figure 1), which we have been able to isolate in the pure condition as the double salt $(Et_4N)_4[\mathbf{6}]\cdot 2LiCl$.[1] We have demonstrated by variable-temperature ^{1}H NMR that reaction 1 in Me_2SO solution is an equilibrium and favors single cubane **1** with increasing temperature.[1] As seen in Figure 2, at 297 K the reaction is shifted toward **6** with increasing concentration (1−25 mM), also consistent with an equilibrium system. At the lower concentrations, six of the nine possible H_a resonances are observable. The spectrum at 25 mM evidences two additional H_a signals, which presumably are elicited by cluster−cation interactions. Owing to bridge cleavage by chloride in reaction 1, solutions of **6** containing free chloride invariably also contain **1**, whose concentration is diminished at high concentrations of **6** and low temperature. Because of favorable redox potential differences, the two clusters in equilibrium are detectable by voltammetry. The potentials in Table 1 for **1**/**6** and other clusters define one criterion of double cubane formation: resolvable reduction steps of the double cubane separated by 230−330 mV, with the first potential more negative than that of the initial reduction of the precursor single cubane. In the case of **1**/**6**, the potential difference is 200 mV in DMF and arises mainly from the larger negative charge of **6**.

(2) Reactivity. Although **6** experiences partial sulfido bridge cleavage by chloride in solution, it exhibits remarkable stability

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(9) Demadis, K. D.; Coucouvanis, D. *Inorg. Chem.* **1995**, *34*, 436.

(10) See Figure 12 of ref 1.

(11) Mascharak, P. K.; Papaefthymiou, G. C.; Armstrong, W. H.; Foner, S.; Frankel, R. B.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 2851.

Table 1. Redox Potentials of Sulfido- and Oxo-Bridged Double $MoFe_3S_4$ Cubanes and Related Single Cubane Clusters at 297 K

cluster	solvent	$E_{1/2}$, V^a
$[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_3]^{2-}$	DMF	−0.99
$[(Meida)MoFe_3S_4(OC_6H_5)_3]^{2-}$	DMF	−1.03
$[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4CH_3)_3]^{2-}$	DMF	−1.09
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-}$	DMF	−1.17, −1.47
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4CH_3)_2]_2(\mu_2\text{-}S)\}^{4-}$	DMF	−1.24, −1.53
$[(Meida)MoFe_3S_4(SEt)_3]^{2-}$	MeCN	−1.18
$\{[(Meida)MoFe_3S_4(SEt)_2]_2(\mu_2\text{-}S)\}^{4-}$	MeCN	−1.28, −1.55
$[(Meida)MoFe_3S_4Cl_3]^{2-}$	DMF	−0.81^b
$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$	DMF	−1.01, −1.34^b
$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-}$	DMF	−1.15, −1.42
$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}^{4-}$	DMF	−1.25, −1.48

[a] Vs SCE; $E_{1/2} = (E_{p,a} + E_{p,c})/2$. [b] Reference 1.

toward the attack of water and the stronger acid Et_3NH^+. Treatment of **6** (10 mM) in Me_2SO with 300 equiv of water or 5 equiv of Et_3NH^+ caused no appreciable reaction. However, on slow exposure to air, the sulfido bridge of **6** was gradually cleaved, leading to formation of single cubane **1**. Under anaerobic conditions, **6** can generally undergo ligand substitution reactions on terminal Fe sites with common ligands such as ArO^- and RS^-. Treatment of **6** with slightly more than 4 equiv of NaL (L = EtS^-, ArO^-) in Me_2SO caused immediate and quantitative conversion to the bridged double cubanes **7**−**10** (Figure 1) in reaction 2. Because of equilibrium 1, the products

$$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-} + 4NaL \rightarrow \{[(Meida)MoFe_3S_4L_2]_2(\mu_2\text{-}S)\}^{4-} + 4NaCl \quad (2)$$

include the corresponding single cubanes **2**−**5** whose amounts depend on the concentration of the starting cluster **6**. In these systems, terminal chloride substitution proceeds without appreciable bridge cleavage by the strong nucleophiles ethanethiolate or areneoxide.

B. $\{[(Meida)MoFe_3S_4(OAr)_2]_2(\mu_2\text{-}S)\}^{4-}$**. (1) Single Cubanes** $[(Meida)MoFe_3S_4(OAr)_3]^{2-}$**.** We have reported the preparation of the first member **3** of this cluster family by the reaction of 3 equiv of sodium *p*-cresolate with **1** in acetonitrile.[1] Clusters **4** and **5** were prepared in high yields by analogous reactions. The ^1H NMR spectra of these clusters are readily assigned, as shown by the comparisons in Figure 3. Sets of ArO^- signals in a 2:1 intensity ratio, including the ^{19}F resonances of **4** in Figure 4, are consistent with cluster mirror symmetry. The H_a resonances are located at or near 13.5 ppm. Cyclic voltammetry of **3**−**5** reveals one chemically reversible step near −1.0 V with the potential order **4** < **5** < **3** consistent with the electron-donating tendencies of the *para* substituents (Table 1).

