

Insertion of $[VFe_3S_4]^{2+}$ and $[MoFe_3S_4]^{3+}$ Cores into a Semirigid Trithiolate Cavitand Ligand: Regiospecific Reactions at a Vanadium Site Similar to That in Nitrogenase

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The previously synthesized and structurally characterized cubane-type cores $[VFe_3S_4]^{2+}$ and $[MoFe_3S_4]^{3+}$ were inserted into the semirigid trithiolate ligand LS_3 (1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(*p*-tolylthio)benzenate (3⁻), anion of **3**) to afford the clusters $[VFe_3S_4(LS_3)(solvent)_3]^-$ (**6**), $[MoFe_3S_4(LS_3)(Cl_4cat)(solvent)_2]^{2-}$ (**9**) (solvent = DMF, Me₂SO; Cl₄cat = tetrachlorocatecholate(2⁻)), and $[MoFe_3S_4(LS_3)(dmpe)(SEt)]^-$ (**10**) (dmpe = 1,2-bis(dimethylphosphino)ethane). In these and related clusters, **3** binds at the Fe sites. Core volumes of **6**, **9**, and **10** (ca. 9.5–9.6 Å³) are similar to those of the previously inserted $[Fe_4S_4]^{2+}$ core and thus ensure a closely comparable fit in the ligand cavity. With **6**, the ligand directs substitution to the V site, leading to regiospecific reactions that were monitored by isotropic ¹H NMR shifts effected by the $S = 3/2$ cluster ground states. In small excess, Cl⁻, SCN⁻, PhCCPh, Et₃N, and N₂ and CO (saturated solutions) do not bind, *p*-cresolate and azide bind weakly with some decomposition, and hydrotris(pyrazolyl)borate(1⁻) and CN⁻ bind completely. Quaternary ammonium salts of $[VFe_3S_4(LS_3)(HB(pz)_3)]^{2-}$ (**7**) and $[VFe_3S_4(LS_3)(CN)_3]^{4-}$ (**8**), as well those of **6**, **9**, and **10**, were isolated on a preparative scale. Cluster **8** exhibits a reversible oxidation at a potential 0.50 V more negative than that of the corresponding process of **6**, indicating that strongly binding, anionic ligands can modulate redox potentials and associated stabilities of cluster oxidation states. It is concluded that the V site is, overall, less reactive toward substitution than monosolvated Mo sites in clusters related to **9**. The V site in **6** is, by X-ray absorption spectroscopic criteria, quite similar to that in the recently discovered V nitrogenases. The applicability of $[VFe_3S_4]^{2+}$ clusters as models of the V site in native clusters is considered.

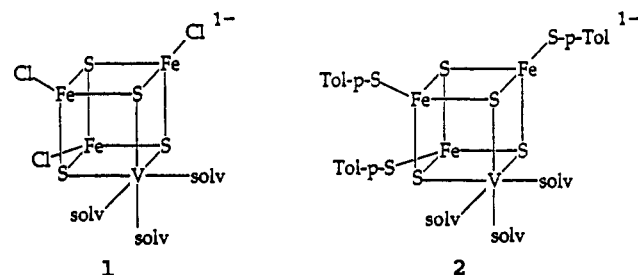
Introduction

Research carried out in this laboratory on the structural, electronic, and reactivity features of clusters containing cubane-type $MoFe_3(\mu_3-S)_4$ ¹⁻¹⁰ and $VFe_3(\mu_3-S)_4$ ¹¹⁻¹⁴ core units has been motivated by the resemblance of coordination environment in these clusters to those in the native clusters of the molybdenum and vanadium cofactors of nitrogenases. The structural criteria are Mo K- and L-edge XANES^{9,15} of intact proteins, cofactors, and synthetic clusters, the comparative results of Mo and V EXAFS of proteins and FeMo cofactor,¹⁶⁻²⁰ and X-ray crystallographic results for synthetic clusters.¹⁰⁻¹³ For example, the EXAFS of the FeV protein of *Azotobacter vinelandii* has been analyzed in terms of these interactions:²⁰ 3 ± 1 V-Fe at 2.76 (3) Å, 3–4 V-S at 2.33 (3) Å, and 2–3 V-N/O at 2.15 (3) Å. For the cluster $[VFe_3S_4Cl_3(DMF)_3]^-$ ¹¹⁻¹³ the corresponding crystallographic data

are 3 V-Fe at 2.777 (5) Å, 3 V-S at 2.336 (5) Å, and 3 V-O at 2.130 (17) Å. Encouraging agreements such as this between these metric features of native and synthetic cubane-type clusters mark the latter as the best available models of the local coordination units in the former.²¹

The reactivity of $MoFe_3S_4$ clusters has been explored in detail.¹⁻⁸ In clusters such as $[MoFe_3S_4Cl_3((al)_2cat)(solvent)_2]^{2-}$ ²² where the Fe (Cl⁻) and Mo (solvent) sites are in competition by having the indicated labile ligands, regiospecific reactions are normally observed. Thus, thiolate reacts preferentially at the Fe sites until they are completely substituted, whereas 1 equiv of PEt₃ or cyanide binds at the Mo site exclusively.⁴ Certain nitrogenase pseudo-substrates also react at the Mo site.⁷ One drawback of these clusters is that they possess only one labile coordination position at the Mo site. Methods for their synthesis always leave one catecholate or diphosphine coordinated to the Mo atom. It has not yet proven possible to remove this ligand with retention of the core structure. However, the reactivity information obtained may prove useful in interpreting ligand-binding reactions of native clusters. One clear example is furnished by the reaction of thiolate with the FeMo cofactor,²³ which results in binding at a Fe site.

