

Molybdenum Atom Ligand Substitution Reactions of MoFe₃S₄ Cubane-Type Clusters: Synthesis and Structures of Clusters Containing Mo-Bound Pseudosubstrates of Nitrogenase

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Abstract: The ligand substitution chemistry of the title clusters, containing a Mo atom in a coordination environment similar (by EXAFS criteria) to that in nitrogenase, has been further developed. Reaction of [Mo₂Fe₇S₈(SEt)₁₂]²⁻ with tetrachlorocatechol (Cl₄catH₂) yields the doubly bridged double cubane [Mo₂Fe₆S₈(SEt)₆(Cl₄cat)₂]⁴⁻ (**1**). This and analogous clusters form the solvated, spin-quartet, single cubanes [MoFe₃S₄(SR)₃(cat*)(MeCN)]²⁻ (**2**) in acetonitrile solution. These species undergo a number of Fe and Mo site-specific ligand substitution reactions, which are summarized and include catechol exchange at the Mo site. Reaction of **2** (R = *p*-C₆H₄Cl; cat* = 3,6-diallylcatecholate) with excess Cl₄catH₂ and catechol (catH₂) yields [Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat*)₂]⁴⁻ (cat* = Cl₄cat, cat (**3**)). (Et₄N)₃(**3**) crystallizes in monoclinic space group *P*2₁/*n* with *a* = 18.25 (2) Å, *b* = 22.08 (3) Å, *c* = 26.21 (3) Å, β = 99.43 (10)°, and *Z* = 4. The anion consists of two MoFe₃S₄(S-*p*-C₆H₄Cl)₂(cat) subclusters joined by two Mo-S(R)-Fe bridges whose elongated bonds contribute to the ready cleavage to **2** in acetonitrile. The ligand binding reactions of **2** and its W analogue were investigated by ¹H NMR spectroscopy. In ~10 mM solutions reactions of 1 equiv of the nitrogenase-related ligands L = CN⁻, N₃⁻, N₂H₄, NH₃, PhNHNH₂, and piperidine were found to be nearly quantitative at 298 K. Spectra at 240 K unambiguously demonstrated binding from the appearance of inequivalent R-substituent resonances in a 2:1 intensity ratio, consistent with [MFe₃S₄(SR)₃(cat*)L]²⁻³⁻ clusters (**4**, M = Mo, W) of C₃ symmetry. By variation of R and cat* groups using substitution reactions, diffraction quality crystals of **4** with L = CN⁻ and N₃⁻ were obtained. (Et₄N)₃[MoFe₃S₄(SEt)₃(Cl₄cat)(CN)] crystallizes in orthorhombic space group *Pnma* with *a* = 22.793 (5) Å, *b* = 19.274 (3) Å, *c* = 12.456 (2) Å, and *Z* = 4. (Et₄N)₃[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)N₃] crystallizes in space group *P*2₁/*n* with *a* = 19.158 (9) Å, *b* = 18.56 (1) Å, *c* = 20.15 (1) Å, β = 105.96 (5)°, and *Z* = 4. The Mo-L portions of these single cubanes are linear (L = CN⁻) or bent (L = N₃⁻, Mo-N-N = 125 (1)°), and Mo-C (2.19 (3) Å) and Mo-N (2.17 (2) Å) bond distances are consistent with an intermediate oxidation state (III, IV) of the Mo atom. The results of this and prior investigations have defined means for systematic and specific manipulation of all noncore ligands in [MoFe₃S₄]³⁺ single cubanes, results that should be pertinent to the development of substrate-reducing systems based on reduced ([MoFe₃S₄]²⁺) single-cubane clusters.

In order to examine reaction chemistry at a molybdenum atom site that, by EXAFS criteria,^{2,4} is structurally similar to that in the iron-molybdenum cofactor (FeMo-co) of nitrogenase, we have developed a synthetic route to the solvated single cubanes [MoFe₃S₄(SR)₃(al₂cat)(solv)]²⁻ (**1**)³⁻⁵ and [MoFe₃S₄Cl₃(al₂cat)(solv)]²⁻ (**2**)⁶ (al₂cat = 3,6-diallylcatecholate). Schematic structures of these and other clusters are provided in Figure 1. Proof of the existence of solvated clusters has been obtained by the structure determination of **2** (solvent = THF).⁶ The coordinated solvent molecules in **1** and **2** are substitutionally labile, being in rapid equilibrium with bulk solvent.^{5,6}

The different reactivity properties of ligands bound to Mo and Fe sites have allowed development of an extensive and site-specific cluster substitution chemistry, the leading aspects of which are summarized in Figure 1. The scheme refers to reactions in acetonitrile with, usually, stoichiometric quantities of reactants; of the bound solvent molecules Me₂SO, DMF, and MeCN, the last is the most readily displaced. The fundamental precursor cluster type is **1**, generated in solution by the solvent-induced cleavage of the bridged double cubanes [Mo₂Fe₆S₈(SR)₆(R'cat)₂]⁴⁻.

The latter are synthesized from the Fe(III)-bridged double cubanes [Mo₂Fe₇S₈(SR)₁₂]^{3-7,8} by reaction with 3,6-disubstituted catechols.⁵ Thiolate ligands at Fe sites are readily substituted in reactions 1 and 2 with electrophiles to afford **3** and **2**,^{5,6} respectively. The chloride ligands are easily replaced in reaction 3,⁶ which recovers **1**. In reactions 4 and 5 ligands L = CN⁻ and Et₃P displace solvent to form **4** and **5**,^{5,6,9,10} respectively; additional cyanide in reaction 6 gives the tetrasubstituted cluster **6**. Further evidence of the lability of bound solvent is provided by other examples of reaction 5, yielding **5** with L = RO⁻ and RS⁻.^{5,6,9,10} In the ligand displacement reaction 7 leading to **7** the binding affinity order at the Mo site has been shown to be PhS⁻ < Et₃P < CN⁻.⁶ Demonstration of the existence of ligated clusters follows from ¹H NMR spectra^{5,6,9,10} (vide infra) and the isolation and structure determination of the Et₄N⁺ salt of [MoFe₃S₄(S-*p*-C₆H₄Cl)₄(al₂cat)]^{3-9,10} (**5**, R = *p*-C₆H₄Cl, L = *p*-ClC₆H₄S⁻).

Clusters **1-7** have the [MoFe₃S₄]³⁺ (α) core oxidation level and, in common with FeMo-co,¹¹ S²⁻ ground states.^{5,6,9,10,12} All are chemically or electrochemically reducible by one electron as in, e.g., reaction 8, which affords the reduced solvated cluster **9** with the [MoFe₃S₄]²⁺ (β) oxidation level. One example of **9**,

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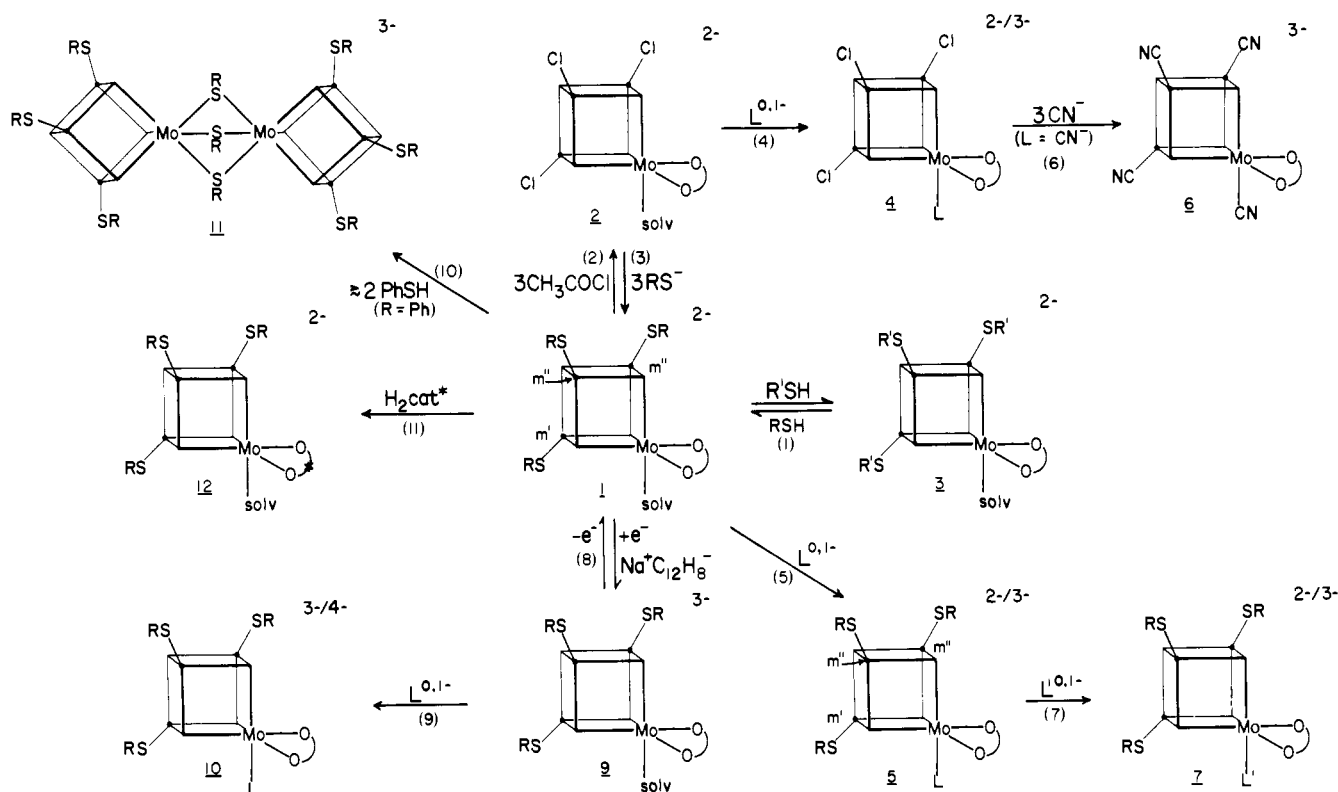
REACTIONS OF MoFe₃S₄ SINGLE-CUBANES

Figure 1. Schematic summary of reactions 1–11 of MoFe₃S₄ single-cubane clusters in acetonitrile solution demonstrated in this and prior investigations^{5,6,9,10,13} (● = Fe, solvent = MeCN; L, L' = generalized ligand).

[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(a₁cat)(EtCN)]³⁻, has been isolated¹³ and shown to have an *S* = 2 ground state.¹² Phosphines and CN⁻ bind in reaction 9 to afford the reduced ligated clusters **10**, which have been detected in solution.^{9,10,13}

Under essentially stoichiometric conditions, reactions 1–3 are specific to Fe sites and reactions 4, 5, 7, and 9 are specific to Mo sites. The analogous tungsten clusters have been shown to undergo some of the same reactions.^{5,10} In this investigation two new reactions of **1** have been demonstrated: the single → double-cubane conversion reaction **10** resulting in formation of triply bridged **11** and the catechol ligand exchange reaction **11** affording **12**. Reaction **11** is a further example of a Mo site-specific process that, in combination with reactions 1 and 5, has led to the crystallization of certain ligated clusters **5** containing pseudo-substrates (L = CN⁻, N₃⁻, PhNHNH₂) of nitrogenase. Proof of the occurrence of reaction **11** is provided by an X-ray structure determination, and the structures of cyanide- and azide-bound clusters **5** are described. This is the initial report of the syntheses and properties of MoFe₃S₄ single cubanes containing ligands related to substrates or substrate reduction products of nitrogenase.

Experimental Section

Preparation of Compounds. (Et₄N)₃. Separate solutions of 3.25 g (50 mmol) of NaN₃ and 8.35 g (50 mmol) of Et₄NCl in 100 mL of 1:2 v/v acetone/methanol were mixed and the resultant solution was evaporated to dryness in vacuo. The residue was treated with 100 mL of acetonitrile. After the mixture was stirred for 2 h, NaCl was removed by filtration and the filtrate was condensed in vacuo to 20 mL. Addition of 25 mL of ether and cooling to 0 °C caused separation of a white microcrystalline solid, which was collected and dried in vacuo. This material was recrystallized from dry methanol to give the product as white crystals in 80% yield (ν_{N_3} 2000 cm⁻¹).

In the following preparations all operations were carried out under a pure argon atmosphere with use of degassed solvents. Volume reduction and drying steps were performed in vacuo.

(Et₄N)₃[Mo₂Fe₇S₈(SEt)₁₂]. An earlier synthesis of this compound⁷ has been improved. Reaction of (NH₄)₂MoS₄^{14,15} with 2 equiv of NaOMe in methanol afforded Na₂MoS₄, which may be isolated by solvent removal or crystallized from a concentrated methanol solution by addition of ether. The prior procedure⁷ was followed with these modifications: (i) the source of [MoS₄]²⁻ is a slurry prepared by addition of 2 equiv of Et₄NCl to a solution of Na₂MoS₄ in ethanol; (ii) the total reaction mixture volume was >850 mL of ethanol for the mol ratio of reactants MoS₄²⁻ (18 mmol):3.5FeCl₃:12NaSEt; (iii) the mixture was efficiently stirred; and (iv) Celite was used to remove NaCl from acetonitrile extracts of the crude product. This method does not require preisolation of (Et₄N)₂MoS₄^{15,16} and routinely gives the product in yields of >75% without contamination by (Et₄N)₃[Mo₂Fe₆S₈(SEt)₉].