(2) Synthesis and Properties. The double cubanes **8**−**10** are conveniently prepared in ca. 70% isolated yields by the cluster coupling reaction 3 in Me_2SO solution. Addition of THF/ether (1:1 v/v) precipitated the desired cluster but left LiOAr in solution. The ^1H NMR spectra of the isolated salts of **8**−**10** are devoid of signals from free areneoxide, indicating that none of these clusters was contaminated with LiOAr salts. The driving force for this reaction is apparently the higher affinity of the iron sites for sulfide than areneoxide. Reaction 3 is currently the best method for the preparation of sulfido-bridged double cubanes free of ligand that in sufficient amount might effect bridge cleavage, as in reaction 1.

$$2[(Meida)MoFe_3S_4(OAr)_3]^{2-} + Li_2S \rightarrow \{[(Meida)MoFe_3S_4(OAr)_2]_2(\mu_2\text{-}S)\}^{4-} + 2LiOAr \quad (3)$$

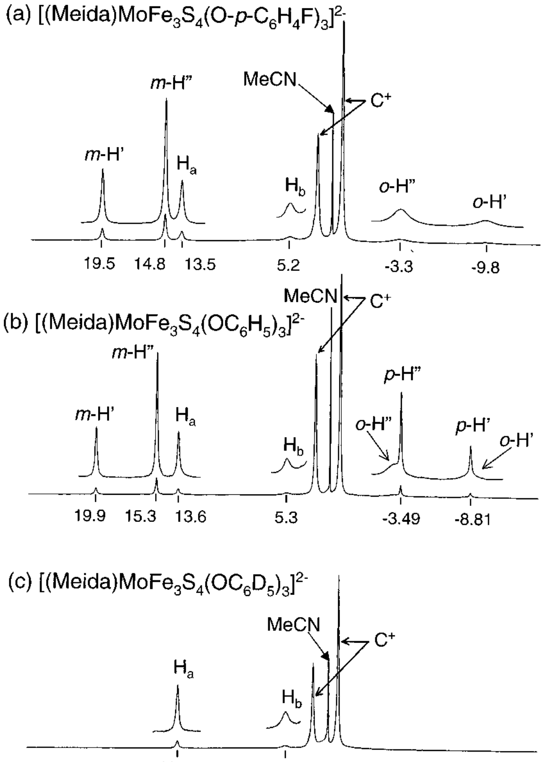


Figure 3. ^1H NMR spectra of $[(Meida)MoFe_3S_4(OAr)_3]^{2-}$ in CD_3CN at 297 K: (a) Ar = $p\text{-}C_6H_4F$; (b) Ar = C_6H_5; (c) Ar = C_6D_5. Signal assignments are indicated.

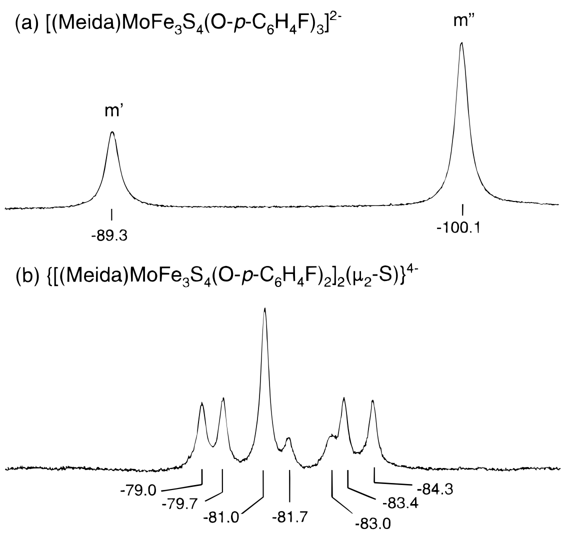
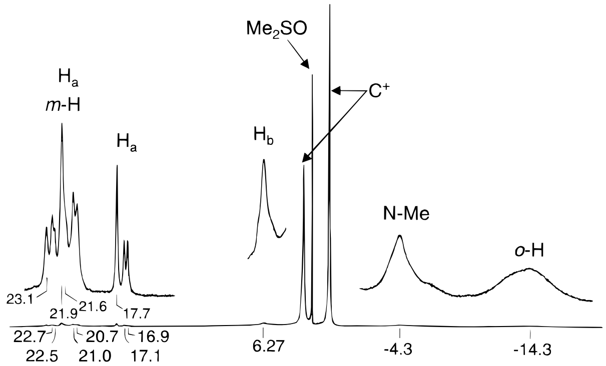


Figure 4. ^{19}F NMR spectra in $Me_2SO\text{-}d_6$ at 297 K: (a) $[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_3]^{2-}$; (b) $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-}$.