As the foregoing Mo cluster, $[VFe_3S_4Cl_3(DMF)_3]^-$ (**1**) contains chloride at the Fe sites but has three potentially displaceable solvent molecules at the V site. Its reactivity properties and those



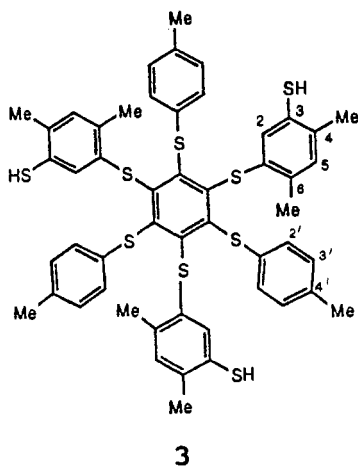
of derivative clusters are largely unexplored. However, several observations are pertinent. With 3 equiv of *p*-toluenethiolate,

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- (22) Abbreviations: (al)₂cat, 3,6-diallylcatecholate(2⁻); Cl₄cat, tetrachlorocatecholate(2⁻); dmpe, 1,2-bis(dimethylphosphino)ethane; HB(pz)₃, tris(2-pyrazolyl)hydroborate(1⁻); *p*-tol, *p*-tolyl; pz, pyrazolyl; solv, solvent.
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substitution occurs exclusively at the Fe sites.¹² The resultant cluster $[\text{VFe}_3\text{S}_4(\text{S-}i\text{-tol})_3(\text{solv})_3]^-$ (**2**) decomposes in the presence of additional thiolate, preventing determination of thiolate binding to the V site. With cyanide, **2** reacts at both types of sites, making it difficult to obtain regiospecificity.

Recently, in this laboratory the synthesis of the trithiol ligand 1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(*p*-tolylthio)benzene ($\text{L}(\text{SH})_3$, **3**) has been accomplished.^{24,25} Its



trianion acts as semirigid tridentate ligand to the cubane-type Fe_4S_4 unit, allowing the synthesis of the clusters $[\text{Fe}_4\text{S}_4(\text{LS}_3)\text{L}]^{2-}$ ($\text{L}' = \text{Cl}^-, \text{RS}^-$) in which Fe sites have been differentiated in a 3:1 ratio. Substitution reactions occur regiospecifically at the unique site.²⁴⁻²⁶ In this work we have determined that the ligand captures VFe_3S_4 and MoFe_3S_4 clusters by binding at the Fe sites only. We have utilized the resultant vanadium cluster $[\text{VFe}_3\text{S}_4(\text{LS}_3)(\text{sol})_3]^-$ to examine the reactivity of the V site in its cubane-type environment, which is related to the coordination unit of native FeV-cofactor cluster.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere with use of standard Schlenk techniques or an inert atmosphere box. Solvents were purified by distillation and degassed before use. The compounds $(\text{NH}_4)_3[\text{VS}_4]$,²⁷ $(\text{Et}_4\text{N})_4[\text{MoFe}_3\text{S}_4(\text{SEt})_6(\text{Cl}_4\text{cat})_2]$ ⁷ (which forms $[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{Cl}_4\text{cat})(\text{sol})]^{2-}$ (**4**) in coordinating solvents), and $(\text{Et}_4\text{N})[\text{MoFe}_3\text{S}_4(\text{SEt})_4(\text{dmpe})]$ ⁸ (**5**) were prepared as previously described. Ligand **3** was obtained by an improved version of the synthesis.²⁵ Anhydrous FeCl_2 (99.99%) was obtained from Cerac; other solvents and reagents were used as received.

$(\text{Me}_4\text{N})[\text{VFe}_3\text{S}_4(\text{Cl}_3(\text{DMF})_3] \cdot 2\text{DMF}$ (1**).** An earlier synthesis of this compound^{11,12} has been improved to increase the yield and eliminate contamination by ammonium salts. A solution of 6.6 g (52 mmol) of anhydrous FeCl_2 in 300 mL of DMF was treated with 3.0 g (13 mmol) of $(\text{NH}_4)_3[\text{VS}_4]$. After being stirred overnight, the brown reaction mixture was filtered and ether (200 mL) was added. The mixture was cooled to -20°C , the nearly colorless supernatant was decanted, and the gummy residue was washed with ether and dried in vacuo. A slurry of 1.5 g (10 mmol) of Me_4NBr in 200 mL of acetonitrile was added to this material, and the mixture was stirred for 6 h. Some white solid was removed by filtration, and the filtrate was evaporated in vacuo. The residue was redissolved in 200 mL of DMF. Diffusion of 150 mL of ether into the solution maintained at 5°C afforded 5.2 g (58%) of pure product as a highly crystalline black solid. Its ^1H NMR spectrum in Me_2SO showed no trace of a signal at 7.2 ppm due to NH_4^+ . The spectroscopic properties of this sample are identical with those reported earlier;¹² it was used without further purification.

$(\text{Me}_4\text{N})[\text{VFe}_3\text{S}_4(\text{LS}_3)(\text{DMF})_3]$ (6**).** In 20 mL of DMF, 0.082 g (0.98 mmol) of NaSEt and 0.300 g (0.32 mmol) of trithiol **3** was stirred under dynamic vacuum for 2 h. The orange solution was added to a solution

of 0.280 g (0.313 mmol) of **1** in 20 mL of DMF. An immediate reaction occurred, and after the mixture was stirred for 30 min, a red-brown solution was obtained. The solution was filtered, the filtrate was cooled to 5°C , and 50 mL of ether was diffused into the solution. A microcrystalline red-brown solid was collected, washed with ether, and dried in vacuo to afford 0.405 g (81%) of product. Upon addition of 40 mL of ether to the filtrate, a second crop of product (0.030 g) was collected for a total yield of 87%. An analytical sample was obtained by recrystallization from DMF/ether. Absorption spectrum (DMF): λ_{max} (ϵ_{M} , $\text{M}^{-1}\text{cm}^{-1}$) 380 (sh, 19 100), 455 (sh, 11 000) nm. ^1H NMR ($\text{Me}_2\text{SO}-d_6$, 296 K, anion): δ 2.27 (4'-Me), 6.49 (3'-H), 7.18 (2'-H), 8.86 (4-Me), 12.0 (6-Me), 14.5 (5-H). Anal. Calcd for $\text{C}_{60}\text{H}_{78}\text{Fe}_3\text{N}_4\text{O}_3\text{S}_3\text{V}$: C, 48.48; H, 4.95; Fe, 10.56; N, 3.53; S, 26.26; V, 3.21. Found: C, 47.21; H, 4.84; Fe, 10.70; N, 3.60; S, 26.32; V, 3.24.