(Et₄N)₃[Mo₂Fe₇S₈(SEt)₆(Cl₄cat)₂]. A solution of 4.5 g (18 mmol) of *o*-C₆H₄(OH)₂¹⁷ (Cl₄catH₂) in 130 mL of acetonitrile was treated with 5.2 mL (37 mmol) of Et₃N. The mixture was transferred onto 6.5 g (3.3 mmol) of (Et₄N)₃[Mo₂Fe₇S₈(SEt)₁₂] and 2.5 g (12 mmol) of Et₄NBr, both as solids. The reaction vessel was slightly evacuated and the contents was stirred for 20 h at ambient temperature. The initially homogeneous reaction mixture developed a deep red color and a microcrystalline solid deposited. After the reaction mixture was cooled at -20 °C for 2 h the product was collected, washed with acetonitrile (2 × 50 mL), and dried. The brown crystalline product obtained at this point was pure by the ¹H NMR criterion and was suitable for use in other reactions. An analytical sample was obtained by extraction of this solid with 300 mL of acetonitrile (leaving a residue of 4.1 g (57%)). The extract was concentrated to 200 mL and was cooled overnight at -20 °C. The solid was collected, washed with 50 mL of acetonitrile, and dried; 1.3 g (18%) of pure brown-black crystalline product was obtained. Anal. Calcd for C₅₆H₁₁₀Cl₈Fe₆Mo₂N₂O₄S₁₄: C, 31.10; H, 5.12; Cl, 13.11; Fe, 15.49; Mo, 8.87; N, 2.60; S, 20.75. Found: C, 30.49; H, 5.00; Cl, 13.15; Fe, 15.90; Mo, 9.09; N, 2.56; S, 20.75. Absorption spectrum (acetonitrile): λ_{max}

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390 (ϵ_M 36 300), 300 (sh, 48 000), 260 (sh, 64 400) nm. $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$): -52.6 (CH_2), -4.30 (CH_3) ppm. Treatment of the reaction mixture filtrate with 2.1 g (10 mmol) of Et_4NBr followed by volume reduction to ~ 60 mL and storage at -20°C for several days gave a dark red precipitate. This material was collected, washed with 1:1 v/v ether/acetonitrile, dried, and extracted with 2×40 mL of propionitrile. The extracts were combined and stored at -20°C for ~ 24 h. The dark red crystals were collected, washed with 1:1 v/v ether/propionitrile, and dried. This material was identified as $(\text{Et}_4\text{N})_3[\text{Fe}(\text{Cl}_4\text{cat})_3]$ (61%) by absorption spectral comparison with an authentic sample prepared by the reaction of $(\text{Et}_4\text{N})[\text{FeCl}_4]$ with 3 equiv of $\text{Na}_2\text{C}_6\text{Cl}_4\text{O}_2$ and excess Et_4NBr in acetonitrile.

$(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{Cl}_4\text{cat})_2]$. A slurry of 3.7 g (1.4 mmol) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6(\text{Cl}_4\text{cat})_2]$ in 250 mL of acetonitrile was treated with a solution of $p\text{-ClC}_6\text{H}_4\text{SH}$ (1.6 g, 11 mmol) in 100 mL of acetonitrile. The reaction mixture was stirred for 40 min at ambient temperature with periodic evacuation to remove liberated ethanethiol. The volume was reduced to ~ 100 mL and the dense crystalline suspension was stored overnight at -20°C . The solid was collected, washed with 50 mL of 3:1 v/v ether/acetonitrile, and dried to give 2.87 g (64%) of brown-black microcrystalline product. The combined filtrate and washings were condensed to a volume of 30 mL and were diluted with 20 mL of ether; crystallization was allowed to proceed overnight at ambient temperature and then for 24 h at -20°C . The solid was collected, washed with a small portion of 3:1 v/v ether/acetonitrile, and dried to yield an additional 0.70 g (16%) of product. The two crops of product were pure ($^1\text{H NMR}$ spectra) and usable in other reactions. An analytical sample was obtained by recrystallization from acetonitrile/ether and then from cold acetonitrile. Anal. Calcd for $\text{C}_{80}\text{H}_{104}\text{Cl}_4\text{Fe}_6\text{Mo}_2\text{N}_4\text{O}_4\text{S}_{14}$: C, 36.15; H, 3.94; Cl, 18.67; Fe, 12.61; Mo, 7.22; N, 2.11; S, 16.89. Found: C, 36.79; H, 4.01; Cl, 18.35; Fe, 12.32; Mo, 7.06; N, 2.13; S, 16.75. Absorption spectrum (acetonitrile): λ_{max} 448 (ϵ_M 37 000), 356 (43 900) nm. $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$): -13.5 ($m\text{-H}$), $+3.1$ ($br, o\text{-H}$) ppm.

Catecholate Exchange Reactions. (a) $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{cat})_2]$. A slurry of 1.10 g (0.43 mmol) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{al}_2\text{cat})_2]^5$ in 100 mL of acetonitrile was treated with 1.29 g (11.7 mmol) of catechol (catH_2) in a small volume of acetonitrile, after which the mixture became homogeneous. The solution was stirred for 2 h and then condensed to a volume of 20 mL. A dark, oily solid and a nearly colorless supernatant were produced by addition of 80 mL of ether and cooling overnight at -20°C . After the supernatant was decanted the oily residue was dissolved in 30 mL of THF, and this solution was treated with 80 mL of ether. The precipitated oil slowly solidified as the mixture was stirred overnight. The solid was collected and dissolved in 20 mL of acetonitrile. This solution was diluted with 20 mL of ether and was cooled slowly to -20°C . The solid was collected, washed with ether, and dried; 0.63 g (61%) of pure brown-black crystalline product was obtained. Anal. Calcd for $\text{C}_{80}\text{H}_{112}\text{Cl}_6\text{Fe}_6\text{Mo}_2\text{N}_4\text{O}_4\text{S}_{14}$: C, 40.33; H, 4.74; Cl, 8.93; Fe, 14.07; Mo, 8.05; N, 2.35; S, 18.84. Found: C, 41.04; H, 4.43; Cl, 8.86; Fe, 14.23; Mo, 7.70; N, 2.35; S, 18.66. Absorption spectrum (acetonitrile): λ_{max} 432 (sh, ϵ_M 28 300), 348 (sh, 35 400) nm. $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$): -13.32 ($m\text{-H}$), -10.58 ($\text{cat-H}(4,5)$), -8.92 ($\text{cat-H}(3,6)$), $+2.7$ ($br, o\text{-H}$) ppm. Although stored anaerobically, the compound decomposed over the course of several months.

(b) $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{Cl}_4\text{cat})_2]$. A procedure similar to that preceding was followed in a reaction system containing 0.77 g (0.30 mmol) of the initial cluster and 1.53 g (6.17 mmol) of $o\text{-C}_6\text{Cl}_4(\text{OH})_2$ in 80 mL of acetonitrile. The crude product was separated from the excess catechol by precipitation from the acetonitrile solution with ether and reprecipitation from the THF solution with ether. Recrystallization from acetonitrile afforded 0.60 g (74%) of brown-black microcrystals identical in all respects with that obtained by the different method described above.

$(\text{Et}_4\text{N})_3[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{Cl}_4\text{cat})(\text{CN})]$. Reaction of a slurry of 1.0 g (0.40 mmol) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6(\text{Cl}_4\text{cat})_2]$ and 0.16 g (1.0 mmol) of $(\text{Et}_4\text{N})\text{CN}^{18}$ in 65 mL of acetonitrile produced a homogeneous solution. Solvent (25 mL) was removed and the mixture was filtered. The filtrate was condensed to 20 mL, and 60 mL of acetone was added. The solution was cooled to -20°C and crystallization, induced by scratching, was allowed to proceed overnight. The solid was collected, washed with acetone, and dried to give 0.70 g (61%) of black crystalline product. The filtrate from dissolution of this material in 25 mL of acetonitrile was reduced in volume to 15 mL and diluted with three volumes of acetone. This mixture was seeded with crystals from the first isolation, allowed to stand overnight at ambient temperature, and stored

at 5°C for 48 h. The purified product was obtained as black crystals after being washed with acetone and dried. Anal. Calcd for $\text{C}_{35}\text{H}_{72}\text{Cl}_4\text{Fe}_3\text{MoN}_4\text{O}_2\text{S}_7$: C, 35.90; H, 6.11; Cl, 11.46; Fe, 13.54; Mo, 7.75; N, 4.53; S, 18.13. Found: C, 35.83; H, 6.10; Cl, 11.52; Fe, 13.33; Mo, 7.60; N, 4.47; S, 18.26. Absorption spectrum (acetonitrile): λ_{max} 390 (ϵ_M 17 700), 304 (sh, 22 700), 260 (33 000) nm. $^1\text{H NMR}$ (CD_3CN): -79.0 (2, CH_2), -38.3 (4, CH_2), -6.00 (3, CH_2), -4.00 (~ 6 , CH_3) ppm.

$(\text{Et}_4\text{N})_3[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{Cl}_4\text{cat})(\text{CN})]$. A solution of 1.1 g (0.40 mmol) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{Cl}_4\text{cat})_2]$ in 100 mL of acetonitrile was treated with a solution of 0.13 g (0.84 mmol) of $(\text{Et}_4\text{N})\text{CN}^{18}$ in 20 mL of acetonitrile. The mixture was filtered, concentrated to 20 mL, and diluted with 30 mL of ether. The dense crystalline suspension was stored overnight at -20°C . The solid was collected, washed with 2:1 v/v ether/propionitrile and ether, and dried; 0.99 g (82%) of golden-brown microcrystalline product was obtained. An analytical sample was prepared by recrystallization from acetonitrile/ether. Anal. Calcd for $\text{C}_{49}\text{H}_{72}\text{Cl}_3\text{Fe}_3\text{MoN}_4\text{O}_2\text{S}_7$: C, 39.62; H, 4.89; Cl, 16.71; Fe, 11.28; Mo, 6.46; N, 3.77; S, 15.11. Found: C, 39.71; H, 4.67; Cl, 16.69; Fe, 11.38; Mo, 6.44; N, 3.79; S, 15.19. Absorption spectrum (acetonitrile): λ_{max} 443 (ϵ_M 17 900), 350 (22 200), 265 (51 500) nm. $^1\text{H NMR}$ (CD_3CN): -17.7 (2, $m\text{-H}$), -11.3 (4, $m\text{-H}$), $+9.0$ ($br, o\text{-H}$) ppm.

$(\text{Et}_4\text{N})_3[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{N}_3]$. A solution of 0.068 g (0.39 mmol) of $(\text{Et}_4\text{N})\text{N}_3$ in 25 mL of acetonitrile was slowly added to a filtered solution prepared from 0.508 g (0.199 mmol) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{al}_2\text{cat})_2]^5$ in 125 mL of acetonitrile. The reaction mixture was stirred for 2 h, and its volume was reduced to ~ 30 mL. The mixture was maintained at -20°C for ~ 40 h. Dry ether (45 mL) was added, and the mixture was stored at -20°C for 48 h. The solid was collected by filtration, washed with ether, and dried. The pure product was obtained as 0.180 g (63%) of black crystalline solid. Anal. Calcd for $\text{C}_{54}\text{H}_{84}\text{Cl}_3\text{Fe}_3\text{MoN}_6\text{O}_2\text{S}_7$: C, 44.92; H, 5.86; Cl, 7.36; Fe, 11.60; Mo, 6.64; N, 5.82; S, 15.54. Found: C, 44.72; H, 5.66; Cl, 7.41; Fe, 11.39; Mo, 6.49; N, 5.85; S, 15.66. IR: $\nu_{\text{N}_3} = 2032$ cm^{-1} (mull); $\mu = 4.08$ μ_B (acetonitrile, 298 K).

$(\text{Et}_4\text{N})_2[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{PhNHNH}_2)]$. A solution of 0.090 g (0.83 mmol) of phenylhydrazine in 25 mL of acetonitrile was slowly added to a solution prepared from 0.508 g (0.199 mmol) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{al}_2\text{cat})_2]^5$ in 125 mL of acetonitrile. After the reaction mixture was stirred for 1 h, its volume was reduced to ~ 15 mL. The mixture was maintained at -20°C for 4 days. The solid was collected by filtration and dried. The pure product was obtained as 0.153 g (55%) of black crystalline solid. Anal. Calcd for $\text{C}_{52}\text{H}_{72}\text{Cl}_3\text{Fe}_3\text{MoN}_4\text{O}_2\text{S}_7$: C, 45.27; H, 5.26; Cl, 7.71; Fe, 12.14; Mo, 6.55; N, 4.06; S, 16.26. Found: C, 45.12; H, 5.31; Cl, 7.73; Fe, 11.90; Mo, 6.76; N, 4.10; S, 16.21. $\mu = 3.90$ μ_B (acetonitrile, 298 K).

X-ray Structural Determinations. For the three compounds whose structures have been determined, crystal data, intensity collection information, and structure refinement parameters are provided in Table I. Diffraction experiments were performed at $\sim 25^\circ\text{C}$ with a Nicolet R3m four-circle automated diffractometer using graphite-monochromatized $\text{Mo K}\alpha$ radiation. Computer programs were those of the SHELXTL structure determination package (Nicolet XRD Corporation, Fremont, CA). Atomic scattering factors were taken from a standard source.¹⁹

Collection and Reduction of X-ray Data. (a) $(\text{Et}_4\text{N})_3[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{cat})_2]$. Crystals suitable for diffraction experiments were obtained by slow cooling of a warm (45°C) saturated propionitrile solution. A black, irregularly shaped crystal was mounted with Apiezon grease in a glass capillary under an argon atmosphere and the capillary was flame sealed. The final orientation matrix and unit cell parameters were determined from 25 machine-centered reflections having $15^\circ \leq 2\theta \leq 25^\circ$. Selected ω scans were symmetrical and exhibited half-widths of 0.38–0.42°. Three standard reflections, examined after every 60 measurements, showed no sign of decay during the course of the data collection. Data reduction, including Lorentz and polarization corrections, was carried out with the program XTAPE. An empirical absorption correction based on intensity profiles of seven reflections over a range of settings (ψ) of the diffraction vector was applied to the data with the program XEMP. Systematic absences $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) unambiguously established the space group in the monoclinic system as $P2_1/n$.

(b) $(\text{Et}_4\text{N})_3[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{Cl}_4\text{cat})(\text{CN})]$. Thin black plates were obtained from acetone/acetonitrile solution as described for the preparation of the analytical sample. A single crystal (major faces (0,0,1)-(0,0,1)) was mounted under an argon atmosphere in a glass capillary with the aid of hydrocarbon grease, and the capillary was flame sealed. The final orientation matrix and unit cell parameters were determined from

(18) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3678. Andreades, S.; Zahnow, E. W. *Ibid.* **1969**, *91*, 4181.