The NMR spectra of clusters **8**, **9**, and **10**-d_{10} in the 16−25 ppm region demonstrate that isomeric mixtures are formed in reaction 3. The spectra of **8** (Figure 5) and **9** (not shown) are complicated by the overlap of H_a and *m*-H, as shown by comparison with the spectrum of **10**-d_{10} (Figure 5). Cluster **8** shows at least 10 *m*-H + H_a signals, and **10**-d_{10} manifests at least 7 *m*-H features. The spectrum of **9** is even more complicated by the appearance of *p*-CH_3 signals in the same downfield region. Some 7 ^{19}F resonances of **8** (Figure 4) are resolved. While these and other signals cannot be assigned to specific isomers, it is not unlikely that the four equally intense ^{19}F signals (at −79.0, −79.7, −83.4, −84.3 ppm) arise from the C_1 isomer,[10] which we have concluded is the most stable of

(a) $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-}$



(b) $\{[(Meida)MoFe_3S_4(OC_6D_5)_2]_2(\mu_2\text{-}S)\}^{4-}$

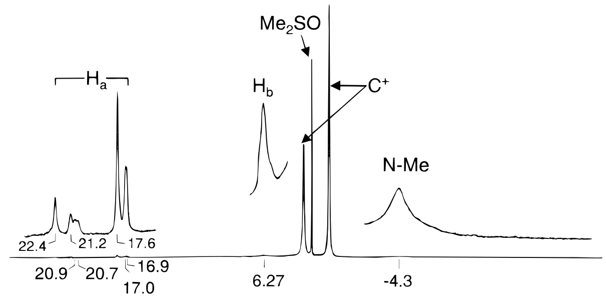


Figure 5. ^1H NMR spectra of $\{[(Meida)MoFe_3S_4(OAr)_2]_2(\mu_2\text{-}S)\}^{4-}$ in $Me_2SO\text{-}d_6$ at 297 K: (a) Ar = $p\text{-}C_6H_4F$; (b) Ar = C_6D_5.

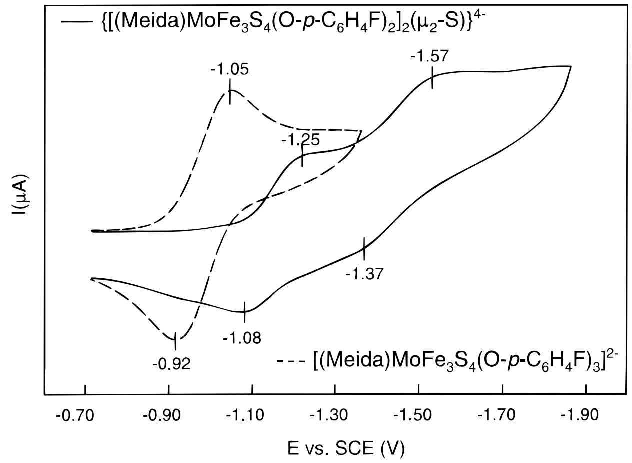


Figure 6. Cyclic voltammograms of $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-}$ (solid line) and $[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_3]^{2-}$ (dashed line) in DMF at 100 mV/s. Peak potentials are indicated.

the four isomers.[1] The cyclic voltammetry of **8**, depicted in Figure 6, satisfies the double cubane criterion. Successive reductions occur at $E_{1/2} = -1.17$ and -1.47 V, with the first step 180 mV more negative than the reduction of single cubane **4** measured separately.

(3) Reactivity. Double cubanes **8**−**10** remain intact in DMF and Me_2SO solutions; no single cubanes are detectable by NMR or electrochemistry. In 5 mM cluster solutions, the addition of 4 equiv of the corresponding phenol or phenolate did not result in detectable bridge cleavage for a period of at least 1 day. When treated with equimolar Li_2S in Me_2SO solution as in reaction 4, the product, formulated as a multiply sulfido-bridged multicubane cluster, was formed immediately. The ^1H and ^{19}F NMR spectra of **12** (not shown) are poorly resolved but quite distinct from those of **8**. Cluster **12** is expected to have four or more isomers when $n \geq 2$; its formation is precedented by the conversion of **6** to **11** under the same conditions. The formulation of **12** is independently supported by the observation that treatment of **11** with a slight excess of $Na(O\text{-}p\text{-}C_6H_4F)$ in Me_2SO affords **12** as the only NMR-detectable product.

$$(n/2)\{[(Meida)MoFe_3S_4(OAr)_2]_2(\mu_2\text{-}S)\}^{4-} + (n/2)Li_2S \rightarrow \{[(Meida)MoFe_3S_4(OAr)](\mu_2\text{-}S)\}_n^{2n-} + n\text{LiOAr} \quad (4)$$