$(\text{Me}_4\text{N})_2[\text{VFe}_3\text{S}_4(\text{LS}_3)(\text{HB}(\text{pz}))_3]$ (7**).** $\text{KHB}(\text{pz})_3$ (0.060 g, 0.240 mol) was added to a solution of 0.400 g (0.240 mol) of **6** in 20 mL of DMF. No color change was observed. The brown solution was stirred for 30 min, and 0.038 g (0.240 mmol) of Me_4NBr was added. After being stirred overnight, the reaction mixture was filtered and 50 mL of ether was layered on top of the brown filtrate. The solid that separated was collected, washed with ether, and dried in vacuo to afford 0.350 g (84%) of product as a black microcrystalline solid. ^1H NMR ($\text{Me}_2\text{SO}-d_6$, 296 K, anion): δ 2.28 (4'-Me), 5.96 (pz 4-H), 6.51 (3'-H), 7.21 (2'-H), 8.57 (4-Me), 12.0 (6-Me), 14.4 (5-H), 16.5 (pz 5-H).

$(\text{Me}_4\text{N})(\text{Et}_4\text{N})_3[\text{VFe}_3\text{S}_4(\text{LS}_3)(\text{CN})_3]$ (8**).** A solution of 0.060 g (0.384 mmol) of $(\text{Et}_4\text{N})\text{CN}$ in 2 mL of DMF was added to a solution of 0.100 g (0.063 mmol) of **6** in 10 mL of DMF. Within 5 min a light brown microcrystalline material formed. After the reaction mixture was stirred for 30 min, the solid was collected by filtration, washed with a small amount of DMF and then with ether, and dried in vacuo to afford 0.105 g (95%) of product. ^1H NMR ($\text{Me}_2\text{SO}-d_6$, 296 K, anion): δ 2.27 (4'-Me), 6.58 (3'-H), 7.11 (2'-H), 7.27 (4-Me), 11.1 (6-Me), 14.0 (5-H).

$(\text{Et}_4\text{N})[\text{MoFe}_3\text{S}_4(\text{LS}_3)(\text{Cl}_4\text{cat})(\text{DMF})_3]$ (9**).** A slurry of 0.500 g (0.527 mmol) of **3** in 30 mL of DMF was added to a solution of 0.570 g (0.263 mmol) of $(\text{Et}_4\text{N})_2[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{Cl}_4\text{cat})(\text{DMF})_3]$ in 20 mL of DMF. The reaction mixture was stirred under dynamic vacuum for 8 h. The red-brown solution was filtered, and ether (100 mL) was layered on top of the filtrate. After 24 h at -20°C , red-brown crystalline material had formed. This was collected, washed with ether, and dried in vacuo to yield 0.895 g (77%) of product. Absorption spectrum (DMF): λ_{max} (ϵ_{M} , $\text{M}^{-1}\text{cm}^{-1}$) 380 (sh, 25 300), 455 (sh, 18 000) nm. ^1H NMR (acetone- d_6 , 296 K, anion): δ 2.16 (4'-Me), 6.56 (3'-H), 7.25 (2'-H), 9.50 (4-Me), 13.3 (6-Me), 14.8 (5-H).

$(\text{Et}_4\text{N})[\text{MoFe}_3\text{S}_4(\text{LS}_3)(\text{dmpe})(\text{SEt})_3]$ (10**).** A slurry of 0.360 g (0.380 mmol) of **3** in 20 mL of DMF was added to a solution of 0.350 g (0.381 mmol) of **5** in 10 mL of DMF. The reaction mixture was stirred under dynamic vacuum for 12 h. The red-brown solution was filtered, and ether (50 mL) was layered on top of the filtrate. After 24 h at -20°C a black-brown crystalline material had formed. This was collected, washed with ether, and dried in vacuo to afford 0.520 g (81%) of product. Absorption spectrum (DMF): λ_{max} (ϵ_{M} , $\text{M}^{-1}\text{cm}^{-1}$) 382 (sh, 23 300), 482 (sh, 13 300) nm. ^1H NMR (CD_3CN , 296 K, anion): δ -3.13 (CH_2CH_3), 2.28 + 2.30 (4'-Me), 6.59 (2'-H), 7.35 (3'-H), 7.90 (CH_2 , dmpe), 8.15 (Me, dmpe), 10.0 + 10.9 (6-Me), 12.4 + 13.7 (4-Me), 14.3 + 15.2 (5-H).

Cluster compounds **7-10**, all of which were obtained in crystalline form, were not analyzed. However, their identity and substantial or full purity were established by ^1H NMR spectroscopy.

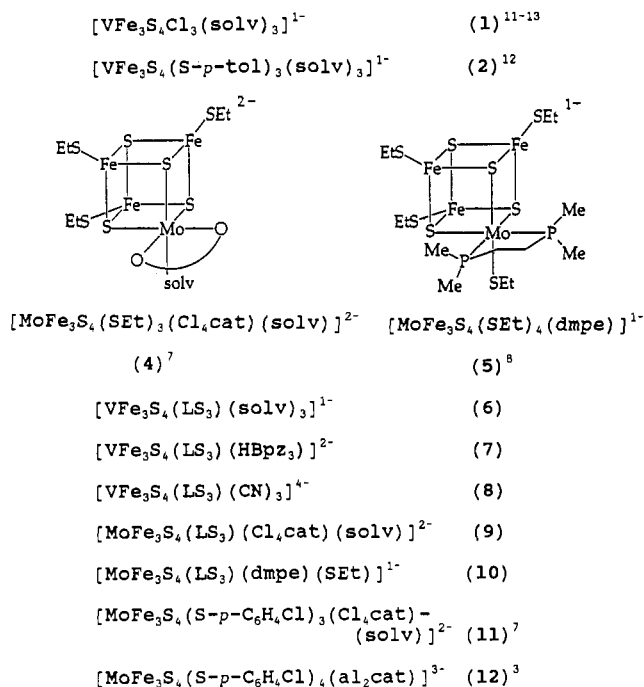
Physical Measurements. All measurements were made under anaerobic conditions. Absorption spectra were determined on a Cary 219 spectrophotometer. ^1H NMR spectra were obtained on a Bruker AM-300 or AM-500 spectrometer; chemical shifts are referenced to Me_2Si internal standard. Electrochemical measurements were made in Me_2SO solutions by using standard PAR instrumentation, a Pt working electrode, 0.2 M (*n*-Bu₄N)(ClO₄) supporting electrolyte, and a SCE reference electrode. Cyclic voltammograms were recorded at 100 mV/s.

