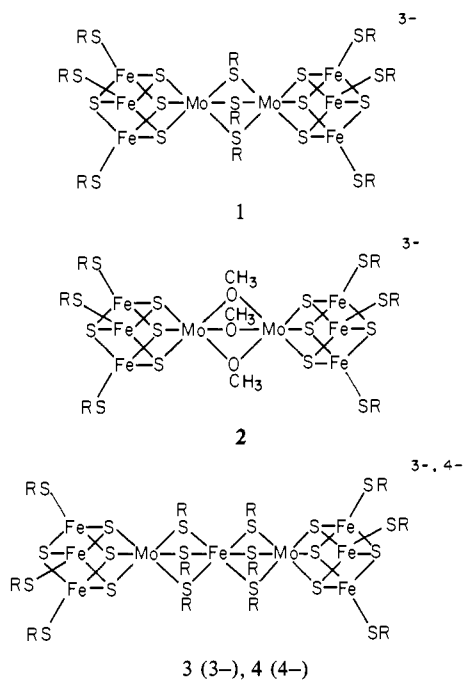# Doubly Bridged Double Cubanes Containing MFe$_3$S$_4$ Clusters (M = Mo, W). Synthesis, Structure, and Conversion to Spin-Quartet Single Clusters in Solution

**W. H. Armstrong, P. K. Mascharak, and R. H. Holm***

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Abstract: Reaction of the Fe(III)-bridged double-cubane clusters [M$_2$Fe$_7$S$_8$(SEt)$_{12}$]$^{3-}$ with the 3,6-disubstituted catechols R'$_2$catH$_2$ in acetonitrile solution at ambient temperature results in bridge cleavage and formation of the new set of clusters [M$_2$Fe$_6$S$_8$(SEt)$_6$(R'$_2$cat)$_2$]$^{4-}$ (M = Mo, W; R' = *n*-Pr, CH$_2$CH=CH$_2$), which are isolated in good yield as Et$_4$N$^+$ salts. The structure of the monoclinic form of (Et$_4$N)$_4$[Mo$_2$Fe$_6$S$_8$(SEt)$_6$(Pr$_2$cat)$_2$] is reported. It crystallizes in space group *C2/c* with *a* = 31.474 (7) Å, *b* = 19.544 (5) Å, *c* = 25.182 (6) Å, β = 141.77 (1)°, and *Z* = 4; the structure was refined to *R* = 4.8% by using 4227 unique data ($F_o^2 > 3\sigma(F_o^2)$). The structure of the centrosymmetric anion is that of a doubly bridged double-cubane cluster. Two MoFe$_3$S$_4$(SEt)$_2$(R'$_2$cat) subclusters, of unexceptional dimensions and containing a Mo–R'$_2$cat chelate ring, are joined by two Mo(μ-SEt)Fe bridges. Bridge bond distances are 0.04–0.09 Å longer than comparable terminal distances. In solution the clusters undergo complete thiolate ligand substitution with arylthiols RSH affording [M$_2$Fe$_6$S$_8$(SR)$_6$(R'$_2$cat)$_2$]$^{4-}$ (R = Ph, *p*-tolyl, *p*-C$_6$H$_4$Cl), several of which have been isolated as Et$_4$N$^+$ salts. In coordinating solvents such as Me$_2$SO, acetonitrile, and DMF at ambient temperature the double cubanes are cleaved to the single cluster solvates [MFe$_3$S$_4$-(SR)$_3$(R'$_2$cat)(solv)]$^{2-}$. On the basis of ^{1}H NMR evidence, all thiolate ligands are present as terminal Fe–SR groups; M atom coordination is completed by a solvent molecule, which is in rapid exchange with bulk solvent. Magnetic susceptibility and EPR spectral properties confirm a *S* = $^3/_2$ ground state. EPR parameters resemble those of the *S* = $^3/_2$ spin system of FeMo proteins and the FeMo cofactor of nitrogenase, suggesting an electronic similarity. Solvate clusters undergo a single one-electron reduction at ca. −1.1 to −1.5 V (vs. SCE). This property together with the lability of coordinated solvent molecules leads to the possibility that (reducible) nitrogenase substrates may be bound and activated at the M atom site.

The chemistry of cubane-type MFe$_3$S$_4$ clusters (M = Mo, W) is under continuing development in this laboratory.[1–4] These species are of significance in inorganic cluster chemistry for they are the only mixed-metal M'$_n$M$_{4-n}$S$_4$ cubane clusters thus far isolated. In addition they are relevant to the Mo–Fe–S cluster(s) in nitrogenase. Of the known MoFe$_3$S$_4$ clusters the triply bridged double cubanes [Mo$_2$Fe$_6$S$_8$(μ-SR)$_3$(SR)$_6$]$^{3-}$ [5,6] (**1**) and

1

2

3 (3−), 4 (4−)

[Mo$_2$Fe$_6$S$_8$(μ-OMe)$_3$(SR)$_6$]$^{3-,4,6}$ (**2**), and the Fe(II, III)-bridged double cubanes [Mo$_2$Fe$_7$S$_8$(μ-SR)$_6$(SR)$_6$]$^{3-,4-7,8}$ (**3**, **4**) are readily assembled from simple reagents.[4–7] Their tungsten analogues have also been prepared.[6,7] Although the compositions of the molybdenum-containing clusters do not correspond to current analytical atom ratios (Fe:S:Mo = (7–8):(4–6):1) for the FeMo cofactor[9–11] (FeMo-co) extractable from FeMo proteins of nitrogenase, EXAFS analyses indicate elements of similarity in the synthetic and native Mo atom coordination units.[5,12] The MoFe$_3$S$_3$ portion of the subclusters in **1**–**4** and additional Mo atom coordination by low Z atoms, possibly simulated by the oxygen atoms in **2** and [MoFe$_4$S$_4$(SEt)$_3$(cat)$_3$]$^{3-}$ [13] (**5**, cat = catecholate dianion), constitute a presently viable structural model for the Mo atom environment in FeMo-co.[12]

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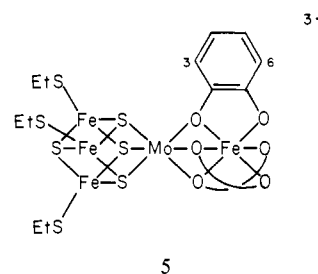
One part of our present studies is directed toward an evaluation of MoFe$_3$S$_4$ clusters (in reduced oxidation levels[4]) as possible simulators of the nitrogenase active site(s) in reductive trans-

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formations of substrates. However, if substrate binding involves a Mo atom, the presently available set of clusters is unsatisfactory in this regard owing to coordination saturation by tightly bound ligands. Single clusters or bridged double cubanes, both having labile terminal ligands at the Mo site, are desirable. Recently we have devised a synthetic route to the *doubly* bridged double cubanes $[M_2Fe_6S_8(SR)_4(\mu\text{-}SR)_2(3,6\text{-}(n\text{-}Pr)_2cat)_2]^{4-2}$ (M = Mo, W) which are more susceptible to bridge substitution/cleavage reactions than are clusters **1–4**. A further important feature of the doubly bridged clusters is that they are immediate precursors to species containing MFe_3S_4 clusters that are magnetically uncoupled from another (sub)cluster or appended paramagnetic fragment such as is present in **1–5**. This situation facilitates comparison of individual cluster electronic properties with those of the $S = {}^3/_2$ native cluster,[14–16] which are unique in biology. Detailed here are the syntheses of molybdenum- and tungsten-containing doubly bridged double cubanes, the crystal structure of a representative member of the set, and solution spectroscopic and redox properties that provide a satisfactory definition of the clusters in solution. Subsequent reports will deal with the reactivity properties of the latter. Certain leading results of this investigation have been described recently.[2]

Experimental Section

Preparation of Compounds. The cluster salts $(Et_4N)_3[M_2Fe_7S_8(SEt)_{12}]$ (M = Mo, W) were prepared as described.[7] Catechol diallyl ether[17] was rearranged to 3,6-diallylcatechol[17,18] $((C_3H_5)_2catH_2)$, which was hydrogenolyzed to 3,6-di-*n*-propylcatechol[19] (Pr_2catH_2). Ring-deuterated $(C_3H_5)_2catH_2$ was required for certain ¹H NMR signal assignments in clusters. It was prepared by refluxing the catechol (10 g) with 21 g of NaOH in 150 mL of D_2O under a dinitrogen atmosphere. After 2 days the mixture was neutralized with acetic acid and the deuterated catechol was isolated from an ether extract. Its NMR spectrum demonstrated >95% deuteration at the 4,5-positions.[20] In the following preparations all operations were performed under a pure dinitrogen atmosphere by using degassed solvents. Benzenethiol was freshly distilled prior to use. The designation for clusters of general formulation $[M_2Fe_6S_8(SR)_6(3,6\text{-}R'_2cat)_2]^{4-}$ (M = Mo, W), synthesized and isolated or generated in solution by the procedures described, is given: **6-Mo, 6-W**, R = Et, R' = *n*-Pr; **7-Mo, 7-W**, R = Et, R' = $CH_2CH=CH_2$; **8-Mo, 8-W**, R = Ph, R' = $CH_2CH=CH_2$; **9-Mo**, R = $p\text{-}C_6H_4Cl$, R' = $CH_2CH=CH_2$; **10-Mo, 10-W**, R = $p\text{-}C_6H_4Me$, R' = *n*-Pr; **11-Mo**, R = $p\text{-}C_6H_4Me$, R' = $CH_2CH=CH_2$.

$(Et_4N)_4[M_2Fe_6S_8(SEt)_6(3,6\text{-}R'_2cat)_2]$ **(6, 7).** $(Et_4N)_3[M_2Fe_7S_8(SEt)_{12}]$ (1 mmol) was stirred with 6-mmol each of 3,6-R'_2catH_2 and Et_4NBr and 12 mmol of Et_3N in 30 mL of acetonitrile for ~16 h. At the end of this time the products separated as black microcrystalline solids, which were collected by filtration. One recrystallization from acetonitrile affords products pure by ¹H NMR spectral criterion. Analytical samples were obtained from a second recrystallization from acetonitrile. All compounds were isolated as black air-sensitive solids. The following data are given for each preparation: mmol of reactant cluster; crude yield; recrystallized yield; λ_{max} (ϵ_M) in acetonitrile; analysis.

(a) $(Et_4N)_4[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]$ **(6-Mo):** 3.56 mmol; 76%; 67%; 396 (37 400), 264 (sh) nm. Anal. Calcd for $C_{68}H_{142}Fe_6Mo_2N_4O_4S_{14}$: C, 39.73; H, 6.96; Fe, 16.30; Mo, 9.33; N, 2.73; S, 21.84. Found: C, 39.89; H, 6.94; Fe, 15.96; Mo, 9.14; N, 2.67; S, 21.45.

(b) $(Et_4N)_4[W_2Fe_6S_8(SEt)_6(Pr_2cat)_2]$ **(6-W):** 1.54 mmol; 70%; 54%; 386 (37 400), 290 (sh) nm. Anal. Calcd for $C_{68}H_{142}Fe_6N_4O_4S_{14}W_2$: C, 36.60; H, 6.41; Fe, 15.02; N, 2.51; S, 20.12; W, 16.48. Found: C, 36.12; H, 6.20; Fe, 14.83; N, 2.53; S, 19.72; W, 16.57.

