

listed in tables, were initially strong but decreased in intensity with time (more rapidly than peaks from **8**). These peaks were all sharp, in keeping with the general observation throughout this work that rates of inversion at sulfur are relatively slow on the NMR time scale when the sulfur atom is incorporated in a chelate ring. Again, peaks due to two diastereomers are resolved (intensity ratio approximately 3:1), including two distinct doublets of doublets in the ^{195}Pt spectrum (Table I). One unusual aspect of the ^1H spectrum is the very low shielding of the resonances due to the methine proton in **7**, near 5.4 ppm (Table II). Because of the complexity of the methylene region of this spectrum, no attempt was made to analyze it in detail. A clear assignment of peaks due to **7** was not possible in the ^{13}C spectrum, because this species disappeared too rapidly from the solution.

Some of the spectra from solutions containing **7** and **8** also showed a number of weaker peaks (e.g., in the ^{15}N spectrum and in the *S*-methyl region of the ^1H spectrum). No attempt was made to assign these in detail. It is possible that some of these peaks were due to *cis*-Pt(NH $_3$) $_2$ (metH-S)(H $_2$ O) $^{2+}$.

Since the S,O-chelate ring in Pt(NH $_3$) $_2$ (metH-S,O) $^{2+}$ (**7**) is seven-membered, it might be expected to be less stable thermodynamically and kinetically than the corresponding six-membered ring in Pt(NH $_3$) $_2$ (mecysH-S,O) $^{2+}$ (**6**). This probably accounts for the greater complexity of the reactions involving methionine. There would be a higher proportion of the aqua complex *cis*-Pt(NH $_3$) $_2$ (metH-S)(H $_2$ O) $^{2+}$ in equilibrium with the chelate, and the rate of ring closure to the S,O-chelate is probably slower than in the mecys analogue. This allows some *cis*-Pt(NH $_3$) $_2$ (metH-S) $^{2+}$ (**8**) to form in the course of the reaction between **1** and methionine. It might also be expected that this factor would allow

much faster isomerization from the S,O- to the S,N-chelate. In fact, from our qualitative observations, the rates of isomerization are comparable for mecys and methionine complexes. The balancing factor is probably a slower rate of formation of the six-membered chelate ring in Pt(NH $_3$) $_2$ (metH-S,N) $^{2+}$ (**5**) from *cis*-Pt(NH $_3$) $_2$ (metH-S)(H $_2$ O) $^{2+}$ than in the corresponding formation of the five-membered ring in Pt(NH $_3$) $_2$ (mecysH-S,N) $^{2+}$ (**3**). We have previously shown that formation of a Pt-N bond to produce a chelate ring is much slower when the ring to be formed is six- rather than five-membered, in amino acid 14 and (aminoalkyl)-phosphonate 27 complexes of platinum.

Conclusion. We have now demonstrated that "metastable" complexes play an important role in the solution chemistry of these complexes with relatively complex ligands, as well as those with simpler amino acids and analogues. 13,14,27 As has been previously noted, 16 the facile loss of coordinated ammonia from diammineplatinum(II) complexes with sulfur donors has some implications when the ultimate fate of ammine-platinum complexes *in vivo* is under consideration.

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Registry No. **1**, 52241-26-6; **2a**, 111349-55-4; **2b**, 111465-01-1; **3a**, 111349-56-5; **3b**, 111465-02-2; **4** (a?), 111465-03-3; **4** (b?), 111464-97-2; **5**, 111349-57-6; **6**, 111464-98-3; **7** (isomer 1), 111464-99-4; **7** (isomer 2), 111465-04-4; **8**, 111465-00-0; *cis*-Pt(NH $_3$) $_2$ (ONO $_2$) $_2$, 41575-87-5; D $_2$, 7782-39-0.

(27) Appleton, T. G.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* **1986**, *25*, 720.