Results and Discussion

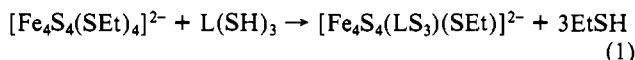
The following clusters are of principal interest in this investigation (solv = DMF, Me_2SO). Clusters **1**, **2**, **4**, **5**, **11**, and **12** have been reported earlier; **1**, **4**, and **5** have been utilized as starting materials for the new clusters **6-10** containing the anion of tridentate ligand **3**. Clusters **11** and **12** are useful for comparison purposes.

Cluster Insertion into Cavitated Ligand. Current evidence indicates that ligand **3** functions as a semirigid cavitated ligand of trigonal symmetry, in which the three coordinating "arms" are on one side of the central benzene ring and the three *p*-tolylthio "legs" are on the other side.^{24,25} The desired reactions of VFe_3S_4 and MoFe_3S_4 clusters, whereby terminal ligands are displaced and

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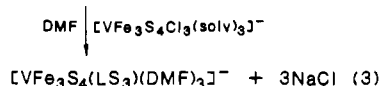
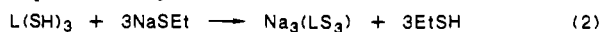


the heterometal cores are inserted into the ligand cavity, are schematically illustrated in Figure 1. The initial example of cluster insertion is ligand substitution reaction 1, which proceeds in high yield and results in the capture of the $[\text{Fe}_4\text{S}_4]^{2+}$ core with liberation of ethanethiol.²⁴⁻²⁶

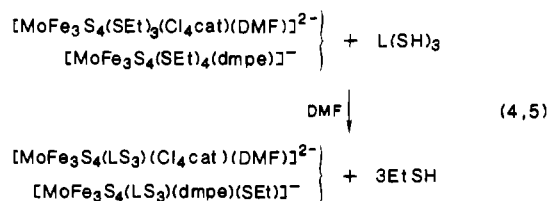


In the reactions that follow, cluster products were isolated as crystalline solids and were unambiguously identified by their ^1H NMR spectra, which are isotropically shifted and well resolved owing to the presence of the $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ cores, each of which has a $S = 3/2$ ground state.^{5,14} The spectra of clusters containing these cores have been extensively investigated^{1-4,7,8,12,23a} and are characterized by shifts that are mainly contact in origin and result from ligand-to-metal antiparallel spin transfer.

Reaction 1 and its precedents proceed essentially quantitatively when an alkanethiolate cluster is treated with a stoichiometric amount of arenethiolate.²⁸ Attempts to insert the $[\text{VFe}_3\text{S}_4]^{2+}$ core by a reaction analogous to (1) failed because of the instability of alkanethiolate cluster precursors. However, when ligand 3 was fully deprotonated by reaction 2, insertion reaction 3 afforded the



desired cluster 6 in almost quantitative yield as its Me_4N^+ salt. The ligand trianion was not isolated but was identified by its ^1H NMR spectrum, which is consistent with effective trigonal symmetry. The $[\text{MoFe}_3\text{S}_4]^{3+}$ core can be inserted by means of stoichiometric reactions 4 and 5 of the alkanethiolate precursor



clusters 4 and 5 with trithiol 3. Isolated yields of product clusters 9 and 10 are ca. 80%.

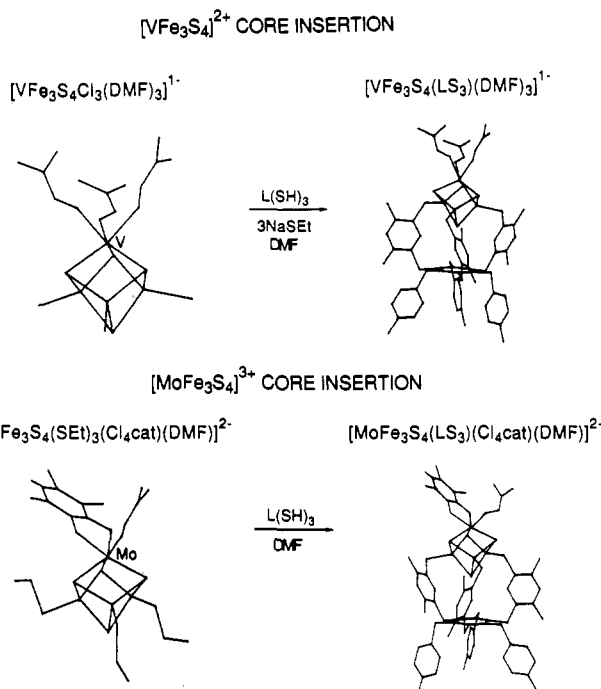


Figure 1. Schematic representation of the insertion of $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ cores into ligand $\text{L}(\text{SH})_3$ (3). The structures of initial clusters 6 and 9 were drawn from atomic coordinates of the same¹³ or a closely related⁷ cluster. The structure of the ligand is that found in $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Se}_4(\text{LS}_3)\text{Cl}]$.²⁵

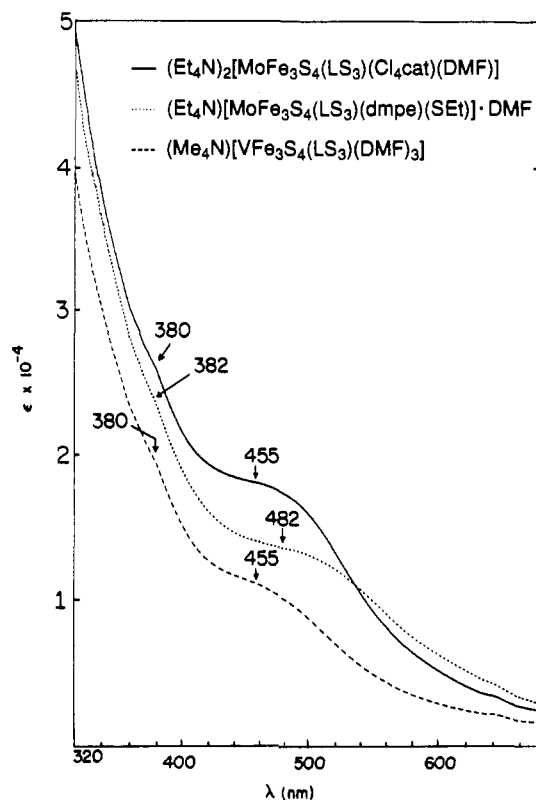


Figure 2. Absorption spectra of clusters 6, 9, and 10 in DMF solutions. The locations of spectral features are indicated.