(19) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for (Et₄N)₄[Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂], (Et₄N)₃[MoFe₃S₄(SEt)₃(Cl₄cat)(CN)], and (Et₄N)₃[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)N₃].MeCN

formula	C ₃₁₁ H ₁₁₂ Cl ₆ Fe ₆ Mo ₂ N ₄ O ₄ S ₁₄	C ₃₇₇ H ₇₅ Cl ₄ Fe ₃ MoN ₄ O ₂ S ₇	C ₄₁₁ H ₇₂ Cl ₇ Fe ₃ MoN ₆ O ₂ S ₇ ·C ₂ H ₃ N
mol. wt.	2382.32	1237.72	1541.25
<i>a</i> , Å	18.25 (2)	22.793 (5)	19.158 (9)
<i>b</i> , Å	22.08 (3)	19.274 (3)	18.56 (1)
<i>c</i> , Å	26.21 (3)	12.456 (2)	20.15 (1)
β, deg	99.43 (10)		105.96 (5)
crystal system	monoclinic	orthorhombic	monoclinic
<i>V</i> , Å ³	10423 (24)	5472 (1)	6890 (7)
<i>Z</i>	4	4	4
<i>d</i> _{calcd.} , g/cm ³	1.52	1.50	1.49
<i>d</i> _{obsd.} ^a , g/cm ³	1.53	<i>d</i>	<i>d</i>
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pnma</i>	<i>P</i> 2 ₁ / <i>n</i>
crystal dimensions, mm	0.45 × 0.40 × 0.25	0.57 × 0.19 × 0.08 ^b	0.67 × 0.34 × 0.09 ^b
radiation	Mo Kα (λ 0.71069 Å)	Mo Kα (λ 0.71069 Å)	Mo Kα (λ 0.71069 Å)
absorption coeff, μ, cm ⁻¹	14.27	14.48	22.8
transmission factors (max/min)	0.48/0.42	1.00/0.34	0.24/0.19
scan speed, deg/min	2.93–29.3 (θ/2θ scan)	2.02–29.3 (θ/2θ scan)	2.02–29.3 (θ/2θ scan)
scan range, deg	2.0 + (2θKα ₁ - 2θKα ₂)	2.2 + (2θKα ₁ - 2θKα ₂)	2.0 + (2θKα ₁ - 2θKα ₂)
background/scan time ratio	0.25	0.30	0.25
data collected	2–40° (+ <i>h</i> , + <i>k</i> , ± <i>l</i>)	4.5–25° (- <i>h</i> , - <i>k</i> , - <i>l</i>) 4.5–50° (+ <i>h</i> , + <i>k</i> , + <i>l</i>)	3–50° in 2θ (± <i>h</i> , -1 to + <i>k</i> , -1 to + <i>l</i>)
total reflections	10555	5382	12217
<i>R</i> _{merge} , % ^c	14.3	2.8	5.9
unique data (<i>F</i> _o ² > 2.5σ(<i>F</i> _o ²))	3364	2035	5062
no. of variables	474	226	464
goodness of fit ^e	1.8	1.5	1.9
<i>R</i> , %	8.7	7.4	7.6
<i>R</i> _w , %	8.4	7.1	7.7

^a Determined by flotation in CCl₄/cyclohexane. ^b Plate-shaped crystal. ^c $R_{\text{merge}} = \frac{1}{N} \sum_{j=1}^{N_i} \frac{|F_j - \bar{F}_j|}{\sum_{j=1}^{N_i} F_j^2}^{1/2}$, where *N*_{*i*} is the number of reflections in a given set, *F*_{*j*} is one member of the set, and \bar{F}_j is the mean. ^d Not determined. ^e Weights for the least squares were calculated from the expression $w = 1/(\sigma^2(F) + 0.0009(F^2))$.

25 machine-centered reflections having 17° ≤ 2θ ≤ 27°. Selected ω scans displayed half-widths of ca. 0.26°, and the scans were well resolved from background. Three standard reflections, examined after every 60 measurements, showed no signs of decay during the course of the data collection. Data reduction and an empirical absorption correction (based on seven intensity profiles) were performed as above. Axial rotation photographs and the systematic absences *Ok*l (*k* + *l* ≠ 2*n*) and *hk*0 (*h* ≠ 2*n*) were consistent with orthorhombic space groups *Pnma* or *Pn*2₁*a*, a nonstandard setting of *Pna*2₁. Simple E statistics favored the centric space group, which was employed for the initial solution and refinement.

(c) (Et₄N)₃[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)N₃].MeCN. This compound was prepared by the reaction of (Et₄N)₃ with (Et₄N)₂[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)(MeCN)]. Plate-like crystals were grown by slow diffusion of ether into an acetonitrile solution of the recrystallized reaction product. A single crystal was mounted under argon in a glass capillary. The final orientation matrix and unit cell parameters were determined from 25 machine-centered reflections having 25° ≤ 2θ ≤ 30°. Selected ω scans displayed half-widths of ca. 0.32°, and the scans were well resolved from background. Data collection was performed with θ/2θ scans. Three standard reflections, examined after every 60 measurements, showed no signs of decay during the course of the data collection. Data reduction and an empirical absorption correction (based on the intensity profiles for eight reflections) were performed as above. The systematic absences *h*0*l* (*h* + *l* ≠ 2*n*) and *0k*0 (*k* ≠ 2*n*) uniquely determined the space group in the monoclinic system as *P*2₁/*n*.

Solution and Refinement of Structures. (a) (Et₄N)₄[Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]. The direct methods option SOLV of the x program was employed. Trial positions of the Mo, Fe, and core S atoms were taken from the E map derived from the unique phase set with the next-to-highest combined figure of merit. The remaining non-hydrogen atoms were located by subsequent difference Fourier maps. The asymmetric unit consists of a complete anion and four counterions. The structure was refined by the blocked-cascade least-squares method. No correction was made for the presence of extinction. All Mo, Fe, S, and Cl atoms except Cl(1) were refined anisotropically; remaining atoms had isotropic temperature coefficients. Phenyl rings were treated as rigid, regular hexagons with a C–C bond length of 1.395 Å. Counterions 1 and 2 were unexceptional and were refined without constraints. Cations 3 and 4 were severely disordered; these were treated as rigid groups with C–N and C–C bond lengths of 1.49 and 1.54 Å, respectively, and with idealized angles about the central N atom. Chemically equivalent C atoms in the disordered cations were refined with common isotropic temperature factors. Fixed contributions for the hydrogen atoms (C–H bond length of 0.96 Å) with thermal parameters set to 1.2× that of the bonded carbon

were included in the final stages of the refinement for all appropriate carbon atoms except those of the disordered cations.

(b) (Et₄N)₃[MoFe₃S₄(SEt)₃(Cl₄cat)(CN)]. The direct methods option SOLV of the x program was employed. The three phase sets with the highest combined figures of merit were identical but for choice of origin, and the set with the most convenient fractional coordinates for the trial positions of the Mo, Fe, and S atoms was selected. The positions of the remaining non-hydrogen atoms were determined by subsequent difference Fourier maps. The asymmetric unit for this initial model contained 0.5 of the anion and 1.5 cations; the remaining atoms were generated by reflection through the mirror plane at *y* = 1/4. In the course of refinement, inspection of certain interatomic dimensions and thermal motion parameters suggested that the anion could not be modeled with crystallographically imposed mirror symmetry. Comparison of the intensities of Friedel pairs did not indicate a noncentrosymmetric space group, and attempted refinements in *Pn*2₁*a* were ill-behaved and failed to converge. Consequently, a disordered treatment in the centrosymmetric space group was necessary. The asymmetric unit of the final model consisted of one complete cation at a general position, one half-cation on the mirror plane at *y* = 1/4, and one complete anion of half-occupancy. The remaining cation atoms are generated by reflection symmetry; the Et₄N⁺ ions are well-ordered and exhibit no exceptional features. The atoms Mo, S(2), C(1), and N(1) are constrained to lie in the mirror plane; this crystallographic symmetry element is no longer a perfect bisector of the catecholate ring, nor is it a cube diagonal plane. Reflection in the mirror plane results in the superposition of two half-occupancy anions; in the final refined model the mirror-related vectors Mo–Fe(1) and Mo–Fe(1') subtend an angle of 11.3°. This model was refined by the full-matrix least-squares method. No correction was made for the presence of extinction. Bond lengths formally equivalent under exact C₂ symmetry were set equal to a refined variable by the method of added observational equations. Anisotropic thermal parameters were refined for the Mo, Fe, S(2,3,5), C(1), and N(1) atoms. Remaining S and Cl atoms have independent isotropic thermal parameters; remaining O and C atoms of the anion that were previously related by the idealized mirror plane were refined with common isotropic temperature factors. Fixed contributions from the hydrogen atoms (C–H bond length of 0.96 Å) with thermal parameters set at 1.2× that of the bonded carbon atom were included in the final stages of the refinement.

(c) (Et₄N)₃[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)N₃].MeCN. Trial positions of the core Mo, Fe, and S atoms were obtained from the direct-methods solution consistent with the Patterson function, and the remaining non-hydrogen atoms were determined by subsequent difference Fourier maps. The structure was refined by the blocked cascade least-squares method. Hydrogen atom contributions were calculated as described above. All

Table II. Fractional Atom Coordinates ($\times 10^4$) of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{cat})_2]^{4-}$

atom	x	y	z
Mo(1)	4925 (2) ^a	2861 (1)	1819 (1)
Mo(2)	1607 (2)	2745 (1)	1833 (1)
Fe(1)	3617 (2)	2962 (2)	1173 (2)
Fe(2)	4732 (3)	2354 (2)	850 (2)
Fe(3)	4780 (3)	3576 (2)	950 (2)
Fe(4)	2906 (3)	2706 (2)	2508 (2)
Fe(5)	1820 (3)	1924 (2)	2633 (2)
Fe(6)	1687 (3)	3126 (2)	2844 (2)
S(1)	4124 (5)	2068 (4)	1497 (4)
S(2)	4193 (5)	3739 (4)	1628 (3)
S(3)	3981 (5)	3048 (5)	372 (4)
S(4)	5730 (5)	2912 (4)	1184 (4)
S(5)	2455 (4)	1941 (4)	1968 (3)
S(6)	2278 (5)	3568 (4)	2244 (4)
S(7)	2516 (5)	2457 (4)	3268 (3)
S(8)	783 (5)	2513 (5)	2424 (4)
S(9)	2332 (4)	2923 (4)	1033 (3)
S(10)	4934 (5)	1562 (5)	333 (4)
S(11)	5160 (6)	4413 (5)	566 (4)
S(12)	4192 (5)	2696 (4)	2624 (3)
S(13)	1583 (6)	968 (5)	2868 (4)
S(14)	1114 (6)	3743 (5)	3359 (4)
O(1)	5603 (10)	2220 (9)	2224 (7)
O(2)	5656 (11)	3374 (9)	2340 (7)
C(1)	6134 (17)	2460 (15)	2584 (12)
C(2)	6629 (19)	2105 (18)	2929 (13)
C(3)	7227 (22)	2397 (19)	3276 (15)
C(4)	7217 (23)	2982 (20)	3298 (15)
C(5)	6673 (21)	3397 (18)	2969 (14)
C(6)	6153 (16)	3102 (14)	2627 (11)
O(3)	963 (11)	2193 (9)	1308 (7)
O(4)	875 (12)	3346 (10)	1440 (8)
C(7)	496 (19)	2513 (17)	974 (14)
C(8)	11 (22)	2202 (20)	591 (15)
C(9)	-535 (23)	2526 (20)	198 (17)
C(10)	-514 (19)	3111 (17)	287 (13)
C(11)	-99 (18)	3482 (17)	665 (13)
C(12)	422 (20)	3130 (18)	1056 (14)

^a Estimated standard deviation given in parentheses in this and succeeding tables.

atoms of the anion were refined with anisotropic thermal parameters except for the C atoms of the thiolate ligands, which were treated isotropically. The asymmetric unit consists of a complete anion, three complete Et_4N^+ ions, and a molecule of acetonitrile. The counterion containing N(4) is disordered over two orientations differing only in the position of methylene C atoms; the refined occupancies of the two orientations were constrained to a sum of unity and converged to 0.58 (1) and 0.42 (1). The solvate molecule is disordered between three overlapping orientations totalling to five atomic positions, which were refined with a common isotropic temperature factor. No H-atom contribution was included for the acetonitrile molecule. The geometry of the solvent model is very irregular and could not be corrected by the application of observational constraints to the bond lengths. The presence of the acetonitrile solvate molecule was further confirmed by ^1H NMR spectroscopy.

Positional parameters of the three clusters are listed in Tables II-IV; selected interatomic distances and angles are compiled in Tables V and VI.²⁰

Other Physical Measurements. Absorption spectra were determined on a Cary Model 219 spectrophotometer. ^1H NMR spectra were measured at 300 MHz on a Bruker WM-300 spectrometer. Chemical shifts at fields above and below that of Me_4Si internal standard are designated as positive and negative, respectively. Ligands used in the NMR binding studies were commercial samples; anhydrous hydrazine (Aldrich) and phenylhydrazine were distilled from KOH.