(c) $(Et_4N)_4[Mo_2Fe_6S_8(SEt)_6((C_3H_5)_2cat)_2]$ **(7-Mo):** 4.23 mmol; 92%; 64%; 396 (36 200), 305 (sh), 260 (sh) nm. Anal. Calcd for

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $(Et_4N)_4[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]$

formula (mol wt)	$C_{68}H_{142}Fe_6Mo_2N_4O_4S_{14}$ (2055.77)
a, Å	31.474 (7)
b, Å	19.544 (5)
c, Å	25.182 (6)
β, deg	141.77 (1)
cryst system	monoclinic
V, Å³	9586 (3)
Z	4
d_{calcd}, g/cm³	1.42
d_{obsd},[a] g/cm³	1.44
space group	$C2/c$
cryst dimens,[b] mm	0.24 × 0.32 × 0.44
radiation	Mo Kᾱ (λ 0.710 69 Å)
abs coeff, μ, cm⁻¹	14.63
takeoff angle, deg	3.0
scan speed, deg/min	3.0–29.3 ($\theta/2\theta$ scan)
scan range, deg	$2.8 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$
bkgd/scan time ratio	0.25
data collected	2θ of 4–48°; $+h, +k, \pm l$
unique data ($F_o^2 > 3.0\sigma(F_o^2)$)	4227
no. of variables	445
goodness of fit	0.98
R, %	4.8
R_w, %	5.1

a Determined by flotation in CCl_4/cyclohexane.   *b* Rectangular prism.

$C_{68}H_{134}Fe_6Mo_2N_4O_4S_{14}$: C, 39.89; H, 6.60; Fe, 16.36; Mo, 9.37; N, 2.74; S, 21.92. Found: C, 39.40; H, 6.44; Fe, 16.27; Mo, 9.28; N, 2.75; S, 21.61.

(d) $(Et_4N)_4[W_2Fe_6S_8(SEt)_6((C_3H_5)_2cat)_2]$ **(7-W):** 2.05 mmol; 88%; 56%; 388 (37 500), 300 (sh) nm. Anal. Calcd. for $C_{68}H_{134}Fe_6N_4O_4S_{14}W_2$: C, 36.73; H, 6.07; Fe, 15.07; N, 2.52; S, 20.19; W, 16.54. Found: C, 36.01; H, 6.01; Fe, 14.65; N, 2.52; S, 19.89; W, 16.42. In this preparation the starting cluster compound was $(Et_4N)_4[W_2Fe_7S_8(SEt)_{12}]^7$ rather than the trianion salt. The formation of the product in good yield indicates that Fe(II)- and Fe(III)-bridged double cubanes[7] can both be employed in the synthetic procedure.

$(Et_4N)_4[M_2Fe_6S_8(SR)_6((C_3H_5)_2cat)_2]$ **(8, 9).** To a slurry of 1.0 mmol of the Et_4N^+ salt of 7-Mo or 7-W in 300 mL of acetonitrile was added a solution of 6.3 mmol of the arenethiol in 50 mL of acetonitrile. The initial cluster salt dissolved readily, and the solution became orange-brown within ~5 min. The reaction mixture was stirred and subjected to intermittent reduced pressure (to remove liberated ethanethiol) over a 12-h period. After volume reduction to ~20 mL and filtration, slow cooling of the filtrate afforded small quantities of crystalline product. Yields were improved by the addition of propionitrile, further volume reduction, and cooling to -20 °C. The resultant black, air-sensitive, crystalline product was collected by filtration, washed with cold propionitrile or acetone, and dried in vacuo. The yields given below refer to the quantity of material obtained at this point.

(e) $(Et_4N)_4[Mo_2Fe_6S_8(SPh)_6((C_3H_5)_2cat)_2]$ **(8-Mo):** 0.73 mmol; 44%; 436 (35 300), 354 (39 800) nm. The material isolated after crystallization from acetonitrile was analyzed. Its ¹H NMR spectrum indicates the presence of acetonitrile as do analytical data, which conform to a bis(acetonitrile) solvate formulation. Anal. Calcd for $C_{96}H_{140}Fe_6Mo_2N_6O_4S_{14}$: C, 47.69; H, 5.84; Fe, 13.86; Mo, 7.94; N, 3.47; S, 18.56. Found: C, 47.10; H, 5.75; Fe, 14.09; Mo, 8.12; N, 3.42; S, 18.58.

(f) $(Et_4N)_4[W_2Fe_6S_8(SPh)_6((C_3H_5)_2cat)_2]$ **(8-W):** 0.90 mmol; 36%; 424 (35 700), 350 (39 700), 292 (sh), 256 (sh) nm. Anal. Calcd for $C_{92}H_{134}Fe_6N_4O_4S_{14}W_2$: C, 43.99; H, 5.38; Fe, 13.34; N, 2.23. Found: C, 44.25; H, 5.38; Fe, 12.70; N, 2.32. This compound is more unstable to decomposition than any other isolated in this work. ¹H NMR spectra of freshly prepared solutions are in agreement with the indicated formulation (see text).

(g) $(Et_4N)_4[Mo_2Fe_6S_8(S\text{-}p\text{-}C_6H_4Cl)_6((C_3H_5)_2cat)_2]$ **(9-Mo):** 1.12 mmol; 51%; 435 (35 500), 362 (41 500), 305 (sh), 264 (90 700) nm. Owing to low solubility the addition of propionitrile was not required. Anal. Calcd for $C_{92}H_{128}Cl_6Fe_6Mo_2N_4O_4S_{14}$: C, 43.46; H, 5.07; Cl, 8.37; Fe, 13.18; Mo, 7.55; N, 2.20; S, 17.65. Found: C, 42.95; H, 4.95; Cl, 8.41; Fe, 13.59; Mo, 7.46; N, 2.30; S, 17.78.

Ligand Substitution Reactions. Certain clusters were generated in solution by these reactions but were not isolated. To ~10 mM Me_2SO solutions prepared from $(Et_4N)_4[M_2Fe_6S_8(SEt)_6(R'_2cat)_2]$ (R' = *n*-Pr, C_3H_5) was added a solution of 3.2 equiv of *p*-toluenethiol/M atom. After

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the mixture was stirred under dynamic vacuum for 1.5 h at ambient temperature, substitution was complete, as shown by ^{1}H NMR spectra, yielding clusters derived from **10-Mo**, **10-W**, and **11-Mo**. In the case of the latter the reaction was followed by NMR after the addition of each equivalent (see text).

Structure Determination of Monoclinic (Et₄N)₄[Mo₂Fe₆S₈(SEt)₆-(Pr₂cat)₂] (6-Mo). Collection and Reduction of X-ray Data. A black air-sensitive crystal, obtained by diffusion of THF into an acetonitrile solution, was sealed in a glass capillary under an Ar atmosphere. Diffraction experiments were performed with a Nicolet R3M four-circle automated diffractometer with a Mo X-ray tube equipped with a graphite monochromator. Data collection parameters are summarized in Table I. The orientation matrix and unit-cell parameters were determined by using 25 machine-centered reflections which had 2θ values between 14 and 22°. The crystal exhibited broad (full width at half-height $\sim 0.7°$) but symmetrical ω scans. No significant decay of intensity of three standard reflections recorded after every 60 reflections was observed. Data reduction and an empirical absorption correction were performed by the program XTAPE of the SHELXTL structure determination program package. The systematic absences hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$) are consistent only with the monoclinic space groups $C2/c$ and Cc. Statistical analysis of the data by the program GECOR indicated a centric space group. Solution and refinement of the structure confirmed space group $C2/c$. Crystal data are given in Table I.

Solution and Refinement of the Structure. The Mo atom position was determined from a Patterson map. The remaining non-hydrogen atoms of the anion and the cations were located from subsequent difference Fourier maps. The structure was refined by using the blocked cascade least-squares method. Fixed contributions from hydrogen atoms with thermal parameters set at 1.2 times that of the bonded carbon atom were included in the final stage of refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters except for one methylene carbon atom in the side chain of a Pr₂cat ligand, which was disordered. The asymmetric unit consists of half of the anion and two cations; the remaining atoms are generated by inversion symmetry. The distribution of the disordered carbon atom (C(11)) was modeled with three equally occupied positions. Its C–CH₂ and C–CH₃ distances were short (1.19–1.32 Å) and long (1.74–1.83 Å), respectively. Unique data used in the refinement and final R factors are given in Table I. The following results are tabulated: positional parameters (Table II), selected interatomic distances and angles (Table III), and unweighted least-squares planes (Table IV) of the anion; thermal parameters of the anion (Table S-I); positional and thermal parameters of the cations (Table S-II); calculated and observed structure factors (Table S-III[21]).

Triclinic (Et₄N)₄[Mo₂Fe₆S₈(SEt)₆(Pr₂cat)₂]. Crystals of this form were obtained by slow cooling of an acetonitrile solution. The compound crystallizes in space group $P\bar{1}$ with $a = 13.942$ (4) Å, $b = 19.119$ (3) Å, $c = 19.576$ (3) Å, $\alpha = 89.11$ (1)°, $\beta = 74.54$ (2)°, $\gamma = 75.75$ (2)°, $V = 4867$ (3) Å³, and $Z = 2$. From 6568 data ($F_0^2 > 2.5\sigma(F_0^2)$, $2\theta \leq 43°$) the structure was refined to $R = 5.7\%$ and $R_w = 5.9\%$ by using 883 variables. The asymmetric unit consists of two halves of two independent centrosymmetric anions and four cations. The structures of the subclusters are unimportantly different from those of the monoclinic form. Metrical details of the Mo(μ-SEt)Fe bridge region do differ somewhat, as seen by comparison of the following data (independent values, mean value) with those in Table III: Mo–S = 2.653 (3), 2.647 (4), 2.650 Å; Fe–S = 2.297 (3), 2.309 (3), 2.303 Å; Mo···Fe = 4.274 (3), 4.238 (3), 4.256 Å; Mo···Mo = 5.980 (5), 5.953 (5), 5.976 Å; Fe···Fe = 3.915 (3), 3.885 (4), 3.900 Å; Mo–S–Fe = 119.2, 117.4, 118.3°. Full details of the structure of the triclinic modification are given elsewhere.[22]

Other Physical Measurements. All measurements were performed under anaerobic conditions; solvents were purified by standard procedures and were degassed prior to use. Absorption spectra were recorded on a Cary Model 219 spectrophotometer. EPR spectra were obtained at X-band frequencies using a Varian E-109 spectrometer equipped with a Helitran Model LTD-3-110 temperature controller. Electrochemical measurements were made with standard Princeton Applied Research instrumentation using a glassy carbon working electrode; potentials were measured at ~ 25 °C vs. a saturated calomel electrode as reference. ^{1}H NMR spectra were recorded on a Brüker WM-300 spectrometer equipped with a deuterium lock. Chemical shifts downfield and upfield of Me₄Si reference are designated as negative and positive, respectively. Solution magnetic susceptibilities were determined by the NMR method.[23] Solvent susceptibilities were taken from the results of Gerger et al.[24] and diamagnetic corrections from tabulated values.[25]

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(21) See paragraph at the end of this article concerning supplementary material.

