

On the Existence in Solution of Doubly Thiolate-Bridged Double Cubanes Containing the Heterometal [MFe₃S₄] Core (M = Mo, W)

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Clusters of the general type {[MFe₃S₄(SR)₂(cat)]₂(μ₂-SR)₂}⁴⁻ (cat = catecholate) have previously been shown to contain two heterometal cubane-type cores [MFe₃S₄]³⁺ (M = Mo, W) linked by two Fe–S(R)–M bridges such that the cluster has idealized centrosymmetry. These clusters resemble the P-clusters of nitrogenase in that both have two μ₂-SR bridges between cubane (or cuboidal) halves of the cluster. When dissolved in a strongly coordinating solvent or treated with a suitable ligand L^{1–0}, the bridges are cleaved to afford the single cubanes [MFe₃S₄(SR)₃(cat)L/(solv)]^{2–3-}. Because of their relation to P-clusters, the stability and electron transfer properties of the double cubanes have been examined in solution. ¹H NMR spectroscopic and cyclic voltammetric properties of acetonitrile solutions prepared from Et₄N⁺ salts of clusters with R = Et and M = Mo, W are entirely consistent with the presence of bridged double cubanes in solution. Key observations include different chemical shifts of bridging and terminal ethanethiolate ligands and two successive oxidations separated by 150–230 mV. Reduction occurs with twice the diffusion current of the oxidations and results in cleavage to two single cubanes. Bridge strength increases in the order R = Ph < Et (consistent with basicities of the thiolate anions) and M = Mo < W. This work has produced the first demonstration that doubly thiolate-bridged double cubanes of any description remain intact in solution. The synthesis of Fe₄S₄ double cubanes with bis(μ₂-SR) bridges persists as an objective if actual analogues of the P-cluster are to be obtained.

Introduction

The demonstration by protein crystallography that the P-clusters of nitrogenase, depicted as **I** and **II** in Figure 1, are minimally bridged by two cysteinyl sulfur atoms is a powerful factor in the sustained interest in bridged double-cubane clusters. These clusters have the core compositions Fe₈S_{7,8} and function as internal redox centers in the FeMo protein of nitrogenase, passing electrons to the catalytic FeMo-cofactor cluster. Structure **I**, determined by Rees and co-workers,¹ features an intercubane S–S bond between Fe₄(μ₃-S)₄ subclusters, whereas **II**, deduced by Bolin,² has a μ₆-S atom bridging the two cuboidal Fe₄(μ₃-S)₃ halves. If both structures have the same oxidation state, their differences are yet to be reconciled. In iron–sulfur cluster chemistry, no thiolate-bridged double cubanes or double cuboids have been realized experimentally, the closest approach being mono-μ₂-sulfido double cubanes.³ Indeed, these are the only known Fe₄S₄ double-cubane clusters connected through sulfur atoms.⁴

In contrast to Fe₄S₄ clusters, bridged structures predominate in the chemistry of the heterometal double-cubane clusters containing MFe₃(μ₃-S)₄ cores with the metals present in nitrogenase (M = V, Mo) and certain nonbiological metals (M = Nb, W, Re). These are set out as **III–X** in Figure 1. Clusters of the triply bridged type **III**⁵ were the first synthesized in the set of the eight structure types. The Fe(II,III)–hexathiolate-

bridged clusters **IV**^{5c,f,g,6} followed and, thereafter, the doubly thiolate-bridged molybdenum and tungsten clusters **V**,⁷ which are of principal interest in this investigation. Cluster **VI**⁸ is the only example of a cluster similar to **V** involving vanadium. Nearly all of the remaining members of the set, **VII**,⁹ **VIII**,¹⁰ **IX**,¹¹ and **X**,¹² were obtained more recently. Among these is the double cubane {[MoFe₃S₄Cl₂(Cl₄cat)]₂(μ₂-S)₂}⁶⁻ (**VIII**)¹³ with Mo–S–Mo and Fe–S–Fe bridges. In the extensive