Results and Discussion

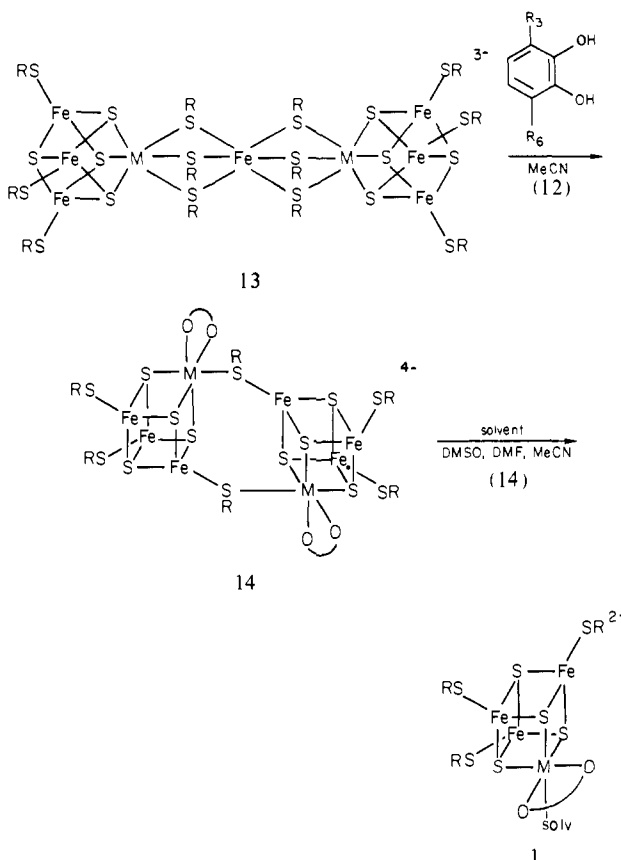
Figure 2 contains specific examples of some of the reactions in Figure 1 which have been investigated in this work. The different reaction types are considered, together with proof of

Table III. Fractional Atom Coordinates ($\times 10^4$) of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6(\text{Pr}_2\text{cat})_2(\text{CN})]^{3-}$

atom	x	y	z
Mo	928 (8)	2500 (0)	794 (1)
Fe(1)	-96 (1)	2640 (3)	1918 (3)
Fe(2)	877 (2)	3261 (3)	2667 (4)
Fe(3)	792 (2)	1857 (3)	2729 (4)
S(1)	404 (3)	3536 (3)	1125 (5)
S(2)	1591 (2)	2500 (0)	2286 (4)
S(3)	233 (3)	2624 (4)	3658 (5)
S(4)	248 (3)	1617 (3)	1242 (5)
S(5)	-1046 (4)	2984 (5)	1849 (7)
S(6)	1235 (4)	4169 (4)	3605 (8)
S(7)	1074 (4)	890 (4)	3623 (8)
Cl(1)	2413 (4)	790 (5)	-563 (8)
Cl(2)	3604 (4)	1500 (6)	-1172 (8)
Cl(3)	3697 (4)	3110 (6)	-1140 (8)
Cl(4)	2581 (5)	3996 (6)	-683 (10)
O(1)	1473 (9)	1802 (12)	-63 (19)
O(2)	1572 (9)	3166 (12)	129 (19)
C(2)	1978 (14)	2097 (16)	-251 (59)
C(3)	2449 (11)	1664 (10)	-540 (31)
C(4)	2996 (8)	1991 (12)	-814 (25)
C(5)	3040 (8)	2684 (11)	-890 (21)
C(6)	2559 (10)	3124 (11)	-578 (31)
C(7)	2014 (14)	2834 (17)	-295 (58)
C(1)	545 (10)	2500 (0)	-822 (19)
N(1)	358 (9)	2500 (0)	-1685 (17)
C(1S)	1592 (19)	4600 (34)	2403 (50)
C(2S)	2128 (18)	4317 (28)	2722 (39)
C(3S)	1630 (19)	420 (34)	2756 (52)
C(4S)	2128 (18)	563 (30)	2146 (36)
C(5S)	-1381 (18)	2713 (21)	3040 (32)
C(6S)	-1650 (27)	2051 (32)	2969 (58)

products obtained from spectroscopic and X-ray diffraction results.

Synthesis of Doubly Bridged Double Cubanes. Reaction 12 has been shown to effect removal of the bridging Fe(III) atom of **13**, affording the doubly bridged double cubanes **14** ($M = \text{Mo}, \text{W}; R = \text{Et}$) as Et_4N^+ salts. Structure **14** has been established for $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6(\text{Pr}_2\text{cat})_2]^{4-}$ by X-ray analysis.⁵ The rationale



(20) See paragraph at the end of this article regarding supplementary material available.

Table IV. Fractional Atom Coordinates (×10⁴) of [Mo₂Fe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)N₃]³⁻

atom	x	y	z
Mo	8788 (1)	5878 (1)	2230 (1)
Fe(1)	7346 (1)	5950 (1)	1537 (1)
Fe(2)	8208 (1)	5012 (1)	1108 (1)
Fe(3)	8331 (1)	6436 (1)	917 (1)
S(1)	7904 (2)	4966 (2)	2122 (2)
S(2)	9249 (2)	5638 (2)	1264 (2)
S(3)	7349 (2)	5737 (2)	419 (2)
S(4)	8083 (2)	6920 (2)	1854 (2)
S(5)	6164 (2)	6109 (2)	1528 (2)
S(6)	8170 (2)	3964 (2)	521 (2)
S(7)	8414 (2)	7255 (2)	116 (2)
Cl(1)	11016 (2)	7462 (2)	2992 (2)
Cl(2)	12424 (2)	6582 (3)	3656 (3)
Cl(3)	12319 (2)	4930 (3)	3905 (3)
Cl(4)	10797 (2)	4167 (2)	3450 (3)
Cl(5)	6205 (4)	5882 (3)	4661 (3)
Cl(6)	938 (3)	2082 (3)	1821 (4)
Cl(7)	927 (3)	9474 (3)	1298 (3)
O(1)	9684 (5)	6559 (5)	2599 (5)
O(2)	9594 (5)	5163 (5)	2800 (5)
N(1)	8609 (7)	6076 (8)	3233 (7)
N(2)	9073 (7)	6250 (7)	3744 (7)
N(3)	9502 (9)	6453 (9)	4232 (8)
C(1)	6193 (8)	6087 (8)	2429 (7)
C(2)	6769 (10)	6241 (10)	2897 (9)
C(3)	6787 (12)	6192 (11)	3603 (10)
C(4)	6140 (11)	5976 (11)	3789 (10)
C(5)	5605 (11)	5825 (10)	3308 (10)
C(6)	5539 (11)	5856 (10)	2587 (10)
C(7)	8931 (8)	3445 (8)	917 (8)
C(8)	9173 (10)	2938 (9)	518 (9)
C(9)	9778 (10)	2524 (10)	795 (10)
C(10)	10153 (10)	2591 (10)	1454 (9)
C(11)	9962 (11)	3103 (10)	1902 (10)
C(12)	9352 (9)	3530 (9)	1590 (9)
C(13)	9128 (7)	7860 (7)	489 (7)
C(14)	9703 (9)	7681 (9)	1018 (8)
C(15)	10265 (10)	8192 (10)	1260 (9)
C(16)	10227 (9)	8869 (9)	971 (8)
C(17)	9659 (8)	9038 (9)	456 (8)
C(18)	9116 (9)	8527 (8)	185 (8)
C(19)	10286 (8)	6204 (7)	2905 (6)
C(20)	10966 (7)	6545 (8)	3107 (7)
C(21)	11595 (8)	6146 (9)	3424 (7)
C(22)	11538 (7)	5423 (8)	3527 (6)
C(23)	10869 (8)	5080 (8)	3315 (7)
C(24)	10237 (7)	5465 (8)	3017 (7)

Table V. Selected Bond Distances (Å) and Angles (deg) of [Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]⁴⁻

Bond Distances			
Mo(1)-S(1)	2.347 (9)	Mo(2)-S(5)	2.345 (9)
Mo(1)-S(2)	2.362 (9)	Mo(2)-S(6)	2.352 (9)
Mo(1)-S(4)	2.395 (10)	Mo(2)-S(8)	2.384 (10)
Mo(1)-S(12)	2.703 (9)	Mo(2)-S(9)	2.685 (9)
Mo(1)-O(1)	2.057 (18)	Mo(2)-O(3)	2.057 (19)
Mo(1)-O(2)	2.082 (18)	Mo(2)-O(4)	2.039 (21)
Fe(1)-S(1)	2.284 (10)	Fe(4)-S(5)	2.270 (10)
Fe(1)-S(2)	2.250 (9)	Fe(4)-S(6)	2.271 (10)
Fe(1)-S(3)	2.313 (11)	Fe(4)-S(7)	2.290 (11)
Fe(1)-S(9)	2.316 (9)	Fe(4)-S(12)	2.317 (10)
Fe(2)-S(1)	2.264 (11)	Fe(5)-S(5)	2.246 (11)
Fe(2)-S(3)	2.288 (10)	Fe(5)-S(7)	2.255 (10)
Fe(2)-S(4)	2.255 (10)	Fe(5)-S(8)	2.289 (10)
Fe(2)-S(10)	2.279 (12)	Fe(5)-S(13)	2.260 (12)
Fe(3)-S(2)	2.250 (11)	Fe(6)-S(6)	2.269 (11)
Fe(3)-S(3)	2.249 (10)	Fe(6)-S(7)	2.270 (10)
Fe(3)-S(4)	2.276 (10)	Fe(6)-S(8)	2.274 (10)
Fe(3)-S(11)	2.267 (12)	Fe(6)-S(14)	2.288 (13)
O(1)-C(1)	1.346 (33)	O(3)-C(7)	1.322 (39)
O(2)-C(6)	1.237 (33)	O(4)-C(12)	1.287 (41)
C(1)-C(2)	1.408 (45)	C(7)-C(8)	1.403 (51)
C(1)-C(6)	1.421 (45)	C(7)-C(12)	1.390 (54)
C(2)-C(3)	1.453 (50)	C(8)-C(9)	1.493 (55)
C(3)-C(4)	1.294 (61)	C(9)-C(10)	1.312 (58)
C(4)-C(5)	1.513 (55)	C(10)-C(11)	1.406 (48)
C(5)-C(6)	1.360 (45)	C(11)-C(12)	1.495 (49)
S(9)-C(13)	1.719 (27)	S(12)-C(31)	1.753 (24)
S(10)-C(19)	1.741 (25)	S(13)-C(37)	1.768 (23)
S(11)-C(25)	1.762 (26)	S(14)-C(43)	1.814 (25)

Angles			
S(1)-Mo(1)-S(2)	103.8 (3)	S(5)-Mo(2)-S(6)	103.6 (3)
S(1)-Mo(1)-S(4)	101.7 (3)	S(5)-Mo(2)-S(8)	102.2 (3)
S(1)-Mo(1)-S(12)	79.7 (3)	S(5)-Mo(2)-S(9)	80.2 (3)
S(1)-Mo(1)-O(1)	87.6 (6)	S(5)-Mo(2)-O(3)	86.7 (6)
S(2)-Mo(1)-S(4)	101.8 (3)	S(6)-Mo(2)-S(8)	101.8 (4)
S(2)-Mo(1)-S(12)	86.6 (3)	S(6)-Mo(2)-S(9)	87.6 (3)
S(2)-Mo(1)-O(2)	88.4 (6)	S(6)-Mo(2)-O(4)	88.7 (6)
S(4)-Mo(1)-O(1)	90.3 (6)	S(8)-Mo(2)-O(3)	87.5 (6)
S(4)-Mo(1)-O(2)	91.8 (6)	S(8)-Mo(2)-O(4)	92.2 (7)
S(12)-Mo(1)-O(1)	80.7 (6)	S(9)-Mo(2)-O(3)	82.2 (6)
S(12)-Mo(1)-O(2)	84.7 (6)	S(9)-Mo(2)-O(4)	82.9 (7)
O(1)-Mo(1)-O(2)	76.7 (7)	O(3)-Mo(2)-O(4)	78.0 (8)
S(1)-Fe(1)-S(2)	109.6 (3)	S(5)-Fe(4)-S(6)	108.7 (3)
S(1)-Fe(1)-S(3)	104.4 (4)	S(5)-Fe(4)-S(7)	103.4 (4)
S(2)-Fe(1)-S(3)	103.9 (4)	S(6)-Fe(4)-S(7)	104.6 (4)
S(1)-Fe(2)-S(3)	105.9 (4)	S(5)-Fe(5)-S(7)	105.4 (4)
S(1)-Fe(2)-S(4)	108.9 (4)	S(5)-Fe(5)-S(8)	108.5 (4)
S(3)-Fe(2)-S(4)	102.7 (4)	S(7)-Fe(5)-S(8)	102.9 (4)
S(2)-Fe(3)-S(3)	105.9 (4)	S(6)-Fe(6)-S(7)	105.4 (4)
S(2)-Fe(3)-S(4)	109.3 (4)	S(6)-Fe(6)-S(8)	108.0 (4)
S(3)-Fe(3)-S(4)	103.2 (4)	S(7)-Fe(6)-S(8)	102.8 (4)
Mo(1)-S(1)-Fe(1)	71.3 (3)	Mo(2)-S(5)-Fe(4)	72.1 (3)
Mo(1)-S(1)-Fe(2)	73.1 (3)	Mo(2)-S(5)-Fe(5)	73.6 (3)
Fe(1)-S(1)-Fe(2)	72.5 (3)	Fe(4)-S(5)-Fe(5)	73.1 (3)
Mo(1)-S(2)-Fe(1)	71.7 (3)	Mo(2)-S(6)-Fe(4)	72.0 (3)
Mo(1)-S(2)-Fe(3)	73.1 (3)	Mo(2)-S(6)-Fe(6)	73.4 (3)
Fe(1)-S(2)-Fe(3)	72.6 (3)	Fe(4)-S(6)-Fe(6)	72.6 (3)
Fe(1)-S(3)-Fe(2)	71.5 (3)	Fe(4)-S(7)-Fe(5)	72.5 (3)
Fe(1)-S(3)-Fe(3)	71.5 (3)	Fe(4)-S(7)-Fe(6)	72.3 (3)
Fe(2)-S(3)-Fe(3)	73.4 (3)	Fe(5)-S(7)-Fe(6)	74.3 (3)
Mo(1)-S(4)-Fe(2)	72.3 (3)	Mo(2)-S(8)-Fe(5)	72.1 (3)
Mo(1)-S(4)-Fe(3)	72.0 (3)	Mo(2)-S(8)-Fe(6)	72.7 (3)
Fe(2)-S(4)-Fe(3)	73.5 (3)	Fe(5)-S(8)-Fe(6)	73.5 (3)
Mo(2)-S(9)-Fe(1)	119.9 (3)	Mo(1)-S(12)-Fe(1)	121.1 (3)
Mo(2)-S(9)-C(13)	112.9 (11)	Mo(1)-S(12)-C(31)	114.3 (9)
Fe(1)-S(9)-C(13)	102.7 (10)	Fe(4)-S(12)-C(31)	101.4 (8)
Mo(1)-O(1)-C(1)	113.1 (18)	Mo(2)-O(3)-C(7)	111.2 (20)
Mo(1)-O(2)-C(6)	117.5 (19)	Mo(2)-O(4)-C(12)	116.1 (21)

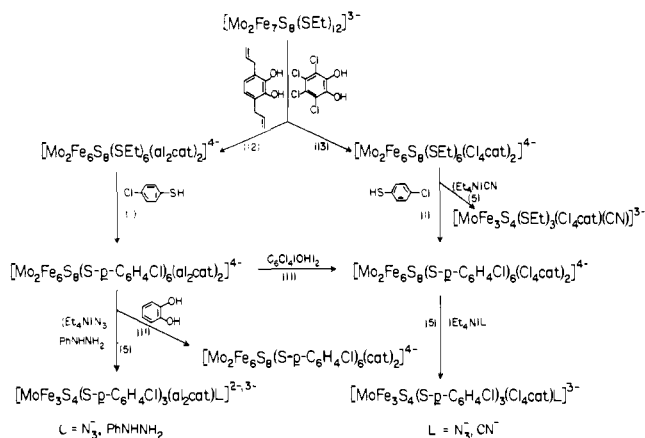


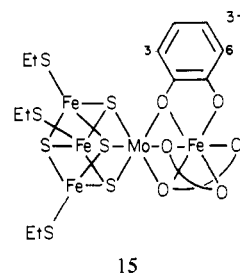
Figure 2. Summary of cluster reactions carried out in this investigation. The formulas of isolated products are given; in solution the doubly bridged double cubanes are converted to the solvated single cubanes **1**.