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Table II. Positional Parameters for $[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]^{4-}$

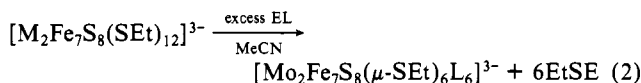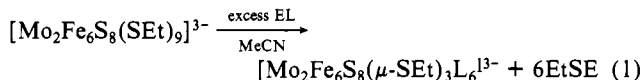| atom	x	y	z
Mo	0.39037 (3)^a	0.10684 (3)	0.40985 (4)
Fe(1)	0.44354 (5)	0.03234 (5)	0.38192 (6)
Fe(2)	0.39831 (5)	0.16133 (5)	0.31724 (7)
Fe(3)	0.30725 (5)	0.05956 (5)	0.24767 (6)
S(1)	0.36450 (9)	−0.00766 (9)	0.3622 (1)
S(2)	0.49059 (9)	0.1311 (1)	0.4582 (1)
S(3)	0.3043 (1)	0.1673 (1)	0.2777 (1)
S(4)	0.3782 (1)	0.0671 (1)	0.2461 (1)
S(5)	0.47863 (9)	0.05077 (9)	0.5661 (1)
S(6)	0.4035 (1)	0.2564 (1)	0.2699 (2)
S(7)	0.2016 (1)	0.0203 (1)	0.1246 (2)
C(1)S(5)^b	0.4299 (4)	0.0024 (5)	0.5673 (6)
C(2)S(5)	0.4409 (6)	0.0273 (7)	0.6330 (7)
C(1)S(6)	0.3881 (6)	0.3272 (6)	0.2995 (7)
C(2)S(6)	0.4310 (7)	0.3288 (7)	0.3910 (8)
C(1)S(7)	0.1642 (9)	0.016 (1)	0.157 (2)
C(2)S(7)	0.131 (2)	0.044 (2)	0.143 (3)
O(1)	0.4111 (2)	0.1928 (2)	0.4748 (3)
O(2)	0.3244 (2)	0.0950 (2)	0.4077 (3)
C(1)	0.3280 (4)	0.1442 (4)	0.4484 (4)
C(2)	0.3748 (4)	0.1973 (4)	0.4846 (4)
C(3)	0.3812 (4)	0.2511 (4)	0.5271 (4)
C(4)	0.3410 (4)	0.2484 (4)	0.5328 (5)
C(5)	0.2962 (4)	0.1958 (4)	0.4989 (5)
C(6)	0.2870 (4)	0.1430 (4)	0.4536 (5)
C(7)	0.4291 (5)	0.3106 (5)	0.5603 (7)
C(8)	0.4266 (8)	0.3706 (7)	0.589 (1)
C(9)	0.4730 (8)	0.4278 (7)	0.613 (1)
C(10)	0.2383 (6)	0.0836 (6)	0.4161 (9)
C(11A)^c	0.244 (2)	0.023 (2)	0.424 (2)
C(11B)	0.175 (2)	0.087 (2)	0.362 (2)
C(11C)	0.185 (1)	0.073 (1)	0.333 (2)
C(12)	0.155 (1)	0.000 (1)	0.343 (2)

^{a} Estimated standard deviations in parentheses in this and succeeding tables. ^{b} The labeling schemes for the SEt and Pr₂cat ligands are S–C(1)S–C(2)S and
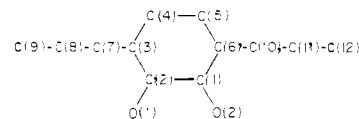
^{c} Disordered methylene carbon atom.

Results and Discussion

Synthesis of Doubly Bridged Clusters. Several prior attempts have been made to cleave bridges present in double cubanes. Treatment of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ and $[M_2Fe_7S_8(SEt)_{12}]^{3-}$ (M = Mo, W) with the electrophiles (EL) acetyl chloride and thiols at ambient temperature results in reactions 1 and 2.[3] Under

$$[Mo_2Fe_6S_8(SEt)_9]^{3-} \xrightarrow[\text{MeCN}]{\text{excess EL}}$$
$$[Mo_2Fe_6S_8(\mu\text{-SEt})_3L_6]^{3-} + 6EtSE \quad (1)$$

$$[M_2Fe_7S_8(SEt)_{12}]^{3-} \xrightarrow[\text{MeCN}]{\text{excess EL}}$$
$$[Mo_2Fe_7S_8(\mu\text{-SEt})_6L_6]^{3-} + 6EtSE \quad (2)$$

$$L = Cl, RS$$

conditions which preserve subcluster structure these reactions afford clean substitution of terminal thiolate ligands but do not disrupt bridges even when excess reagent is employed. In a second attempt, based on the high affinity of catecholate for Fe(III),[26] reaction 3 was found to give **5** in $\sim 40\%$ purified yield.[13] No other

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Table III. Selected Interatomic Distances (Å) and Angles (Deg) in [Mo$_2$Fe$_6$S$_8$(SEt)$_6$(Pr$_2$cat)$_2$]$^{4-}$

MoFe$_3$S$_4$(SEt)$_2$(Pr$_2$cat) Subcluster			
Mo–S(1)	2.362 (2)	Mo···Fe(1)	2.695 (2)
Mo–S(2)	2.371 (3)	Mo···Fe(2)	2.748 (2)
Mo–S(3)	2.377 (2)	Mo···Fe(3)	2.755 (2)
mean	2.370 (8)^a	mean	2.733 (33)
Mo···S(4)	3.908 (4)	Fe(1)···Fe(2)	2.719 (2)
Mo–O(1)	2.062 (6)	Fe(1)···Fe(3)	2.707 (2)
Mo–O(2)	2.047 (10)	Fe(2)···Fe(3)	2.711 (2)
mean	2.055	mean	2.712 (6)
Fe(1)–S(1)	2.259 (4)	Fe(1)···S(3)	3.870 (3)
Fe(1)–S(2)	2.268 (3)	Fe(2)···S(1)	3.900 (3)
Fe(1)–S(4)	2.311 (3)	Fe(3)···S(2)	3.911 (2)
Fe(2)–S(2)	2.278 (3)	mean	3.894 (21)
Fe(2)–S(3)	2.263 (4)	O(1)···O(2)	2.591 (8)
Fe(2)–S(4)	2.285 (3)	S(1)···S(2)	3.725 (3)
Fe(3)–S(1)	2.264 (3)	S(1)···S(3)	3.671 (3)
Fe(3)–S(3)	2.263 (3)	S(1)···S(4)	3.585 (5)
Fe(3)–S(4)	2.269 (4)	S(2)···S(3)	3.696 (3)
mean	2.273 (16)	S(2)···S(4)	3.596 (3)
Fe(2)–S(6)	2.281 (4)	S(3)···S(4)	3.574 (5)
Fe(3)–S(7)	2.250 (3)	mean	3.64
mean	2.266	C(1)–O(2)	1.34 (1)
C(1)S(6)–S(6)	1.81 (2)	C(2)–O(1)	1.35 (2)
C(1)S(7)–S(7)	1.90 (5)	C(1)–C(2)^b	1.40 (1)
O(1)–Mo–O(2)	78.2 (3)	C(2)–C(3)	1.40 (2)
O(1)–Mo–S(2)	88.0 (2)	C(3)–C(4)	1.38 (2)
O(1)–Mo–S(3)	90.5 (1)	C(4)–C(5)	1.37 (1)
O(2)–Mo–S(1)	86.6 (2)	C(5)–C(6)	1.39 (2)
O(2)–Mo–S(3)	90.2 (2)	C(6)–C(1)	1.40 (2)
S(1)–Mo–S(2)	103.8 (1)	mean	1.39 (1)
S(1)–Mo–S(3)	101.6 (1)	Mo–S(1)–Fe(1)	71.3 (1)
S(2)–Mo–S(3)	102.2 (1)	Mo–S(1)–Fe(3)	73.1 (1)
Fe(1)–Mo–Fe(2)	59.9 (1)	Mo–S(2)–Fe(1)	71.0 (1)
Fe(1)–Mo–Fe(3)	59.6 (1)	Mo–S(2)–Fe(2)	72.4 (1)
Fe(2)–Mo–Fe(3)	59.0 (1)	Mo–S(3)–Fe(2)	72.6 (1)
mean	59.5 (1)	Mo–S(3)–Fe(3)	72.8 (1)
S(1)–Fe(1)–S(2)	110.8 (1)	mean	72.2
S(1)–Fe(1)–S(4)	103.3 (1)	Fe(1)–S(1)–Fe(3)	73.5 (1)
S(2)–Fe(1)–S(4)	103.5 (1)	Fe(1)–S(2)–Fe(2)	73.5 (1)
S(2)–Fe(2)–S(3)	109.0 (1)	Fe(1)–S(4)–Fe(2)	72.5 (1)
S(2)–Fe(2)–S(4)	104.0 (1)	Fe(1)–S(4)–Fe(3)	72.5 (1)
S(3)–Fe(2)–S(4)	103.6 (1)	Fe(2)–S(3)–Fe(3)	73.6 (1)
S(1)–Fe(3)–S(3)	108.4 (1)	Fe(2)–S(4)–Fe(3)	73.1 (1)
S(1)–Fe(3)–S(4)	104.5 (1)	mean	73.1
S(3)–Fe(3)–S(4)	104.1 (1)		

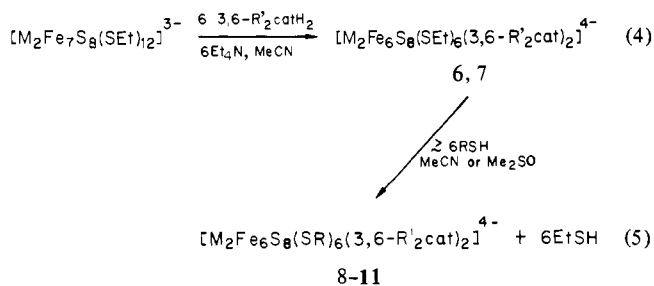| Mo(μ-SEt)Fe Bridge			
Mo–S(5)	2.689 (2)	Mo–S(5)–Fe(1')	122.2 (1)
Fe(1')–S(5)	2.305 (3)	S(5)–Mo–O(1)	81.5 (2)
Mo···Fe(1')	4.377 (4)	S(5)–Mo–O(2)	81.5 (2)
		S(5)–Mo–S(1)	84.6 (2)
Mo···Mo'	6.038 (4)	S(5)–Mo–S(2)	84.4 (2)
Fe(1)···Fe(1')	4.048 (3)	S(5)–Fe(1')–S(1')	112.1 (2)
Mo···S(1')	5.163 (4)	S(5)–Fe(1')–S(2')	115.1 (2)
Mo···S(2')	5.211 (4)	S(5)–Fe(1')–S(4')	111.2 (2)
Fe(1)···S(1')	4.135 (5)	S(5)–Mo–Fe(1)	91.3 (1)
Fe(1)···S(2')	4.195 (5)		
S(1)···S(1')	5.292 (6)		
S(2)···S(2')	5.394 (6)		
S(1)···S(2')	3.831 (5)		
C(5)–S(5)	1.82 (2)		

^{a} The standard deviation of the mean was estimated from $\sigma \approx s = [(\Sigma x_i^2 - n\bar{x}^2)/(n-1)]^{1/2}$; when no value is given, the variations exceed those expected from a sample taken from the same population. ^{b} *n*-Pr C–C distances: C(3)–C(7) = 1.53 (2) Å; C(6)–C(10) = 1.52 (2) Å; C(7)–C(8) = 1.41 (3) Å; C(8)–C(9) = 1.54 (3) Å. Atom C(11) is disordered.

reaction product has as yet been purified to an extent sufficient for identification nor have we thus far been able to detach the

$$[Mo_2Fe_7S_8(SEt)_{12}]^{3-} \xrightarrow[MeCN]{6H_2cat,\ 6Et_3N} [MoFe_4S_4(SEt)_3(cat)_3]^{3-}$$
$$\mathbf{5}$$

$$(3)$$
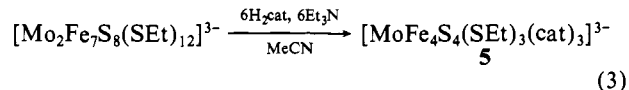
Fe(cat)$_3$$^{3-}$ subunit from the Mo site in **5**. However, this cluster has provided a direction for further investigation of bridge cleavage reactions.