Given that the Si−O bond energy exceeds that of Si−S by ca. 40 kcal/mol,[12] reaction of Me_3SiCl with an areneoxide double cubane is expected to remove the oxygen ligands and leave the sulfido bridge intact. Indeed, reaction 5 proceeded swiftly and yielded **6** as the only cluster product. In another test of the relative reactivities of areneoxide and sulfide in a double cubane toward electrophiles, a solution of **8** in Me_2SO was treated with 4 equiv of $(Et_3NH)Cl$. Reaction 6 occurred rapidly, affording essentially quantitative formation of **6**. The importance of these reactions is that they suggest means of removal of terminal ligands with retention of the sulfido bridge, a desirable feature of any rearrangement of a double cubane to the cofactor topology.[13]

$$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-} + 4Me_3SiCl \rightarrow \{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-} + 4Me_3SiOC_6H_4\text{-}p\text{-}F \quad (5)$$

$$\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}S)\}^{4-} + 4(Et_3NH)Cl \rightarrow \{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-} + 4Et_3N + 4p\text{-}FC_6H_4OH \quad (6)$$

C. $\{[(Meida)MoFe_3S_4(SEt)_2]_2(\mu_2\text{-}S)\}^{4-}$. Unlike **1** and **3**−**5**, single cubane **2** in Me_2SO exhibits only a slow reaction with Li_2S, even in large excess (∼10:1). In contrast, reaction of **2** with Et_4NSH quickly generated double cubane **7** with the liberation of EtSH. However, the conversion under stoichiometric conditions was incomplete, affording the ∼2:1 **7**:**2** mole ratio. Addition of excess hydrosulfido did not significantly increase the amount of **7**, and other (unidentified) cluster species were formed. We have already observed that reaction 2 (L = EtS^-) affords **7**, but this too results in a mixture of products because of the presence of **1**. While **7** has not been generated or isolated in the pure condition, we briefly offer evidence that it does possess a double cubane structure. Single cubane **2** exhibits the well-resolved ^1H NMR spectrum shown in Figure 7a. Upon partial conversion to **7**, the pattern of H_a resonances at 14−19 ppm in Figure 7b is observed. Except for a 2 ppm upfield shift, this pattern strongly resembles the H_a spectrum of **6**, whose double cubane structure has already been demonstrated.[1] In the 40−120 ppm region (not shown), 10 $FeSCH_2$ resonances appear, of which two arise from **2**. The remaining are eight of the nine possible resonances from an isomeric mixture of double cubanes. When measured separately as in Figure 8a, **2** shows a single reversible reduction at $E_{1/2} = -1.18$ V. Voltammetric examination of **7** in Figure 8b reveals two coupled reductions separated by 270 mV, the first of these being 100 mV negative of the reduction of **2**, whose presence is in accord with the ^1H NMR spectrum of a solution in which **7** is generated from **2**. The ^1H NMR and voltammetric features of **7** are clearly consistent with a mixture of isomeric double cubanes.

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[12] Tacke, R.; Wannagat, U. *Top. Curr. Chem.* **1979**, *84*, 5.

[13] Huang, J.; Holm, R. H. Research in progress.

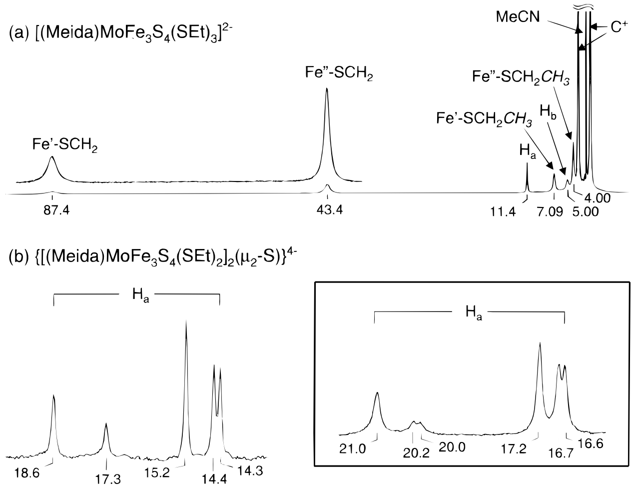

Figure 7. ^{1}H NMR spectra in CD_3CN at 297 K: (a) $[(Meida)MoFe_3S_4(SEt)_3]^{2-}$; (b) H_a signals of $\{[(Meida)MoFe_3S_4(SEt)_2]_2(\mu_2\text{-}S)\}^{4-}$; (inset) H_a signals of $\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$ for comparison with (b).