Clusters 6, 9, and 10 were identified by their spectroscopic properties. The absorption spectra in Figure 2 of the product clusters, when compared with those of the precursors,^{7,8,12} show substantial red shifts of the intense lowest energy LMCT band. In the cases 4 (390 nm)/9 (455 nm) and 5 (402 nm)/10 (482 nm), the shifts are largely due to the replacement of an alkanethiolate with an arenethiolate ligand, an effect always observed with $[\text{Fe}_4\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ clusters. The pairs 2 (433 nm)/6

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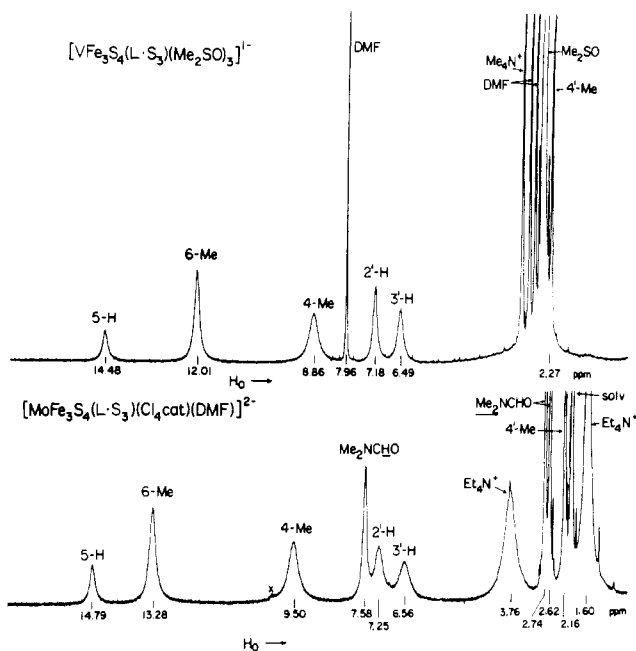


Figure 3. ^1H NMR spectra of clusters **6** (top) and **9** (bottom) in $\text{Me}_2\text{SO}-d_6$ and acetone- d_6 solutions, respectively, at 296 K. The signal assignments are indicated (cf. formula 3).

(455 nm) and **11** (448 nm⁷)/**9** (455 nm) evidence much smaller red shifts because of the presence of terminal arenethiolate ligands only. At least with **9** and **10**, the absorption spectra clearly indicate binding to the LS_3 ligand system.

Incisive identification of all clusters is afforded by their ^1H NMR spectra. Those of **6** and **9** are presented in Figure 3. Ligand numbering is given in formula 3; note that signals of the legs are designated with primes. In these and other spectra, the paramagnetically broadened 2-H signals were not located. Signal assignments are based on those for $[\text{Fe}_4\text{S}_4(\text{LS}_3)\text{L}']^{2-}$ clusters ($\text{L}' = \text{Cl}^-, \text{RS}^-$).²⁴ The present spectra and those of Fe_4S_4 clusters differ primarily in the greater line widths and isotropic shifts, which are larger for the heterometal clusters because of their greater paramagnetism. The spectra of **6** and **9** are indicative of trigonal symmetry. In the latter case, this arises from previously described fluxionality at the Mo site that involves solvent dissociation, chelate ring reorientation, and solvent rebinding.⁴ This behavior is not possible in **10**, where a strongly binding ligand has replaced solvent. Consequently, the effective cluster symmetry is reduced to C_{2v} and is manifested in the spectrum of **10** in acetonitrile (not shown) by the splittings of 5-H, 4- and 6-Me, and 4'-Me signals into doublets with a 2:1 intensity ratio. Signal assignments were checked by preparing the cluster containing $\text{dmppe}-d_{12}$.⁸

The absorption and ^1H NMR spectral results prove that the core insertion reactions in Figure 1 have occurred and that the resultant clusters have trigonal (**6**, **9**) or 2-fold (**10**) symmetry in solution. The facile capture of $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ cores is consistent with size considerations. The core volumes of **1**,¹³ **5**,⁸ and $[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_4(\text{al})_2\text{cat}]^{2-}$ (related to **4**) are nearly the same (9.56–9.62 Å³) and are 1.1–1.7% smaller than that of the $[\text{Fe}_4\text{S}_4]^{2+}$ core (9.73 Å³) as incorporated in $[\text{Fe}_4\text{S}_4(\text{LS}_3)\text{Cl}]^{2-}$.²² Ligand **3** is sufficiently flexible that it also readily accommodates the larger $[\text{Fe}_4\text{Se}_4]^{2+}$ core (10.71 Å³).²⁵

Reactions at the Vanadium Site. Ligand substitution reactions of clusters of the types $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{cat})(\text{sol})]^{2-}$ and $[\text{MoFe}_3\text{S}_4(\text{SR})_3(\text{cat})(\text{sol})]^{2-}$ have been thoroughly investigated. Inasmuch as regiospecific reactions at the Mo or Fe sites occur in nearly all cases,^{1–8} solvated cluster **9** offers no advantage in this respect. The next event of substitution will occur at the Mo site. Of the previously prepared VFe_3S_4 clusters, **1** contains particularly labile ligands at both metal sites. Reaction with 3 equiv of *p*-toluenethiolate occurs exclusively at the Fe sites, leading to **2**. While this cluster might be expected to direct any further reactions to the V site, it has proven rather unstable to certain additional

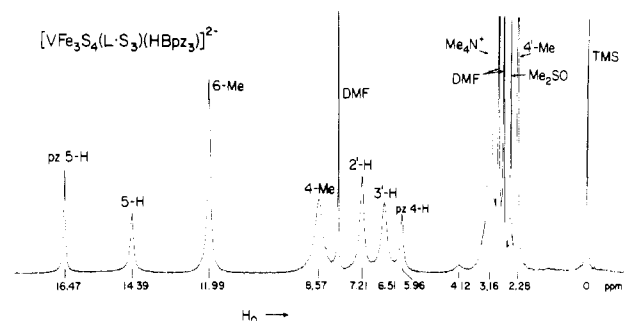
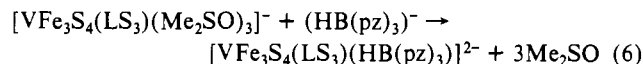


Figure 4. ^1H NMR spectrum of cluster **7** in $\text{Me}_2\text{SO}-d_6$ solution at 296 K. The signal assignments are indicated.