In the structure of **5** in the crystalline state[13] the three Fe–SEt groups are directed away from the directly opposite catecholate rings. In certain rotational conformations possible in solution the methyl groups closely approach the 3-H atom of the opposite ring. When the 3 substituent is methyl or larger, these conformations lead to approaches well within van der Waals distances. Sufficiently large 3 substituents will, in addition, generate unavoidable and unfavorable steric interactions with the sulfur atoms. These circumstances indicate probable steric destabilization of structure **5** and formation of another product in a variant of reaction 3 with appropriate 3,6-disubstituted catechols. Of the latter the 3,6-diallyl[17,18] and 3,6-di-*n*-propyl[19] derivatives are readily accessible. Their employment in reaction 4 results in smooth formation of

$$[M_2Fe_7S_8(SEt)_{12}]^{3-} \xrightarrow[6Et_4N,\ MeCN]{6\ 3,6-R'_2catH_2} [M_2Fe_6S_8(SEt)_6(3,6-R'_2cat)_2]^{4-}$$
$$\mathbf{6,7}$$

$$(4)$$

$$\downarrow \begin{array}{c} 2\ 6RSH \\ MeCN\ or\ Me_2SO \end{array}$$

$$[M_2Fe_6S_8(SR)_6(3,6-R'_2cat)_2]^{4-} + 6EtSH$$
$$\mathbf{8-11}$$

$$(5)$$

clusters **6** and **7** (M = Mo, W), obtained in ~60% yield after purification of their Et$_4$N$^+$ salts.[27] Unlike **1** and **3** clusters **6** and **7** undergo complete thiolate ligand substitution with arenethiols (reaction 5, vide infra). Catecholate ligands are retained in the product clusters **8–11**. The Et$_4$N$^+$ salts of certain R' = *n*-Pr clusters are quite soluble in acetonitrile and proved difficult to crystallize. Those with R' = C$_3$H$_5$ and R = Ph (**8**-Mo, **8**-W) and *p*-C$_6$H$_4$Cl (**9**-Mo) are readily crystallized and were obtained in ~40–50% purified yield. Other clusters (**10**-Mo, **10**-W, **11**-Mo) were generated in solution for examination but were not isolated.

Structure of (Et$_4$N)$_4$[Mo$_2$Fe$_6$S$_8$(SEt)$_6$(Pr$_2$cat)$_2$]. This compound has been crystallized in triclinic and monoclinic modifications. Because most of the differences in metrical features of the anions in the two crystals are chemically insignificant, only the structure of the monoclinic form is described in detail. Its crystal structure consists of well-separated cations and anions. As shown in Figure 1 the structure of cluster **6**-Mo, which has a crystallographically imposed symmetry center, is of the double-cubane type. A stereoview is provided in Figure 2. Interatomic distances and angles are collected in Table III, and certain least-squares planes and positional deviations therefrom are presented in Table IV. The cluster consists of two MoFe$_3$S$_4$ subclusters in which two of the Fe atoms are terminally coordinated by ethanethiolate ligands. The two subclusters are joined by two Mo(μ-SEt)Fe bridges, a component not previously encountered in other structurally characterized double cubanes.[4,5,8,28-32]

(27) Other reaction products have not been identified but dark red solids, presumably (Et$_4$N)$_3$[Fe(3,6-R'$_2$cat)$_3$], have been observed to separate from reaction mixture filtrates upon standing.

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Double Cubanes Containing MFe₃S₄ Clusters

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Table IV. Unweighted Least-Squares Planes of $[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]^{4-}$

$Ax + By + Cz = D$ (Orthogonalized Coordinates)

plane no.	A	B	C	D
1	0.6439	-0.4181	0.6408	4.5728
2	0.1816	0.8995	0.3975	3.6606
3	0.7401	0.1302	-0.6597	5.3157
4	0.7271	0.1163	-0.6766	7.4551
5	0.1757	0.8934	0.4135	1.3434
6	0.6388	-0.4064	0.6533	2.2853
7	0.6548	0.7318	-0.1891	6.3771
8	0.9782	-0.2068	-0.0182	6.9822
9	-0.3284	0.9294	-0.1686	-0.6615
10	0.5586	0.3387	0.7571	4.0064
11	-0.0612	-0.3535	0.9334	-2.0287
12	-0.3711	0.5291	0.7631	-2.6359
13	0.6692	0.7182	-0.1906	6.4730

Deviations (Å) from Plane Numbers 1–13

atom	1	2	3	4	5	6
Mo	-0.121	-0.136	0.142			
Fe(1)	-0.139			-0.188	0.181	
Fe(2)		-0.155		-0.190		0.174
Fe(3)			0.162		0.186	0.176
S(1)	0.130		-0.152		-0.185	
S(2)	0.130	0.145		0.190		
S(3)		0.146	-0.152			-0.176
S(4)				0.187	-0.182	-0.174

atom	7	8	9	10	11	12
Mo	0.003	0.011	-0.007			
Fe(1)	-0.003			0.013	0.018	
Fe(2)		-0.012		-0.012		0.007
Fe(3)			0.008		-0.018	-0.007
S(1)		-0.009		-0.009		0.005
S(2)			0.006		-0.013	-0.005
S(3)	-0.002			0.009	0.013	
S(4)	0.002	0.009	-0.006			

plane 13	Mo	Mo	Fe(1)	Fe(1')	S(5)	S(5')
dev, Å	-0.013	0.013	0.019	-0.019	0.016	-0.016
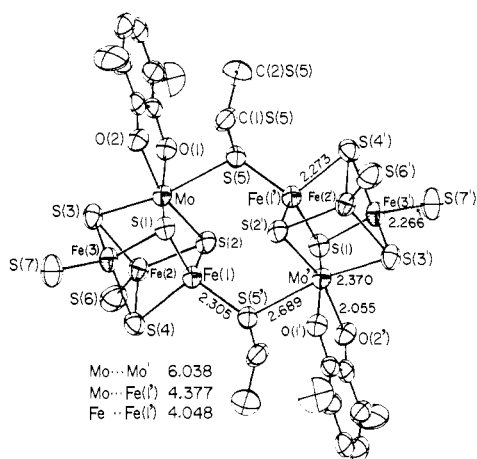
Figure 1. Structure of $[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]^{4-}$ (**6-Mo**), showing 50% probability ellipsoids, selected (mean) interatomic distances, and the atom labeling scheme. Ethyl groups of terminal thiolate and the ethyl portions of catecholate ligands are omitted; primed and unprimed atoms are related by the inversion center.

Subclusters in **6-Mo** exhibit dominant trigonal distortion with respect to the Mo–S(4) diagonal as the idealized threefold axis. Each face (MoS₂Fe, Fe₂S₂, planes 1–6) is a decidedly nonplanar rhombus; atomic deviations from diagonal planes 7–12 are much smaller. Metrical features are very similar to those of some six other clusters of types $\mathbf{1–5}^{5,8,13,28-30}$ containing the subcluster $[MoFe_3S_4]^{3+}$ oxidation level in common with that of **6-Mo**. This situation is illustrated by comparison of appropriate mean values

in Table III with the following ranges of mean bond distances in other clusters: Mo–S = 2.34 (2)–2.39 (2) Å; Mo⋯Fe = 2.71 (2)–2.75 (1) Å; Fe⋯Fe = 2.69 (1)–2.72 (1) Å; Fe–S = 2.25 (3)–2.27 (2) Å; Fe–SR = 2.23 (1)–2.26 (1) Å. In idealized trigonal symmetry the nine Fe–S distances divide into sets of six and three. The former set averages to 2.266 (7) Å. The latter set, involving the S(4) atom, contains the long Fe(1)–S(4) distance of 2.311 (3) Å. This bond lengthening is associated with the involvement of atom Fe(1) in the Mo(μ-SEt)Fe bridge unit and may reflect a degree of strain in the subcluster structure. Two Mo atom coordination sites external to the subclusters are occupied by chelating Pr₂cat ligands. Their C–O bond lengths (1.34 (1), 1.35 (2) Å) are indicative of the Pr₂cat²⁻ rather than the semi-quinone or quinone oxidation level.[33] Values of Mo–O distances (2.062 (6), 2.047 (10) Å) are larger than terminal Mo–O bond lengths cis to Mo=O groups in catecholate,[33,34] salicylaldiminate,[35] and β-diketonate[36] complexes of Mo(VI) (range 1.92–2.01 Å). The differences in mean Mo–O (cis) bond lengths between MoO₂(PhCOCHCOPh)₂[36] (1.993 Å) and Mo(acac)₃[37] (2.071 (3) Å), the most appropriate comparison currently available, suggests an effective Mo oxidation state in **6-Mo** below VI and near III. From an analysis of ⁵⁷Fe isomer shifts in clusters of different oxidation levels, we have offered the (mean) oxidation states $Fe^{2.67+}$ and Mo^{3+} as reasonable descriptors of charge distribution in clusters with the $[MoFe_3S_4]^{3+}$ oxidation level.[4]

Distorted octahedral and tetrahedral coordination of the Mo and Fe(1) atoms, respectively, is completed by binding to the S(5) atom of a bridging ethanethiolate ligand. The two Mo(μ-SEt)Fe bridges, with angles at the S(5,5') atoms of 122.2 (1)°, dispose the two subclusters such that six atoms of the bridges are nearly coplanar (plane 13, Table IV) and the distance of closest approach is 3.831 (5) Å (S(1)⋯S(2')). Metal–metal and the remaining S⋯S atom approach distances between the two closest subcluster faces occur in the 4.0–6.0-Å range. Of these the Mo⋯Mo' separation of 6.038 (4) Å is the longest. The bridging S(5)–Et group is disposed so as to reduce steric interference with adjacent Pr₂cat and S(6')–Et ligands. Certain rotational conformations of the S(5)–Et and n-Pr (but not S(6')–Et) groups can bring the two into van der Waals contact, but destabilizing steric interactions involving the S(5) atom are clearly absent.

The Fe(1)–S(5') bond distance of 2.305 (3) Å is 0.039 Å longer than the mean value of the two terminal Fe–SEt distances. In the triclinic form the bridge mean distance exceeds the mean of the four independent terminal distances (2.248 (5) Å) by 0.055 Å. The Mo–S(5) bond distance is 2.689 (2) Å; in the triclinic modification the mean of the two independent values is 2.650 Å. Taking terminal (cis) Mo(IV)–SR distances in complexes of different structures as a rough guide,[38] their range of 2.24–2.41 Å would appear to suggest a bond elongation in the vicinity of 0.3–0.4 Å as a consequence of bridge formation. Further, the Mo–S bridge bonds are ~0.08–0.12 Å longer than the indistinguishable values (2.559 (8)–2.568 (4) Å) of bridge Mo–SR bond distances in four well-refined structures of **1**, **3**, and **4** containing $[MoFe_3S_4]^{3+}$ subclusters.[5,8,30] As shown below, only the latter estimate of bond elongation is meaningful. It and the comparable increases in Fe–S bond lengths imply weaker and more reactive bridge bonds in **6-Mo** and related doubly bridged double cubanes compared to **1** and **3**,[3] a matter examined in the following sections.