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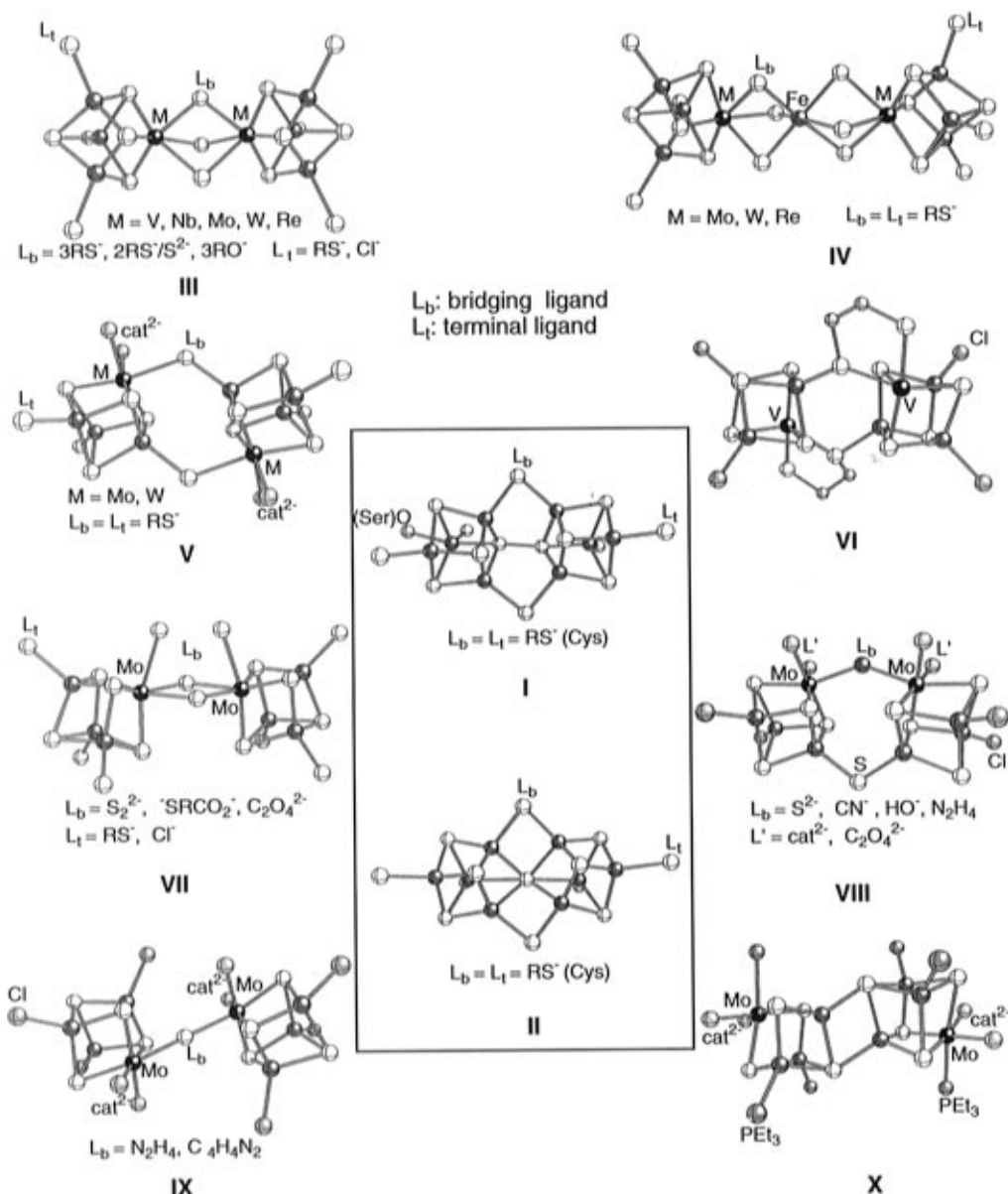
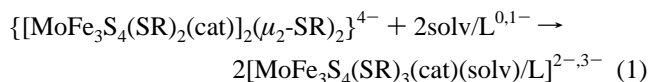


Figure 1. Depictions of the two structures **I** (Rees *et al.*¹) and **II** (Bolin²) of nitrogenase P-clusters, and of all known structural types **III**–**X** of bridged heterometal (MFe₃S₄) double cubanes. Bridging and terminal ligands are indicated, but not all combinations may occur with a given metal. The catechol chelate rings in **V** and **VIII**–**X** and the S–S bond in the bis(μ_2 : η^2 : η^2 -S₂) cluster **VII** are omitted for clarity.

development of MFe₃S₄ cluster chemistry,¹⁴ considerable emphasis has been placed on obtaining *single* cubanes in order to simplify the electronic structures, but primarily because then, as now, the unbridged MoFe₃S₄ fragment provides the best synthetic representation of the molybdenum coordination environment in the cofactor cluster. A highly effective route has been reaction 1, in which a double cubane **V** is cleaved by a coordinating solvent such as Me₂SO or DMF or by an exogenous unidentate ligand L to afford single cubanes. The initial Mo–S(R)–Fe bridge typically has the bond distances



Mo–S = 2.70 Å and Fe–S = 2.31 Å.⁷ Without exception, cleavage leaves the Fe–S bond intact and the solvent or added ligand is bound at the distorted octahedral molybdenum site in

a position necessarily *cis* to the catechol oxygen atoms. The structures of two type **V** clusters⁷ and several single cubane^{14,15} reaction products have been established by X-ray structure determinations.