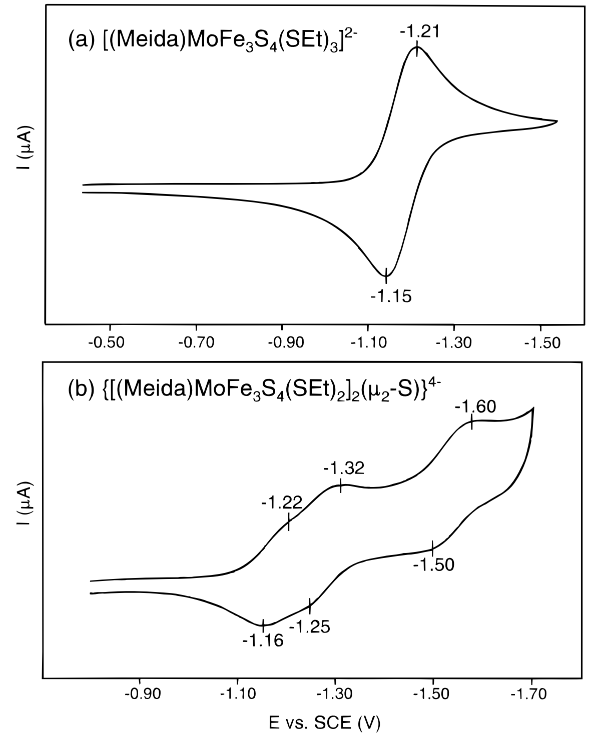

Figure 8. Cyclic voltammograms of (a) $[(Meida)MoFe_3S_4(SEt)_3]^{2-}$ and (b) $\{[(Meida)MoFe_3S_4(SEt)_2]_2(\mu_2\text{-}S)\}^{4-}$ in MeCN at 20 mV/s. Peak potentials are indicated. The first reduction wave in (b) is due to $[(Meida)MoFe_3S_4(SEt)_3]^{2-}$, whose presence was confirmed by ^{1}H NMR (see text).

Oxo-Bridged Double Cubanes. The synthesis and stability of sulfido-bridged double cubanes comprised of $[Fe_4S_4]^{2+}$ and/or $[MoFe_3S_4]^{3+}$ individual cubanes raises the matter of the existence of other single atom-bridged clusters with Fe−X−Fe links. Recently, we have prepared and structurally characterized $\{[Fe_4Se_4(LS_3)]_2Se\}^{4-}$, crystallographically inequivalent examples of which have Fe−Se−Fe bridge angles in the 113−116° range.[1,8] It is entirely likely that other selenide-bridged species can be prepared. Somewhat more interesting are oxo-bridged species, the first example of which was detected in the equilibrium 7 and studied electrochemically in Me_2SO solution.[7]

$$[Fe_4S_4(LS_3)(OH)]^{2-} \rightleftarrows 2\{[Fe_4S_4(LS_3)]_2O\}^{4-} + H_2O \quad (7)$$

The equilibrium was established by the addition of LiOH to a solution of $[Fe_4S_4(LS_3)Cl]^{2-}$ in Me_2SO containing <2% water (v/v). The reaction was shifted to the left with increasing amounts of water. The proposed μ-oxo double cubane exhibited coupled reductions at −1.24 and −1.47 V, which are of equal intensity in differential pulse voltammetry. These values are comparable with those of $\{[Fe_4S_4(LS_3)]_2S\}^{4-}$ in acetonitrile (−1.26, −1.50 V) and with the double cubane potentials in Table 1. Neither cluster in reaction 7 was isolated. Oxo-bridged clusters are not directly pertinent to the double cubane rearrangement concept noted earlier. However, resonance Raman results are not inconsistent with the presence of $Fe^{III}-O-Fe^{III}$ bridges in two bacterial 6-Fe/S proteins.[14] Because of the possible further occurrence of oxo bridges in iron−sulfur proteins, we have demonstrated the existence of Fe−O−Fe bridges in double cubanes as part of this investigation.

$\{[(Meida)MoFe_3S_4L_2]_2(\mu_2\text{-}O)\}^{4-}$ (L = Cl^-, $p\text{-}FC_6H_4O^-$, $C_6D_5O^-$). (1) Synthesis. Clusters **13**−**15** (Figure 1) are readily prepared in ca.70% isolated yield by the coupling reaction 8,

$$2[(Meida)MoFe_3S_4L_3]^{2-} + 2NaOEt + H_2O \rightarrow \{[(Meida)MoFe_3S_4L_2]_2(\mu_2\text{-}O)\}^{4-} + 2NaL + 2EtOH \quad (8)$$

analogous to reactions 1 and 3. Cluster **13** was also obtained by the reaction of single cubane **1** in acetonitrile with 1 equiv of Me_4NOH. The precipitated product when dissolved in Me_2SO gave an ^{1}H NMR spectrum identical with the product of reaction 8. The oxo (rather than hydroxo) formulation of these clusters is based on an elemental analysis of $(Et_4N)_4$[**13**], which requires four cations per anion.