(33) For a review of molybdenum catecholate complexes, cf.: Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

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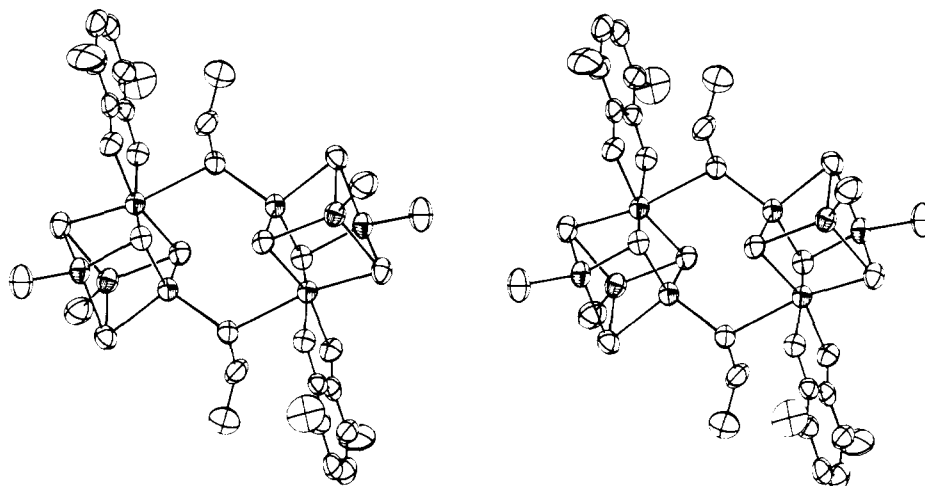
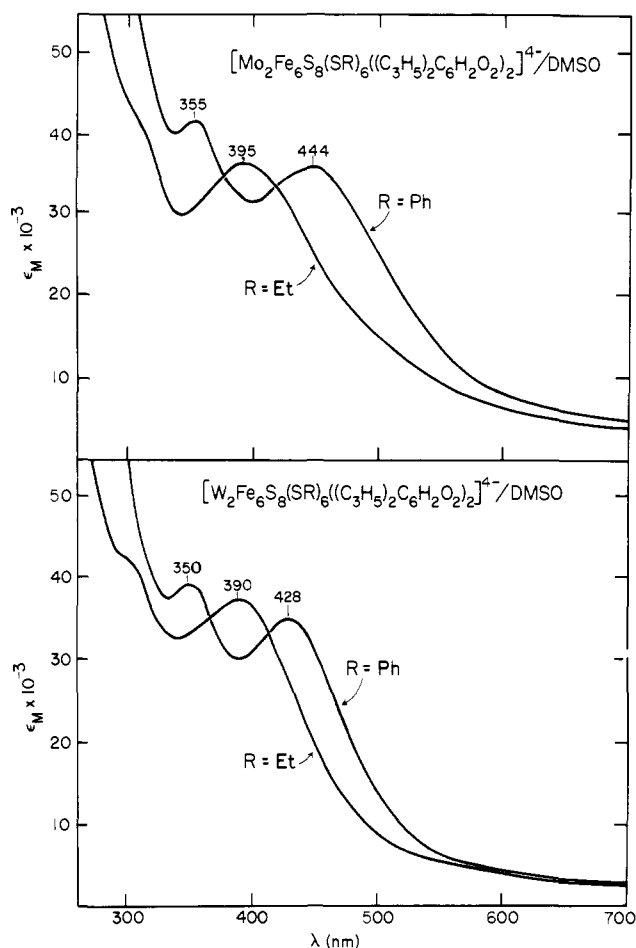**Figure 2.** Stereoview of the structure of **6**-Mo presented in Figure 1.

Figure 3. UV–visible spectra of 0.2–0.3 mM Me$_2$SO solutions prepared from Et$_4$N$^+$ salts of **7**-Mo and **8**-Mo (top) and **7**-W and **8**-W (bottom).
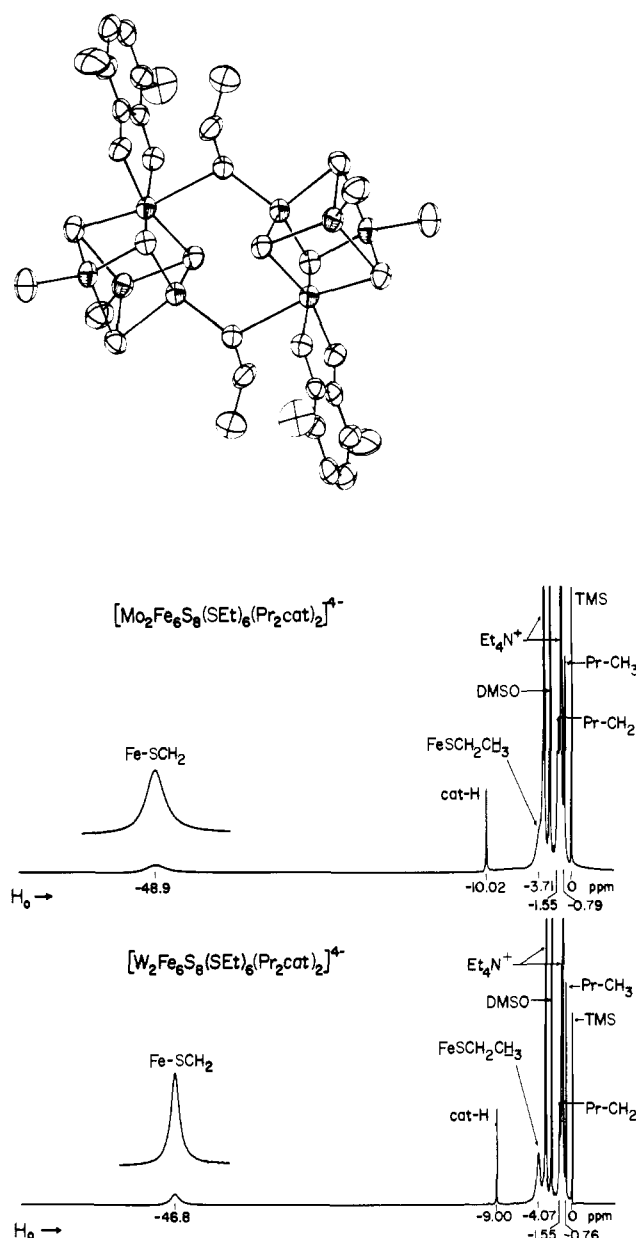

Figure 4. ^{1}H NMR spectra (300 MHz, 297 K) of ∼15 mM Me$_2$SO-d_6 solutions prepared from Et$_4$N$^+$ salts of **6**-Mo and **6**-W. Signal assignments are indicated.

Properties of Solute Clusters. The doubly bridged structure established for **6**-Mo as its crystalline Et$_4$N$^+$ salt is considered to apply to other isolated clusters **6–9** in the solid state (vide infra) inasmuch as all members of the set have analogous compositions. Solutions prepared from the cluster salts have been examined by spectroscopic and electrochemical methods in an attempt to determine whether the doubly bridged double-cubane arrangement remains intact in polar aprotic solvents such as Me$_2$SO, DMF, and acetonitrile. Certain of these properties are compared with those of **1–5**, for which there is unequivocal evidence that bridging interactions are retained in solution.[3-7,13] At the outset it is noted that all clusters are paramagnetic and that properties of R′ = *n*-Pr

and C$_3$H$_5$ species at parity of M and R are essentially identical. Examination of one or both types of R′-substituted clusters was dictated by solubility and availability of compounds.

(a) **Absorption Spectra.** Shown in Figure 3 are the spectra of Me$_2$SO solutions prepared from molybdenum and tungsten cluster salts with R = Et (**7**-Mo, **7**-W) and R = Ph (**8**-Mo, **8**-W). These spectra, which are useful for characterization purposes, are typical of those afforded by all members of the cluster set **6–11**. The small blue shifts of band maxima in tungsten vs. molybdenum species have been observed previously in other MFe$_3$S$_4$-type double cubanes.[5,7] Band maxima near 390 nm (**7**-Mo, **7**-W) and the appearance of two absorption features in the 350–450-nm range (**8**-Mo, **8**-W) are found in the spectra of **1–5** with corresponding (alkyl, phenyl) R groups.[3-5,7,13,39] The extinction coefficients of ≲20 000/MFe$_3$S$_4$ cluster for the (lower energy) visible bands are similar to those found for **1** (R = Et,[5] Ph[39]) and **5**.[13] These spectral consistencies support the presence of the MFe$_3$S$_4$ entity in the solute clusters, but cannot distinguish among doubly bridged or

(39) Christou, G.; Hageman, R. V.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 7600.

Table V. Magnetic Moments, ¹H Isotropic Shifts, and Signal Intensities of Clusters in Me₂SO-d_6 Solutions at ~299 K

cluster	$\mu_{MFe_3S_4}$,[h] μ_B	$(\Delta H/H_0)_{iso}$,[a] ppm (relative intensity)						
		SCH₂	SCH₂CH₃	cat-H	o-H	m-H	p-H, -Me	(CH₃CH₂)₄N⁺
6-Mo	4.14	−46.4 (2.9)	−2.5	−3.56 (1)				
7-Mo	4.09	−46.7 (2.8)	−2.6	−3.60 (1)				(13[f])
7-Mo (DMF-d_7)	b	−47.3 (2.7)	c	−2.68 (1)				(13[f])
8-Mo	4.09			−4.00 (1)	c	−5.81 (2.8)	+10.4	(8.4,[g] 14[f])
8-Mo (CD₃CN)	4.05			−2.01 (1)	c	−5.99 (2.9)	+10.2	(13[f])
9-Mo	4.13			−4.10 (1)	+10.4	−5.82 (3.0)		(7.3,[g] 12[f])
10-Mo	b			−4.17 (1)	+10.2	−5.83 (2.9)	−9.83 (4.7)	(9.0[g])
6-W	4.19	−44.3 (2.8)	−2.83 (3.8)	−2.54 (1)				(8.2[g])
7-W	4.14	−44.7 (3.1)	−2.85 (3.6)	−2.45 (1)				(8.4,[g] 12[f])
8-W	4.03			−2.69 (1)	+8.84	−5.56 (3.2)	+9.58	(8.8,[g] 14[f])
10-W	b			−2.89 (1)	+8.6	−5.61 (3.0)	−9.39 (4.7)	(8.8[g])
1 (R = Et)	4.05[d]	−52.9[f]	−3.37[f]					
1 (R = Ph)[e]	4.03				c	−6.61	+11.4	
2 (R = Ph)[e]	b				c	−6.25	+10.4	

[a] $(\Delta H/H_0)_{iso} = (\Delta H/H_0)_{obsd} - (\Delta H/H_0)_{dia}$; diamagnetic shifts are taken as those of free thiols or catechols. [b] Not determined. [c] Signal not resolved. [d] Reference 4. [e] Reference 6. [f] CH₃ resonance. [g] CH₂ resonance. [h] μ $(\mu_B) = 2.828\ (\chi^M T)^{1/2}$.
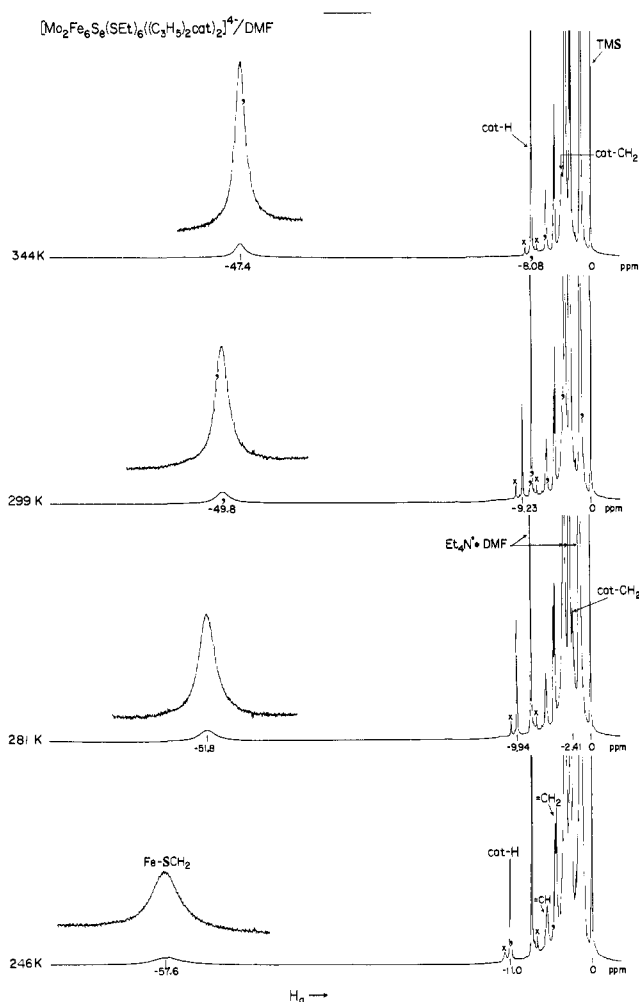
Figure 5. Variable-temperature ¹H NMR spectra (300 MHz) of a ~10 mM solution of the Et₄N⁺ salt of 7-Mo in DMF-d_7. Signal assignments are indicated (x = impurity).