Given the importance of single MFe₃S₄ cubanes in biologically related cluster chemistry, an aspect that continues today with the use of such species as catalytic reductants,¹⁶ the precursor clusters **V** have remained largely unexamined except for crystal structure determinations. Indeed, the double-cubane status has never been investigated in solution, the presumption being that strongly coordinating solvents efficiently cleave these clusters. ¹H NMR spectra of *ca.* 10 mM solutions prepared from salts of molybdenum- and tungsten-containing species **V** in acetonitrile, DMF, or Me₂SO at ambient temperature have not revealed the presence of double-cubane clusters.^{7,15} With

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the emergence of the bridged P-cluster structures **I** and **II**, we have returned to the matter of thiolate-bridged double cubanes, their stability in solution, and the associated matter of redox behavior. We are particularly concerned with the intrinsic stability of an intercubane thiolate bridge; i.e., is its existence in type **V** clusters an effect of the solid state, or is it of sufficient robustness to survive in a solution medium? While such clusters cannot be said to be strict analogues of the bridge interactions in the native clusters, they are presently the only molecules which allow examination of Fe-(μ_2 -SR) bonds in cubane clusters.

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere. Solvents were purified as appropriate and degassed prior to use. 3,4,5,6-Tetrachlorocatechol was purified by sublimation; 3,6-diallylcatechol was prepared by rearrangement of catechol diallyl ether at 165 °C under dinitrogen for 6 h followed by vacuum distillation. The compounds $(Et_4N)_4[M_2Fe_6S_8(SET)_6(al_2cat)_2]$ ($M = Mo, W$)^{7a} and $(Et_4N)_4[Mo_2Fe_6S_8(SET)_6(Cl_4cat)_2]$ ^{7b} were prepared as previously described.

Physical Measurements. All measurements were performed under anaerobic conditions. ¹H NMR spectra were measured on a Bruker AM-500 spectrometer. Electrochemical measurements were performed at ambient temperature in acetonitrile solutions with a PAR Model 263 potentiostat/galvanostat using a Pt working electrode, 0.1 M (Bu₄N)-(PF₆) or 0.1–0.2 M NaBPh₄ supporting electrolyte, and an SCE reference electrode.

Results and Discussion

Clusters **1–11** are of principal interest in this work; **1–3** and **9–11** are double cubanes of type **V**, **8** is a double cubane of type **III**, and **4–7** are solvated or ligated single cubanes. In past and present work, these clusters were employed as their Et₄N⁺ salts.

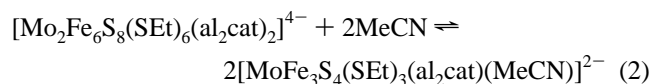
For simplicity, compounds are referred to by their anion number.

$[Mo_2Fe_6S_8(SET)_6(Cl_4cat)_2]^{4-}$	1 (V)
$[Mo_2Fe_6S_8(SET)_6(al_2cat)_2]^{4-}$	2 (V)
$[W_2Fe_6S_8(SET)_6(al_2cat)_2]^{4-}$	3 (V)
$[MoFe_3S_4(SET)_3(Cl_4cat)(solv)]^{2-}$	4
$[MoFe_3S_4(SET)_3(al_2cat)(solv)]^{2-}$	5
$[WFe_3S_4(SET)_3(al_2cat)(solv)]^{2-}$	6
$[MoFe_3S_4(SET)_3(Cl_4cat)(CN)]^{3-}$	7
$[Mo_2Fe_6S_8(OMe)_3(SBu^t)_6]^{3-}$	8 (III)
$[Mo_2Fe_6S_8(SET)_6(Pr_2cat)_2]^{4-}$	9 (V)
$[Mo_2Fe_6S_8(SPh)_6(al_2cat)_2]^{4-}$	10 (V)
$[Mo_2Fe_6S_8(S-p-C_6H_4Cl)_6(cat)_2]^{4-}$	11 (V)

Behavior in Solution. The reaction of type **V** clusters with strongly coordinating solvents is exemplified by treatment of **1** and **3** with Me₂SO. The compounds dissolve instantly; the ¹H NMR spectra a and b in the inset of Figure 2 are entirely consistent with the formation of solvated single cubanes **4** and **6**. Because these clusters are fluxional at the molybdenum and tungsten sites owing to rapid solvent dissociation and attendant reorientation of the catecholate chelate ring,¹⁵ the spectra correspond to trigonally symmetric species. Ethanethiolate signals are isotropically shifted owing to the paramagnetism of the clusters, which have an $S = 3/2$ ground state.¹⁷ In general, isotropic shifts of $[MFe_3S_4]^{3+}$ clusters ($M = Mo, W$) are very sensitive to the nature of the terminal and Mo-bound ligands, apparently through a complicated interplay of contact and dipolar interactions.