of using bulky 3,6-disubstituted catechols followed from expected steric destabilization of [MoFe₄S₄(SET)₃(cat)]³⁻ (**15**) by interaction of sufficiently large catecholates 3-substituents and nearby EtS groups. Cluster **15** is the (only isolated) product from an analogous cluster system containing catechol itself.²¹ Here

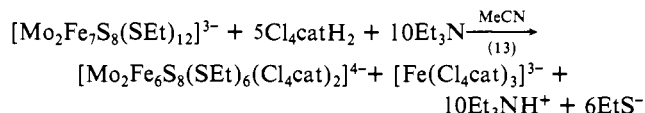
Table VI. Selected Interatomic Distances (Å) and Angles (deg) of [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)(N₃)³⁻ (A) and [MoFe₃S₄(S*t*)₃(Cl₄cat)(CN)³⁻ (B)^a

	A	B
Distance		
Mo-S(2)	2.391 (5)	2.396 (6)
Mo-S(1)	2.361 (4)	2.363 (5)
Mo-S(4)	2.361 (4)	2.368 (5)
Mo-O(1)	2.098 (9)	2.119 (10)
Mo-O(2)	2.120 (9)	2.119 (10)
Mo-N(1)/Mo-C(1)	2.172 (15)	2.194 (25)
Mo...Fe(1)	2.735 (2)	2.737 (4)
Mo...Fe(2)	2.747 (2)	2.759 (4)
Mo...Fe(3)	2.751 (2)	2.727 (4)
Fe(1)-S(1)	2.275 (4)	2.295 (8)
Fe(1)-S(4)	2.270 (4)	2.283 (8)
Fe(1)-S(3)	2.289 (4)	2.294 (7)
Fe(2)-S(2)	2.255 (4)	2.242 (6)
Fe(3)-S(2)	2.257 (4)	2.272 (6)
Fe(2)-S(3)	2.279 (4)	2.278 (7)
Fe(3)-S(3)	2.279 (4)	2.268 (7)
Fe(2)-S(1)	2.274 (5)	2.266 (6)
Fe(3)-S(4)	2.258 (5)	2.277 (6)
Fe(1)...Fe(3)	2.690 (3)	2.720 (6)
Fe(1)...Fe(2)	2.699 (3)	2.690 (6)
Fe(2)...Fe(3)	2.691 (3)	2.713 (7)
Fe(1)-S(5)	2.279 (5)	2.265 (10)
Fe(2)-S(6)	2.268 (4)	2.256 (6)
Fe(3)-S(7)	2.253 (5)	2.264 (6)
Angle		
S(2)-Mo-O(1)	87.2 (3)	91.2 (7)
S(2)-Mo-O(2)	87.0 (3)	82.3 (7)
S(2)-Mo-N(1)/S(2)-Mo-C(1)	167.8 (3)	164.3 (6)
S(2)-Mo-S(1)	102.0 (1)	100.6 (2)
S(2)-Mo-S(4)	101.4 (1)	103.2 (2)
S(1)-Mo-S(4)	103.0 (1)	103.6 (4)
S(1)-Mo-O(2)	89.9 (3)	84.6 (8)
S(4)-Mo-O(1)	87.7 (3)	92.7 (8)
O(1)-Mo-O(2)	77.4 (3)	77.3 (5)
Mo-N(1)-N(2)	124.9 (12)	
Mo-C(1)-N(1)		178.1 (22)
N(1)-N(2)-N(3)	176.5 (16)	
Fe(1)-S(1)-Mo	72.3 (1)	71.9 (2)
Fe(1)-S(4)-Mo	72.4 (1)	72.1 (2)
Fe(2)-S(2)-Mo	72.4 (1)	72.9 (2)
Fe(3)-S(2)-Mo	72.5 (1)	71.5 (2)
Fe(2)-S(1)-Mo	72.7 (1)	73.1 (2)
Fe(3)-S(4)-Mo	73.1 (1)	71.9 (2)
Fe(2)-S(2)-Fe(3)	73.2 (1)	73.9 (3)
Fe(2)-S(3)-Fe(3)	72.4 (1)	73.3 (2)
Fe(1)-S(3)-Fe(2)	72.4 (1)	72.1 (2)
Fe(1)-S(3)-Fe(3)	72.2 (1)	73.2 (2)
Fe(1)-S(1)-Fe(2)	72.8 (1)	72.3 (2)
Fe(1)-S(4)-Fe(3)	72.9 (1)	73.3 (3)
S(2)-Fe(2)-S(3)	104.1 (2)	103.2 (2)
S(2)-Fe(3)-S(3)	104.0 (2)	102.7 (2)
S(1)-Fe(2)-S(2)	109.2 (2)	108.6 (3)
S(4)-Fe(3)-S(2)	109.1 (1)	110.5 (3)
S(1)-Fe(2)-S(3)	104.5 (2)	106.2 (3)
S(4)-Fe(3)-S(3)	104.9 (2)	104.0 (3)
S(1)-Fe(2)-S(2)	109.2 (2)	108.6 (3)
S(4)-Fe(3)-S(2)	109.1 (2)	110.5 (3)
S(1)-Fe(1)-S(3)	104.1 (2)	106.2 (3)
S(4)-Fe(1)-S(3)	104.2 (2)	102.9 (3)
S(4)-Fe(1)-S(1)	108.9 (1)	108.7 (3)
S(5)-Fe(1)-S(3)	106.6 (2)	110.6 (3)
S(6)-Fe(2)-S(1)	117.2 (2)	115.4 (4)
S(7)-Fe(3)-S(4)	113.7 (2)	112.8 (4)

^a The clusters possess approximate C_s symmetry, the mirror plane passing through Mo, S(2), Fe(1), and S(3). Those dimensions related by the pseudomirror are listed consecutively.

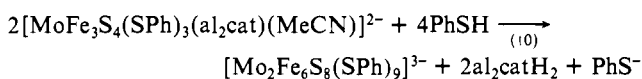


reaction 13 gave the product cluster in >60% yield as its Et₄N⁺ salt when Cl₄catH₂ was used in small excess.²² The isolation of



(Et₄N)₃[Fe(Cl₄cat)₃] in a yield (61%) comparable to that of product **14** reveals the fate of the bridging Fe(III) atom of reactant cluster **13**. If the steric argument is correct substituents as small as a chlorine atom are effective in promoting the formation of **14**. Double cubanes **14** are cleaved in reaction 14 in donor solvents to the solvated single cubanes **1** (M = Mo, W).^{5,10,23} As depicted in Figure 1, these are the reactive species in solution.

Single-Cubane → Double-Cubane Conversion. The ligand exchange reaction 1 (R = Et, R' = Ar) is of substantial synthetic utility.^{5,10,23} On occasion a paramagnetic minority product has been observed by ¹H NMR spectroscopy, particularly if excess thiol is used. The situation is illustrated by the NMR spectra of the reaction system [MoFe₃S₄(SPh)₃(al₂cat)(MeCN)]²⁻/nPhSH in Figure 3. The solution prepared from a slightly impure sample of (Et₄N)₄[Mo₂Fe₆S₈(SPh)₆(al₂cat)₂]⁵⁻ gives a spectrum containing the phenyl and al₂cat ring-H signals of **1** (R = Ph) and also a weak resonance at -13.79 ppm. Addition of increasing quantities of benzenethiol causes diminution and ultimately elimination of the -8.56 and -13.33 ppm resonances of **1**. The final spectrum, at n = 30 equiv, corresponds to that of [Mo₂Fe₆S₈(SPh)₉]³⁻,^{24,25} whose triply bridged double-cubane structure **11** (R = Ph) has been demonstrated by X-ray analysis.²⁶ The limiting stoichiometry of the process, which results in removal of the catecholate ring of **1** and attendant single-cubane → double-cubane conversion, is given in reaction 10. This does not account for



the large excess of thiol required for appreciable conversion in the 0.5-h reaction intervals examined. This matter is considered below. No intermediate clusters were detected in the NMR spectra. The inertness of bridging ligands of **11** to further reactions with thiols²⁷ renders reaction 10 irreversible. Contamination of samples of **14** with **11** can be avoided by careful control of the stoichiometry of reaction 1 and/or purification of products by recrystallization.

Catecholate Exchange Reactions. While reaction 10 is not of synthetic value, its occurrence suggested another type of pro-

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

(22) The product quantity written as 6Et₃NH⁺ + 6EtS⁻ in reaction 13 more likely exists as free amine and thiol in acetonitrile, implying that 4 equiv of reactant amine would suffice. However, because of the sensitivity of clusters to acid the ratio Et₃N/catechol = 2:1 has been used in reactions 12⁵ and 13 to ensure neutralization of all acid formed.

(23) Mascharak, P. K.; Smith, M. C.; Armstrong, W. H.; Burgess, B. K.; Holm, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 7056.

(24) Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2820.

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

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

(27) Palermo, R. E.; Power, P. P.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 173.

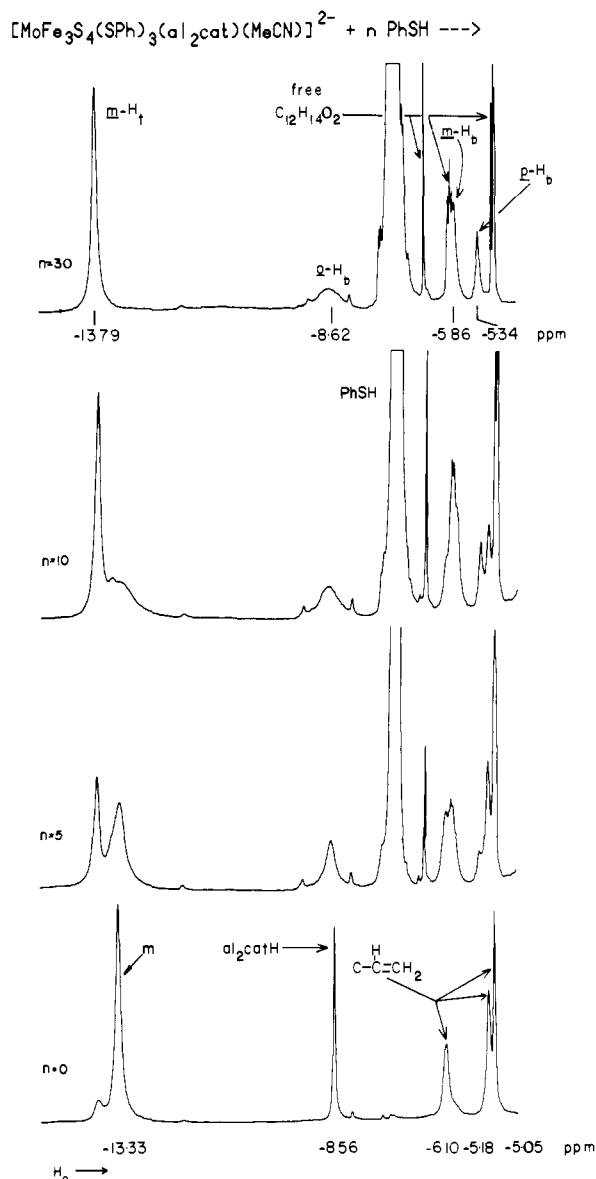


Figure 3. ¹H NMR spectra (297 K) of the system [MoFe₃S₄(SPh)₃(al₂cat)(MeCN)]²⁻ (**1**) + *n* = 0, 5, 10, 30 equiv of PhSH/Mo in CD₃CN solution. Spectra were measured ~0.5 h after the addition of thiol. Signal assignments are indicated (t = terminal, b = bridging ligand of **11**, R = Ph). The upfield region in which (other) *o*-H and *p*-H signals of **1** and **11** occur is not shown. The systems with added thiol are not necessarily at equilibrium.

tonation reaction specific to Mo atom sites, viz., the ligand exchange reaction 11 (Figure 1). Such reactions are expected to be essentially thermoneutral and under statistical control. Treatment of [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(al₂cat)(MeCN)]²⁻ with ~10 equiv of Cl₄catH₂ afforded a 74% yield of the Et₄N⁺ salt of [Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(Cl₄cat)₂]⁴⁻. This material proved identical with that isolated from the reaction of [MoFe₃S₄(SEt)₃(Cl₄cat)(MeCN)]²⁻ and *p*-ClC₆H₄SH. In a similar reaction involving ~14 equiv of catechol (Et₄N)₄[Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]⁴⁻ (61%) was obtained. ¹H NMR spectra in Me₂SO-*d*₆ were consistent with formation of the substituted single cubanes **12** in solution. The spectra revealed retention of thiolate ligands²⁸ and the absence (Cl₄cat) or presence (cat) of catecholate

(28) Note that in the structurally similar cubane clusters [Fe₃S₄(SR)₄]²⁻ thiolate ligands are replaceable by excess phenol to form [Fe₃S₄(OPh)₄]²⁻.²⁹ No products containing catecholate groups bound to Fe sites were isolated in this work.

(29) Cleland, W. E.; Averill, B. A. *Inorg. Chim. Acta* **1981**, *56*, L9. Cleland, W. E.; Holtman, D. A.; Sabat, M.; Ibers, J. A.; DeFotis, G. C.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 6021.

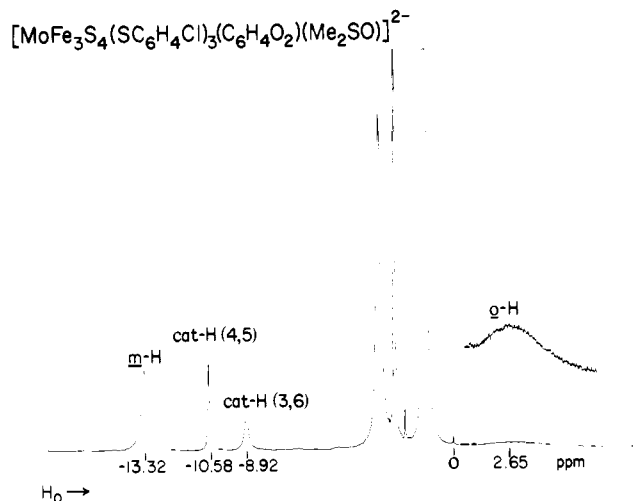


Figure 4. ¹H NMR spectrum (297 K) of the single-cubane **1** formed in a Me₂SO-*d*₆ solution prepared from (Et₄N)₄[Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]. Signal assignments are indicated. The relative integrated intensities are 5.9(*m*-H):2.0(cat-H(4,5)):1.9(cat-H(3,6)).