Figure 6. ¹H NMR spectra (300 MHz, 297 K) of equilibrium systems in Me₂SO-d_6 solutions initially 9.5 mM in the Et₄N⁺ salt of 7-Mo, to which n = 1–3 equiv of p-toluenethiol/Mo atom has been added. The −10 to −20 ppm region is shown; signal assignments for each (3–n,n) species are given (x = impurity).

Figure 7. ¹H NMR spectra (300 MHz, 297 K) of ~10 mM solutions of the Et₄N⁺ salts of 8-Mo and 8-W in Me₂SO-d_6. Signal assignments are indicated.

some other bridged structure or single (nonbridged) clusters.

(b) ¹H NMR Spectra. These spectra provide the best means of probing the nature of clusters in solution. Consequently, a rather extensive body of results is provided. Selected spectra are presented in Figures 4–8; isotropic shifts at ~299 K measured mainly in Me₂SO-d_6 solutions are collected in Table V. Also tabulated are relative intensities of those resonances that are sufficiently well resolved to be meaningfully integrated. Intensities of other signals are normalized to those of catecholate ring protons (cat-H), which were assigned by comparison with the spectra of
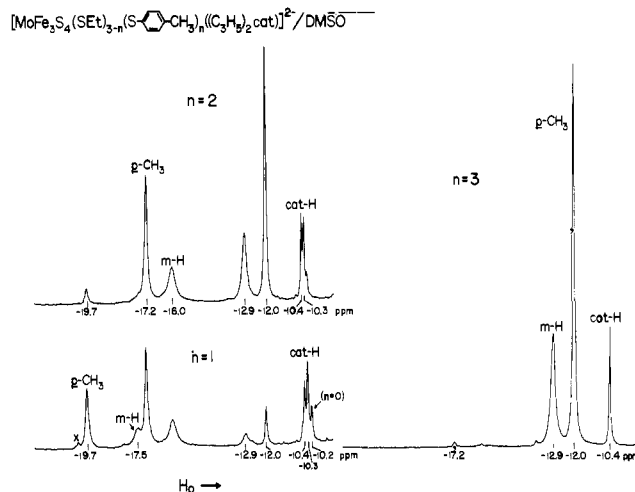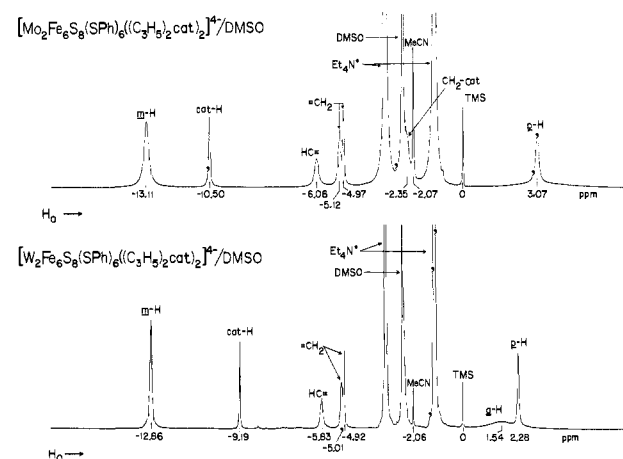
clusters synthesized from 3,6-$(C_3H_5)_2C_6D_2(OH)_2$. The following features apply to the spectra of all solute clusters present in solutions prepared from $(Et_4N)_4[M_2Fe_6S_8(SR)_6(3,6-R'_2cat)_2]$ (6–9) or generated in solution (10, 11) by reaction 5. (i) Resonances are isotropically shifted as a consequence of cluster paramagnetism, which affords magnetic moments per (sub)cluster
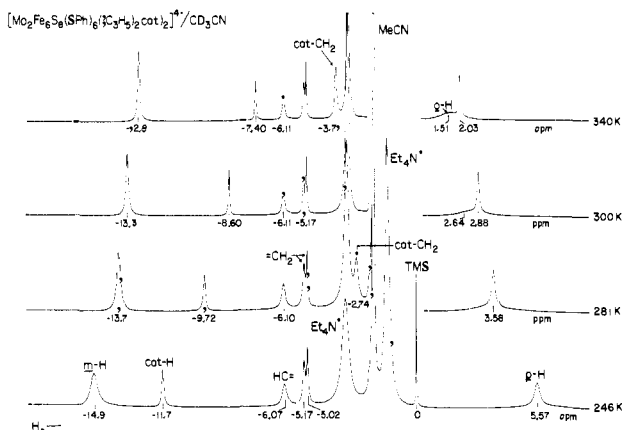
Figure 8. Variable-temperature ^1H NMR spectra (300 MHz) of a $\sim$10 mM solution of the Et_4N^+ salt of 8-Mo in CD_3CN. Signal assignments are indicated.

μ_{MFeS_4} = 4.0–4.2 μ_B at ambient temperature. (ii) Only *one* set of RS signals is observed. (iii) Relative signal intensities correspond to the ratio RS:R'$_2$cat:Et$_4$N$^+$ = 3:1:2 which, together with analytical data of crystalline salts, demonstrates the solute cluster minimal formulation $[MFe_3S_4(SR)_3(3,6-R'_2cat)]^{2-}$. (iv) The resonances in the figures and in Table V are the only ones detected at the indicated temperatures in ±400-ppm sweeps vs. the Me$_4$Si reference signal. Some specific cases are considered next in order to illustrate these spectral features. Attention is directed to RS and cat-H signals, which undergo the largest isotropic shifts.[40]

Spectra of the cluster pair 6-Mo and 6-W in Me$_2$SO-d_6, shown in Figure 4, display three isotropically shifted signals. Two of these arise from the EtS groups and the other from cat-H. Narrower line widths are a consistent feature of the spectra of tungsten-containing clusters. On the basis of the spectrum of 1 (R = Et, Table V) and signal intensities of the tungsten cluster, the resonances near −47 and −4 ppm are assigned, as indicated, to Fe–SEt units.[41] When examined at 246–344 K, the cluster present in a DMF-d_7 solution prepared from the salt of 7-Mo gives comparable results. The spectra, shown in Figure 5, reveal SCH$_2$ and cat-H signals whose isotropic shifts decrease with increasing temperature; the SCH$_2$CH_3 resonance is not resolved. No additional SEt or cat-H signals are observed above or below ambient temperature.

Because of the possibility that the broad SCH$_2$ resonances and unresolved SCH$_2$CH_3 signals in the preceding systems may have prevented detection of more than one solute species, clusters with R = Ph and *p*-tolyl have been examined. Shown in Figure 6 are the spectra resulting from the addition of 1–3 equiv of *p*-toluenethiol/Mo atom to a Me$_2$SO-d_6 solution prepared from the Et$_4$N$^+$ salt of 7-Mo. Each species gives a single set of *p*-CH$_3$, *m*-H, and cat-H signals. Upon the addition of 3 equiv of thiol the spectrum simplifies to three isotropically shifted lines and the SCH$_2$ signal at lower field is abolished. Complete ligand substitution (reaction 5) has occurred to generate a cluster derived from 11-Mo. Spectra of clusters derived from 10-Mo and 10-W (Table V) were obtained similarly. Complete substitution is verified by comparison with the spectra in Figure 7 of the cluster species present in Me$_2$SO-d_6 solutions prepared from the salts of 8-Mo and 8-W. The spectrum of the latter species is particularly well resolved, with one set of R = Ph resonances and one cat-H signal clearly evident. Spectra of the molybdenum cluster in

CD$_3$CN solution at 246–340 K are presented in Figure 8. Other than resolution of the broad ortho-H signal at the highest temperatures no new signals appear. From signal intensities and isotropic shift comparisons with 1 and 2 (both with R = Ph, Table V), it is concluded that all arenethiolate ligands are present in the form of Fe–SR units. As with the R = Et clusters no signals attributable to Mo–SR and/or Mo(μ-SR)Fe structural components were detected at any temperature.

The foregoing results demonstrate the occurrence of reaction 6. The doubly bridged double-cubane structure 12 present in the crystalline state[42] undergoes bridge disruption in the process of dissolution in polar, coordinating solvents such as Me$_2$SO, acetonitrile, and DMF. Presumably the process is initiated by
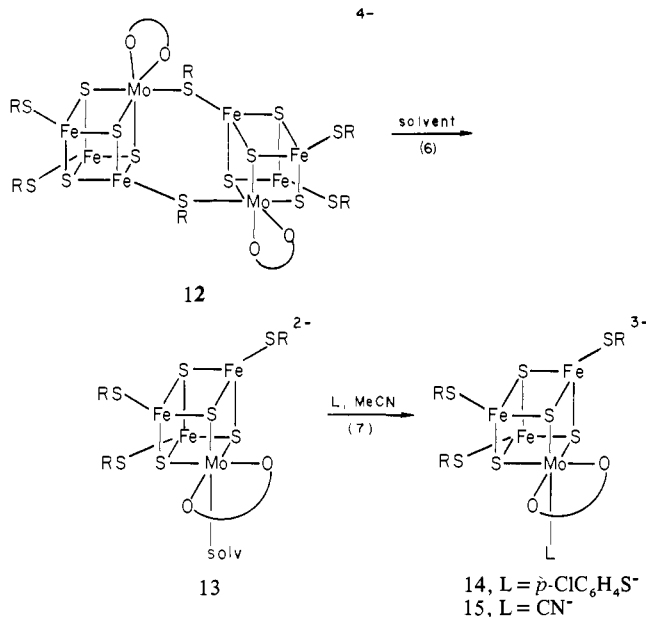
solvent-induced cleavage of the elongated Mo–SR bridge bond. Whatever are the mechanistic details, there is no question that bridging thiolate ligands in solid-state structures become terminal Fe–SR ligands in the solute clusters. For the latter the formulation $[MFe_3S_4(SR)_3(3,6-R'_2cat)_2(solv)]^{2-}$ (13) is proposed, in which a solvent molecule completes the coordination sphere of the Mo (or W) atom. Another possibility is a solvent-bridged double cubane, $[M_2Fe_6S_8(SR)_6(3,6-R'_2cat)_2(\mu\text{-solv})]^{4-}$, but this appears highly improbable in acetonitrile solution.

Spectral feature (ii) poses an apparent inconsistency with structure 13 (or the solvent-bridged structure). Iron atom sites are inequivalent in a 2:1 ratio (C_s cluster symmetry) yet only a single set of RS resonances is found at temperatures down to $\sim$240 K. This observation is rendered even more interesting by the sensitivity of isotropic shifts to changes in cluster composition. Shifts of cat-H signals are notably solvent dependent (Table V), and *p*-tolyl shifts are remarkably sensitive to the extent of substitution on a cluster (Figure 6). The matter was resolved by examination of the products of reaction 7. Treatment of an acetonitrile solution of $[MoFe_3S_4(S-p-C_6H_4Cl)_3((C_3H_5)_2cat)$-

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(40) Resonances of CH$_2$ groups directly attached to catecholate rings are also isotropically shifted but to a much smaller extent. These signals are often overlapped by cation or solvent features and are not useful for identification of solute species.