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

Reduction of *n*-C $_5$ H $_{11}$ N $_3$ Catalyzed by Single Cubane Clusters with Mo-Fe-S and Fe-S Cores, Mediated with Methyl Viologen in Aqueous Micellar Solutions

Koji Tanaka, Makoto Moriya, Satoshi Uezumi, and Toshio Tanaka*

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The Mo-Fe-S double cubane cluster [Mo $_2$ Fe $_6$ S $_8$ (SC $_6$ H $_4$ -*p*-*n*-C $_8$ H $_{17}$) $_6$ (O $_2$ C $_6$ Cl $_4$) $_2$] $^{4-}$ bridged by two SC $_6$ H $_4$ -*p*-*n*-C $_8$ H $_{17}$ $^-$ anions is dissociated into two [MoFe $_3$ S $_4$ (SC $_6$ H $_4$ -*p*-*n*-C $_8$ H $_{17}$) $_3$ (O $_2$ C $_6$ Cl $_4$)L] $^{2-}$ (**1**; L = DMF, Me $_2$ CO) single cubane clusters in polar organic solvents, such as DMF and Me $_2$ CO. The solvent molecule coordinated to the molybdenum of the MoFe $_3$ S $_4$ core is easily substituted by *n*-C $_5$ H $_{11}$ N $_3$. In the corresponding single cubane cluster with the Fe $_4$ S $_4$ core, [Fe $_4$ S $_4$ (SC $_6$ H $_4$ -*p*-*n*-C $_8$ H $_{17}$) $_4$] $^{2-}$ (**2**), however, the thiolate ligand is substituted by *n*-C $_5$ H $_{11}$ N $_3$ only in the reduced 3- state. Both **1** and **2** function as catalysts for the reduction of *n*-C $_5$ H $_{11}$ N $_3$ by Na $_2$ S $_2$ O $_4$ in aqueous Triton X-100 micellar solutions, giving an equal amount of *n*-C $_5$ H $_{11}$ NH $_2$ and N $_2$. The reduction is enhanced efficiently by the addition of methyl viologen dication (MV $^{2+}$). The MV $^{2+}$ radical cation formed by the reduction of MV $^{2+}$ with Na $_2$ S $_2$ O $_4$ effectively transfers electrons to **1** to reduce *n*-C $_5$ H $_{11}$ N $_3$ not only with two electrons but also with six and eight electrons, affording N $_2$ H $_4$ and NH $_3$ as well as *n*-C $_5$ H $_{11}$ NH $_2$ and N $_2$. On the other hand, **2** catalyzes only the two-electron reduction even in the presence of MV $^{2+}$ to give *n*-C $_5$ H $_{11}$ NH $_2$ and N $_2$, suggesting that **1** is superior to **2** as a catalyst for the multielectron reduction of *n*-C $_5$ H $_{11}$ N $_3$.

Introduction

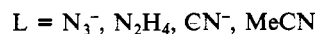
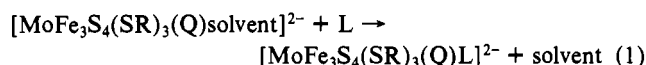
Nitrogenase is composed of iron-sulfur and molybdenum-iron-sulfur proteins, the former protein of which functions as an electron-transfer catalyst from a reduced species of ferredoxin to the latter protein involving molybdenum-iron cofactors (MoFe-co) and Fe $_4$ S $_4$ clusters. 1 The MoFe-co may be an active center for the reduction of dinitrogen to ammonia and is believed to involve novel molybdenum-iron-sulfur clusters; 2 the most probable atomic ratios of Mo:Fe:S in the MoFe-co have been reported as 1:6-8:8-9. 3 The spectroscopic study on the MoFe-co suggests

that both molybdenum and iron atoms are placed in a sulfide-rich coordination spheres. 4 Along this line, various Mo-Fe-S clusters have been prepared as models of the MoFe-co. 5 Among those,

- (1) (a) Dalten, H.; Mortenson, L. E. *Bacteriol. Rev.* **1972**, *231*. (b) Mortenson, L. E.; Thorneley, R. N. F. *Annu. Rev. Biochem.* **1979**, *48*, 387.
- (2) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 348.
- (3) (a) Nelson, M. J.; Lery, M. A.; Orme-Johnson, W. H. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 147. (b) Yang, S. S.; Pan, W. H.; Friesen, G. D.; Burgess, B. K.; Corbin, J. L.; Stiefel, E. I.; Newton, W. E. *J. Biol. Chem.* **1982**, *257*, 8042.

