(σ-carb)(CO)(RCN)(PPh_3)] (**2a**, R = CH_3, and **2b**, R = C_6H_5) were prepared as previously reported.[10] The reactant alkenes and alkynes were commercial samples used without further purification. Infrared spectra were obtained with a Perkin-Elmer Model 457 and calibrated against polystyrene film. ^1H NMR spectra were recorded on a Bruker WP-60 FT NMR instrument at 60 MHz in $CDCl_3$ or C_6D_6 solutions. Melting points were determined by a conventional hot-stage microscope and are uncorrected. Molecular weights were obtained by a Mechrolab Model 301A osmometer.

[Ir(H)[σ-$CHCH_2C(O)OC(O)$](σ-carb)(CO)(CH_3CN)(PPh_3)] (3). An excess of maleic anhydride (144 mg, 1.5 mmol) was added to a solution of complex **2a** (380 mg, 0.51 mmol) in benzene (5 mL) at room temperature under argon atmosphere. After a few minutes, addition of hexane (10 mL) afforded a white solid. This crude product was separated and further purified by recrystallization from hexane/benzene (1:1) to give 340 mg (yield 80%) of pure **3**.

Ir(H)[σ-$CH_2CH_2C(O)OCH_3$](σ-carb)(CO)(PPh_3) (4). Methyl acrylate (0.2 mL, 0.2 mmol) was added to a dichloromethane solution of **2b** (162 mg, 0.2 mmol; in 2 mL of CH_2Cl_2) at room temperature under argon. After 1 h of stirring, removal of the solvent under vacuum and recrystallization of the residual solid from CH_2Cl_2/CH_3OH gave white crystals of pure **4** (142 mg, 90%): mol wt ($CHCl_3$) found 820, calcd 790.

Ir(H)[σ-$CH_2CH_2C(O)OC_2H_5$](σ-carb)(CO)(PPh_3) (5). Complex **5** was prepared as **4** by reacting the dihydride **2a** with ethyl acrylate in dichloromethane. The yield of white crystals of **5** was 85%.

Ir(H)[σ-$CH(CO_2CH_3)CH_2C(O)OCH_3$]($\sigma$-carb)(CO)($PPh_3$) (6). Methyl fumarate (200 mg, 1.39 mmol) was reacted with complex **2b** (405 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) solution under argon. The resulting mixture was stirred at room temperature for 5 min. Then, methanol (10 mL) was added, and the precipitate so formed was separated by filtration and further purified by recrystallyzation from CH_2Cl_2/CH_3OH (1:1). Pure white crystals of **6** were obtained in a yield of 80% (337 mg). Following the same procedure, complex **6** was obtained by reacting the complex **2a** or **2b** with methyl maleate in place of methyl fumarate.

Ir(H)[σ-$C(C_6H_5){=}CH(CO_2C_2H_5)$]($\sigma$-carb)(CO)($C_6H_5CN$)($PPh_3$) (7). A solution of 403 mg (0.5 mmol) of complex **2b** in 5 mL of benzene was treated with an excess of $C_6H_5C{\equiv}CCO_2C_2H_5$ (122 mg, 0.7 mmol) at room temperature. After 10 min of stirring, the solvent was removed under reduced pressure to give a white solid; this was then crystallized from hexane/benzene (1:1) to give 417 mg (85%) of white crystals of pure **7**.

Ir(H)[σ-$C(CO_2CH_3){=}CH(CO_2CH_3)$]($\sigma$-carb)(CO)($CH_3CN$)($PPh_3$) (8a). A solution of the dihydride **2a** (745 mg, 1 mmol) and dimethyl acetylendicarboxylate (0.5 mL, 5 mmol) in benzene (10 mL) was stirred for a few minutes at room temperature under argon. Then, upon addition of hexane (20 mL), a precipitate was formed which was further purified by recrystallization from hexane/benzene (1:1) to give 816 mg (92%) of white crystals of **8a**: mol wt ($CHCl_3$) found 880, calcd 886.9.

Ir(H)[σ-$C(CO_2CH_3){=}CH(CO_2CH_3)$]($\sigma$-carb)(CO)($C_6H_5CN$)($PPh_3$) (8b). As with the complex **8a**, this was prepared by treating 805 mg (1 mmol) of the dihydride **2b** with 5 mmol (0.5 mL) of $C(CO_2CH_3){\equiv}C(CO_2CH_3)$ in benzene (10 mL). Addition of hexane caused precipitation of **8b** that was then purified by recrystallization from hexane/benzene to give 900 mg (95%) of white crystals of pure product: mol wt ($CHCl_3$) found 920, calcd 949.

Ir(H)[σ-$C{=}CHC(O)OC(O)$](σ-carb)(CO)(C_6H_5CN)(PPh_3) (9). A slow stream of anhydrous hydrogen chloride was passed into a benzene solution of **8b** (300 mg in 8 mL) for 10 h at room temperature. The white solid so formed was purified by recrystallization from hexane/benzene to give white crystals of pure **9** in essentially quantitative yield: mol wt ($CHCl_3$) found 890, calcd 903.

Acknowledgment. We thank the Italian Research Council, CNR, for a grant in support of this research.

Registry No. **2a**, 70700-92-4; **2b**, 70700-93-5; **3**, 79255-31-5; **4**, 79255-30-4; **5**, 79255-29-1; **6**, 79255-28-0; **7**, 79255-27-9; **8a**, 79255-26-8; **8b**, 79255-25-7; **9**, 79272-63-2.

Contribution from the Departments of Chemistry,
Harvard University, Cambridge, Massachussetts 02138, and Stanford University, Stanford, California 94305

Ligand Substitution Properties of the MFe_3S_4 Double-Cubane Cluster Complexes $[Mo_2Fe_6S_8(SR)_9]^{3-}$ and $[M_2Fe_7S_8(SR)_{12}]^{3-}$ (M = Mo, W)

R. E. PALERMO,[1] P. P. POWER, and R. H. HOLM*[1]

Received May 6, 1981

Reactions of the double-cubane clusters $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ (**1**) and $[M_2Fe_7S_8(SEt)_{12}]^{3-}$ (**3**, M = Mo, W) with benzenethiol and acetyl chloride have been investigated in order to ascertain ligand substitution propensities of thiolate ligands. These complexes contain individual $MoFe_3S_4(SEt)_3$ clusters connected by $(\mu\text{-SEt})_3$ or $(\mu\text{-SEt})_3Fe^{III}(\mu\text{-SEt})_3$ bridging groups and thus offer as potential reaction sites both terminal and bridging thiolate sulfur atoms. Reactions of **1** with 1–6 and larger equiv of reagent were monitored by UV–visible spectrophotometry, ^1H NMR spectroscopy, and differential-pulse polarography. The limiting substituted species formed were $[Mo_2Fe_6S_8(\mu\text{-SEt})_3(SPh)_6]^{3-}$ (**5**) and $[Mo_2Fe_6S_8(\mu\text{-SEt})_3Cl_6]^{3-}$ (**4**), salts of which were isolated in good yield when reactions with $\gtrsim$6 equiv of reagent were conducted on a preparative scale. Preparative reactions of **3** and $\gtrsim$6 equiv of reagent afforded isolated salts of $[Mo_2Fe_7S_8(\mu_2\text{-SEt})_6(SPh)_6]^{3-}$ (**8**) and $[M_2Fe_7S_8(\mu\text{-SEt})_6Cl_6]^{3-}$ (**7**). Similarly, $[W_2Fe_6S_9(SEt)_8]^{3-}$ (**2**) yielded $[W_2Fe_6S_8(\mu\text{-S})(\mu\text{-SEt})_2(S\text{-}p\text{-tol})_6]^{3-}$ (**6**) with *p*-toluenethiol. Structures of all products are fully documented by spectroscopic and electrochemical properties. These results lead to the conclusion that the two electrophilic reagents effect only terminal ligand substitution under reaction conditions (Me_2SO or acetonitrile solutions, ambient temperature, stoichiometric or (specified) excess of reagent) that leave intact individual cluster structures. A reported exception to this consistent reactivity pattern, viz., formation of $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ from the reaction of **1** with excess 2-hydroxyethanethiol, was not confirmed. By comparison of properties of authentic $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$, prepared by direct synthesis, the ligand exchange product isolated in this work was shown to be $[Mo_2Fe_6S_8(\mu\text{-SEt})_3(SCH_2CH_2OH)_6]^{3-}$. The bridge structure of the precursor cluster is retained, as in the formation of **4**–**8** by similar reactions.

Introduction

Three structural types of double-cubane cluster complexes containing MFe_3S_4 core units, $[Mo_2Fe_6S_8(SR)_9]^{3-}$[2] (**1**), $[M_2Fe_6S_9(SR)_8]^{3-}$[2,3] (**2**), and $[M_2Fe_7S_8(SR)_{12}]^{3-}$[3] (**3**) (M = Mo, W), shown in Figure 1, have been prepared and characterized in these laboratories. Structures of the Mo clusters **1**–**3** have been established by X-ray crystallography.[2,4] In

---

(1) Harvard University.

(2) Wolff, T. E.; Berg, J. M.; Hodgson, K. O.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 4140.

(3) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4694.