(41) In making this assignment due note is taken of the larger SCH$_2$CH_3 shifts of tungsten clusters in the pairs 6-Mo/6-W and 7-Mo/7-W. The reverse behavior is consistently found for the isotropic shifts of 1–4 and their tungsten analogues with R = Et.[6,7] Similarly, larger isotropic shifts of R = Ph and *p*-tolyl resonances are observed with molybdenum clusters in this (Table V) and other work.[6]

(42) The existence of the doubly bridged arrangement 12 was further investigated by X-ray examination of a cluster salt containing R = Ph. $(Et_4N)_4[Mo_2Fe_6S_8(SPh)_6((C_3H_5)_2cat)_2]\cdot2MeCN$ (8-Mo), obtained by slow cooling of a concentrated acetonitrile solution, crystallizes in triclinic space group $P\bar{1}$ with a = 12.893 (5) Å, b = 14.904 (3) Å, c = 16.718 (3) Å, α = 105.43 (1)°, β = 104.98 (2)°, γ = 100.35 (2)°, V = 2883 (1) Å^3, and Z = 1. Because of a linear decay in intensities of $\sim$40% during data collection and severe disorder in one allyl group, a full report of the structure of this compound will be deferred until a more suitable crystalline form is obtained. However, a decay correction was applied and the structure was solved and refined to R = 6.4% (R_w = 6.7%) from 2807 unique data ($F_o^2 > 2.0\sigma(F_o^2)$, $2\theta \leq 35°$) by using 427 variables. The anion is found in the doubly bridged double-cubane structure of 6-Mo. Subcluster and bridge metrical features are very similar to those of 6-Mo. The bridge Mo–S and Fe–S distances are 2.681 (4) and 2.306 (5) Å, respectively. The acetonitrile molecules are not coordinated.
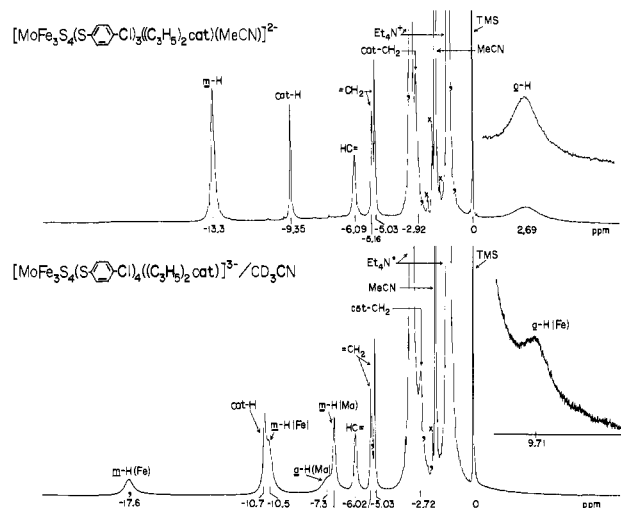
Double Cubanes Containing MFe₃S₄ Clusters

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Figure 9. ¹H NMR spectra (300 MHz, 297 K) of a ~5 mM CD₃CN solution of the Et₄N⁺ salt of 9-Mo (top) and of a ~5 mM CD₃CN solution of (Et₄N)₃[MoFe₃S₄(S-p-C₆H₄Cl)₄((C₃H₅)₂cat)] (bottom). Signal assignments are indicated (x = impurity).

(MeCN)]²⁻ (from the Et₄N⁺ salt of 9-Mo) with 1.0 equiv of (Et₄N)L led to the formation of the ligated clusters **14** and **15**. These have been isolated in >60% yield as analytically pure Et₄N⁺ salts and have been thoroughly characterized. The single cluster structure **14** of (Et₄N)₃[MoFe₃S₄(S-p-C₆H₄Cl)₄((C₃H₅)₂cat)] has been confirmed by X-ray diffraction. Full details of the synthesis, properties, and structures of single clusters are given elsewhere.[43] Several results pertinent to the present investigation of solvated clusters are noted.

Cluster dimensions of **14** are similar to those of **6**-Mo. For present purposes the most significant structural feature is a terminal thiolate ligand bonded to the Mo atom at a distance of 2.600 (3) Å. This result shows that in the two crystalline forms of **6**-Mo the Mo–SEt bonds are lengthened by 0.05–0.09 Å as a consequence of bridge formation. The ¹H NMR spectra of **14** and its immediate precursor in CD₃CN solutions are compared in Figure 9. The spectrum of the latter is typical of a solvated cluster. The spectrum of **14** contains several new features. The two resonances at −7.1 and −7.3 ppm are assigned to the molybdenum thiolate ligand from signal intensities and their absence in the spectrum of **15**. Two m-H resonances of iron thiolate ligands with a 2:1 intensity ratio are observed at −10.5 and −17.6 ppm,[44] consistent with structure **14**. The weighted average of these shifts (−12.9 ppm) is close to the shift of the acetonitrile solvate (−13.3 ppm). These findings provide a satisfactory explanation of the apparent equivalence of Fe sites in the solvated clusters **13**. From the structures of **6**-Mo and **14** the Mo–R′₂cat chelate ring and one MoFeS₂ face of **13** are expected to be roughly coplanar. Dissociation of a bound solvent molecule could allow spatial readjustment of the chelate ring such that, upon subsequent binding of solvent, the ring returns with equal probability to its original orientation or to one of two others displaced by ~90°. In this manner the chelate ring becomes "coplanar" with each of the three MoFeS₂ faces. Evidently these processes occur at rates sufficient to afford time-averaged trigonal symmetry at the Mo atom and consequent equilibration of the Fe sites.

(c) EPR Spectra. Demonstration of the existence of the solvated single clusters **13** in solution allows the unperturbed magnetic properties of [MoFe₃S₄]³⁺ clusters to be examined for the first time. Hereafter these species are referred to as **6–11**, with the solvate form specified. The solution magnetic moments in Table V are consistent with occupancy of a $S = {}^3/_2$ spin state, for which
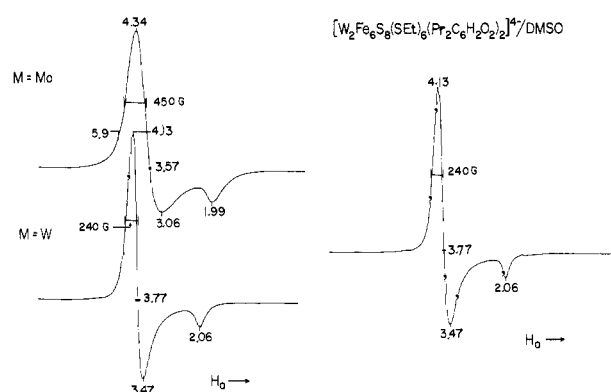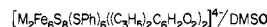

Figure 10. X-Band EPR spectra (~7 K) of ~10 mM Me₂SO solutions of **8**-Mo·Me₂SO and **8**-W·Me₂SO (left) and **6**-W·Me₂SO (right). Signal widths at half-height and selected g values are indicated. Spectra were recorded with 40-G modulation amplitude and 5-mW microwave power.

Table VI. EPR Parameters of Synthetic and Natural Mo–Fe–S Clusters

species	g_x	g_y	g_z	$|E/D|$	ref
A. vinelandii FeMo protein	3.65	4.32	2.01	0.055[b]	47, 48
C. pasteurianum FeMo protein	3.77	4.29	2.01	0.06	16, 48
FeMo-co	3.3	4.6	(2.0)[a]	0.11	14
8-Mo·Me₂SO	(3.7)[a]	4.34	1.99	0.06	c
[Fe(MoS₄)₂]³⁻(aq)	2.57	5.34	1.73	~0.2	50

[a] Not resolved. [b] $D \approx +6\ cm^{-1}$. [c] This work.

the spin-only moment is 3.87 μ_B. In the range 257–317 K the susceptibilities of **8**-Mo·MeCN and **8**-W·MeCN closely adhere to a linear T^{-1} dependence, with magnetic moments of 4.05 and 4.01 μ_B, respectively. Ground-state properties have been further investigated by EPR spectroscopy; because of fast electron-spin relaxation satisfactory spectra were obtained at $T \lesssim 15$ K.

X-Band EPR spectra of **6**-Mo, **7**-Mo, **8**-Mo, **6**-W, and **8**-W in the solid state are extremely complex, with numerous signals observed at ~0.5–7 kG. In Me₂SO solutions prepared at 0.5–15 mM the spectra of the R = Et clusters **6**-Mo and **7**-Mo remain complex and resemble the solid-state spectra. This behavior is attributed to reformation of the doubly bridged structure **12** when solutions containing **13** are frozen. Magnetic interactions between subclusters and perhaps intermolecular interactions produce the complicated spectra that are observed.[45] Under similar conditions the spectra of **1–5**, which contain isoelectronic [MoFe₃S₄]³⁺ (sub)clusters, are also rather complicated but are different from those found in this work. The spectra in these cases must also be those of $S = {}^3/_2$ (sub)clusters (e.g., **1**, Table V) that are magnetically perturbed.

Compared to the preceding results the spectra of Me₂SO solutions presented in Figure 10 are much simpler. These spectra correspond to $S = {}^3/_2$ spin systems that are apparently magnetically dilute and are associated with single cluster solvates. The spectra show that **6**-W·Me₂SO in contrast to **6**-Mo·Me₂SO does not revert to its double-cubane form in frozen solution and provide examples of the observation that all R = aryl species remain in the single-cluster solvate form in frozen solutions.[46] From expressions for principal g values of the $S = {}^3/_2$ case in rhombic symmetry[47] the assignments in Table VI are made. The large

(43) Armstrong, W. H.; Mascharak, P. K.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 1699. Mascharak, P. K.; Armstrong, W. H.; Mizobe, Y.; Holm, R. H. *J. Am. Chem. Soc.*, submitted for publication.

(44) In spectra at lower temperatures the meta H and cat-H resonances near −11 ppm in Figure 9 are resolved, permitting determination of the stated intensity ratio.

(45) For an example cf. Figure 2 of ref 2.

(46) The **8**-Mo–solvate form is found after freezing 0.5–15 mM Me₂SO solutions and is also found in frozen solutions of nitromethane and acetone, among other solvents tested. Compared to R = Et the R = aryl groups may provide a steric barrier to formation of the double-cubane structure when solutions are rapidly frozen at 77 K. The R = Ph group does not prevent the formation of the latter structure, as shown by its presence in the Et₄N⁺ salt of **8**-Mo.[42] In no case has evidence been obtained for the presence of solvate clusters in materials crystallized from (as opposed to being frozen in) solutions.

Table VII. Redox Potentials of Clusters in Me_2SO Solutions

cluster[a]	$E_{1/2},$[b] V	cluster[a]	$E_{1/2},$[b] V
6-Mo, 7-Mo	−1.33	8-W	−1.33
8-Mo	−1.13	1 (R = Et)[c]	−1.32,[d] −1.53[e]
9-Mo	−1.08	1 (R = Ph)[c]	−1.02,[d] −1.23[e]
10-Mo	−1.17	2 (R = Ph)[c]	−1.05,[d] −1.25[e]
6-W, 7-W	−1.53		

[a] ~2 mM, Me_2SO solvates. [b] $E_{1/2} = (E_{p,c} + E_{p,a})/2$, vs. SCE, $i_{p,c}/i_{p,a} \sim 1$, 0.1 M (n-Bu$_4$N)ClO$_4$ supporting electrolyte. [c] Reference 4. [d] $E_{1/2}$ (3−/4−). [e] $E_{1/2}$ (4−/5−).

line width (450 G) of the low-field signal obscures the g_x feature which is given the indicated estimated value since the $g_\perp = 4$ resonance of the axial case is nearly symmetrically split in the presence of small values of the rhombicity parameter $[E/D]$. These transitions occur in the $m_s = \pm^1/_2$ Kramers doublet of the $S = ^3/_2$ spin system. Spectra of 6-W·Me$_2$SO and 8-W·Me$_2$SO are similar in appearance but with smaller anisotropy, narrower lines (without resolution of g_x, g_y), and $g_z > 2$, indicating an anisotropic Zeeman interaction. Experiments aimed at determination of the sign of D are in progress.