A considerably different behavior is encountered with **1** and **3** in acetonitrile, in which the compounds are much less soluble. Spectra a and d in Figure 2 correspond to saturated solutions of **1** and **3**, respectively, at 297 K with solid present. By increasing the temperature or adding solid NaBPh₄ (*ca.* 15 equiv), the compounds completely dissolve. The spectra clearly differ from those of the single cubanes, and correspond to species with the centrosymmetry of type **V** clusters. Resonances are assignable on the basis of relative intensities and isotropic shifts. In spectra a–c of the molybdenum cluster **1**, the signal with the largest isotropic shift is assigned to the bridging methylene protons, whose ethanethiolate group is bonded to two clusters. In spectrum a, this feature occurs at 98.2 ppm. The pair of signals at 16.9 and 16.5 ppm correspond to terminal Fe–SCH₂ groups whose protons are diastereotopic.¹⁸ The signal at 8.89 ppm is associated with the methyl group of bridging ethanethiolate by reason of its chemical shift. Methyl signals of terminal ligands are not resolved and occur at 2.77 ppm. The addition of NaBPh₄ accentuates the chemical shift difference between the Fe–SCH₂ groups, presumably by an ion-pairing effect. The tungsten cluster **3** behaves in a related manner, as seen from inspection of spectra d–f. Because of overlap with the al₂cat ligand, the methyl resonance of the terminal thiolate ligands was not located. The observed smaller isotropic shifts and narrower line widths are a consistent property of $[WFe_3S_4]^{3+}$ vs $[MoFe_3S_4]^{3+}$ clusters.^{5cd,7} The spectra of **1** and **3** are consistent with retention of the doubly bridged structure **V** in acetonitrile solution.²¹

Further evidence for existence of the doubly bridged structure **V** in solution is obtained with cluster **2**. A saturated solution of this cluster in acetonitrile at 297 K affords the three Fe–SCH₂ resonances of Figure 3a. The signals at 16.6 and 91.5 ppm derive from the double cubane whereas that at 53.3 ppm is in the range of single cubanes (Figure 2, inset). This chemical shift is essentially the average value (54.1 ppm) of the other two signals, confirming assignment²¹ of the 16.6 ppm signal to the terminal ligands. Increasing the temperature to 313 K leaves only the resonance of **5** (Figure 3b), indicating the operation of equilibrium **2**. Addition of solid NaBPh₄ evidently stabilizes **2** at the expense of **5** and induces a pronounced asymmetry in the feature at 15.6 ppm (Figure 3c).



Electron Transfer Reactions. Relevant cyclic voltammograms a–d of solutions prepared from double cubanes **1–3** are set out in Figure 4. The behavior of three clusters in acetonitrile (Figure 4, voltammograms a–c) is essentially the same. All show a single chemically reversible reduction step ($i_{pc}/i_{pa} = 1$) with a diffusion current *ca.* twice that of each of the two

(18) The appearance of two methylene signals has three limiting origins: (i) diastereotopism of the protons in a given group, with any inequivalence of the two methylene groups a secondary effect; (ii) static or fluxional centrosymmetry, in which event the two groups are inequivalent; (iii) *syn* and *anti* conformers, with any inequivalence of the two groups within a conformer a secondary effect. Regarding i, resolvable diastereotopism of terminal Fe–SCH₂ protons has been observed previously¹⁹ but its occurrence in MFe_3S_4 clusters is, in our experience, most infrequent. In ii, fluxional centrosymmetry requires inversion at the bridging sulfur atoms, a process which may occur in the Fe–S(Et)–Mo bridges of type **IV** clusters.^{5c} Concerning iii, **9** (monoclinic form),^{7a} two inequivalent molecules of **9** (triclinic form),²⁰ and **10**²⁰ are centrosymmetric with the *anti* conformation, whereas **11**^{7b} exists in the *syn* conformation.