0020-1669/82/1321-0173$01.25/0 © 1982 American Chemical Society

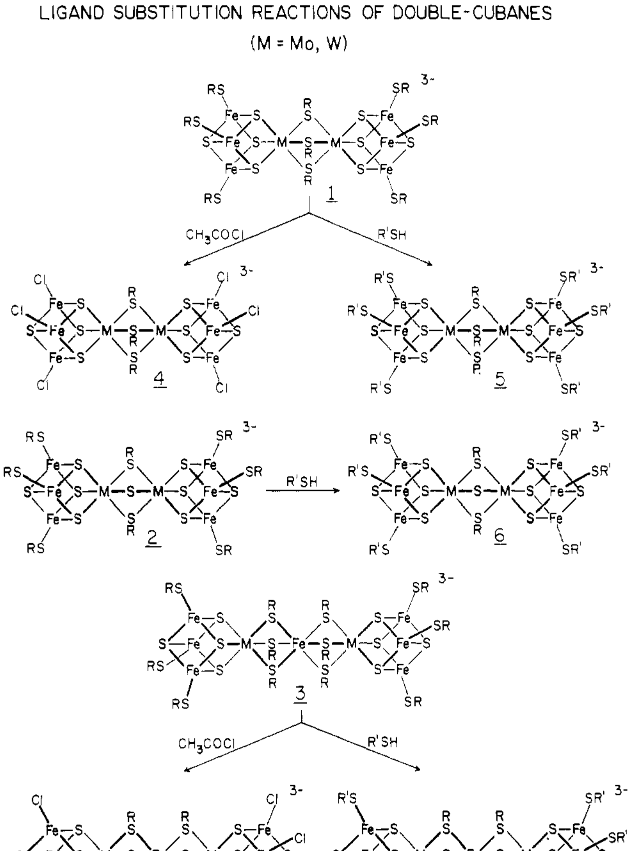
LIGAND SUBSTITUTION REACTIONS OF DOUBLE-CUBANES (M = Mo, W)

Figure 1. Schematic structures of $[M_2Fe_6S_8(SR)_9]^{3-}$ (**1**), $[M_2Fe_6S_9(SR)_8]^{3-}$ (**2**), and $[M_2Fe_7S_8(SR)_{12}]^{3-}$ (**3**) and their ligand substitution products from reactions with acetyl chloride (**4**, **7**) and thiols (**5**, **6**, **8**).

addition, Christou, Garner, and their co-workers have prepared a number of Mo and W double-cubanes of type **1** and have characterized them spectroscopically[5,6] and structurally.[7-10] Because the complexes **1**–**3** are the only examples of heterometallic cubane-type clusters $M^*_nM_{4-n}S_4$, their continued investigation is merited on this basis alone. A further significant aspect of these clusters is the distinct similarity of their Mo EXAFS[2] with those of FeMo proteins of several nitrogenases.[11] This relationship implies an extent of correspondence, as yet unknown in full detail, between the synthetic and native Mo coordination environments and suggests that clusters **1**–**3** or derivatives thereof might be elaborated to species capable of reducing nitrogenase substrates.

Essentially complete oxidation of the strongly reducing cluster $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ by excess benzenethiol with concomitant H_2 evolution has recently been reported.[12] Whereas reaction schemes involving ligand protonation followed by internal electron transfer affording a transient metal hydride can be entertained in this case, any reductive transformations of other nitrogenase substrates such as acetylene and N_2 almost certainly will require initial binding to a cluster metal site. If MFe_3S_4-type clusters are to have such reaction potentiality, information as to thiolate ligand substitution properties of their initially synthesized forms **1**–**3** must be acquired. This situation bears an obvious resemblance to that encountered earlier with the clusters $[Fe_4S_4(SR)_4]^{2-}$. Here it has been shown that thiolate ligands are subject to the stepwise reactions (eq 1)

$$[Fe_4S_4(SR)_4]^{2-} + nEL \rightleftharpoons [Fe_4S_4(SR)_{4-n}L_n]^{2-} + nRSE \quad (1)$$

with the generalized electrophile EL affording substituted clusters.[13] Reactions with thiols[14] and acyl halides[13,15] are the best developed and can lead to complete substitution. An acetylene reduction system based on reduced, substituted Fe_4S_4 clusters has been devised.[16] In a necessary prelude to examining the reactions of reduced MFe_3S_4-type clusters with substrates (other than protonic acids), certain ligand substitution reactions of **1** (M = Mo), **3** (M = Mo, W), and **2** (M = W) have been investigated. Details of this work are reported here; several leading results were adumbrated earlier.[3] While this research was in progress, Christou, Garner, et al. have briefly described the reactions of **1** (M = Mo) with 2-hydroxyethanethiol[8] and benzoyl halides[17] and certain properties of the product complexes.[6,8,17]

Experimental Section

Preparation of Compounds. Quaternary ammonium salts of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$, $[W_2Fe_6S_9(SEt)_8]^{3-}$, $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$, and $[W_2Fe_7S_8(SEt)_{12}]^{3-}$ were prepared as described elsewhere.[2,3] In the syntheses which follow, all steps were conducted under a pure argon or dinitrogen atmosphere. For use in syntheses and physical measurements, solvents and reagents were purified by distillation: acetonitrile, from calcium hydride; methanol and ethanol, from the respective magnesium alkoxide; THF and diethyl ether, from Na/K alloy; acetyl chloride, from PCl_5 and then quinoline. Other materials were used as received.

$HSCD_2CH_2OH$. This compound was prepared from ethyl bromoacetate-d_2[18] by reaction sequence 2 whose steps were carried out

$$BrCD_2CO_2Et \xrightarrow{i} PhCH_2SCD_2CO_2Et \xrightarrow{ii} PhCH_2SCD_2CH_2OH \xrightarrow{iii} HSCD_2CH_2OH \quad (2)$$

conventionally. Reagents and yields are indicated as follows: (i) sodium hydride and phenylmethanethiol in DMF, 86% (pure); (ii) lithium aluminum hydride in ether, 95% (crude); (iii) sodium in liquid ammonia, ether extraction, distillation, 25%.

$(Et_4N)(SPh)$. This compound was prepared by reaction of equimolar amounts of benzenethiol and sodium methoxide in methanol followed by addition of an equimolar quantity of dry Et_4NBr. After solvent removal in vacuo, extraction of the residue with acetonitrile, and addition of ether to the extract filtrate, the product was collected and recrystallized from acetone. The compound was utilized as a soluble source of benzenethiolate ion in polar organic solvents.

$(Et_4N)_3[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]$ (1; R = CH_2CH_2OH). A solution of 0.161 mol of $NaSCH_2CH_2OH$ in 100 mL of methanol (from 3.72 g of sodium and 13.3 g of 2-mercaptoethanol) was added to a filtered solution of 6.54 g (40.3 mmol) of $FeCl_3$ in 40 mL of methanol. To this mixture was added 3.50 g (13.4 mmol) of $(NH_4)_2MoS_4$.[19]

---

(4) Wolff, T. E.; Berg, J. M.; Power, P. P.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1980**, *19*, 430.

(5) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2354.

(6) Christou, G.; Garner, C. D.; Miller, R. M.; Johnson, C. E.; Rush, J. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2363.

(7) Christou, G.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1978**, 740.

(8) Christou, G.; Garner, C. D.; Mabbs, F. E.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 91.

(9) Acott, S. R.; Christou, G.; Garner, C. D.; King, T. J.; Mabbs, F. E.; Miller, R. M. *Inorg. Chim. Acta* **1979**, *35*, L337.

(10) Christou, G.; Garner, C. D.; Miller, R. M.; King, T. J. *J. Inorg. Biochem.* **1979**, *11*, 349.

(11) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398.

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

(13) Johnson, R. W.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5338.

(14) Que, L., Jr.; Bobrik, M. A.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4168.

(15) Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578.

(16) McMillan, R. S.; Renaud, J.; Reynolds, J. G.; Holm, R. H. *J. Inorg. Biochem.* **1979**, *11*, 213.

(17) Christou, G.; Garner, C. D. *J. Chem. Soc., Chem. Commun.* **1980**, 613.

(18) Blomquist, A. T.; Hiscock, B. F.; Harp, D. N. *J. Org. Chem.* **1966**, *31*, 4121.

After 20 h of stirring, the reaction mixture was filtered into a stirred solution of 7.34 g (34.9 mmol) of Et_4NBr in 50 mL of 2:3 v/v methanol/acetone. The suspension of crystalline material was stirred briefly and cooled to −15 °C for 10 h, and the solid product was collected by filtration. After being washed with 2:1 v/v THF/acetonitrile, the solid was extracted with 2 × 150 mL of warm (50 °C) methanol. The combined filtered extracts were reduced in volume by 75 mL in vacuo. The solution was warmed to 40 °C, ~80 mL of acetone was added, and the mixture was cooled to −15 °C for 20 h. The crystalline solid was collected by filtration, washed with cold 2:1 v/v acetone/methanol, and dried in vacuo; 9.54 g (76%) of pure product as black-green crystals was obtained. An analytical sample was obtained by recrystallization from acetonitrile/acetone. Anal. Calcd for acetone monosolvate, $C_{45}H_{111}Fe_6Mo_2N_3O_{10}S_{17}$, M_r = 1926.5 (acetonitrile monosolvate, $C_{44}H_{108}Fe_6Mo_2N_4O_9S_{17}$, M_r = 1909.5): C, 28.06 (27.68); H, 5.81 (5.70); Fe, 17.39 (17.55); Mo, 9.96 (10.05); N, 2.18 (2.93); O, 8.31 (7.54); S, 28.30 (28.55). Found: C, 28.15; H, 6.04; Fe, 17.68; Mo, 10.00; N, 2.71, O, 7.09; S, 28.45 (sum 100.12).

$(Et_4N)_3[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SPh)_6]$ (5; R = Et, R′ = Ph). A solution of 2.07 g (1.20 mmol) of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ in 50 mL of acetonitrile was treated with 0.830 g (7.96 mmol) of benzenethiol in a small volume of acetonitrile. The mixture was stirred for 40 min under reduced pressure at ambient temperature, after which the volume was reduced by half in vacuo. The homogeneous solution was warmed to ~55 °C, and 30 mL of a 2:1 v/v THF/ether mixture was added. Continued stirring converted the oily portion of the product to a solid. After storage at −15 °C for 24 h, the product was collected by filtration, washed with 2:1 v/v THF/ether until the washings were clear, and dried in vacuo. The filtrate from a solution of this material in 60 mL of acetonitrile was reduced in volume to 20 mL while maintained at 55 °C. The stirred solution deposited crystals upon cooling to ambient temperature. After dilution to 50 mL with 2:1:1 v/v acetonitrile/THF/ether, the mixture was kept at −15 °C overnight. The product was collected by filtration, washed with the ternary solvent mixture, and dried in vacuo; 1.14 g (47%) of pure red-black crystalline product was obtained. Anal. Calcd for $C_{66}H_{105}Fe_6Mo_2N_3S_{17}$: C, 39.39; H, 5.26; Fe, 16.65; Mo 9.53; N, 2.09; S, 27.08. Found: C, 39.50; H, 5.21; Fe, 16.61; Mo, 9.40; N, 2.10; S, 27.09. Absorption spectrum (acetonitrile): λ_{max} 254 (sh, ϵ_M 77 200), 346 (sh, 43 100), 418 (sh, 35 500) nm.