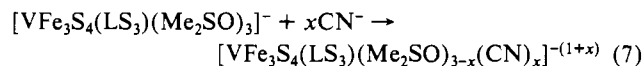
ligands including thiolate. As noted at the outset, 1–6 equiv of cyanide reacts at both Fe and V sites. Multiple ^1H NMR signals appear,²⁹ including those of free thiolate after 2 equiv. Cluster **6** is satisfactory for the examination of reactions at the V site solvated with Me_2SO or DMF. Some decomposition was observed by NMR spectroscopy in acetonitrile and THF, and reactions were not pursued in those solvents. Reaction systems initially containing 20 mM **6** were monitored by ^1H NMR in Me_2SO solutions.

No reaction was observed between **6** and 2–6 equiv of Cl^- , SCN^- , PhCCPh , and Et_3N or with CO in a saturated solution. Hydrosulfide or *p*-toluenethiolate caused decomposition of the cluster. With 1–3 equiv of $(\text{Et}_4\text{N})(p\text{-MeC}_6\text{H}_4\text{O})$, the cluster monosubstituted at the V site was identified by ^1H NMR spectroscopy and some decomposition was observed. With $(\text{Et}_4\text{N})\text{N}_3$, an equilibrium mixture of substituted species occurs but complete substitution was not achieved even with 12 equiv. Reaction 6



occurs quantitatively with a stoichiometric quantity of ligand. The spectrum of the product cluster **7**, shown in Figure 4, indicates a trigonally symmetric species with isotropically shifted signals of pyrazolyl protons³⁰ and an upfield displacement of the 4-Me resonance by 0.29 ppm. Other ligand signals are nearly unshifted.

The reactions of cluster **6** with $n = 1, 3,$ and 5 equiv of $(\text{Et}_4\text{N})\text{CN}$ afford the NMR spectra in Figure 5. The results can be interpreted in terms of reaction 7; clusters are abbreviated as



$[3-x, x]$. At $n = 1$, new isotropically shifted features appear just downfield of the 5-H, 6-Me, and 4-Me signals of $[3,0] = \mathbf{6}$. The $[3,0]$ and $[2,1]$ clusters are diminished at $n = 3$ where $[1,2]$ becomes dominant. At $n = 5$, substitution is complete with the formation of $[0,3] = \mathbf{8}$. The final spectrum indicates a trigonally symmetric product in which cyanide must be bound at the V site because of the retention of isotropically shift resonances of the LS_3 ligand, all of which are significantly shifted from their positions in the spectrum of **6**. Compound **8** was isolated as a sparingly soluble, microcrystalline solid. When **8** is dissolved in Me_2SO , an equilibrium mixture of **8** and $[1,2]$ is formed.

Electron-Transfer Behavior. Cyclic voltammograms of four VFe_3S_4 clusters in Me_2SO solutions are presented in Figure 6. The behavior of **2** is representative of a larger set:¹² a chemically reversible oxidation at +0.1 to –0.4 V and an irreversible reduction below ca. –1.4 V vs SCE. Clusters **2** and **6** have nearly identical behavior, with $E_{1/2} = -0.33$ and –0.34 V, respectively. Coulometry of **6** over a 30-min period gave $n = 1.01$ for oxidation and $n = 0.93$ for rereduction. Further, solutions of the oxidized form were found to be stable for at least 12 h by cyclic voltammetry. These

(29) There are a total of 16 mono- through hexasubstituted clusters, of which 12 are distinguishable in principle by NMR.

(30) Resonances are tentatively assigned on the basis of line widths. The 3-H resonance, from that proton nearest to the V site, was not detected, presumably because of paramagnetic broadening.

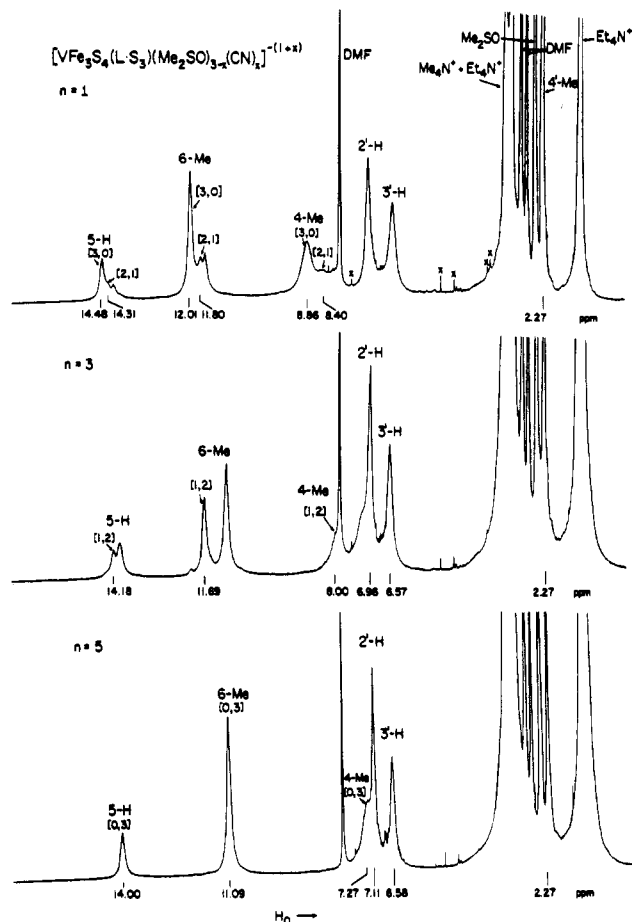


Figure 5. ^1H NMR spectra for reaction of cluster 6 with $n = 1, 3,$ and 5 equiv of $(\text{Et}_4\text{N})\text{CN}$ in $\text{Me}_2\text{SO}-d_6$ solution at 296 K. The signal assignments of product clusters $[3-x,x]$ are indicated; $[0,3] = 8$.

observations demonstrate the stability of the oxidized cluster. Cluster 7 differs from all others in having a reversible one-electron reduction ($E_{1/2} = -1.52$ V). Certainly the most interesting result is the effect of cyanide binding. The potential of 8 ($E_{1/2} = -0.84$ V) is shifted by -0.50 V vs that of 6. A related but smaller shift (-0.27 V) has been found between 11 (solv = MeCN) and its monocyano adduct.³ The greater shift here doubtless arises in large part by an increase in overall cluster negative charge by 3 units.