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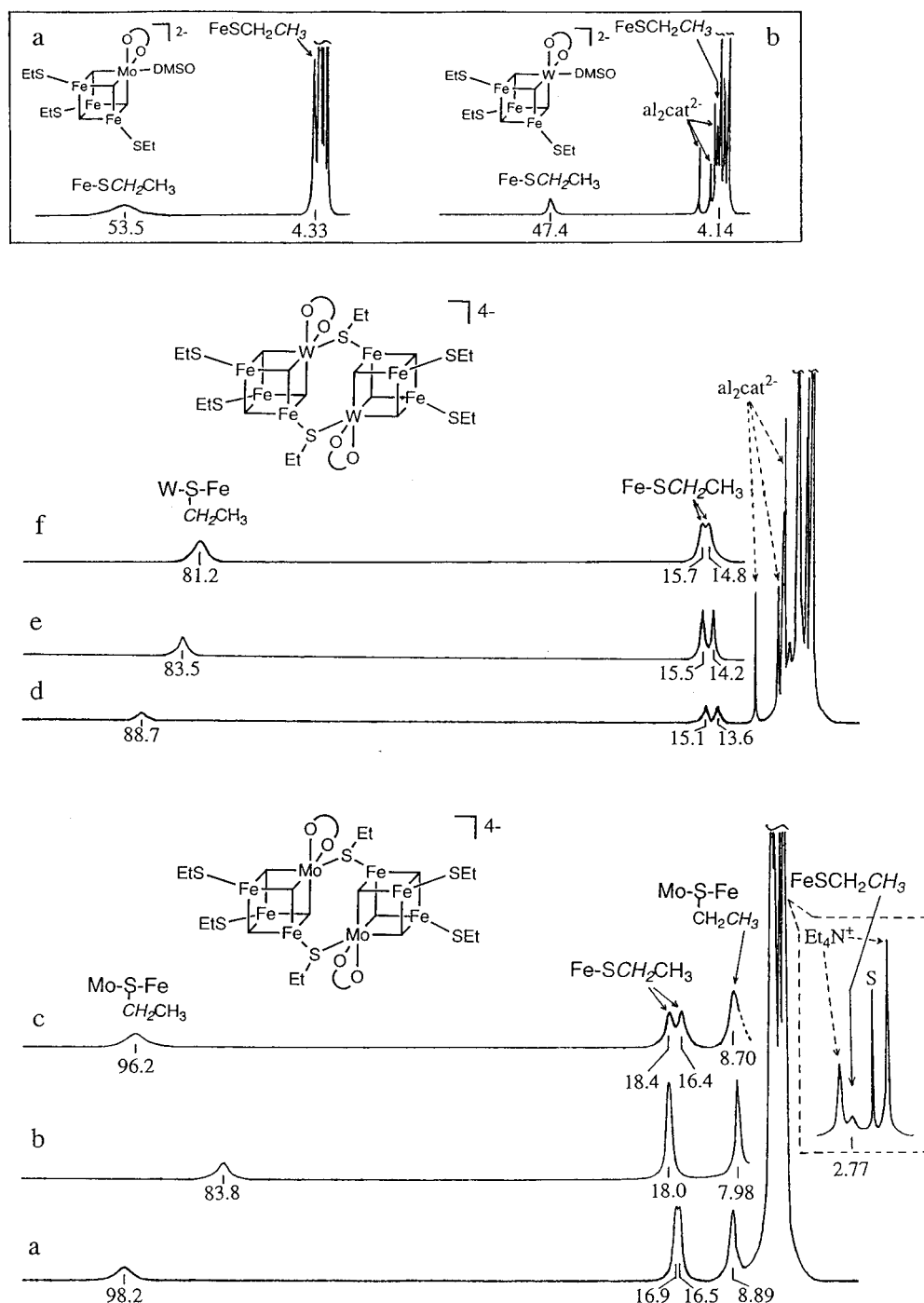
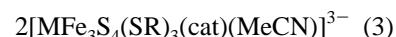
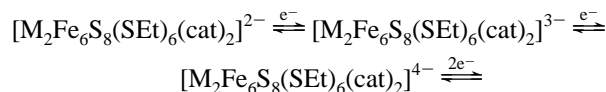


Figure 2. Inset: ¹H NMR spectra of single cubanes **4** (a) and **6** (b) in Me₂SO at 297 K. ¹H NMR spectra in CD₃CN: **1** (a) at 297 K, (b) at 333 K, and (c) in the presence of NaBPh₄ at 297 K; **3** (d) at 297 K, (e) at 313 K, and (f) in the presence of NaBPh₄ at 297 K. Signal assignments are indicated.

oxidation steps whose half-wave potentials are separated by 150–230 mV. For **1** (Figure 4a), the potentials are $E_{1/2} = -0.11, -0.27,$ and -1.31 V. This cluster evidenced an unidentified impurity feature at -0.44 V, which was of variable intensity in different runs, but its apparent current height never exceeded that of either oxidation reaction. The behavior of **2** and **3** (Figure 4, spectra b and c) was somewhat cleaner; the potentials of **2** are $E_{1/2} = -0.28, -0.43,$ and -1.32 V and of **3** are $E_{1/2} = -0.34, -0.57,$ and -1.51 V. A solution in Me₂SO prepared from **2** affords a voltammogram (Figure 4d) with one oxidation and one reduction step of nearly equal diffusion current, indicating the formation of the single cubane **5**.

These observations are entirely consistent with the electron transfer series 3. The initial core oxidation state of **1–3** is

$[\text{MFe}_3\text{S}_4]^{3+}$ ($S = 3/2$), which in the two-electron step is reduced



to $[\text{MFe}_3\text{S}_4]^{2+}$, a characterized oxidation level with $S = 2.17$. Our results do not differentiate between the reduction of either component in equilibrium 2. The two successive, closely spaced oxidations provide persuasive evidence for the existence of the double-cubane structure **V** in species which have been oxidized to the $\{[\text{MFe}_3\text{S}_4]^{3+}[\text{MFe}_3\text{S}_4]^{4+}\}$ and $\{[\text{MFe}_3\text{S}_4]^{4+}\}_2$ oxidation levels. Decreased bridge binding affinity with core reduction