$(Et_4N)_3[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SCH_2CH_2OH)_6]$ (5; R = Et, R′ = CH_2CH_2OH). A solution of 2.02 g (1.17 mmol) of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ in 100 mL of acetonitrile was treated with 5.00 mL (71.3 mmol, 61 equiv) of 2-hydroxyethanethiol. The stirred mixture was heated to ca. 50 °C and maintained at that temperature for 2.5 h during which time the vessel was periodically evacuated. About 25 mL of solvent was removed in vacuo, and 60 mL of warm acetone was added. After being cooled to room temperature, the mixture was maintained at −20 °C for several days. After collection by filtration, the product was washed with acetone and dried in a stream of dinitrogen, affording 1.58 g (70%). This material was recrystallized from 1:1 v/v acetonitrile/acetone and recovered in 69% yield as black needles. Anal. Calcd for acetone monosolvate, $C_{45}H_{111}Fe_6Mo_2N_3O_7S_{17}$, M_r = 1878.5 (acetonitrile monosolvate, $C_{44}H_{108}Fe_6Mo_2N_4O_6S_{17}$, M_r = 1861.5): C, 28.77 (28.39); H, 5.96 (5.85); Fe, 17.84 (18.00); Mo, 10.21 (10.31); N, 2.24 (3.01); O, 5.96 (5.16); S, 29.02 (29.28). Found: C, 28.76; H, 6.17; Fe, 17.73; Mo, 9.96; N, 2.32; O, 5.10; S, 29.94 (sum 99.98).

$(Et_4N)_3[Mo_2Fe_6S_8(\mu\text{-}SEt)_3Cl_6]$ (4; R = Et). A solution of 2.01 g (1.17 mmol) of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ in 70 mL of acetonitrile was treated with 0.59 g (7.5 mmol) of acetyl chloride. An immediate color change from dark green to brown ensued. After stirring for 40 min, ~30 mL of solvent was removed in vacuo. The mixture was warmed to 50 °C and stirred until it became homogeneous. The solution was cooled to ambient temperature, and 30 mL of 1:1 v/v THF/ether was added, causing separation of a solid. The solution was warmed to 50 °C, stirred until nearly homogeneous, and kept at −15 °C overnight. The solid was collected by filtration, washed with 1:1 v/v THF/ether, and dried in vacuo. Recrystallization of this material (1.37 g, 75%) from acetonitrile afforded 0.86 g (47%) of pure product as dark brown needles. Anal. Calcd for $C_{30}H_{75}Cl_6Fe_6Mo_2N_3S_{11}$: C, 22.95; H, 4.81; Cl, 13.55; Fe, 21.34; Mo, 12.22; N, 2.68; S, 22.46. Found: C, 24.10; H, 4.80; Cl, 13.60; Fe, 21.11; Mo, 11.90; N, 2.46; S, 22.24. Absorption spectrum (acetonitrile): λ_{max} 246 (ϵ_M 61 800), 545 (sh, 4030) nm.

$(Et_4N)_3[Mo_2Fe_7S_8(\mu\text{-}SEt)_6(SPh)_6]$ (8; R = Et, R′ = Ph). A solution of 0.43 g (3.9 mmol) of benzenethiol in 10 mL of acetonitrile was added to a stirred solution of 1.2 g (0.61 mmol) of $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$ in 25 mL of acetonitrile. The procedure followed was the same as that for the preparation of $(Et_4N)_3[W_2Fe_6S_9(\mu\text{-}SEt)_2(SC_6H_4\text{-}p\text{-}CH_3)_6]$ (see below). Recrystallization of the collected solid from a minimum volume of warm acetonitrile/THF afforded 0.90 g (65%) of pure product as red-black crystals. Anal. Calcd for $C_{72}H_{120}Fe_7Mo_2N_3S_{20}$: C, 38.40; H, 5.37; Fe, 17.36; Mo, 8.52; N, 1.87; S, 28.48. Found: C, 38.30; H, 5.31; Fe, 17.30; Mo, 8.70; N, 2.02; S, 28.50.

$(Me_3NCH_2Ph)_3[Mo_2Fe_7S_8(\mu\text{-}SEt)_6(SPh)_6]$ (8; R = Et, R′ = Ph). A suspension of 1.01 g (0.50 mmol) of $(Me_3NCH_2Ph)_3[Mo_2Fe_7S_8(SEt)_{12}]$ in 45 mL of acetonitrile was treated with a solution of 0.40 g (3.6 mmol) of benzenethiol in 5 mL of acetonitrile. The stirred reaction mixture was warmed to 50 °C for 2 h and periodically evacuated to remove liberated ethanethiol. Considerable crystalline material separated by the end of this time; slow cooling to 5 °C resulted in the deposition of more crystals. This solid was collected by filtration, washed with THF, and dried in vacuo; 0.58 g (50%) of pure product as brown-black crystals was obtained. The compound was identified by coincidence of spectroscopic and electrochemical properties with those of the Et_4N^+ salt. Absorption spectrum (acetonitrile): λ_{max} 257 (ϵ_M 104 000), 346 (sh, 65 200), 410 (sh, 55 400) nm.

$(Me_3NCH_2Ph)_3[Mo_2Fe_7S_8(\mu\text{-}SEt)_6Cl_6]$ (7; R = Et). $(Me_3NCH_2Ph)_3[Mo_2Fe_7S_8(SEt)_{12}]$ (1.09 g, 0.54 mmol) was dissolved in 100 mL of acetonitrile by stirring for 90 min at 50 °C. A solution of 0.28 g (3.5 mmol) of acetyl chloride in 25 mL of acetonitrile was added; the intense green color of the solution rapidly lightened. The reaction mixture was stirred for 90 min, and the volume was reduced to ~30 mL. Addition of 10 mL of THF caused separation of a crystalline solid. After storage of the reaction mixture overnight at −15 °C, the solid was collected, washed with cold 2:1 v/v THF/acetonitrile, and dried in vacuo. Pure product (0.62 g, 62%) was obtained as black crystals. Anal. Calcd for $C_{42}H_{78}Cl_6Fe_7Mo_2N_3S_{14}$: C, 26.98; H, 4.21; Cl, 11.38; Fe, 20.91; Mo, 10.26; N, 2.25; S, 24.01. Found: C, 26.91; H, 3.78; Cl, 10.98; Fe, 22.70; Mo, 9.90; N, 2.90; S, 23.04. Absorption spectrum (acetonitrile): λ_{max} 247 (ϵ_M 74 900) nm.

$(Et_4N)_3[W_2Fe_7S_8(\mu\text{-}SEt)_6Cl_6]$ (7; R = Et). A solution of 0.22 g (2.8 mmol) of acetyl chloride in 20 mL of acetonitrile was added to a stirred solution of 1.0 g (0.47 mmol) of $(Et_4N)_3[W_2Fe_7S_8(SEt)_{12}]$ in 30 mL of acetonirile. The dark red-brown color of the initial solution immediately lightened. Stirring for 1 h afforded a rather pale solution and a small amount of crystalline material. Maintenance of this solution at −20 °C for 6 h yielded more solid, which was collected by filtration. Pure product was obtained as dark brown crystals in ~80% yield. Anal. Calcd for $C_{36}H_{90}Cl_6Fe_7N_3S_{14}W_2$: C, 21.78; H, 4.57; Cl, 10.71; Fe, 19.69; N, 2.12; S, 22.61; W, 18.52. Found: C, 22.01; H, 4.60; Cl, 10.85; Fe, 19.80; N, 2.12; S, 22.10; W, 18.61.

$(Me_3NCH_2Ph)_3[W_2Fe_7S_8(\mu\text{-}SEt)_6Cl_6]$ (7; R = Et). This compound was obtained starting with $(Me_3NCH_2Ph)_3[W_2Fe_7S_8(SEt)_{12}]$ by the same procedure as in the preceding preparation. Anal. Calcd for $C_{42}H_{78}Cl_6Fe_7N_3S_{14}W_2$: C, 24.66; H, 3.84; Cl, 10.40; Fe, 19.11; N, 2.05; S, 21.95; W, 17.98. Found: C, 24.60; H, 3.75; Cl, 10.20; Fe, 19.01; N, 2.26; S, 21.80; W, 18.31.

$(Et_4N)_3[W_2Fe_6S_9(\mu\text{-}SEt)_2(SC_6H_4\text{-}p\text{-}CH_3)_6]$ (6; R = Et, R′ = $p\text{-}C_6H_4CH_3$). A solution of 0.38 g (3.1 mmol) of *p*-toluenethiol in 10 mL of acetonitrile was added to a stirred solution of 0.96 g (0.51 mmol) of $(Et_4N)_3[W_2Fe_6S_9(SEt)_8]$ in 20 mL of acetonitrile. The reaction mixture was heated to 50 °C for 2 h during which time it changed to a more pronounced red-brown color. Over this period, the reaction vessel was periodically evacuated to remove liberated ethanethiol and to afford a final solution volume of ca. 20 mL. The solution was then cooled to −20 °C for 12 h. The crystalline red-brown solid was collected by filtration and washed with ether; 0.91 g (79%) of pure product was obtained. Anal. Calcd for $C_{70}H_{112}Fe_6N_3S_{17}W_2$: C, 37.48; H, 5.03; Fe, 14.94; N, 1.87; S, 24.30; W, 16.39. Found: C, 37.60; H, 5.11; Fe, 14.90; N, 1.75; S, 24.55; W, 16.30.