The comparison of EPR parameters of FeMo proteins,[16,47,48] FeMo-co,[14] and 8-Mo·Me$_2$SO presented in Table VI suggests a definite similarity in the electronic structures of natural and synthetic Fe–Mo–S clusters. The $S = ^3/_2$ spin system of the proteins, initially recognized in the period 1972–1975,[47,49] is now well documented as is the same system in FeMo-co.[14] Spectra of 8-Mo·Me$_2$SO and FeMo-co contain broader lines than in native protein spectra but the g_x, g_y anisotropy is resolved in cofactor spectra. Close inspection of the spectra of 8-Mo·Me$_2$SO and other Mo (but not W) solvate clusters indicates a weak shoulder with $g \approx 5.9$. This may be the counterpart of the resolved $g \approx 5.9$ signal in FeMo-co spectra, which has been assigned to the g_z feature of very low transition probability in the upper $m_s = \pm^3/_2$ Kramers doublet of the $S = ^3/_2$ system.[14] Lastly, it is noted that another Mo–Fe–S cluster, [Fe(MoS$_4$)$_2$]$^{3-}$, exhibits a $S = ^3/_2$ EPR spectrum.[50] In this species the Fe and Mo atoms occupy tetrahedral coordination sites and are separated by 2.740 (1) Å.[51] The relation of this cluster to that in native proteins and FeMo-co appears less direct than for MoFe$_3$S$_4$ clusters. Spectral rhombicity is much larger (Table VI) and Mo EXAFS data[12] are less compatible with the native Mo atom coordination environment.

(d) **Redox Properties.** Solvate clusters in Me_2SO and acetonitrile solutions exhibit single one-electron reductions that are chemically reversible by the criterion $i_{p,c}/i_{p,a} \simeq 1$. Typical cyclic voltammograms are shown in Figure 11 and half-wave potentials are listed in Table VII. One or more irreversible reductions are encountered at potentials more negative than ca. −2.0 V. In their first reduction steps these clusters do not show the coupled subcluster redox processes that are resolved for 1–4 and their tungsten analogues.[3,4,7,52] This is a necessary but not sufficient property[53] for identification of the redox-active species as single clusters. Potentials follows the R substituent dependence previously observed for triply bridged double-cubane clusters.[4,52] Perhaps the most interesting feature of redox properties is the difference in
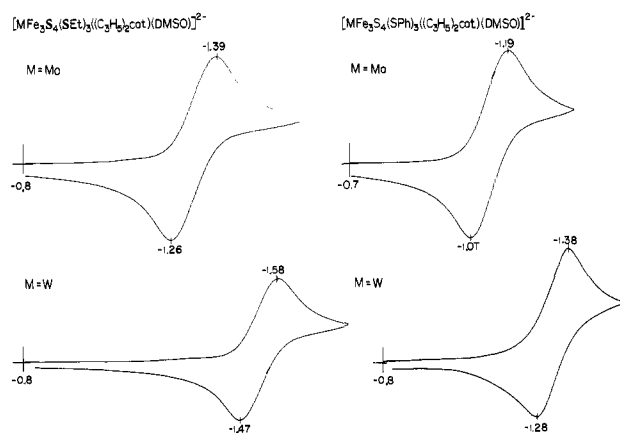

Figure 11. Cyclic voltammograms (100 mV/s) of ~2 mM solutions of the Me_2SO solvates of 7-Mo and 7-W (left) and 8-Mo and 8-W (right). Peak potentials vs. SCE are given.

potentials $E_{1/2}$(Mo) − $E_{1/2}$(W) = 0.20 V for three cluster pairs in Table VII. For the double cubanes 1–4 this difference is much smaller (ca. 0.10 V[7,52]) and for the 3−/4− step of [M$_2$Fe$_6$S$_8$-(SEt)$_9$]$^{3-}$ the sign of the difference (−0.04 V) is reversed.[52] The metal dependence of solvate cluster potentials lies on the edge of the corresponding potential differences of metal-centered (M-(V)−M(IV)) reductions of certain mononuclear complexes, which span 0.2−0.5 V.[54,55] This result suggests a larger contribution of molybdenum and tungsten orbitals in the molecular orbitals involved in the redox process than is the case for 1–4.

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

(i) Cleavage reactions of the Fe-bridged double cubanes [M$_2$Fe$_7$S$_8$(SEt)$_{12}$]$^{3-,4-}$ (3, 4) with certain 3,6-disubstituted catechols yield a new set of doubly bridged double cubanes, [M$_2$Fe$_6$S$_8$-(SEt)$_6$(R′$_2$cat)$_2$]$^{4-}$ (M = Mo, W; R′ = n-Pr, C$_3$H$_5$), isolable as Et$_4$N$^+$ salts. With ≥3 equiv of RSH/M atom these species undergo complete thiolate ligand substitution affording [M$_2$Fe$_6$S$_8$(SR)$_6$(R′$_2$cat)$_2$]$^{4-}$ clusters (R = Ph, p-tolyl, p-C$_6$H$_4$Cl), several of which have been isolated.

(ii) Crystal structures of Et$_4$N$^+$ salts of [Mo$_2$Fe$_6$S$_8$(SR)$_6$-(R′$_2$cat)$_2$]$^{4-}$ (monoclinic and triclinic forms of R = Et and R′ = n-Pr; R = Ph, R′ = C$_3$H$_5$[42]) reveal that the MoFe$_3$S$_4$(SR)$_2$ subclusters are joined by two Mo(μ-SR)Fe bridges. Compared to terminal bond lengths the Fe–SR and Mo–SR bridge distances are elongated by ~0.04−0.06 Å and ~0.05−0.09 Å, respectively.

(iii) In solutions of coordinating solvents (Me_2SO, acetonitrile, DMF) at ambient temperature the doubly bridged double cubanes cleave to the solvated single clusters [MFe$_3$S$_4$(SR)$_3$(R′$_2$cat)-(solv)]$^{2-}$, at least partly as a consequence of the lengthened bridge bonds noted in (ii). Demonstration of solvated clusters follows from ^{1}H NMR integrated signal intensities and the presence of single sets of isotropically shifted RS signals which can only arise from terminal Fe–SR groups. The solvent molecule is bound to the M atom, completing distorted octahedral coordination, and is in fast exchange with bulk solvent.

(iv) Solvated single clusters have magnetic moments of 4.0−4.2 μ_B in fluid solutions (250−320 K) consistent with a $S = ^3/_2$ ground state. EPR spectra in frozen solutions (≤15 K) correspond to a $S = ^3/_2$ spin system in rhombic symmetry; large line widths prevent resolution of the g_x, g_y components of the $m_s = \pm^1/_2$ Kramers doublet. EPR parameters are close to those of FeMo proteins and FeMo-co, suggesting an electronic similarity between the synthetic and native Mo–Fe–S clusters.

(v) Solvated single clusters exhibit a single one-electron reduction reaction at potentials less negative than −2.0 V vs. SCE.

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Potentials of tungsten-containing clusters are 0.20 V more negative than those of their molybdenum analogues. This property, together with the lability of coordinated solvent molecules, leads to the possibility that reduced clusters in the presence of a protic source may be able to bind and effect reductive transformations of nitrogenase substrates. This matter and other structural, electronic, and reactivity features of individual MFe_3S_4-type clusters are under investigation.
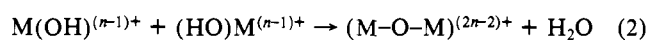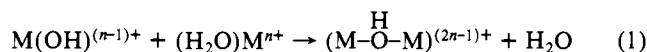
closure of results prior to publication.

The Hydrogen Oxide Bridging Ligand (H3O2−). 1. Dimerization and Polymerization of Hydrolyzed Trinuclear Metal Cluster Ions
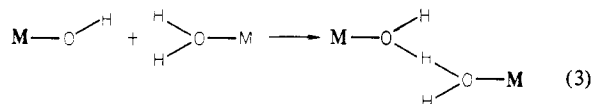
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Abstract: Trinuclear metal cluster ions of molybdenum and tungsten undergo hydrolysis in aqueous solutions. By the addition of various counterions such as Cl⁻, Br⁻, I⁻, and NCS⁻ to this solution several hydrolysis products with different degrees of polymerization have been crystallized. The preparation and X-ray structural characterization of six new compounds are reported; full structural details are presented for two compounds. The two compounds are isomorphous having the formula $\{[M_3O_2-(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}Br\cdot6H_2O$, in compound **1**, M = Mo, and in **2**, M = W. They crystallized in space group $P\bar{1}$ with the following cell dimensions: **1**, $a = 14.358$ (4) Å, $b = 12.114$ (3) Å, $c = 11.402$ (2) Å, $\alpha = 111.08$ (2)°, $\beta = 105.69$ (3)°, $\gamma = 66.74$ (2)°, $V = 1680$ (2) Å³, and $Z = 1$; **2**, $a = 14.316$ (3) Å, $b = 12.115$ (2) Å, $c = 11.423$ (2) Å, $\alpha = 111.14$ (2)°, $\beta = 105.59$ (2)°, $\gamma = 66.59$ (2)°, $V = 1677$ (2) Å³, and $Z = 1$. Dimerization and polymerization occur by formation of a hydrogen oxide ligand (H3O2−), bridging between two metal atoms of adjacent cluster ions. The H3O2− unit appearing in structures **1** and **2** is symmetric with an O–O separation of 2.52 (1) Å and 2.50 (1) Å, respectively.

$M(OH)^{(n-1)+}$, the primary product of hydrolysis of a metal aquo ion $M(OH_2)^{n+}$, often undergoes condensation reactions to form hydrolytic dimers and polymers.[1] It is generally assumed that the metal atoms in these dimers and polymers are bridged by μ-hydroxo or μ-oxo ligands.[2,3] These bridges are formed by elimination of a water molecule from a pair of ions (eq 1 and 2).

$$M(OH)^{(n-1)+} + (H_2O)M^{n+} \rightarrow (M\overset{H}{-}O-M)^{(2n-1)+} + H_2O \quad (1)$$

$$M(OH)^{(n-1)+} + (HO)M^{(n-1)+} \rightarrow (M-O-M)^{(2n-2)+} + H_2O \quad (2)$$

This work reveals the existence of a different kind of bridging by means of a new ligand, the μ-hydrogen oxide ligand, H3O2−. Bridging by this ligand may be accomplished by formation of a strong hydrogen bond between the hydroxo ligand of one metal ion and the water ligand of the other ion. Formation of this H3O2− bridge does not require the elimination of a water molecule (eq 3).

$$M-O\overset{H}{\diagup} + \overset{H}{\diagdown}O-M \longrightarrow M-O\diagup\overset{H}{\underset{\diagdown O-M}{}}\quad (3)$$

Recent work on trinuclear clusters of the early transition elements in aqueous solution showed the existence of triangular species with a new type of structure, namely, M_3X_{17} shown in Figure 1.[4–6] Molybdenum, tungsten, and niobium form a variety of M_3X_{17} triangular clusters all of which have the general formula $[M_3(\mu_3\text{-}X)_2(\mu\text{-}B)_6(H_2O)_3]^{n\pm}$ (X = O, CCH₃; B = O₂CR, SO₄). Clusters of group 6 metals are obtained by reaction of the hexacarbonyls with carboxylic acids.[4,5] The niobium cluster is obtained by the reduction of Nb(V) in sulfuric acid.[6]

Almost all of the reports on the M_3X_{17} clusters dealt with two major aspects: (a) the preparation and (b) the structural characterization of these species.

The present work is part of a project exploring the chemistry of the M_3X_{17} metal clusters in aqueous solution including the substitution and electron-transfer reactions.

In a preliminary communication we reported the discovery of the complex ion $\{[M_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ (M = Mo,

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