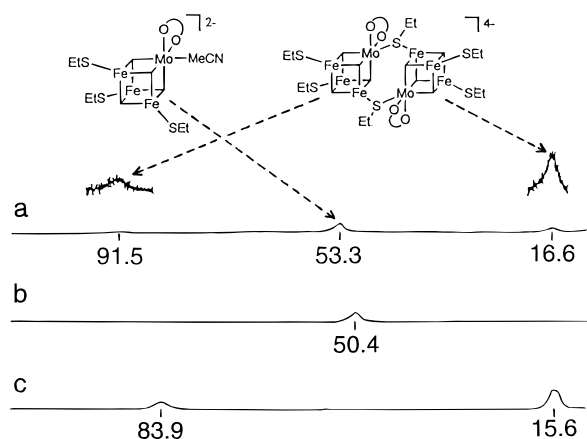


Figure 3. ^1H NMR spectra of CD_3CN solutions prepared from **2** (a) at 297 K (~ 2 mM), (b) at 313 K, (c) and in the presence of NaBPh_4 (15 equiv). Resonances arise from the methylene groups of **2** and single cubane **5**, as indicated.

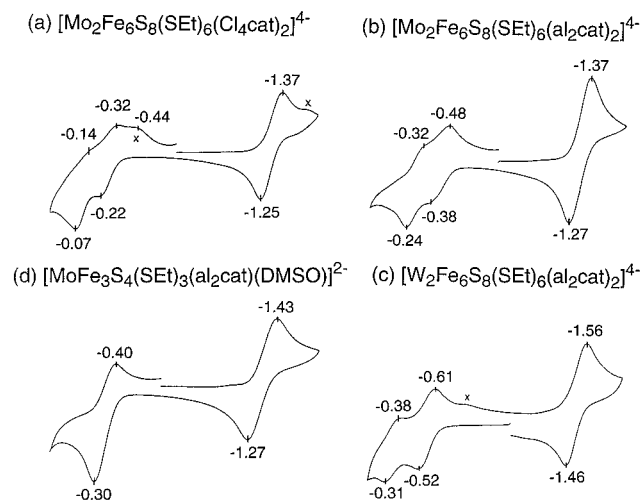


Figure 4. Cyclic voltammograms at ambient temperature (100 mV/s, 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$): (a) **1** in acetonitrile; (b) **2** in acetonitrile; (c) **3** in acetonitrile; (d) solution prepared from **2** in Me_2SO containing **5**. Peak potentials and impurity features (x) are indicated.

is an intuitively reasonable result.²² A redox series spanning these oxidation levels is not without precedent. For example, cluster **8** (type **III**, $\text{L}_b = \text{MeO}^-$) undergoes two one-electron reductions and oxidations,^{5c} thereby forming a five-membered series terminated by the $\{[\text{MoFe}_3\text{S}_4]^{z-}\}_2$ oxidation states with $z = 4+$ and $2+$. The potentials $E_{1/2}$ (**3**) $<$ $E_{1/2}$ (**2**) are consistent with the normal order of tungsten vs molybdenum; *viz.*, tungsten complexes are more difficult to reduce than their molybdenum analogues.

Under certain conditions, the two-electron step of series 3 can be circumvented. The cyclic voltammogram of **1** in acetonitrile in the presence of 0.1 M NaBPh_4 , provided in Figure

- (21) Over the range 297–337 K, the signals at 98.2 and 8.89 ppm (Figure 2a) exhibit a Curie dependence of chemical shift, as expected for a simple paramagnet. We note certain unexpected features of the pair of terminal $\text{Fe}-\text{SCH}_2$ signals of **1–3** at *ca.* 13–18 ppm (Figure 2). The chemical shifts are unusual, given that the analogous resonances occur at 45–47 ppm (Me_2SO) in the solvated single cubanes **5** and **6**^{7a} and at 38(2) and 79(1) ppm (CD_3CN) in the (nonfluxional) single cubane **7**.^{7b} These shifts exhibit anti-Curie behavior, an effect that is evident in Figures 2a,b and 2d,e. Despite these features, signal intensities and multiplicities permit no other assignment.
- (22) In this context, we note the related reaction $[\text{Fe}_2(\text{edt})_4]^{2-} + 2e^- \rightarrow 2[\text{Fe}(\text{edt})_2]^{2-}$ in acetonitrile^{23a} ($\text{edt} = 1,2$ -ethanedithiolate) and the electron transfer series $[\text{Fe}_2(\text{tfd})_4]^{0,1-2-}/2[\text{Fe}(\text{tfd})_2]^{2-}$ in dichloromethane^{23b} ($\text{tfd} = (\text{CF}_3)_2\text{C}_2\text{S}_2$). In both cases, reduction to the $\text{Fe}(\text{II})$ state breaks the two $\text{Fe}-(\mu_2\text{-SR})-\text{Fe}$ bonds of the binuclear species.