Physical Measurements. All measurements were performed under strictly anaerobic conditions. Electrochemical determinations were carried out with standard Princeton Applied Research instrumentation with use of a glassy-carbon working electrode. Potentials were obtained at ~25 °C vs. a saturated calomel reference electrode; solutions

---

(19) Krüss, G. *Justus Liebigs Ann. Chem.* **1884**, *255*, 6.

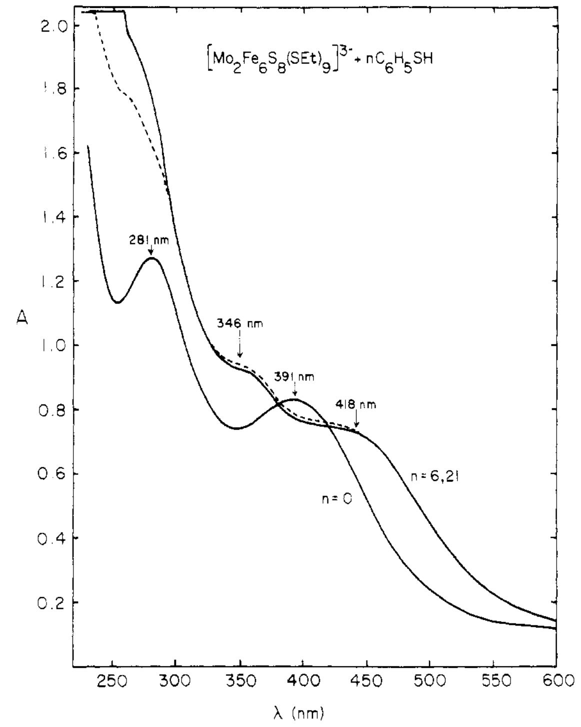

Figure 2. Absorption spectra in acetonitrile solution of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ ($n = 0$) and its reaction product with $n = 6$ (- - -) and 21 equiv (—) of benzenethiol. Reactions were conducted under reduced pressure.

contained 0.1 M $(n\text{-}Bu_4N)(ClO_4)$ as supporting electrolyte. Absorption spectra were determined on Cary Models 17 and 219 spectrophotometers. ^1H NMR spectra were obtained with a Varian XL-100-15 spectrometer and Bruker HXS-360 and WM-300 spectrometers. In accordance with the usual convention for paramagnetic molecules, shifts downfield and upfield of Me_4Si internal reference are designated as negative and positive, respectively. The solvents acetonitrile-d_3 and Me_2SO-d_6 were dried over 3-Å molecular sieves and calcium hydride, respectively, prior to use. Crystal data for $(Et_4N)_3[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]$ and $(Et_4N)_3[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SCH_2CH_2OH)_6]$, obtained with single crystals from preparative samples giving the analytical results quoted above, were determined by use of a Nicolet R3m four-circle diffractometer (Mo Kα radiation). Both crystals displayed hexagonal lattices and axial rotation photographs indicated Laue symmetry $6/m$. In each case systematic absences $00l$ ($l \neq 2n$) limited the choice of space groups of $P6_3$ or $P6_3/m$. Data were collected for determination of unit cell parameters but were not refined for unambiguous space group assignment.

Results and Discussion

So that ligand substitution propensities of the double-cubane clusters $[Mo_2Fe_6S_8(SEt)_9]^{3-}$[2] (1) and $[M_2Fe_7S_8(SEt)_{12}]^{3-}$[3,4] (3; M = Mo, W) with electrophiles could be established, their reactions with acetyl chloride and benzenethiol have been examined in acetonitrile or Me_2SO solutions at ambient temperature. These two reagents were among those employed in the original demonstrations of the occurrence of reaction 1[13-15,20] which, as will be seen, bears a close parallel to those described here. Compared to $[Fe_4S_4(SR)_4]^{2-}$ species, clusters **1** and **3** offer *two* potential nucleophilic thiolate sites in the form of bridging and terminal sulfur atoms. In **3** the bridging fragment $(\mu_2\text{-}SEt)_3Fe(\mu\text{-}SEt)_3$ has been shown to contain Fe(III).[3,4] In most instances, reaction products have been subjected to total elemental analysis, in several cases as two different salts. These results indicate retention of the double-cubane structure and therewith the extent, but not the position(s), of ligand substitution under specified reaction conditions. Because structures of products were not established by X-ray crystallography, a substantial body of spectroscopic and electrochemical data is presented which suffices to demonstrate product structures resulting from reactions with ≥6 equiv of electrophile.

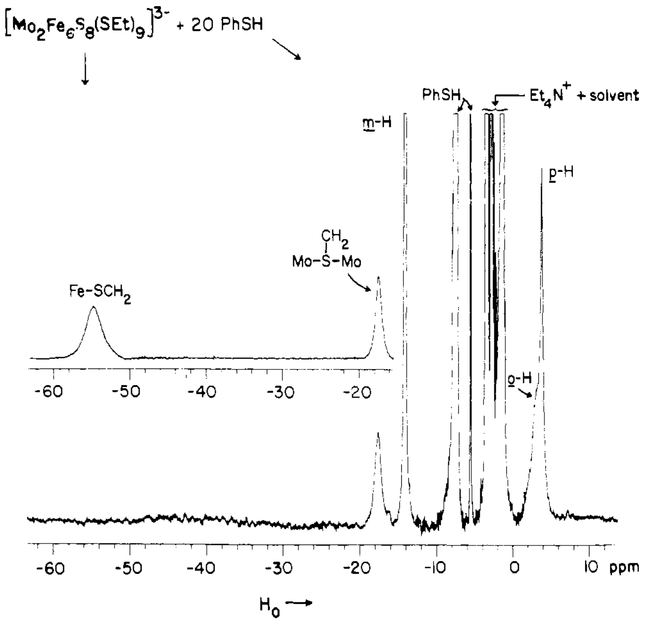

Figure 3. ^1H NMR spectra (360 MHz) of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ (downfield region—insert) and its reaction product with 20 equiv of benzenethiol in Me_2SO-d_6 solution at ~22 °C. Signal assignments are indicated.

Reactions of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$. (a) With Benzenethiol. As shown in Figure 2, reaction of **1** with 6 equiv of thiol results in elimination of the original bands at 281 and 391 nm and formation of a new chromophore with prominent shoulders at ~346 and ~418 nm. The lack of significant spectral differences with 21 equiv of thiol indicates that reaction in the 6 equiv system is complete. ^1H NMR examination of the reaction system after addition of 20 equiv of thiol reveals the spectral changes in Figure 3. The terminal SCH_2 signal at −54.1 ppm is abolished[21] whereas the bridging SCH_2 feature, originally at −17.1 ppm, is retained with full intensity and is barely shifted (−17.0 ppm). Also generated by thiol reaction are sharp resonances at −13.8 and +3.7 ppm and a discernible broad shoulder on the downfield side of the latter. These signals arise from contact interactions[22] and, based on the well-defined spectrum of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$,[3,5] are assigned as shown in Figure 3. No resonances attributable to the μ-SPh groups as in the latter cluster were detectable. When reaction systems with <6 equiv of thiol were monitored by NMR, incompletely substituted species were observed. However, the spectra do not permit distinction between preferential substitution on an individual cluster (I, II) or random substitution on both.

The foregoing results support identification of the product of reaction 3 with $n \geq 6$ equiv as the terminally substituted

$$[Mo_2Fe_6S_8(SEt)_9]^{3-} + nPhSH \rightleftharpoons [Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SEt)_{6-n}(SPh)_n]^{3-} + nEtSH \quad (3)$$

cluster **5** (Figure 1; R = Et, R′ = Ph). Product formulation was confirmed by synthesis of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_3(SPh)_6]$ using $n = 8$ equiv of thiol in reaction 3, which was conducted under reduced pressure in order to displace the equilibrium toward product by removal of ethanethiol. The properties of

---

(20) Bobrik, M. A.; Que, L., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 285.

(21) This behavior cannot always be observed for the $FeSCH_2CH_3$ signal (~−5 ppm) because in certain salts it is obscured by cation resonances.

(22) All clusters examined in this investigation are paramagnetic.

Table I. Potentials of Double-Cubane Clusters in Acetonitrile Solution

double-cubane	E(Fe(III,II))	clusters $E(\mathrm{I_{Ox,Red}})$	clusters $E(\mathrm{II_{Ox,Red}})$
$[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SEt)_6]^{3-\,a}$		−1.27	−1.46
$[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SPh)_6]^{3-\,a}$		−1.01	−1.19
$[Mo_2Fe_6S_8(\mu\text{-}SEt)_3Cl_6]^{3-\,a}$		−0.83	−1.01
$[Mo_2Fe_7S_8(\mu\text{-}SEt)_6(SEt)_6]^{3-}$	−0.89[a]	−1.57[b]	−1.62[b]
$[Mo_2Fe_7S_8(\mu\text{-}SEt)_6(SPh)_6]^{3-}$	−0.72[a]	−1.29[b]	−1.38[b]
$[Mo_2Fe_7S_8(\mu\text{-}SEt)_6Cl_6]^{3-}$	−0.62[a]	−1.14[b]	−1.24[b]
$[MoFe_3S_4Cl_3(\mu\text{-}SEt)_3MoFe_3S_4Cl_3]^{3-}$ (a)[c]		−0.85	−1.04
$[MoFe_3S_4Cl_3(\mu\text{-}SEt)_3MoFe_3S_4(SEt)Cl_2]^{3-}$ (b)		*d*	−1.16
$[MoFe_3S_4Cl_3(\mu\text{-}SEt)_3MoFe_3S_4(SEt)_2Cl]^{3-}$ (c)		*d*	~−1.28
$[MoFe_3S_4Cl_3(\mu\text{-}SEt)_3MoFe_3S_4(SEt)_3]^{3-}$ (d)		−0.91	*d*
$[MoFe_3S_4(SEt)Cl_2(\mu\text{-}SEt)_3MoFe_3S_4(SEt)_3]^{3-}$ (e)		−1.06	*d*
$[MoFe_3S_4(SEt)_2Cl(\mu\text{-}SEt)_3MoFe_3S_4(SEt)_3]^{3-}$ (f)		−1.20	~−1.47
$[MoFe_3S_4(SEt)_3(\mu\text{-}SEt)_3MoFe_3S_4(SEt)_3]^{3-}$ (g)		−1.30	−1.49

[a] $E = (E_{p,c} + E_{p,a})/2$ (50 mV/s). [b] $E_{p,c}$ (50 mV/s). [c] For species a–g, E_p values from DPP are given. [d] Not located. Note that certain coincidences in potentials are not improbable. For example, reductions of doubly chloro-substituted I in species 4,2 and 3,3 are not likely to differ appreciably inasmuch as substitution in II has little effect on the potentials of I.