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

(1) The heterometal cubane-type cores $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ cores can be inserted in the semirigid ligand 3 either by chloride displacement with the ligand trianion (6) or alkane-thiolate substitution with the protonated ligand (9, 10). These results further demonstrate the affinity of thiolate ligands for Fe sites and, with related findings,²⁴⁻²⁶ show that the ligand is sufficiently flexible to accommodate $\text{MFe}_3(\text{S}/\text{Se})_4$ cores ($\text{M} = \text{Fe}, \text{V}, \text{Mo}$) of volumes in the approximate range $9.5-10.7 \text{ \AA}^3$.

(2) Tridentate ligand 3 does not significantly arrest the slow decomposition of the solvated $[\text{VFe}_3\text{S}_4]^{2+}$ core in weakly coordinating solvents (MeCN, THF) but does sufficiently stabilize Fe sites that substitution reactions at the V site can be examined in 6.

(3) Despite its trisolvated condition, the V site in 6 is not especially reactive. Of the ligands tested, it binds weakly and incompletely *p*-cresolate and azide when present in excess but does bind completely the relatively strong ligands $(\text{HB}(\text{pz})_3)^-$ and CN^- in trigonally symmetric 7 and 8, respectively, which were isolated as quaternary ammonium salts. The lack of further reactivity of 8 in the presence of 9 equiv of CN^- illustrates the regiospecificity enforced by ligand 3. In contrast to 6, monosolvated clusters 9 and 11 (and the W analogue of 11) stoichiometrically bind a much larger variety of ligands, including R_3P , RS^- , RO^- , CN^- , N_3^- ,

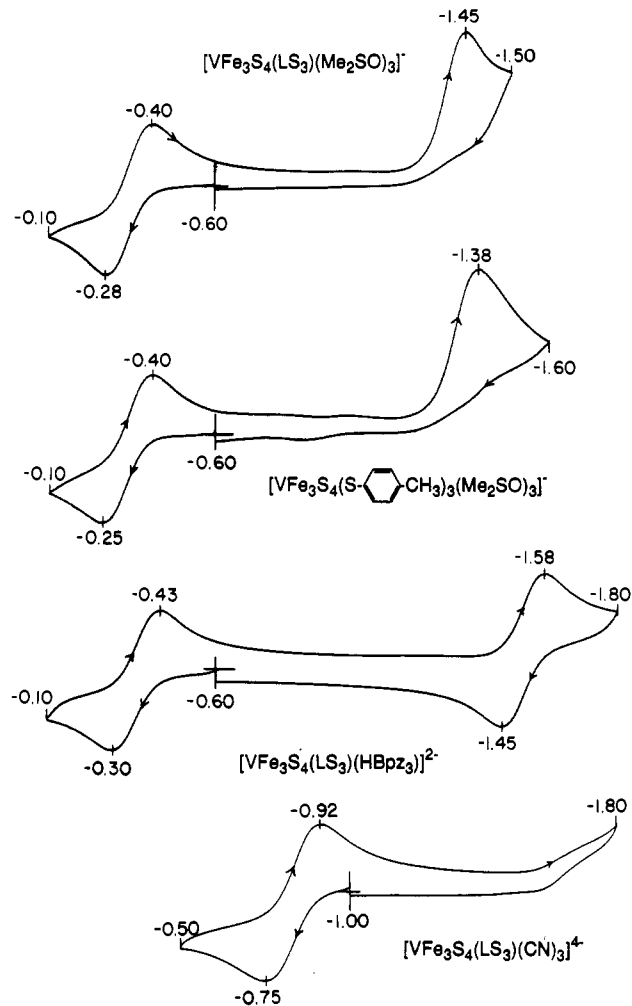


Figure 6. Cyclic voltammograms (100 mV/s) of clusters 6, 2, 7, and 8 in Me_2SO solutions. The peak potentials vs SCE are indicated.

PhNNH_2 , amines, and NH_3 .¹⁻⁸ As the VFe_3S_4 clusters, these species do not bind dinitrogen.

(4) $[\text{VFe}_3\text{S}_4]^{2+}$ clusters generally exhibit a chemically reversible oxidation and an irreversible reduction. The 0.50-V negative shift of potential between 6 and the tricyano cluster 8 for the $[\text{VFe}_3\text{S}_4]^{3+,2+}$ redox step illustrates more clearly than heretofore the influence of strong anionic ligands on cubane cluster potentials, there being no prior example of this effect among the extensively studied Fe_4S_4 clusters.

The value of $[\text{VFe}_3\text{S}_4]^{2+}$ clusters in structural studies of the native V-Fe-S cluster in nitrogenases is made apparent by the employment of 1 as a structural model for the V site as examined by X-ray absorption spectroscopy.^{19,20} Their appropriateness as spectroscopic and reactivity models is under further investigation in this and another laboratory. However, it is now evident that the trisolvated V site as encountered in 1, 2, and 6 (solv = DMF, Me_2SO) is insufficiently reactive to bind detectably enzyme substrates or pseudosubstrates. If a more reduced state of the clusters is required, the irreversible reductions at very negative potentials do not indicate easy accessibility to that state. We have not yet isolated clusters in the $[\text{VFe}_3\text{S}_4]^{3+}$ oxidation state, which we anticipate to be stable. On the basis of the results for 8, this state is decidedly stabilized by strong anionic ligands. Modulation of redox potentials and associated stabilities of the more oxidized states in cubane-type clusters is of potential biological significance and is under active investigation. Lastly, the recognition of another alternative nitrogenase from *A. vinelandii*,³¹ which contains neither V nor Mo but does contain Fe and sulfide, provides one case in

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which binding and activation of substrates (N_2 , H^+ , C_2H_2) cannot involve any metal but Fe. It remains to be discovered if heterometals (V, Mo) execute a binding and/or activating function in their nitrogenases.