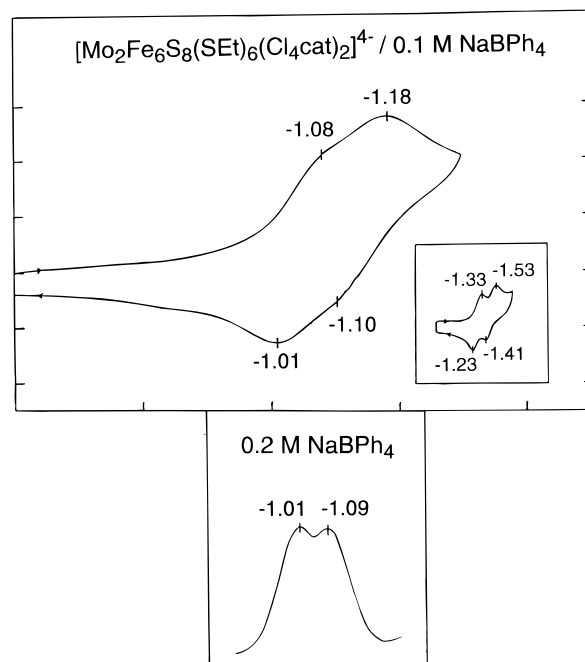


Figure 5. Cyclic voltammogram (100 mV/s) at ambient temperature of **1** in acetonitrile with 0.1 M NaBPh_4 supporting electrolyte. Inset: voltammogram of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6]^{3-}$ in acetonitrile.^{5c} The lower trace is a differential pulse voltammogram in acetonitrile with 0.2 M NaBPh_4 supporting electrolyte. Peak potentials are indicated.

5, does not show the single two-electron reduction step found with 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ present (Figure 4). Instead, two electron transfer steps are observed with $E_{1/2} \approx -1.05$ and -1.14 V. This behavior is related to that of the type **III** clusters $[\text{M}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{3-}$, which in general show two reversible reductions (Figure 5, inset). In the presence of 0.2 M NaBPh_4 , two steps of evidently equal current height are resolved with $E_p = -1.01$ and -1.09 V. These two redox steps are reasonably assigned to the intact double cubane, in which case another instance of stabilization of structure **V** by ion pairing with Na^+ is apparent. The positive potential shifts of *ca.* 200 mV must be a consequence of ion pairing, which reduces the cluster negative charge and facilitates reduction.

Cluster Interaction with Sodium Ions. The double-cubane clusters exhibit an interesting behavior toward sodium ions, as already observed in the stabilization of the bridged structure. As a general rule, sodium salts tend to be insoluble or sparingly soluble in acetonitrile. One exception is NaBPh_4 , which is freely soluble in acetonitrile. Further, the Et_4N^+ salts of **1–3** are sparingly soluble in acetonitrile, but become much more soluble in the presence of NaBPh_4 . Shown in Figure 6 is the behavior of the $\text{Fe}-\text{SCH}_2$ signals of **1** in the presence of 0–60 equiv of NaBPh_4 . With no salt present, a broadened, apparently double signal occurs. As the salt concentration is increased, the two signals split and become well resolved at *ca.* 20 equiv. Cluster **3** (15 mM) behaves similarly, except that the two signals merge at 3 equiv and thereafter separate and become well resolved at *ca.* 30 equiv and remain so to at least 100 equiv of salt (not shown). In both systems, the equal intensities of the resolved signals suggest that cause of the inequivalence is the diastereotopism of the methylene protons. No signals attributable to a single cubane were observed in either system.

These results provide further evidence for the interaction of sodium ions with double cubanes. We cannot prove the mode of interaction, but draw attention to the structural information in Figure 7, where part a depicts the core structure of the clusters in the crystalline state.^{7,20} The sites most likely to bind Na^+

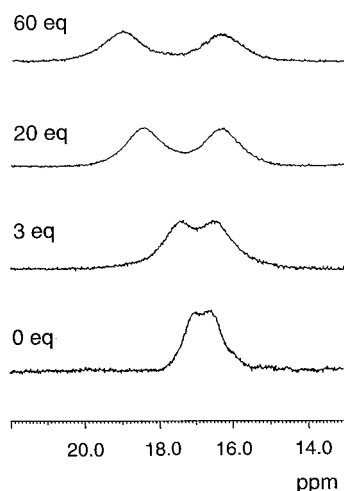


Figure 6. The behavior of the Fe-SCH₂ resonances of **1** (10 mM) in acetonitrile solution at 297 K in the presence of 0–60 equiv of NaBPh₄.