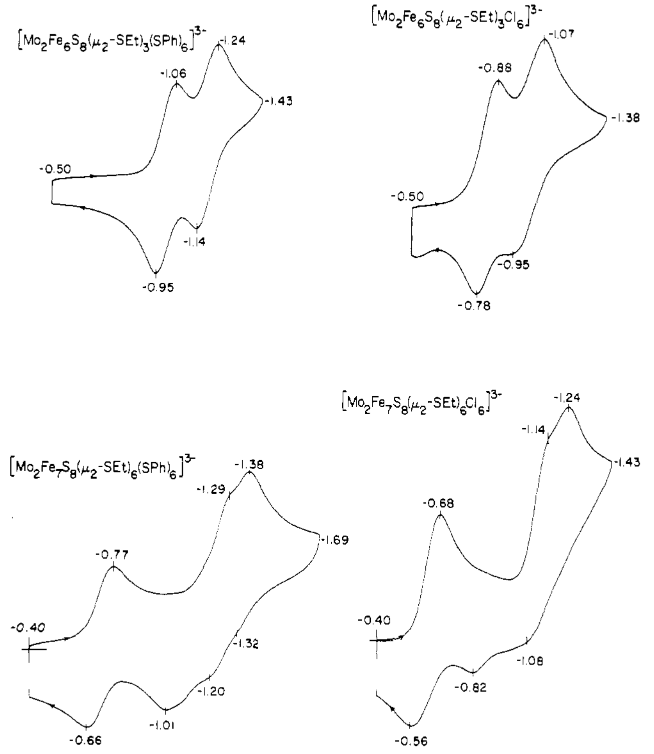

Figure 4. Cyclic voltammograms in acetonitrile solutions of isolated cluster compounds of types **4**, **5**, **7**, and **8**. Peak potentials at ~25 °C vs. SCE measured at 50 mV/s are indicated.

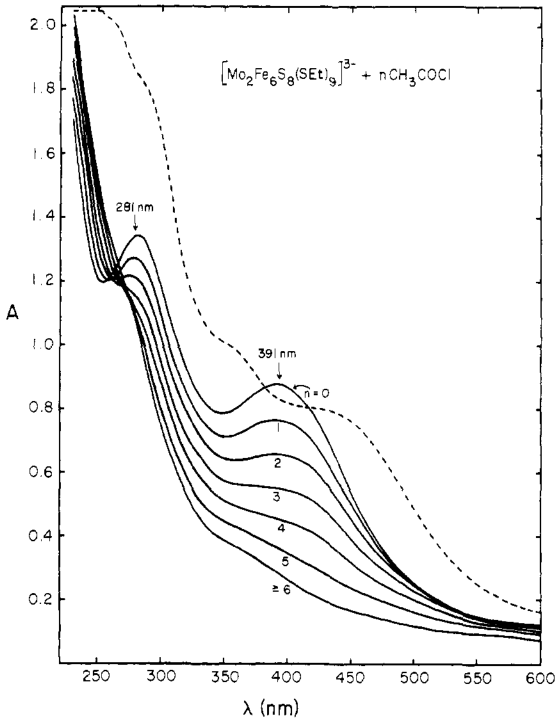

Figure 5. Absorption spectra in acetonitrile solution of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ ($n = 0$) and its reaction products with n = 1–6 equiv of acetyl chloride (—) and of the n = 6 system with 6.9 equiv of $(Et_4N)(SPh)$ (- - -).

the isolated compound are the same as those in Figures 2 and 3. Retention of the double-cubane structure follows from the voltammetric behavior in Figure 4 and the potential data in Table I. Successive reductions of clusters I and II with a potential separation of 0.18 V are observed, a behavior entirely analogous to that of type **1** clusters of proven structure.[3,6] The anodic potential shift upon terminal ligand substitution (0.26 for I, 0.27 V for II) is consistent with that found for $[Fe_4S_4(SR)_4]^{2-/3-}$ couples (R = Et, Ph; 0.29 V[23]).

(b) With Acetyl Chloride. Absorption spectral changes attendant to the addition of 1–6 equiv of acetyl chloride to a solution of **1** are displayed in Figure 5. The two peaks of the initial cluster are monotonically diminished in intensity until, in the 6-equiv system, the visible spectrum becomes nearly featureless. Addition of 6.9 equiv of $(Et_4N)(SPh)$ to this system generates the spectrum of $[Mo_2Fe_6S_8(SEt)_3(SPh)_6]^{3-}$ (compare with Figure 2), whose intensity corresponds to 99% formation of the mixed thiolate cluster. Use of 9 equiv of acetyl chloride afforded the same spectrum as in the 6-equiv system; addition of 11 equiv of $(Et_4N)(SPh)$ resulted in 97% spectral recovery of $[Mo_2Fe_6(SEt)_3(SPh)_6]^{3-}$. Addition of larger amounts of the benzenethiolate reagent in both the 6- and 9-equiv systems produced no significant changes in the visible region. Reaction systems with 1–9 equiv of acetyl chloride have been examined by ^1H NMR spectroscopy; spectra are presented in Figure 6. The initial broad terminal $S\text{-}CH_2$ resonance (−55.7 ppm) is split and reduced in intensity after addition of the first few equivalents of acetyl chloride, consistent with terminal substitution and the formation of species with inequivalent ligands. At the concentrations employed, terminal resonances are undetectable in systems with ≳3 equiv.[21] Simultaneously, the bridging SCH_2 signal (−17.5 ppm) is broadened and reduced in apparent intensity, and a new feature grows in near +4 ppm. At 6 equiv of reagent, the latter signal disappears and the bridging signal emerges

---

[23] DePamphilis, B. V.; Averill, B. A.; Herskovitz, T.; Que, L., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4159.

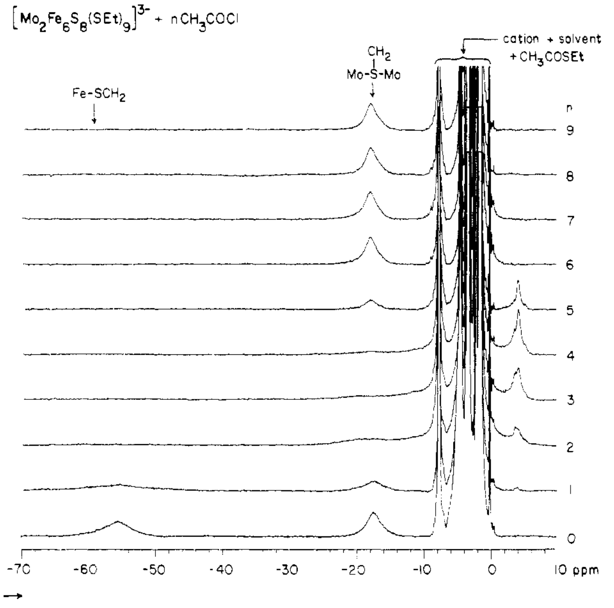

Figure 6. ^1H NMR spectra (100 MHz) of $(Et_3NCH_2Ph)_3$-$[Mo_2Fe_6S_8(SEt)_9]$ ($n = 0$) and its reaction products with n = 1–9 equiv of acetyl chloride in CD_3CN solution at ~25 °C. Signal assignments are indicated.

at −18 ppm with the same intensity as in the spectrum of the initial cluster. No further spectral changes were observed with 7–9 equiv of acetyl chloride. Although alterations in bridging signal resonances with 1–5 equiv of reagent cannot be satisfactorily explained,[24] the spectra do allow the conclusions that when 6 equiv of terminal thiolate ligands have been removed, the initial bridge structure is intact, and no further reaction occurs with three additional equivalents. When 13–20 equiv of reagent are used with reaction times as long as 16 h, bridging SCH_2 resonances are strongly diminished in intensity. Treatment of these systems with ~35 equiv of benzenethiolate results in appearance of ^1H NMR signals characteristic of $[Fe(SPh)_4]^{2-}$[25] and other isotropically shifted, unidentified resonances, indicating fragmentation of individual clusters.

Confirmation of the product of reaction 4 with $n = 6$ equiv

$$\begin{tikzcd}
{[Mo_2Fe_6S_8(SEt)_9]^{3-} + nCH_3COCl} \arrow[d, "(4)"'] \\
{[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SEt)_{6-n}Cl_n]^{3-} + nCH_3COSEt} \arrow[d, "(5)"', "6PhS^-\ (n = 6)"] \\
{[Mo_2Fe_6S_8(SEt)_3(SPh)_6]^{3-} + 6Cl^-}
\end{tikzcd}$$

as the terminally substituted cluster **4** (R = Et) was obtained by isolation of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_3Cl_6]$ by reaction of **1** with a slight excess (7%) of acetyl chloride. The properties of this compound correspond to those of the n = 6–9 equiv reaction product generated in solution (Figures 5 and 6).