NMR spectra of **13**−**15** are presented in Figures 9 and 10. A general observation is that H_a resonances tend to be slightly less shifted downfield and not as well resolved as that of analogous sulfido-bridged clusters. Thus, **13** exhibits four H_a signals (Figure 9) compared to six for **6**.[1] Three or four H_a resonances are observed for **14** and **15**; at least five ^{19}F signals occur over 1.8 ppm for **14** (Figure 10). Here the lesser resolution is particularly obvious; sulfido-bridged **8** generates seven peaks over 5.3 ppm (Figure 4b).

The cyclic voltammogram of **13** in DMF, presented in Figure 11, consists of two reductions separated by 270 mV and occurring at potentials significantly more negative (−1.15, −1.42 V) than those of the sulfido analogue **6** (Table 1). In this regard, it is unlikely that **13** in solution is hydroxo-bridged with a 3− charge; potentials more positive than those of **6** with a 4− charge would be expected.[15] As seen in Figure 12, two coupled reductions, separated by 230 mV, are also observed for **14** in DMF solution. Note that in Figures 11 and 12 after scanning of the two reductions and their reoxidations, redox steps appear at less negative potentials that are absent unless the voltammogram is first extended in the cathodic direction. With **13**, a feature is observed with $E_{1/2} = -0.83$ V, essentially the same as the potential for **1**. With **14**, a feature occurs at $E_{pc} = -0.94$ V. We attribute both of these features to single cubanes formed by bridge rupture. Cluster reduction should increase the basicity of the oxo atom and enhance bridge

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(14) de Vocht, M. L.; Kooter, I. M.; Bulsink, I. M.; Hagen, W. R.; Johnson, M. K. *J. Am. Chem. Soc.* **1996**, *118*, 2766.

(15) Although negative evidence, we note also the absence of an O−H stretching band in the IR spectrum of **13**. The double cubane $\{[(Cl_4cat)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)(\mu_2\text{-}OH)]^{5-}$, having a Mo−O(H)-Mo bridge, exhibits a sharp O−H stretch at 3490 cm^{-1}: Coucouvanis, D.; Challen, P. R.; Koo, S.-M.; Davis, W. M.; Butler, W.; Dunham, W. R. *Inorg. Chem.* **1989**, *28*, 4181. (Cl_4cat = tetrachlorocatecholate(2−).)

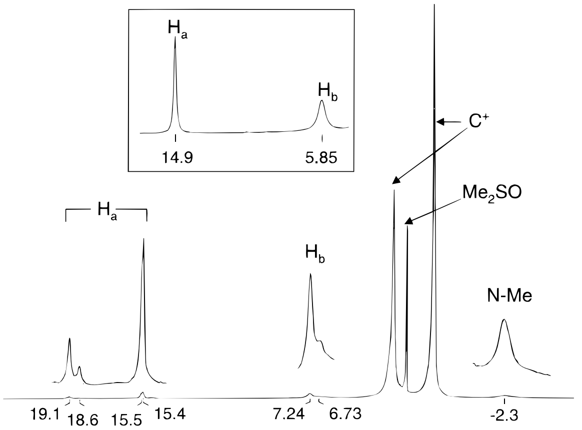
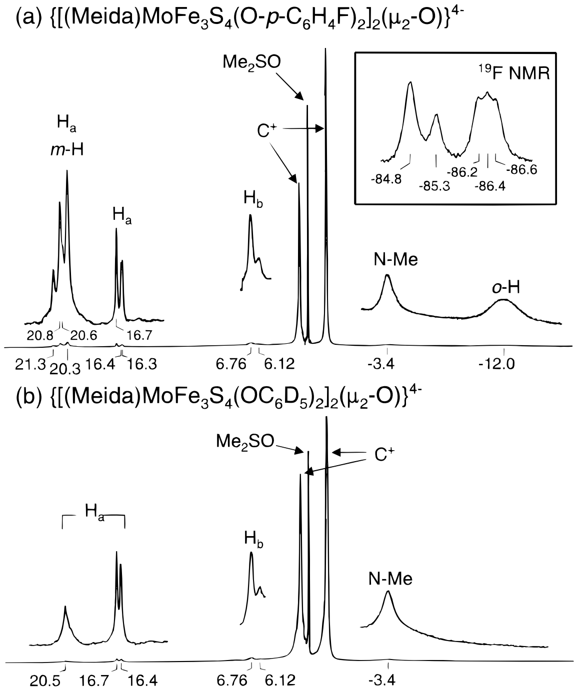


Figure 9. ^1H NMR spectrum of $\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-}$ in $Me_2SO\text{-}d_6$ at 297 K. The inset shows the spectrum of the product from reaction of this cluster with 2 equiv of $(Et_3NH)Cl$ in the same solvent.