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O₂ and CO Binding to "Jellyfish" Type Iron(II) Porphyrins

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The syntheses of "jellyfish" type iron(II) porphyrins and their O₂ and CO affinities in the presence of an excess axial base (1,2-dimethylimidazole) in toluene are reported, together with the O₂ affinities for the corresponding cobalt(II) porphyrins. The O₂ affinities for the Co(II) porphyrins decreased with an increase in the steric bulk of the fences appended to the porphyrin plane, on which the axial base binding occurs. On the other hand, the O₂ and CO affinities for the Fe(II) porphyrins did not exhibit a trend similar to that observed for the O₂ affinities for the Co(II) porphyrins. From the measurements of ¹H NMR spectra for both O₂ and CO adducts of the Fe(II) porphyrins, the conformations of cavities were significantly different in the Fe(II) porphyrin having pivalamide groups as fences, though the ¹H NMR signals of protons in the cavities were similar among the corresponding free-base porphyrins. Thus, steric effects of the cavities are responsible for the reduced O₂ and CO affinities of the Fe(II) porphyrin. Electronic paramagnetic resonance (EPR) spectra for the bisligated Fe(III) porphyrins were measured in CDCl₃ at 77 K, and the changes in the crystal field parameters are also discussed.

In the preceding paper,¹ we reported that O₂ affinities of "jellyfish" type Co(II) porphyrins vary with changes in the fence structures around the axial base binding site, while the cavity structures around the O₂ binding site remain unchanged (Figure 1). To explain these results, we postulated that the structural changes around the axial base induce variations in the orientation (ϕ) of the axial base plane with respect to a N(porphyrin)-Co-N(porphyrin) axis. Hence, it follows that changes in the strength of the π -electron interaction between the axial base and cobalt(II) will result in changes in O₂ affinities.

In order to elucidate on the mechanism of the changes in O₂ affinities for jellyfish porphyrinato Co(II) and Fe(II) complexes, this paper describes the syntheses of jellyfish iron(II) porphyrins and reports their O₂ and CO affinities, together with the O₂ affinities for the corresponding Co(II) porphyrins. ¹H NMR spectra for the O₂ and CO adducts of Fe(II) porphyrins were also measured to examine the environments near O₂ and CO binding sites (cavities) of these complexes. In order to obtain data on the changes in ϕ of jellyfish Fe(II) porphyrins, EPR spectra of their Fe(III) complexes were measured in the presence of excess 1-methylimidazole (1-MeIm) in frozen CDCl₃, and the changes in ϕ are discussed on the basis of the differences in the crystal field parameters.²

Experimental Section

General Information. Electronic spectra were recorded on a Hitachi 340 spectrophotometer. Affinities of O₂ and CO were determined by spectrophotometric titration using the flow method.³ Affinities of O₂ for Co(II) porphyrins were determined as previously described.^{1,4} The Fe(II) porphyrins were prepared by mixing⁵ Fe(III) porphyrins in toluene with aqueous sodium dithionite under Ar. After separation of the two phases, the toluene layer was transferred under Ar into a cell mounted with a rubber septum equipped with gas-inlet and -outlet tubes. A excess amount of 1,2-dimethylimidazole (1,2-Me₂Im) was added to the solution under Ar, and various partial pressures of O₂ or CO were passed through

the solution via the gas-inlet and -outlet tubes. Temperatures of the solutions were maintained at 25 ± 0.1 °C by the use of a constant-temperature circulation pump (Neslab Model RTE-8) and a variable-temperature cell holder (Hitachi). Various partial pressures of O₂ or CO were obtained by a Gas Mixture instrument (Kofloc Model GM-3A) constructed of mass flow controllers and flowmeters. The concentration of 1,2-Me₂Im was 0.07 M, while concentrations of Fe(II) porphyrins and Co(II) porphyrins were ca. 1×10^{-5} and ca. 5×10^{-5} M, respectively. The spectra were recorded in the 600-460-nm range for Co(II) porphyrins and in the 500-350-nm range for Fe(II) porphyrins. $P_{1/2}$ values (half-saturation gas pressures for O₂ or CO binding) were calculated by using the method of Beugelsdijk and Drago.⁶ Reversibility was checked after the last CO or O₂ addition by purging with N₂ gas (7 mL/min) for 30 min; more than 90% reversibility was achieved after 2 h of carbonylation for the Fe(II) porphyrins and oxygenation for the Co(II) porphyrins. The reversibilities achieved after 2 h of oxygenation were more than 75%, 80%, and 90% for [Fe(Az-piv $\beta\beta$)], [Fe(Az-val $\beta\beta$)], and [Fe(Az-P)], respectively.

EPR spectra were recorded at 77 K on a JEOL FE2XG instrument operating at the X band. The magnetic field was calibrated with a NMR gaussmeter (JEOL ES-FC4), and the frequency was calibrated with MnO₂ ($g = 2.0034$). Concentrations of EPR samples were ca. 5×10^{-3} M for Fe(III) porphyrins in CDCl₃.

Proton NMR spectra were recorded on a JEOL GSX-400 and a JEOL FX-100 spectrometer. Preparations of NMR samples were as follows: The Fe(III) porphyrin was reduced in aqueous sodium dithionite and CH₂Cl₂ under Ar; the dichloromethane layer was washed with degassed H₂O and the solvent stripped off by passing Ar; the reduced product was dissolved in degassed toluene-*d*₈ containing 1,2-Me₂Im, and the solution was transferred to an NMR tube via a stainless steel tube; the solution was exposed to an atmosphere of O₂ or CO at room temperature; spectra for the O₂ and CO adducts were obtained at -20 and 24 °C, respectively; concentrations of the Fe(II) porphyrins and 1,2-Me₂Im were ca. 5×10^{-3} and 0.07 M, respectively.

Materials. Toluene was stirred with concentrated H₂SO₄ and then washed with 5% NaOH and H₂O, dried over CaCl₂, and distilled. 1-MeIm and 1,2-Me₂Im were vacuum-distilled from KOH. Silica gel (Wakogel C-200) was used for column chromatography. The 8.97% O₂ in N₂ mixture and the 995 ppm of CO in N₂ mixture were commercially obtained.

Synthesis. 5 β ,15 β -Bis(2-pentanamidophenyl)-10 α ,20 α -bis(nonanediamidodi-*o*-phenylene)porphyrin (H₂-Az-val $\beta\beta$), 5 β ,15 β -Bis[2-(2,2-dimethylpropanamido)phenyl]-10 α ,20 α -bis(nonanediamidodi-*o*-phenylene)porphyrin (H₂-Az-piv $\beta\beta$), 5,15-diphenyl-10 α ,20 α -bis(nonanediamidodi-*o*-phenylene)porphyrin (H₂-Az-P), and their cobalt(II) complexes were prepared by the previously described method.¹

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