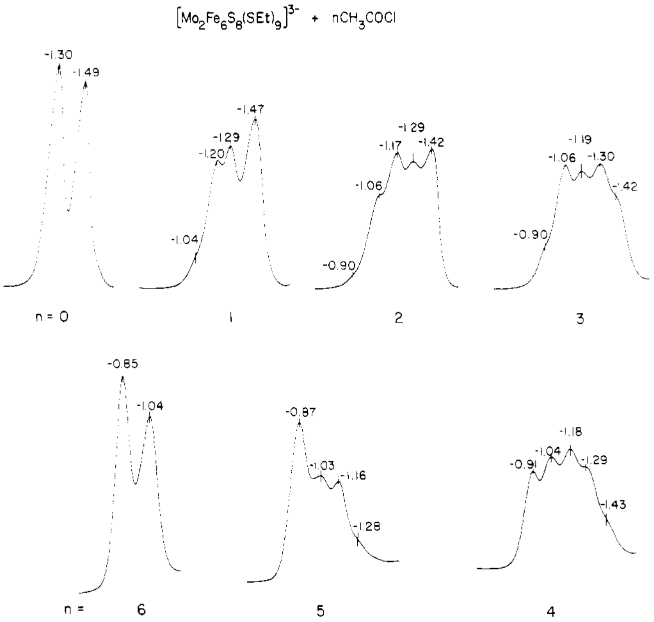

Figure 7. Differential-pulse polarograms in acetonitrile solution of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ ($n = 0$) and its reaction products with n = 1–6 equiv of acetyl chloride. Peak potentials at ~25 °C vs. SCE are indicated.

Moreover, the virtually quantitative substitution reaction 5 with excess benzenethiolate and the two-step redox behavior of the isolated compound (Figure 4) support cluster structure **4**. It is further observed that diminished visible absorption intensity and markedly anodic potential shifts (Table I; vide infra) are found with $[Fe_4S_4Cl_4]^{2-}$[15] when compared to $[Fe_4S_4(SEt)_4]^{2-}$.[23] The presence of terminal chloride ligands in the former cluster has been proven by an X-ray structure determination.[26]

The reactant and product ($n = 6$) clusters of reaction 4 exhibit two one-electron redox steps separated by 0.19 V and peak potential differences for individual clusters I and II of 0.45 V when measured by differential-pulse polarography (DPP; Table I). The latter value corresponds to a mean potential shift of +0.15 V per chloride substituted in I or II and suggests that partially substituted 6–*n*,*n* species may be detected and their potentials determined. The situation is similar to that of $[Fe_4S_4(SR)_{4-n}Cl_n]^{2-}$ systems for which the mean potential shift is +0.14/Cl (R = Et, *t*-Bu[13,15,23]) and the distribution of 4–*n*,*n* species is approximately statistical.[13] In the present case, the situation is more complicated. For systems with n = 0–6, there are 13 isomers of 7 different clusters,[27] corresponding to at least 14 distinct redox processes expected to occur in a 0.64-V interval (−1.49 to −0.85 V). Values of certain potentials have been obtained based on the reasonable assumptions that clusters I and II with the most chloride ligands are reduced at the least negative potentials in the ranges −0.85 to −1.30 V for I and −1.04 to −1.49 V for II and that the distribution of species from reactions with n equiv of reagent is essentially statistical.[27] Based on results already described, each n-equiv reaction is taken to be complete.

Shown in Figure 7 are DP polarograms of reaction systems of **1** with n = 0–6 equiv of acetyl chloride. Contained in Table

---

(24) If, as we[3] and others[5] have argued, bridging group shifts are predominantly dipolar in origin, the appearance of one or more signals near +4 ppm may arise from partially substituted clusters which lack the (assumed) axial magnetic anisotropy of initial cluster **1** or hexasubstituted species **4** (Figure 1). The possibility that rhombic anisotropy arises in part by bridge cleavage, or formation of chlorobridged species, appears unlikely. The upfield resonance is abolished upon passing from the 5- to the 6-equiv reaction system, requiring re-formation of the (μ-SEt)$_3$ bridge in the process if this possibility obtains.

(25) Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054.

(26) Bobrik, M. A.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1977**, *16*, 1851.

(27) This enumeration excludes enantiomers and isomers due to bridging ethyl group orientations. The species 4,2, 3,3, and 2,4 have three isomers each. The statistical mole fraction of a species is $N_{6-n,n} = f_{SEt}^{6-n} f_{Cl}^{n} 6!/n!(6-n)!$, where f is the fraction of total ligand in the indicated form. This relationship does not include statistical weighting of isomers of a given 6–*n*,*n* species. A statistical distribution of species appears reasonable inasmuch as terminal ligand binding sites are separated by ca. 6–7 Å.

I are potentials a–g which have been evaluated from these results. Limiting potentials a and g are those of the 0,6 and 6,0 species, respectively. In the $n = 1$ system, the major constituents[27] are $N_{6,0} = 0.334$, $N_{5,1} = 0.402$, and $N_{4,2} = 0.201$. Accordingly, the −1.20 and −1.47-V peaks (f) are assigned to reduction of monosubstituted I and unsubstituted II in 5,1, with the latter potential considered a fair approximation of the influence of substitution in one cluster on the potential of the other. In the $n = 2$ system ($N_{4,2} = 0.329$), a clear shoulder is evident which develops into a peak at −1.06 V (e) with $n = 3$ ($N_{4,2} = 0.234$). Because this is the second feature positive of the potential of unsubstituted I, it is assigned to reduction of doubly substituted I in 4,2. Similarly, the potential at −0.91 V (d) in the $n = 4$ system ($N_{3,3} = 0.219$), which appears as a shoulder with $n = 2,3$, is associated with reduction of triply substituted I in 3,3. Assignment of the remaining potentials, −1.16 (b) and −1.28 V (c), made primarily from the $n = 5$ system, were arrived at by similar reasoning. The assigned potentials correspond to shifts of +0.10 to 0.15 V/Cl. Four of the expected 14 potentials could not be evaluated. While potentials b–f for incompletely subsituted species may not be exactly correct owing to peak shifts from overlapping current–voltage curves, they are regarded at the least as good estimates. The procedure for their evaluation is illustrative and can be applied to other systems.

Reactions of $[M_2Fe_7S_8(SEt)_{12}]^{3-}$. Inasmuch as individual clusters in **1** and **3** have the same oxidation level,[2,3] comparable reactivity of terminal thiolate ligands with electrophiles is anticipated. This behavior has been confirmed in experiments less extensive than those with **1** and conducted on a preparative scale by utilization of **3** with M = Mo, W. Reaction of **3**-Mo with a small excess of benzenethiol afforded a crystalline $Me_3NCH_2Ph^+$ salt whose ^1H NMR spectrum is presented in Figure 8. The CH_2 (−55.7 ppm) and CH_3 (−4.5 ppm) resonances of terminal SEt groups of the initial cluster **3** (not shown) are absent. The two resonances of the methylene protons (−24.4, −17.5 ppm) and the methyl resonance (−0.81 ppm) of the bridging SEt groups are retained but are shifted (−23.6, −11.7, −1.43 ppm). New signals at −13.9 and +3.7 ppm are clearly due to contact-shifted *m*-H and *p*-H, respectively. Together with the cyclic voltammogram in Figure 4 which, except for potential differences (Table I), corresponds to that of **3**-Mo, these results establish structure of the product cluster of reaction 6 as **8** (R = Et, R′ = Ph). Similarly, the

$$[Mo_2Fe_7S_8(SEt)_{12}]^{3-} + 6PhSH \rightarrow [Mo_2Fe_7S_8(\mu\text{-}SEt)_6(SPh)_6]^{3-} + 6EtSH \quad (6)$$

product of reaction 7 conducted with a small excess of acetyl

$$[M_2Fe_7S_8(SEt)_{12}]^{3-} + 6CH_3COCl \rightarrow [M_2Fe_7S_8(\mu\text{-}SEt)_6Cl_6]^{3-} + 6CH_3COSEt \quad (7)$$

chloride has been shown to have structure **7** (R = Et). The NMR spectrum of $[Mo_2Fe_7S_8(SEt)_6Cl_6]^{3-}$ (Figure 8) shows as the only cluster resonances those of methylene (−38.4, −26.5 ppm) and methyl (+1.6 ppm) portions of bridging SEt groups, which are appreciably displaced from their positions in **3**-Mo. The cyclic voltammogram of this cluster (Figure 4) is also consistent with **7**. This structure for $[W_2Fe_7S_8(SEt)_6Cl_6]^{3-}$ (bridging SEt, −26.3, −17.8, +1.3 ppm) was correspondingly demonstrated. The existence of two signals from the diastereotopic protons of the fragment $MS(CH_2CH_3)Fe$ is itself conclusive evidence for retention of the bridge structure in the products of reactions 6 and 7.

Treatment of **3**-Mo with *excess* electrophile at ambient temperature gave results similar to those with **1** under comparable conditions. Reaction with 13 equiv of benzenethiol under reduced pressure afforded only **8** (R = Et, R′ = Ph). Incubation with 28 equiv of acetyl chloride for 5 h resulted in strongly diminished bridging SCH_2 resonances. Attempted conversion to **8** by addition of ~40 equiv of $(Et_4N)(SPh)$ yielded signals due to $[Fe(SPh)_4]^{2-}$ as the major product together with other unidentified paramagnetically shifted resonances, observations indicative of cluster degradiation.