(a) $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}^{4-}$

(b) $\{[(Meida)MoFe_3S_4(OC_6D_5)_2]_2(\mu_2\text{-}O)\}^{4-}$

Figure 10. ^1H NMR spectra of $\{[(Meida)MoFe_3S_4(OAr)_2]_2(\mu_2\text{-}O)\}^{4-}$ in $Me_2SO\text{-}d_6$ at 297 K: (a) Ar = $p\text{-}C_6H_4F$; (b) Ar = C_6D_5. Inset: ^{19}F NMR spectrum of $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_5F)_2]_2(\mu_2\text{-}O)\}^{4-}$ under the same conditions.

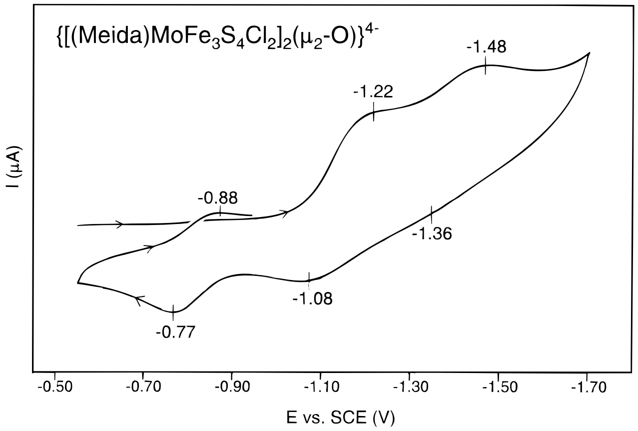
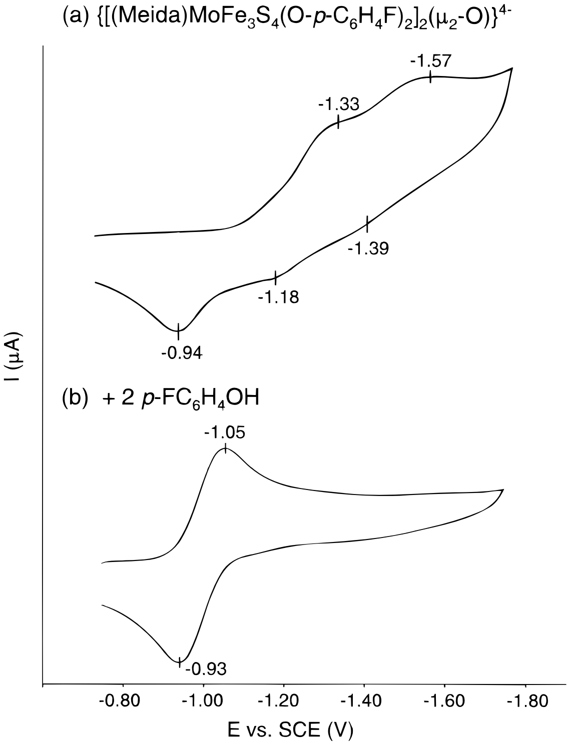

$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-}$

Figure 11. Cyclic voltammogram of $\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-}$ in DMF at 100 mV/s. Peak potentials and scan direction are indicated.


(a) $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}^{4-}$

(b) + 2 $p\text{-}FC_6H_4OH$

Figure 12. Cyclic voltammograms in DMF of (a) $\{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}^{4-}$ and (b) the in-situ reaction product of this cluster and 2 equiv of $p\text{-}FC_6H_4OH$. Peak potentials and the scan direction are indicated.

cleavage by protic impurities. This behavior is not observed for sulfido-bridged double cubanes. The collective analytical, NMR, and electrochemical results suffice to demonstrate that the products of reaction 8 are oxo-bridged double cubanes. Further, the potential differences of these clusters support the previous formulation of an analogous species in reaction 7 for which the two reduction steps are separated by 230 mV.[7]

$$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-} + 2(Et_3NH)Cl \rightarrow 2[(Meida)MoFe_3S_4Cl_3]^{2-} + 2Et_3N + H_2O \quad (9)$$

$$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-} + SH^- \rightarrow \{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-} + OH^- \quad (10)$$

$$\{[(Meida)MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-} + 4p\text{-}FC_6H_4ONa \rightarrow \{[(Meida)MoFe_3S_4(O\text{-}p\text{-}C_6H_4F)_2]_2(\mu_2\text{-}O)\}^{4-} + 4NaCl \quad (11)$$