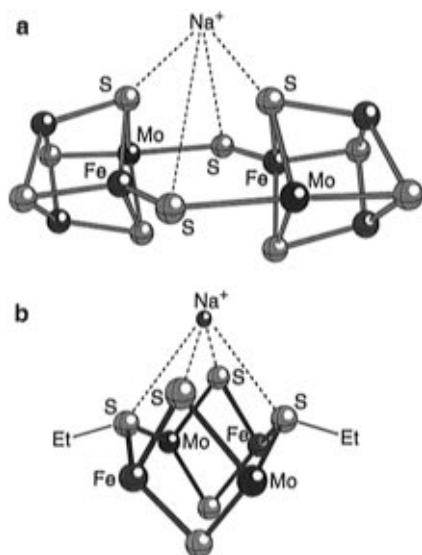


Figure 7. (a) The core and bridges of type **V** double-cubane clusters. (b) The central portion of the cluster in part a in a conformation containing a “boat-shaped” Mo₂Fe₂(μ₂-S)₂(μ₃-S)₂ ring as a possible locus of Na⁺ binding.

are one or both of the μ₂-S atoms and two μ₃-S atoms adjacent to the bridges. If the cluster conformation were *syn*, both μ₂-S atoms might interact if Na⁺ approached the center of the molecule, above the (idealized) Mo₂Fe₂(μ₂-S)₂ plane and on the side opposite the bridging ethyl groups. The bridge region is sufficiently flexible such that a conformation **b** can be achieved, in which the plane in part a is broken and a “boat-shaped” Mo₂Fe₂(μ₂-S)₂(μ₃-S)₂ ring results. This presents a more spatially compact set of three (*anti*) or four (*syn*) sulfur atoms that might bind to Na⁺. With use of the structural data for **9**,^{7a} a molecular modeling study has shown that the distances between “coordinated” Na⁺ and the four sulfur atoms are 2.9–3.0 Å. Among molecular species, these values are similar to the Na⁺–(μ₂-S) distances in [Na₂Fe₁₈S₃₀]⁸⁻, where Na⁺ is bound in the center of a cyclic iron–sulfur cluster.²⁴ Similar interactions are found in [Na₂(Fe₆S₉(SME)₂)₂]⁶⁻.²⁵

Lastly, we emphasize again the beneficial effect of Na⁺ on double cubane cluster stability. As already documented (Figure 3), molybdenum cluster **2** in acetonitrile exists in equilibrium **2** at 297 K and is fully dissociated into the single cubane **5** at 313 K. However, the addition of 15 equiv of NaBPh₄ renders **2** the only NMR-detectable species up to 323 K. Tungsten cluster **3** in acetonitrile is fully cleaved to single cubane **6** at 338 K. However, when 15 equiv of NaBPh₄ are present, only **3** is observed at this temperature. These findings suggest that the added stability arises from Na⁺ interactions with both bridging and core sulfur atoms. These interactions would appear to be promoted by the substantial negative charge (4–) of the double cubanes.

Stability of the Fe–S(R)–M Bridge. We note briefly the effects of components R and M in the bridge. When R = aryl as in **10** and **11**, these double cubanes when placed in acetonitrile at ambient temperature generate the single cubanes [MFe₃S₄–(SR)₃(al₂cat)(MeCN)]²⁻, as determined by a single set of R group resonances in the ¹H NMR spectra.^{7,15a} Evidently the increased basicity of alkyl- vs arylthiolates (manifested by a p*K*_a difference of *ca.* 3.5 for EtSH and PhSH²⁶) affords a considerably stronger bridging interaction. Although we have not pursued the matter beyond the foregoing observations, it seems clear that, on the basis of the behavior of double cubanes **2** and **3** in acetonitrile, the order W > Mo holds for the relative strengths of bridge bonds. No such discrimination is observed in the more strongly coordinating solvents DMF and Me₂SO, where cleavage is complete.

Summary. This investigation provides the first evidence that doubly thiolate-bridged double-cubane clusters of any description can maintain structural integrity in solution. This conclusion is based on the detection of bridging and terminal thiolate resonances, and multiple coupled oxidations in series **3**, both results being entirely consistent with [M₂Fe₆S₈(SEt)₆(cat)₂]⁴⁻. The structures **V** of three analogous clusters in the crystalline state have been established by X-ray diffraction.^{7,20} Coupled redox processes have been observed for sulfide-bridged Fe₄S₄ double cubanes,³ and for the majority of clusters in Figure 1, including doubly bridged **VII**^{9ab} and **VIII**.^{9d,10bc} This behavior is a reasonable criterion for a double-cubane structure, provided the bridges are too long or too unstable upon cluster redox, or do not electronically conjugate the component clusters. One or more of these factors apply to type **IX** clusters, which show one oxidation and one reduction process.¹¹ The stability of type **V** clusters is apparently aided on the one hand by a long Mo–S bond (2.70 Å), which diminishes van der Waals interactions between MFe₂ cubane faces that are held roughly parallel by the bridges, and on the other by rather strong Fe–S bonds (2.31 Å), which are at the long end of Fe–SR terminal bonds (2.25–2.31 Å, R = alkyl) in [Fe₄S₄]^{2+,1+} clusters.²⁷ The problem of the synthesis of bis(μ₂-SR)Fe₄S₄ double cubane as an analogue of the P-cluster **I** (with or without the inter-cubane S–S bond) remains.

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