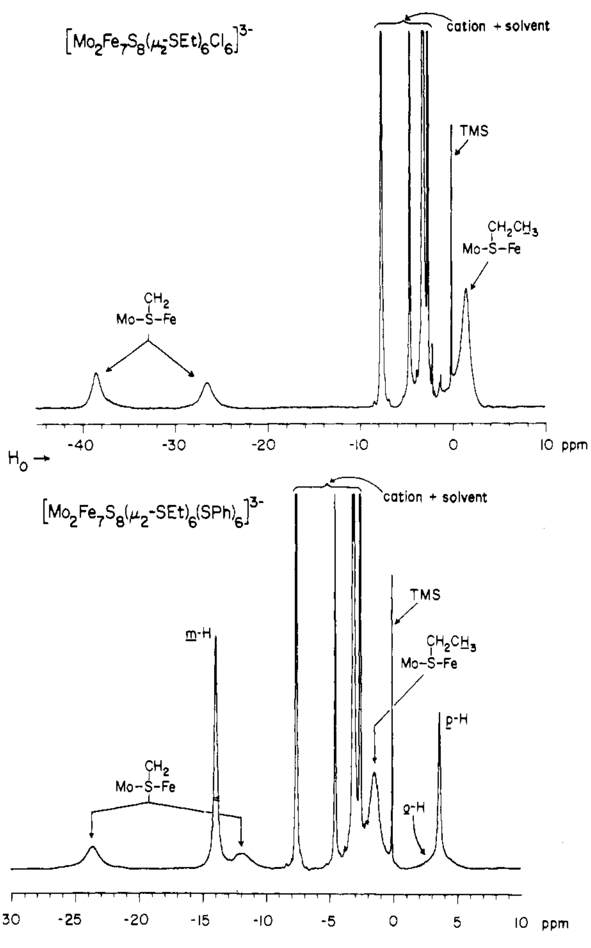

Figure 8. ^1H NMR spectra (100 MHz) of isolated salts of $[Mo_2Fe_7S_8(\mu\text{-}SEt)_6Cl_6]^{3-}$ (upper) and $[Mo_2Fe_7S_8(\mu\text{-}SEt)_6(SPh)_6]^{3-}$ (lower) in $Me_2SO\text{-}d_6$ solutions at ~25 °C. Signal assignments are indicated.

Nature of 2-Hydroxyethanethiolato Clusters. The occurrence of reaction 8 has been briefly described.[8] This process

$$(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9] + 9HOCH_2CH_2SH \rightarrow (Et_4N)_3[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]\cdot Me_2CO + 9EtSH \quad (8)$$

involved reaction of an (unspecified) excess of the thiol with **1** in acetonitrile at ambient temperature, removal of liberated ethanethiol in vacuo, and crystallization of the product from acetonitrile/acetone, yielding the acetone monosolvate. Spectroscopic and electrochemical properties[6] are entirely consistent with a double-cubane structure, which was concluded to be to type **1** with R = CH_2CH_2OH from an X-ray structure determination.[8] The deviation of reaction 8 from the pattern of only terminal ligand substitution observed in this work under comparable experimetal conditions has led to a further examination of the nature of 2-hydroxyethanethiolato clusters formed by direct synthesis and ligand substitution. The product of reaction 8 assumes additional significance owing to its aqueous solubility and the attendant demonstration that it can replace ferredoxin in a H_2-evolving system containing hydrogenase and dithionite.[28]

---

(28) Adams, M. W. W.; Rao, K. K.; Hall, D. O.; Christou, G.; Garner, C. D. *Biochim. Biophys. Acta* **1980**, *589*, 1.

Table II. Comparative Properties of 2-Hydroxyethanethiolato Double-Cubane Clusters

property	direct synthesis $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ [a]	ligand substitution $[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SCH_2CH_2OH)_6]^{3-}$ [a]
λ_{max} (ϵ_M),[h] nm (CH_3CN)	280 (56 700), 386 (38 100)	280 (58 800), 385 (39 100)
E_p,[b] V (DPP) (DMF)	−1.18, −1.37	−1.22, −1.42
chem shifts, ppm		
Me_2SO-d_6	−56, −54 (t-CH_2),[c] −5.57, −4.39[d] (t-CH_2OH), −17.7 (b-CH_2)	−54.9 (t-CH_2), −5.45 (t-CH_2OH), −17.4 (b-CH_2)
CD_3OD	−48.1 (t-CH_2), −4.3 (sh, t-CH_2OH), −17.8 (b-CH_2)[e]	−47.8 (t-CH_2), −4.29 (t-CH_2OH), −17.9 (b-CH_2)
acetylation product[j]	−17.0 (b-CH_2), −1.74 ($OCOCH_3$) ppm[i]	−17.4 (b-CH_2) ppm[i]
crystal data (hexagonal)	$a = 17.198$ (9), $b = 17.206$ (11), $c = 16.432$ (6) Å, $V = 4211$ (3) Å^3 [f]	$a = 16.983$ (5), $b = 16.991$ (4), $c = 16.354$ (4) Å, $V = 4088$ (2) Å^3 [f]
	$a = b = 17.001$ (7), $c = 16.381$ (9) Å, $V = 4100.5$ Å^3 [g]	

[a] Et_4N^+ salts having the compositions described in the Experimental Section. [b] ±10 mV, vs. SCE, glassy-carbon electrode. [c] t = terminal, b = bridging, ligand. [d] Tentative assignment.[31] [e] In this and other cases the b-CH_2CH_2OH and b-CH_2CH_3 resonances are obscured by cation and solvent signals. [f] Space group $P6_3$ or $P6_3/m$. [g] Data from ref 8 for compound formulated as $(Et_4N)_3[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]\cdot Me_2CO$; space group $P6_3/m$. [h] Values based on molecular weights of acetone monosolvates. [i] Me_2SO-d_6 solution. [j] IR data (Nujol mull): $\nu_{CO} = 1735$ cm^{-1}.

So that the nature of the product of reaction 8 could be assessed, authentic $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ was prepared by the standard assembly reaction 9 for type **1** clusters

$$2MoS_4^{2-} + 6FeCl_3 + 17HOCH_2CH_2S^- \rightarrow [Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-} + 4(HOCH_2CH_2S)_2 + 18Cl^- \quad (9)$$

(with ~40% excess thiolate). The product Et_4N^+ salt was recrystallized from methanol/acetone (76% yield). In a second experiment, reaction 8 was conducted with 61 equiv of thiol at 50 °C for 2.5 h under periodic vacuum to remove ethanethiol. The product Et_4N^+ salt was recrystallized from acetonitrile/acetone (69% yield). If the products are taken to contain either of the anions $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ or $[Mo_2Fe_6S_8(SEt)_3(SCH_2CH_2OH)_6]^{3-}$, elemental compositional differences between the unsolvated and solvated forms of a given product or between such forms of the two products are small. Total analyses suggest that both product salts are solvated. Analytical results in the Experimental Section indicate that monosolvates of acetone and acetonitrile are among reasonable formulations.[29]

Corresponding properties of the two 2-hydroxyethanethiolato clusters, designated as the direct synthesis and ligand substitution products, are compared in Table II. Electrochemical results establish a double-cubane structure for both products but cannot distinguish between types **1** and **2**[3] (Figure 1). They do eliminate type **3** clusters,[3] as do analytical results. Although property differences are small, it is clear that the two products do not contain identical clusters. Evidence supporting this assertion is briefly summarized.

(a) Redox Potentials. DPP peak potentials for successive reductions of individual clusters I and II in the two products differ by 40 and 50 mV, respectively, with those of the direct synthesis product being less negative. Under identical conditions potentials of the couples $[Fe_4S_4(SR)_4]^{2-/3-}$ are −1.21 V (R = CH_2CH_2OH) and −1.35 V (R = Et), consistent[30] with the subsitution product having a smaller complement of $HOCH_2CH_2S^-$ ligands.

(b) ^{1}H NMR Spectra. Shown in Figure 9 are spectra of the two products in Me_2SO-d_6 solutions. There is a conspicuous difference, found in the appearance of two overlapping broad

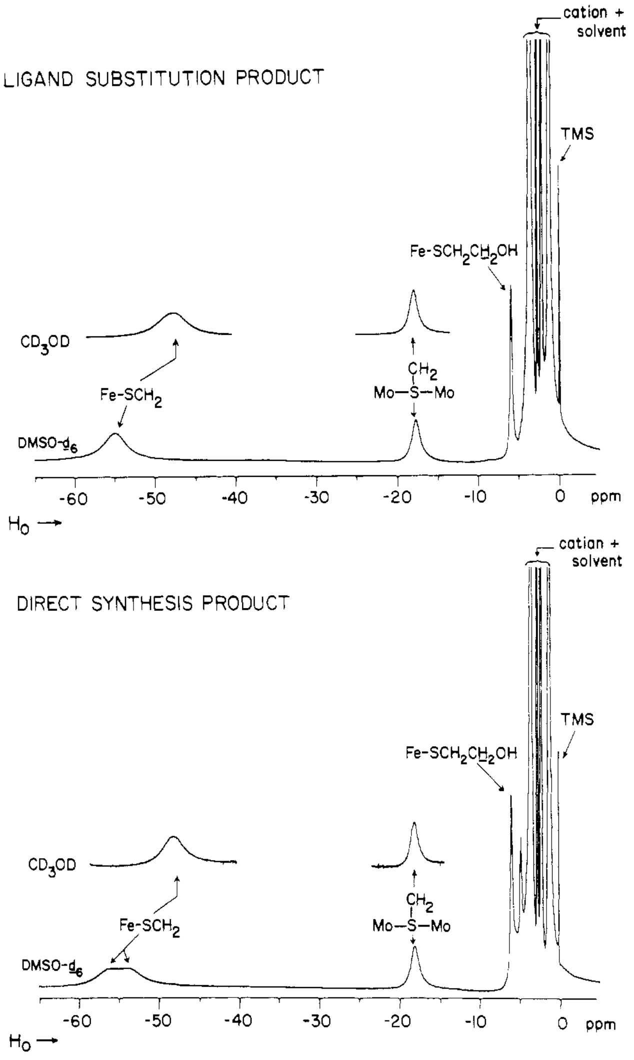

Figure 9. ^{1}H NMR spectra (300 MHz) of 2-hydroxyethanethiolato double-cubane clusters (Et_4N^+ salts) in Me_2SO-d_6 solutions at ~25 °C: upper, ligand substitution product; lower, direct-synthesis product. Inserts in both spectra show the two low-field resonances in CD_3OD solutions. Signal assignments are indicated; chemical shifts are given in Table II.

signals centered at −55 ppm and two sharp signals near −5 ppm in the direct-synthesis product spectrum. The corresponding features in the substitution product spectrum are singlets. The former pair can only be due to $FeSCH_2$ (compare with Figures 3 and 6), and the latter pair is assigned to $FeSCH_2CH_2OH$ groups.[31] These signals are proposed to be doubled because

---

(29) The acetone solvate formulation is supported by the presence of weak bands at 1714 cm^{-1} in the infrared spectra of both compounds in acetonitrile solutions. Note, however, that direct oxygen analyses of the products are in only fair conformance with this formulation.