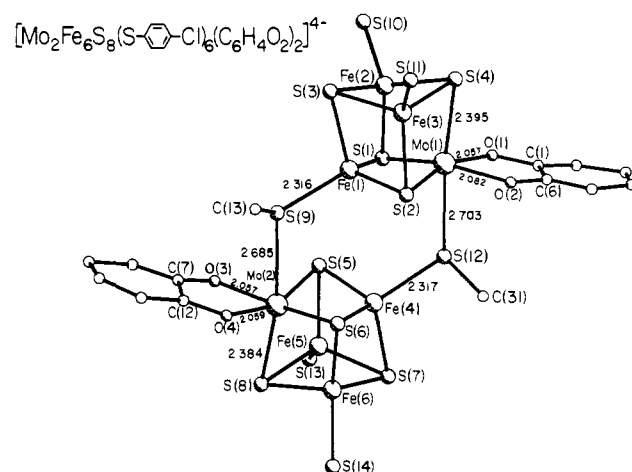


Figure 5. The structure of [Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]⁴⁻ as its Et₄N⁺ salt. Selected bond distances (Å) are given: *p*-C₆H₄Cl groups are omitted for clarity.

ring resonances. The spectrum of the cat-substituted cluster in Me₂SO-*d*₆, shown in Figure 4, is consistent with the solvated cluster structure whose static mirror (*C_s*) symmetry is averaged to trigonal symmetry. Fluxionality at the Mo site has been described earlier in terms of solvent dissociation, degenerate chelate ring reorientation, and solvent rebinding.^{5,6} In the process the Fe sites on (*m*) and related by (*m'*) the mirror plane (**1**, Figure 1) are equilibrated and one set of thiolate resonances is observed. Assignment of the cat-H(4,5) resonance follows from that proven by ligand deuteration in the analogous al₂cat cluster.⁵

In contrast to the facility of reaction 11, a solution of [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(al₂cat)(MeCN)]²⁻ and 13 equiv of the 1,3-diol resorcinol evidenced no appreciable reaction. The starting cluster was obtained in 80% recovery. Comparable results were obtained at temperatures up to 80 °C.

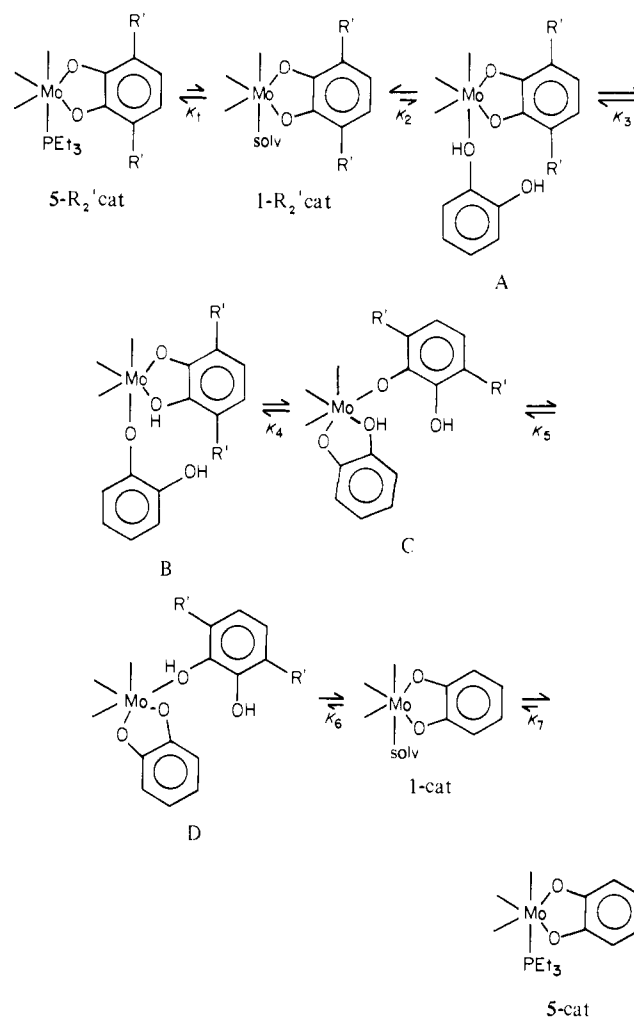
Structure of [Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]⁴⁻. Analytical data for the Et₄N⁺ salt of this cluster conform to the indicated formulation and thus are suggestive of the doubly bridged double-cubane structure **14**. Inasmuch as only one prior proof of this structure exists,⁵ an X-ray study of the compound was undertaken. Its crystal structure is well-behaved except for disorder of two of the cations in the asymmetric unit. The anion structure is of type **14** and is depicted in Figure 5; bond distances and angles are listed in Table V. Principal structural features of the anion are briefly summarized. (i) There is no crystallographically imposed symmetry; each subcluster approximates *C_s* symmetry and the two are related by a pseudo *C₂* axis perpendicular to the plane

Mo(1,2)Fe(1,4). Deviations of core bond distances related by the pseudomirror plane are as large as 0.04 Å but are usually <0.02 Å. (ii) The subclusters contain approximately tetrahedral Fe sites and a distorted octahedral Mo site in which coordination external to the [MoFe₃S₄]³⁺ core is completed by a catechol chelate ring and a bridging S(9,12) atom. (iii) The MoS₂Fe and Fe₂S₂ faces of the subcluster cores are nonplanar rhombs. (iv) The longest Mo–S and Fe–S bonded distances are those that lie in the idealized mirror plane (e.g., Mo(1)–S(4), Fe(1)–S(3)). The Mo–S bonds are presumably lengthened by the trans influence of the bridge sulfur atoms. (v) The subclusters are joined by the bridges Mo(1)–S(12)–Fe(4) (121.3 (3)°) and Mo(2)–S(9)–Fe(1) (119.9 (3)°) with the specified angles. The six bridge atoms are nearly coplanar, with a maximum deviation of 0.037 Å from the unit-weighted least-squares plane in (i). (vi) Bridge thiolate substituents exist in a syn disposition. (vii) The mean Fe–S bridge distance (2.317 Å) exceeds the mean Fe–S terminal distances (2.274 (12) Å) by ~0.04 Å. The mean Mo–S bridge distance (2.694 Å) is 0.094 Å longer than the terminal Mo–S distance in the single cubane [MoFe₃S₄(S-*p*-C₆H₄Cl)₄(al₂cat)]³⁻.^{9,10} As previously,⁵ these elongated bridge bonds are considered to be the dominant cause of the facile cleavage of clusters **14** in donor solvents. Retention of the Fe–SR bond in bridge rupture (Figure 4) is another example of a process specific to a Fe site. The structure of this double cubane is quite similar to that of [Mo₂Fe₆S₈(SEt)₆(Pr₂cat)₂]⁴⁻, which has been described in considerable detail.⁵ The latter, however, has imposed centrosymmetry with anti bridge substituents in the monoclinic form of its Et₄N⁺ salt.⁵ Lastly, the proof of structure **14** for [Mo₂Fe₆S₈(S-*p*-C₆H₄Cl)₆(cat)₂]⁴⁻ demonstrates that catechol chelate 3,6-substituents have no function in stabilizing the doubly bridged configuration in the solid state, although they do appear to be required in synthesis (reaction 12).

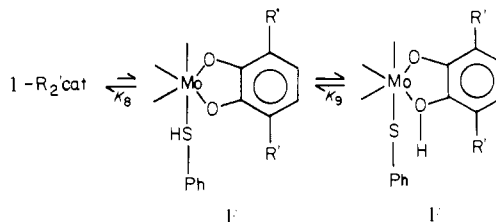
Catechol Exchange Pathway. The usual mechanism for displacement of a bidentate ligand from a coordinatively saturated octahedral complex requires dissociation of one end of the chelate as an initial step, making a binding site available for an incoming ligand.³⁰ In the single cubanes **1** a site is available by solvent replacement, as shown by the synthesis of ligated clusters **5**.^{9,10} (vide infra). To see if the course of reactions 10 and 11 involved prior coordination of PhSH and catechol, respectively, removal of the al₂cat ligand from [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(al₂cat)(PEt₃)]²⁻ (**5**, R = *p*-C₆H₄Cl, L = PEt₃) was examined. This cluster was generated in acetonitrile solution by reaction 5 using 1 equiv of phosphine. Its formation is demonstrated by the NMR spectrum in Figure 6. Because phosphine binding is nonlabile (NMR time scale), separate resonances of ligands at m' and m'' sites (**5**, Figure 1), consistent with C₃ cluster symmetry, are observed. Treatment of the cluster with ≤50 equiv of PhSH at ambient temperature gave no detectable al₂cat removal and formation of **11**, in sharp contrast to the ready occurrence of reaction 10 (Figure 3) with the solvated cluster. However, when the reaction of the phosphine cluster with catechol was examined, a far different result was obtained (Figure 6). Treatment with just 2 equiv of catechol/Mo results in an immediate partial reaction, particularly evident from the doubling of m'-H signals near -19 ppm. Conversion to [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(cat)(PEt₃)]²⁻ is nearly complete at 10 equiv. Signal assignments of this cluster were verified by spectral comparison with an authentic sample generated from [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(cat)(MeCN)]²⁻.

The failure of the phosphine cluster to react with excess PhSH implies a requirement of an available Mo binding site prior to protonation of the al₂cat group. In the catechol exchange reaction the presence of phosphine apparently has little effect on rate-determining aspects. These observations, together with the demonstration of neutral oxygen^{6,31} and phenolate¹⁰ ligand binding at the Mo site, facile substitution of one ligand by another at this site,^{6,31} and no reaction with resorcinol, lead to the following

mechanistic description of catechol exchange. Initial solvated



cluster **1-R₂'cat** binds catechol in step K_2 to form intermediate **A**, which undergoes intramolecular proton transfer from the coordinated hydroxyl group to a chelate oxygen atom (K_3) to form **B**. Step K_4 is a near-degenerate exchange process yielding **C**. Although resorcinol could form intermediates similar to **A** and **B**, the intramolecular step K_4 is impossible. A second proton transfer (K_5) to give **D** followed by dissociation of the doubly protonated ligand (K_6) affords the substituted cluster solvate **1-cat**. If the initial cluster is **5-R₂'cat**, exchange may proceed via a small equilibrium concentration of solvated cluster (K_1) or by direct protonation of catechol and phosphine displacement to give **B**. Phosphine is recaptured in step K_7 in either case. Inhibition of reaction 10 by 1 equiv of PEt₃/Mo may derive in part from the relative magnitudes of binding constants K_1 vs. K_8 , disfavoring formation of **E**, an expected intermediate in reaction of the solvated cluster with thiol. Protonation step K_3 may not be favorable and



must be followed by a second, intermolecular proton transfer to liberate R₂'catH₂, prior to collapse of the single cubanes to the triply bridged cluster **11**. Reactions 10 and 11 both require excess proton donor to approach completion. Under the present proposals the reagent in reaction 10 drives a slow reaction, one step of which is an intermolecular proton transfer. In catechol exchange the

(30) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1968; pp 216-228.

(31) Singh, R.; Holm, R. H., unpublished results.

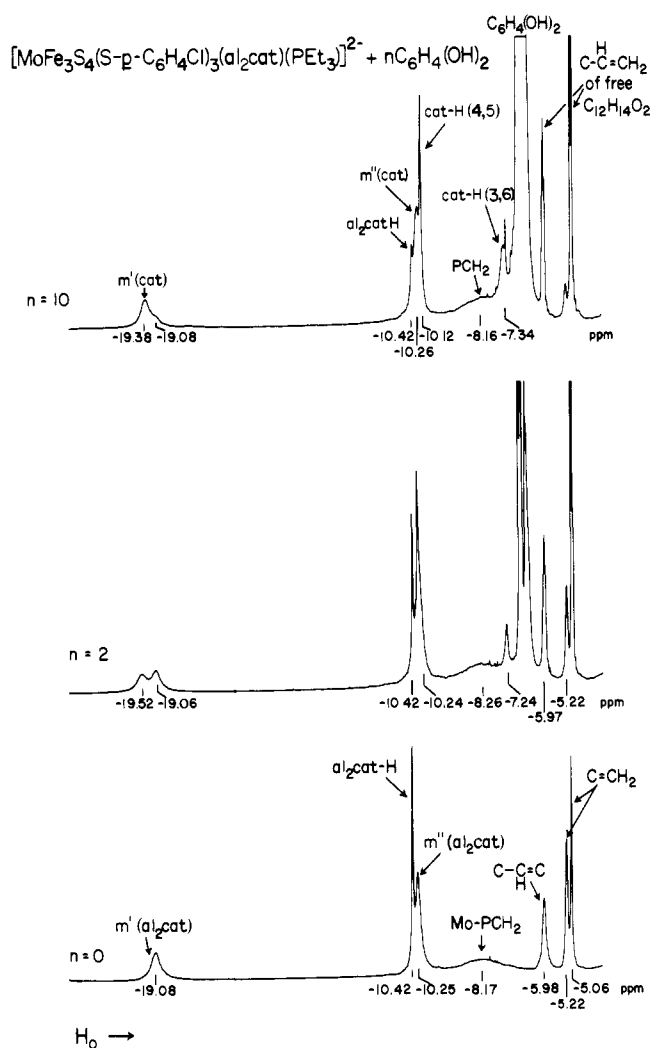


Figure 6. ¹H NMR spectra (297 K) of a CD₃CN solution initially 14 mM in [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(al₂cat)(PEt₃)₂]²⁻, to which the 2 and 10 equiv of catechol/Mo were added. Spectra were recorded ~10 min after addition. Signal assignments are indicated; m' and m'' refer to *m*-H resonances (cf. 5, Figure 1). *o*-H resonances occur at higher fields (not shown).

reagent biases a statistically controlled faster reaction with intramolecular proton transfer to yield the ligand-exchanged cluster.