(2) Reactivity. The oxo-bridged double cubane **13** is considerably more unstable toward the attack of protic reagents than its sulfido-bridged analogue **6**. Unlike the latter, the intercubane bridge in **13** can be readily cleaved by H_2O. However, in *anhydrous* Me_2SO or DMF, **13** is fully intact, as determined by NMR and cyclic voltammetry. When treated with 2 equiv of $(Et_3NH)Cl$ in Me_2SO, the bridge in **13** is completely cleaved in reaction 9. The ^1H NMR spectrum of the reaction product (Figure 9, inset) is identical with that of **1**.[1] When only 1 equiv of $(Et_3NH)Cl$ was added, reaction 9 gave a mixture of **13** and **1**; no other cluster products were observed. That *2* equiv of $(Et_3NH)Cl$ are required to fully cleave the intercubane bridge further excludes the possibility that **13** is a hydroxo-bridged double cubane. Similarly, treatment of **13** with 1 equiv of $(Et_4N)(SH)$ in Me_2SO immediately afforded **6** in reaction 10 whereby an oxo bridge is substituted by sulfido. Terminal ligand substitution is also possible. Stoichiometric reaction 11 proceeds in Me_2SO to form **14** without detectable bridge cleavage.

Clusters **14** and **15** also are completely intact in anhydrous Me_2SO and DMF and undergo reactions analogous to (9) and (10). For example, in stoichiometric reactions **14** is immediately and cleanly transformed to **8** by $(Et_4N)(SH)$ and cleaved to **4** by *p*-FC_6H_4OH in Me_2SO. The latter reaction is readily shown by cyclic voltammetry. The voltammogram in Figure 12a is immediately changed to that in Figure 12b on addition of 2 equiv of the phenol.

Summary. The following are the principal results and conclusions of this investigation.

(i) The cluster $\{[(\mathrm{Meida})MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$ is a prototypic sulfido-bridged Fe−S−Fe double cubane and is prepared by coupling two single cubanes $[(\mathrm{Meida})MoFe_3S_4Cl_3]^{2-}$ with Li_2S.[1] Because it has not been obtained free of chloride, it exists in bridge cleavage equilibrium 1 with the single cubane.

(ii) The areneoxide clusters $\{[(\mathrm{Meida})MoFe_3S_4(OAr)_2]_2(\mu_2\text{-}S)\}^{4-}$ are obtained by the cluster coupling reaction in (i) in Me_2SO. In contrast to chloride and ethanethiolate double cubanes (prepared by similar reactions), these clusters in solution are obtained pure, free of single-cubane contaminants. Despite the presence of single cubanes in the chloride and ethanethiolate cases, the NMR, electrochemical, and reactivity properties of the double cubanes can be examined.

(iii) Oxo-bridged double cubanes $\{[(\mathrm{Meida})MoFe_3S_4L_2]_2(\mu_2\text{-}O)\}^{4-}$ ($L = Cl^-, ArO^-$) with the linkage Fe−O−Fe are prepared by the coupling of single cubanes in Me_2SO using 2 NaOEt/H_2O as the source of oxide. The clusters are obtained free of single cubane impurities. These and the sulfido-bridged double cubanes are isolated as mixtures of as many as four geometrical isomers. They are the first Fe_4S_4 or MFe_3S_4 synthetic clusters with oxo bridges; there is recent evidence for oxo bridges in several iron−sulfur proteins.[14]

(iv) The double cubane formulations in (i)−(iii) are based on criteria developed earlier:[1,16] multiple terminal ligand L and Meida (H_a) resonances consistent with an isomeric mixture; coupled redox reactions of individual cubanes with potential separations near ca. 300 mV and the potentials of the first step ≥100 mV more negative than that of the corresponding single cubane. As the basicity of the terminal ligand increases at constant bridging ligand, this potential difference decreases (Table 1).

(v) Oxo bridges are much more susceptible to protic cleavage than are sulfido bridges. The Fe−O−Fe bridge is readily cleaved by water, Et_3NH^+, HS^-, and ArOH. With 1 equiv of hydrosulfide, the product is $\{[(\mathrm{Meida})MoFe_3S_4Cl_2]_2(\mu_2\text{-}S)\}^{4-}$, thus affording another route to this double cubane. This cluster and $\{[(\mathrm{Meida})MoFe_3S_4Cl_2]_2(\mu_2\text{-}O)\}^{4-}$ undergo terminal ligand substitution with retention of the bridge.

This study has enhanced the scope of sulfido-bridged double cubanes and afforded the first examples of oxo-bridged double cubanes. The reactivity results summarized in Figure 1 and those obtained earlier[1] provide a basis for additional examination of double cubane reaction chemistry, focusing mainly on symmetrical and unsymmetrical clusters of the types $\{[(\mathrm{Meida})MoFe_3S_4L_2]_2(\mu_2\text{-}S)\}^{4-}$ and $\{[(\mathrm{Meida})MoFe_3S_4L_2](\mu_2\text{-}S)(Fe_4S_4Cl_3)\}^{4-}$ [1] and the problem of FeMoco synthesis.

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(16) Despite numerous attempts, no diffraction-quality crystals of any double cubane have been obtained from mixtures of isomers.