(30) When measured under the same conditions, potentials of the couples $[Fe_4S_4(SR)_4]^{2-/3-}$ and $[Mo_2Fe_6S_8(SR)_9]^{3-/4-,4-/5-}$ tend to exhibit a linear relationship upon variation of R (Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H., submitted for publication in *J. Am. Chem. Soc.*). This behavior is apparent from limited data already published.[6]

of hydrogen bonding between hydroxyl groups of terminal and bridging ligands,[32] producing inequivalencies in the former set. Consistent with this proposal is the observation that the doubled features are eliminated in CD_3OD solution, in which medium the spectra of the two products are virtually identical. In an additional experiment, the substitution reaction 8 was conducted with 59 equiv of $HOCH_2CD_2SH$ essentially as described above for the protiothiol, and the product was isolated in 44% yield. Its spectrum in $Me_2SO\text{-}d_6$ contains resonances at −17.4 and −5.44 ppm with the same relative intensities as the corresponding features in the subsitution product spectrum in Figure 9. However, the $FeSCH_2$ resonance at −54.9 ppm was diminished by >90% in intensity. The collective NMR results lead to the conclusion that the ligand substitution product does not contain bridging $HOCH_2CH_2S^-$ ligands. Further, neither product can be a type **2** cluster (Figure 1) for $[Mo_2Fe_6S_9(SEt)_8]^{3-}$ exhibits its bridging SCH_2 resonance at +3.1 ppm and no signal in the vicinity of −17 ppm.[3]

(c) Acetylation Products. The two products were treated with 16–17 equiv of acetyl chloride and 10–20 equiv of 2,6-lutidine in cold (0 °C) acetonitrile. After being warmed to room temperature, the homogeneous reaction mixtures were stirred for 2–3 h. Upon reduction of solvent volume in vacuo and addition of warm (45 °C) ethanol, followed by cooling overnight at 5 °C, the reaction products were isolated. After the products were washed with ethanol and ether, their ^1H NMR and infrared spectra were obtained. The results (Table II) show that the direct synthesis product was esterified in a process proposed as reaction 10 (the product diester was not identified).

$$\begin{aligned}&[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-} + 15CH_3COCl + \\ &\quad 9(\text{base}) \rightarrow [Mo_2Fe_6S_8(\mu\text{-}SCH_2CH_2OCOCH_3)_3Cl_6]^{3-} + \\ &\qquad 6CH_3COSCH_2CH_2OCOCH_3 + 9(\text{base})\cdot HCl \quad (10)\end{aligned}$$

The reaction product lacked a $FeSCH_2$ resonance near −55 ppm, retained the bridging SCH_2 signal, and showed a strong ester carbonyl infrared absorption. The ligand substitution product yielded a nonesterified reaction product, whose properties conform to those of $[Mo_2Fe_6S_8(\mu\text{-}SEt)_3Cl_6]^{3-}$. These results further show the absence of bridging $HOCH_2CH_2S^-$ ligands in the substitution product.

(d) Crystal Data. The direct synthesis and ligand substitution products crystallize in hexagonal space group(s) with cells of similar, but not identical, dimensions. Comparative crystal data for our ligand substitution product and those of the product of reaction 8 as formulated by others[8] make highly probable the identity of the two products.

Summary. From the foregoing evidence, it is concluded that reactions of types **1** and **3** clusters with stoichiometric or (specified) excess quantites of acetyl chloride or thiols result in terminal ligand substitution only. A further example of this regularity is found in the reaction of *p*-toluenethiol and $[W_2Fe_6S_9(SEt)_8]^{3-}$, a type **2** cluster (Figure 1; M = W, R = Et). When carried out on a preparative scale, $(Et_4N)_3[W_2Fe_6S_9(\mu\text{-}SEt)_2(p\text{-}tol)_6]$ was isolated in 79% yield. The structures of this and all other substitution products have been firmly established by their spectroscopic and electrochemical properties. We have been unable to substantiate the one reported exception to the ligand substitution pattern observed here, viz., $[Mo_2Fe_6S_8(\mu\text{-}SCH_2CH_2OH)_3(SCH_2CH_2OH)_6]^{3-}$ as the product of reaction 8 with excess thiol.[8] The crystal structure of the Et_4N^+ salt monoacetone solvate at $R = 9\%$ is described[8] in terms of imposed $3/m$ anion symmetry with disorder of CH_2OH groups of bridging ligands on either side of the mirror plane and of the acetone molecule about the threefold axis. Signs of cation disorder were also noted. Inasmuch as the ligand substitution product obtained here unquestionably is $[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SCH_2CH_2OH)_6]^{3-}$, a reassessment of the crystal structure would appear to be in order. Other formulations and properties of double-cubane substitution products, described in brief by Christou, Garner, et al.,[6,17] are consistent (where comparisons can be made) with those developed in more experimental detail in this investigation.[33]

Evidently, the adjacent metal centers reduce the nucleophilicity of bridging sulfur atoms such that they are not protonated by benzenethiol ($pK_a \approx 6.5$) nor attacked by the strong electrophile acetyl chloride. Kinetic studies of reaction 1 with EL = arylthiols have shown that protonation of bound thiolate is the rate-determining step,[34] and the detection of thioester products when EL = acyl halide[13,15] indicates direct attack of the electrophile on thiolate. Similar processes doubtless occur with the terminal ligands of clusters **1**–**3**.

Demonstration that reactions of cluster types **1** and **3** with thiols and acetyl chloride, summarized in Figure 1, affect specific substitution of terminal ligands provides a foundation for current investigations of cluster reactions with other reagents. Of particular interest are those reactions which effect removal of the more tightly bound bridging thiolates and introduction of relatively labile ligands at the molybdenum atom, a likely substrate binding site, with retention of $MoFe_3S_4$ cubane-type structures. The Fe(III)- (**3**) and Fe(II)-bridged clusters $[Mo_2Fe_7S_8(SR)_{12}]^{3-,4-}$[3,4] are promising in this regard. The $Fe(SR)_6$ bridge fragment can be removed upon reactions with catechols,[35,36] affording species lacking MoSR groups and retaining $MoFe_3S_4(SR)_3$ clusters. These and other substitution reactions of $MoFe_3S_4$ clusters are under continuing study.

Acknowledgment. This research was supported by National Science Foundation Grants CHE 77-04397 and CHE 80-06601. We thank Dr. J. G. Reynolds for the results in Figure 3, Dr. C. L. Coyle for early experimentation, and Dr. G. Christou for useful discussions.

Registry No. $(Et_4N)_3$ (**1**; R = CH_2CH_2OH, M = Mo), 71501-88-7; $(Et_4N)_3$ (**1**; R = Et, M = Mo), 72895-02-4; $(Et_3NCH_2Ph)_3$ (**1**; R = Et, M = Mo), 71899-92-8; $(Et_4N)_3$ (**2**; R = Et, M = W), 72981-31-8; $(Et_4N)_3$ (**3**; R = Et, M = Mo), 73589-29-4; $(Me_3NCH_2Ph)_3$ (**3**; R = Et, M = Mo), 72268-97-4; $(Et_4N)_3$ (**3**; R = Et, M = W), 73589-28-3; $(Me_3NCH_2Ph)_3$ (**3**; R = Et, M = W), 73589-27-2; $(Et_4N)_3$ (**4**; R = Et, M = Mo), 76122-45-7; $(Et_4N)_3$ (**5**; R = Et, R′ = Ph, M = Mo), 79466-72-1; $(Et_4N)_3$ (**5**; R = Et, R′ = CH_2CH_2OH, M = Mo), 79466-71-0; $(Et_4N)_3$ (**6**; R = Et, R′ = $p\text{-}C_6H_4CH_3$, M = W), 79466-73-2; $(Me_3NCH_2Ph)_3$ (**7**; R = Et, M = Mo), 79466-67-4; $(Et_4N)_3$ (**7**; R = Et, M = W), 79466-68-5; $(Me_3NCH_2Ph)_3$ (**7**; R = Et, M = W), 79466-69-6; $(Et_4N)_3$ (**8**; R = Et, R′ = Ph, M = Mo), 79466-75-4; $(Me_3NCH_2Ph)_3$ (**8**; R = Et, R′ = Ph, M = Mo), 79466-74-3; $(NH_4)_2MoS_4$, 15060-55-6; CH_3COCl, 75-36-5.

---

(31) An alternative assignment of the less intense signal (−4.39 ppm) is to bridge CH_2CH_2OH. In $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ the bridge CH_2CH_3 resonance is overlapped by cation resonances.

(32) The possbility of hydrogen-bonding interactions between proximal bridging and terminal CH_2CH_2OH groups is quite apparent from inspection of scale models constructed from the crystallographic coordinates of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$.[2]

(33) However, we view as doubtful the reported formation of $[Mo_2Fe_6S_8(SCH_2CH_2OH)_3Cl_6]^{3-}$ from the product of reaction 8 and (an unspecified amount of) benzoyl chloride.[17] From the results of this study, this material is more likely $[Mo_2Fe_6S_8(\mu\text{-}SEt)_3Cl_6]^{3-}$.

(34) Dukes, G. R.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 528.

(35) Wolff, T. E.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 174.

(36) Armstrong, W. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 6246.