Ligated Single Cubanes. Four clusters were isolated from reaction 5 as Et₄N⁺ salts (Figure 2), whose compositions indicated the presence of cluster 5 with L = CN⁻, N₃⁻, or PhNHNH₂. One purpose of these experiments was to obtain crystals suitable for X-ray analysis of ligand binding at the Mo site. The compound (Et₄N)₃[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(al₂cat)(CN)]¹⁰ proved inadequate in this regard. However, the related compound with R = Et and the Cl₄cat ligand (introduced by reaction 11) provided crystals of better quality. Cluster salts containing azide and phenylhydrazine have not been previously isolated. Suitable crystalline samples of (Et₄N)_{2,3}[MoFe₃S₄(S-*p*-C₆H₄Cl)₃(al₂cat)L] (L = PhNHNH₂, N₃⁻) were not obtained. In the azide case substitution of al₂cat with Cl₄cat afforded diffraction-quality crystals. This compound was not subjected to elemental analysis, and was authenticated by IR and ¹H NMR spectroscopy and a structural determination. No samples of any phenylhydrazine-containing cluster salt suitable for diffraction studies have yet been obtained.

(a) Cluster Structures. The structures of [MoFe₃S₄(SEt)₃(Cl₄cat)(CN)]³⁻ (16) and [MoFe₃S₄(S-*p*-C₆H₄Cl)₃(Cl₄cat)N₃]³⁻ (17) as their Et₄N⁺ salts are provided in Figures 7 and 8, respectively. Metric data are collected in Table VI. These clusters do have the ligated configuration 5; the acetonitrile molecule in the crystal structures of (Et₄N)₃(17)·MeCN is not coordinated.

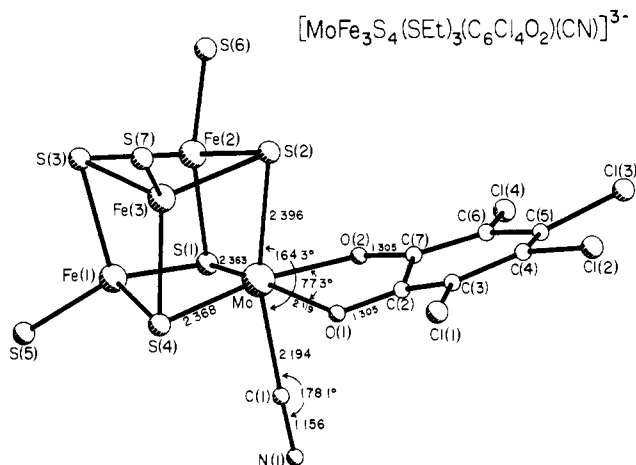


Figure 7. The structure of [MoFe₃S₄(SEt)₃(Cl₄cat)(CN)]³⁻ (16) as its Et₄N⁺ salt. Selected bond distances (Å) and angles are given; ethyl groups are omitted for clarity.

The structure of (Et₄N)₃(16) exhibits a small disorder of the anion which does not affect the Mo-CN group; treatment of the disorder is described in the Experimental Section. Neither anion possesses crystallographically imposed symmetry. The highest idealized symmetry of each is C_s; thus far imposed mirror symmetry has been found only with [MoFe₃S₄Cl₃(al₂cat)(THF)]²⁻.⁶ The metric features of the MoFe₃S₄(SR)₃ portions of 16 and 17 are very similar to each other and to those of two single cubanes^{6,9,10} and two double cubanes⁵ (vide supra), whose structures have been described in detail. The Mo-O(Cl₄cat) bond distances of 2.10 (1)–2.12 (1) Å are somewhat longer than Mo-O(al₂cat) values^{5,6,9,10} (2.045 (4)–2.08 (2) Å), implying weaker bonds in the former case. This is a not unexpected consequence of electro-negative chlorine atoms in the Cl₄cat ligand.

The presence of Mo-CN and Mo-N₃ groups in 16 and 17, respectively, provides final evidence for the site-specific nature of reaction 5 with cyanide and azide. The Mo-C distance of 2.19 (3) Å is consistent with other values in six-coordinate Mo(III,IV)-cyanide complexes.³² The Mo(III) oxidation number assignment is preferred for the core α oxidation level on the basis of ⁵⁷Fe isomer shifts.^{12,24} The essentially linear Mo-CN arrangement (178 (2)°) and the C-N distance (1.16 (3) Å) are standard features of metal-cyanide binding.³²⁻³⁴ Few Mo-azide complexes have been structurally defined.³⁵ One of these, MoN(dppe)₂N₃,^{35b} contains Mo(IV) with a Mo-N₃ distance of 2.20 Å which, however, is probably lengthened by the trans influence of the nitrido ligand. In the *cis-mer*-Mo(VI) complex MoN(bpy)(N₃)₃,^{35a} the mean Mo-N₃ distance is 2.03 Å and in the presumed Mo(II) species [Mo(NO)(H₂NO)(N₃)₄]²⁻,^{35c} this value for Mo-N₃ bonds *cis* to the nitrosyl group is 2.17 Å. On the basis of these limited data the Mo-N distance of 2.17 (2) Å in 17 is compatible with an intermediate oxidation state of Mo. The nonlinear Mo-N₃ arrangement (Mo-N(1)-N(2) = 125 (1)°) and nearly linear azide group (N(1)-N(2)-N(3) = 176 (2)°), as well as the N-N distances, are conventional aspects of non-

(32) (a) [MoO₂(CN)₄]⁴⁻ (2.21 Å): Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 3374. (b) [MoO(H₂O)(CN)₄]²⁻ (2.16 Å): Robinson, P. R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1975**, *14*, 2035. (c) [MoO(CN)₅]³⁻ (2.18 Å), [MoO(H₂O)(CN)₄]²⁻ (two forms, 2.13, 2.19 Å): Weighardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. Z. *Anorg. Allg. Chem.* **1983**, *499*, 44. (d) [Mo₂S₄(CN)₁₂]⁸⁻ (2.19 Å): Müller, A.; Eltzner, W.; Bögge, H.; Jostes, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 795. Mean distances of Mo-C bonds (*cis* to an oxo atom) are given.

(33) Griffith, W. P. *Coord. Chem. Rev.* **1975**, *17*, 177.

(34) Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: London, 1976; pp 1-68.

(35) (a) MoN(bpy)(N₃)₃: Schweda, E.; Strähle, J. Z. *Naturforsch., B* **1980**, *35B*, 1146. (b) MoN(dppe)₂N₃: Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *71*, 21. (c) [Mo(NO)(H₂NO)(N₃)₄]²⁻: Weighardt, K.; Backes-Dahmann, G.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1983**, *22*, 1221. (d) [Mo₂O₂(μ₃-N₃)-(SCH₂CH₂CH₂S)₃]⁻: Bishop, P. T.; Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1052.

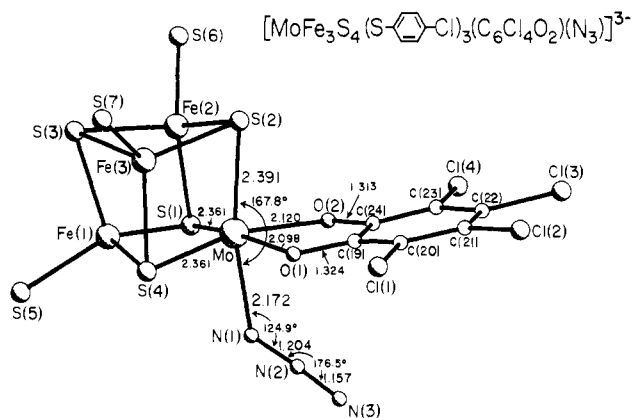


Figure 8. The structure of $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{Cl}_4\text{cat})\text{N}_3]^{3-}$ (17) as its Et_4N^+ salt, acetonitrile solvate. Selected bond distances (Å) and angles are given; $p\text{-C}_6\text{H}_4\text{Cl}$ groups are omitted for clarity.

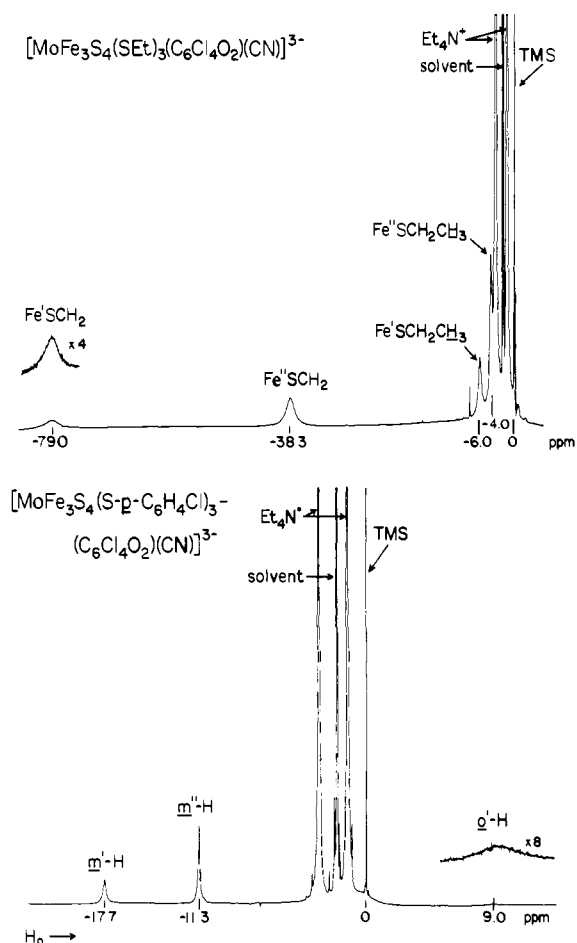


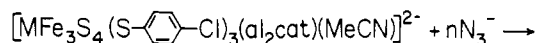
Figure 9. ^1H NMR spectra (297 K) of $[\text{MoFe}_3\text{S}_4(\text{SR})_3(\text{Cl}_4\text{cat})(\text{CN})]^{3-}$ ($\text{R} = \text{Et}, p\text{-C}_6\text{H}_4\text{Cl}$) in CD_3CN solution. Signal assignments are indicated; primes refer to the sites m' and m'' (cf. 5, Figure 1).

bridging metal-azide ligation.³⁵⁻³⁷

(b) Solution Behavior. The interactions of cyanide and a variety of nitrogen-donor ligands with solvated clusters in acetonitrile solutions have been examined by ^1H NMR spectroscopy. Catecholate ring proton chemical shifts are usually quite sensitive to ligand binding in reaction 5, and R-substituent shifts and signal multiplicities reflect the stereochemical integrity of ligated clusters 5. Two examples of these properties have already been seen in Figures 4 and 6. Spectra of the two isolated clusters with $\text{L} = \text{CN}^-$ are shown in Figure 9. Identical spectra are obtained by

(36) Muller, U. *Struct. Bonding (Berlin)* 1973, 14, 141.

(37) Dori, Z.; Ziolo, R. F. *Chem. Rev.* 1973, 73, 247.



$\text{M} = \text{Mo}$

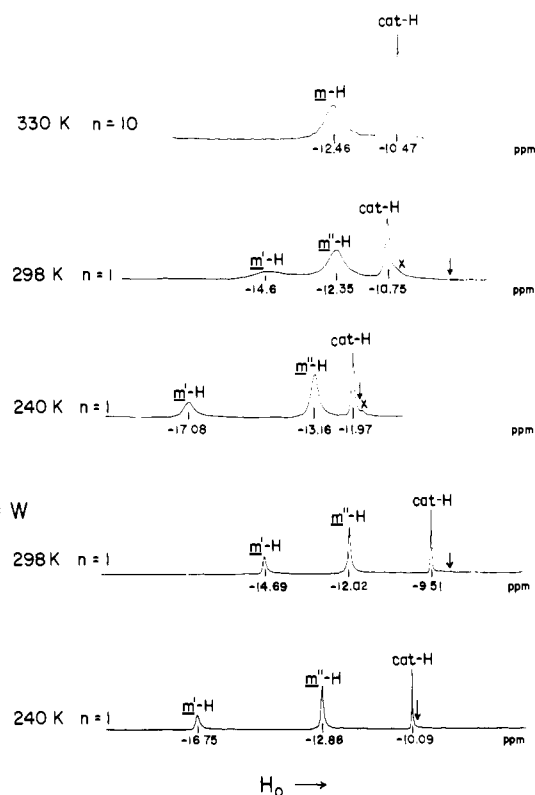


Figure 10. ^1H NMR spectra of $[\text{MFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{N}_3]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$) generated in CD_3CN solutions by reaction with $n = 1$ and 10 equiv of $(\text{Et}_4\text{N})\text{N}_3/\text{M}$. In this and the following figures only downfield spectral regions are shown, signal assignments are indicated (m' and m'' refer to $m\text{-H}$ resonances of 5), cluster concentrations are ~ 10 mM, the arrow gives the catecholate ring proton resonance position of the solvate cluster at the same temperature, and x is an impurity or spectrometer artifact.

the addition of 1 equiv of $(\text{Et}_4\text{N})\text{CN}/\text{Mo}$ to solutions of the acetonitrile solvates. Use of < 1 equiv affords separate spectra of solvated and ligated clusters. Spectra of cyanide clusters are characterized by well-resolved resonances of ligands at m' and m'' sites, which for the $\text{R} = \text{Et}$ case are separated by a remarkable 40.7 ppm³⁸ at 297 K. These observations show that reaction 5 with $\text{L} = \text{CN}^-$ is quantitative and that cyanide clusters are stereochemically rigid. Phosphine- and other cyanide-ligated clusters exhibit these properties.^{6,9,10}

NMR spectra of clusters formed in reaction 5 with $[\text{MFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) and $\text{L} = \text{N}_3^-, \text{PhNHNH}_2, \text{N}_2\text{H}_4, \text{piperidine (pip)}, \text{and } \text{NH}_3$ are set out in Figures 10-12. These spectra are restricted to the regions of catecholate and $m\text{-H}$ resonances. In all cases excess ligand up to the mol ratio $\text{L}/\text{M} = 10:1$ ³⁹ did not perceptibly alter line shapes or change catecholate chemical shifts by > 0.15 ppm (and usually by < 0.05 ppm) compared to 1:1 systems at 298 K. Relative intensities of the signals $m\text{-H}:\text{cat-H} = 3:1$ where line widths permitted meaningful integration. Thus binding occurs at M sites and is, or is nearly, quantitative, reflecting the high

(38) As discussed for other MoFe_3S_4 clusters with the α oxidation level,^{24,25} isotropic shifts of ligands at Fe sites arise from the $S = 3/2$ cluster paramagnetism and are dominantly contact in nature. In the present set of clusters contact shifts are evidenced by upfield and downfield shifts of $o\text{-H}$ and $m\text{-H}$, respectively (Figure 4), and downfield shifts of methylene and methyl protons (Figure 9), all with respect to the free thiols.

(39) A possible exception are the $\text{L} = \text{NH}_3$ systems where saturated ligand solutions were used. We are unaware of any determination of the solubility of ammonia in acetonitrile.

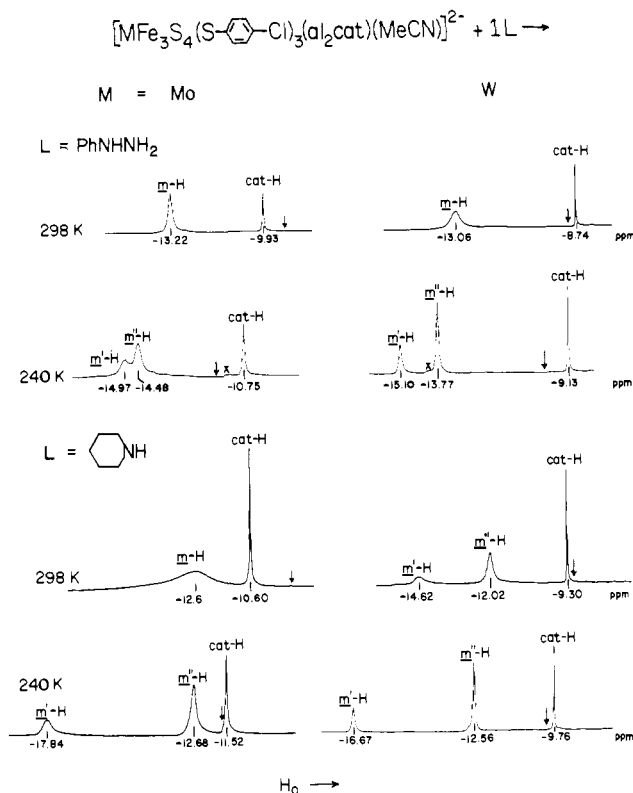


Figure 11. ¹H NMR spectra of $[\text{MFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$ (M = Mo, W) generated in CD_3CN solutions by reaction with 1 equiv of L = PhNHNH₂, piperidine/M.

affinity of these sites for ~ 10 mM L vs. ~ 18 M acetonitrile.⁴⁰ Spectra of the M/N₃⁻ systems (Figure 10) reveal the presence of slow-exchange clusters at 240 K, where m'-H and m''-H signals are separated by ~ 4 ppm. The same behavior applies to the W/N₃⁻ clusters at 298 K⁴¹ where this separation is reduced to ~ 2.7 ppm. The broadened but resolved m'-H and m''-H signals of the Mo/N₃⁻ cluster at 298 K are indicative of intermediate exchange. At ~ 320 K coalescence occurs, signifying equilibration of m' and m'' sites. The 330 K spectrum, recorded in the presence of a 10-fold excess of azide to suppress any ligand dissociation, contains a single m-H resonance at -12.46 ppm. The -7.93 (cat-H) and -12.81 (m-H) ppm signals of $[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$ at this temperature show that the spectrum is not that of the solvated cluster.

Spectra of the remaining systems (Figures 11 and 12) lead to the following qualitative classification of m'/m'' site exchange rates: slow (fully resolved m'-H and m''-H signals) W/PhNHNH₂ (240 K), Mo/pip (240 K), W/pip, N₂H₄ (240–298 K), Mo/N₂H₄ (240 K), M/NH₃ (240 K); intermediate Mo/PhNHNH₂ (240 K), Mo/pip, N₂H₄ (298 K), W/NH₃ (298 K); fast (single m-H resonance) M/PhNHNH₂, Mo/NH₃ (298 K). In several additional experiments 8–10 mM solutions of $[\text{MFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$ were saturated with purified dinitrogen, sealed in NMR tubes under a dinitrogen atmosphere, and examined at 240 and 298 K. Spectra were identical with those of solvated clusters measured under argon, showing that, by the NMR criterion, dinitrogen does not bind to the Mo and W clusters in the α oxidation level in acetonitrile solution.

The means by which sites m' and m'' are equilibrated in the foregoing dynamic systems is not known but must involve a

(40) The shifts in Figures 10–12 may be compared with those of $[\text{MFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$ at 298 (240) K: M = Mo, -9.20 (-11.64) (cat-H), -13.32 (-14.77) ppm (m-H); M = W, -9.10 (-9.99) (cat-H), -13.12 (-14.44) ppm (m-H).

(41) Chemical shifts of m-H and cat-H resonances of MFe₃S₄-type (α) clusters are shifted to higher fields (decreasing contact shift) with increasing temperature^{5,25} owing to decreased paramagnetic susceptibility.^{24,25,42}

(42) Christou, G.; Collison, D.; Garner, C. D.; Acott, S. R.; Mabbs, F. E.; Petrouleas, V. *J. Chem. Soc., Dalton Trans.* **1982**, 1575.

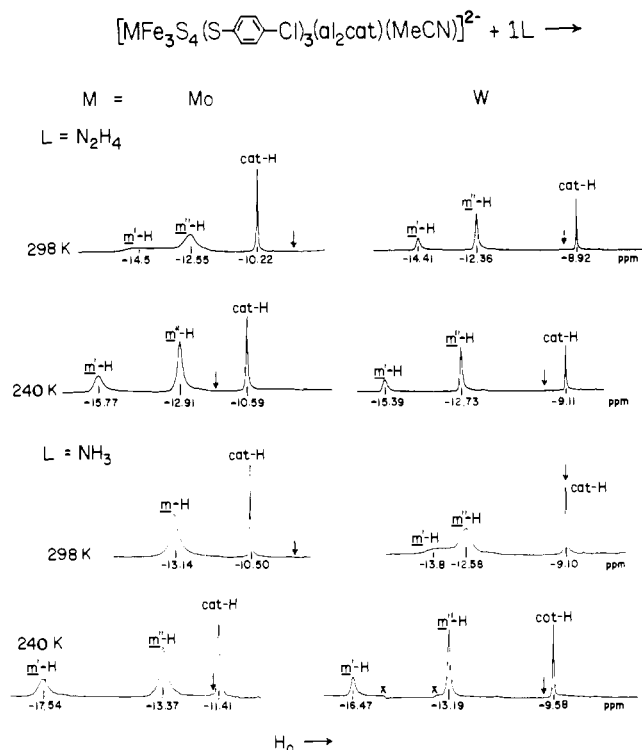


Figure 12. ¹H NMR spectra of $[\text{MFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{L}]^{2-}$ (M = Mo, W) generated in CD_3CN solutions by reaction with 1 equiv of L = N₂H₄/M and a saturated solution of L = NH₃.

trigonal averaging process of catecholate and L ligands. A bimolecular reaction involving ligand exchange and attendant catecholate ring reorientation^{6,43} would have a concentration dependent rate but may be difficult to establish because of limited cluster salt solubility. Likely intramolecular processes include a trigonal twist of the M(cat)L portion or Mo–O/L bond rupture followed by rebinding to yield a degenerate configuration. The latter two processes are of types notoriously difficult to distinguish in DNMR spectra of fluxional metal complexes.⁴⁴ The most important observations are that binding of N donor ligands in reaction 5 is essentially stoichiometric with 1 equiv of L and that W clusters are the more stereochemically rigid.

Summary

The following are the principal findings and conclusions of this investigation.

(1) The Fe(III)-bridged double cubane **13** can be converted to the doubly bridged double cubane $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SET})_6(\text{Cl}_4\text{cat})_2]^{4-}$ (**14**) upon treatment with Cl_4catH_2 (reaction 13); the bridging Fe(III) atom is removed in the form of $[\text{Fe}(\text{Cl}_4\text{cat})_3]^{3-}$. On the basis of steric features other such clusters should be obtainable by use of catechols with 3,6-substituents no larger than chlorine.

(2) The double-cubane structure undergoes bridge cleavage reaction 14 to form the solvated single cubanes **1**, which exhibit a number of Mo and Fe site-specific reactions (Figure 1). The newest of these, the catecholate ligand exchange reaction 11, has been demonstrated by synthesis of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{cat}^*)_2]^{4-}$ (cat* = cat, Cl₄cat) from $[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$ and excess catH_2^* . A pathway for this Mo site-specific reaction is proposed.

(3) The structure of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_6(\text{cat})_2]^{4-}$, synthesized by the methods in (1) and (2), is similar to that of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SET})_6(\text{Pr}_2\text{cat})_2]^{4-5}$ and provides confirmatory evidence that elongated Mo–S(R)–Fe bridge bonds contribute to the facility of cleavage reaction 14.

(43) Cf. Figure 4 of ref 6.

(44) Cf., e.g.: Holm, R. H. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 9.

(4) An example of the single-cubane (**1**) → triply bridged double-cubane (**10**) conversion reaction 10 has been demonstrated; hence the synthetically useful thiolate substitution reaction 1 of solvated clusters **1** should be conducted with minimal thiol. The conversion is suppressed by PEt_3 coordination at the Mo site.

(5) The ligation reaction 5 with the single-cubane acetonitrile solvates **1** at ~ 10 mM and 1 equiv of $\text{L} = \text{CN}^-$, N_3^- , and selected neutral N donor ligands is essentially quantitative at 298 K. Binding occurs exclusively at the Mo (or W) site in the clusters **5**; in solution this property is unambiguously recognized in low-temperature NMR spectra which exhibit resolved $m^{\prime}\text{-H}$ and $m^{\prime\prime}\text{-H}$ resonances indicative of cluster C_3 symmetry. Dinitrogen does not bind to the oxidized (α) clusters in acetonitrile solution. In two cases final proof of site-specific binding was obtained by X-ray analysis of the Et_4N^+ salts of $[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{Cl}_4\text{cat})(\text{CN})]^{3-}$ and $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{Cl}_4\text{cat})\text{N}_3]^{3-}$. Structural features of the Mo-CN (linear) and Mo-N₃ (bent) groups are conventional, and Mo-C/N distances are compatible with an intermediate oxidation state (III, IV) of the Mo atom.

The foregoing results and those of prior investigations,^{5,6,9,10} summarized in Figure 1, have led to systematic and specific manipulation of all noncore ligands in $[\text{MoFe}_3\text{S}_4]^{3+}$ single-cubane clusters. Ligands demonstrated to bind to the clusters include substrates (N_3^- ,⁴⁵ N_2H_4 (poor)), pseudosubstrate (CN^- ,⁴⁶) and the final reduction product (NH_3) of nitrogenase.⁴⁷ Also shown to bind are several derivatives (PhNHNH_2 , pip) of these species. Substrate binding is a necessary step toward activation and reduction. Although cyanide itself is an inhibitor of total electron flow through the enzyme,⁴⁶ the occurrence of Mo-CN binding at some stage of catalysis is not unlikely. Consequently, the structure of the Mo-CN group, and that of Mo-N₃, are potentially useful representations of interactions of these ligands at the catalytic site of the enzyme. The lack of binding by dinitrogen may be due to a combination of factors, including low solubility in acetonitrile, unfavorable competition with solvent, and lack of affinity for oxidized (α) clusters, which also do not bind carbon monoxide in acetonitrile solution.¹⁰ While acetonitrile is an adequate (and relatively inexpensive) solvent for establishing ligand binding properties by NMR spectroscopy, it is not as appropriate for the development of substrate-reducing systems owing to its nitrogen content, potential reducibility, and coordinating ability. Consequently, we have developed single-cubane systems that are soluble in THF and methanol. Future reports will deal with binding and other reactions of nitrogenase-related ligands with

oxidized and reduced ($[\text{MoFe}_3\text{S}_4]^{2+}$, β) clusters in these media. As already demonstrated, β single cubanes can be generated in solution¹⁰ and isolated.¹³ Lastly, the Osaka group⁴⁸ has reported the reduction of several nitrogenase substrates in protic media effected by reduced forms of the triply bridged double cubanes **11**. Because these forms have not been identified, the reactive clusters are unknown. In this laboratory, dihydrogen formation from protic molecules using the reduced double cubanes $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_9]^{4-,5-}$ in acetonitrile solution has been achieved.⁴⁹ Although under these conditions retention of the double-cubane structure is very likely, our working premise that reduction of other substrates at molybdenum requires (at least one) labile binding site continues.

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Registry No. (Et_4N)₃(**13**), 73589-29-4; (Et_4N)₄(**14**), 89345-85-7; (Et_4N)₃(**16**), 89345-91-5; (Et_4N)₃(**17**)-MeCN, 89346-00-9; (Et_4N)₄- $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_6(\text{cat})_2]$, 89345-87-9; (Et_4N)₄- $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_6(\text{Cl}_4\text{cat})_2]$, 89345-89-1; (Et_4N)₄- $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_6(\text{al}_2\text{cat})_2]$, 82247-34-5; (Et_4N)₃- $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{Cl}_4\text{cat})(\text{CN})]$, 89345-93-7; (Et_4N)₃- $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{N}_3]$, 89345-95-9; (Et_4N)₂- $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{PhNHNH}_2)]$, 89345-97-1; (Et_4N)₂- $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{Cl}_4\text{cat})(\text{MeCN})]$, 89363-62-2; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$, 80702-98-3; $[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{Cl}_4\text{cat})(\text{MeCN})]^{2-}$, 89346-01-0; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{PEt}_3)]^{2-}$, 80703-01-1; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{cat})(\text{PEt}_3)]^{2-}$, 89346-02-1; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{cat})(\text{MeCN})]^{2-}$, 89346-03-2; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})(\text{MeCN})]^{2-}$, 80702-98-3; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{N}_3]^{3-}$, 89346-04-3; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{-PhNHNH}_2]^{2-}$, 89345-96-0; $[\text{WFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{Al}_2\text{cat})\text{-PhNHNH}_2]^{2-}$, 89346-05-4; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{pip}]^{2-}$, 89346-06-5; $[\text{WFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{pip}]^{2-}$, 89346-07-6; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{N}_2\text{H}_4]^{2-}$, 89346-08-7; $[\text{WFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{N}_2\text{H}_4]^{2-}$, 89346-09-8; $[\text{MoFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{NH}_3]^{2-}$, 89346-10-1; $[\text{WFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Cl})_3(\text{al}_2\text{cat})\text{NH}_3]^{2-}$, 89346-11-2; nitrogenase, 9013-04-1.

Supplementary Material Available: X-ray structural data for the compounds in Table I, positional parameters not included in Tables II-IV, isotropic and anisotropic thermal parameters, calculated hydrogen atom coordinates and temperature factors, and tables of $10|F_o|$ and $10|F_c|$ (68 pages). Ordering information is given on any current masthead page.

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