- (4) (a) Cramer, S. P.; Hodgson, K. O.; Stiefel, E. I.; Newton, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 2748. (b) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398. (c) Cramer, S. P.; Gillum, W. O.; Hodgson, K. O.; Mortenson, L. E.; Stiefel, E. I.; Chisnell, J. R.; Brill, W. J.; Shah, V. K. *J. Am. Chem. Soc.* **1978**, *100*, 3814. (d) Yamane, T.; Weinger, M. S.; Mortenson, L. E.; Rossmann, M. G. *J. Biol. Chem.* **1982**, *257*, 1221. (e) Conradson, S. D.; Burgess, B. K.; Newton, W. E.; Hodgson, K. O.; McDonald, J. W.; Rubinson, J. F.; Gheller, S. F.; Mortenson, L. E.; Adams, M. W. W.; Maschark, P. K.; Armstrong, W. A.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 7935. (f) Hoffman, B. M.; Venters, R. A.; Roberts, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 4711. (g) Huynh, B. H.; Henzl, M. T.; Christner, J. A.; Zimmermann, R.; Orme-Johnson, W. H.; Munck, E. *Biochim. Biophys. Acta* **1980**, *623*, 124. (h) Flank, A. M.; Weinger, M. W.; Mortenson, L. E.; Cramer, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 1049. (i) Eidsness, M. K.; Flank, A. M.; Smith, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 2746.

a double cubane cluster $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SR})_6\text{Q}_2]^{4+}$ (R = alkyl and aryl group; Q = 3,6-disubstituted catecholate or tetrachlorocatecholate)⁶ has especially been interesting, since in polar organic solvents such as DMF, THF, and acetone the double cubane cluster is readily dissociated into two solvated single cubane clusters with the MoFe_3S_4 core (eq 1), and the solvent molecule is easily



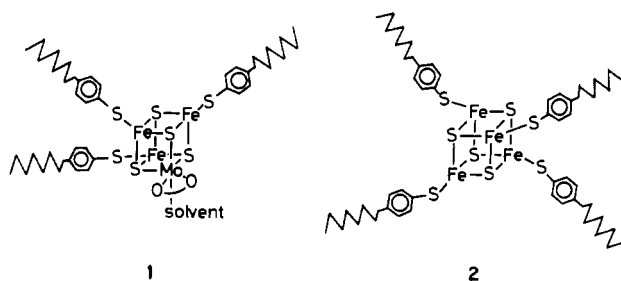
replaced by some of the nitrogenase substrates such as N_3^- , N_2H_4 , CN^- , and CH_3CN .⁶

Although the view that the active site of nitrogenases may be the molybdenum atom of the MoFe-co is generally accepted, no direct evidence that can eliminate the possibility of iron as an active site has been provided so far. In the Fe_4S_4 core of 4-Fe ferredoxins, iron atoms coordinated by three inorganic sulfides and one cysteine sulfur are normally considered to be coordinatively saturated and solely concerned with an electron-transfer catalyst in various biological redox reactions such as N_2 - and CO_2 -fixation, NO_3^- reduction, and so on.⁷ The chemistry of Fe_4S_4 clusters has revealed that alkanethiolates ligated to the iron atoms of an Fe_4S_4 core are labile toward substitution reactions,⁸ and the phenolate ligand of $[\text{Fe}_4\text{S}_4\text{Cl}_2(\text{OC}_6\text{H}_5)_2]^{2-}$ undergoes partial dissociation in polar organic solvents such as DMSO, DMF, and CH_3CN to afford solvated clusters.⁹ On the other hand, the iron atom in the Fe_4S_4 core is known to expand the coordination number from four to five; for instance $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}o\text{-OH})_4]^{2-}$ ¹⁰ and $[\text{Fe}_4\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{SC}_6\text{H}_5)_2]^{2-}$ ¹¹ involve one O-S and two S-S bidentate ligands, respectively. Therefore, if the coordination environment around the iron atom in MoFe-co is similar to that in the Fe_4S_4 core, iron atoms in MoFe-co may be capable of binding nitrogenase substrates by either substitution or addition reaction. Moreover, the reduced species of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ prepared not only chemically but also electrochemically can reduce nitrogenase substrates such as C_2H_2 ,¹² CH_3CN ,¹³ CH_3NC ,¹³ and N_2H_4 ¹⁴ in organic solvents as well as in water. It seems, therefore, to be of importance to clarify the function of the molybdenum in a single cubane MoFe_3S_4 cluster by comparing it with the same type of Fe_4S_4 cluster as catalysts in multielectron reductions of nitrogenase or pseudonitrogenase substrates in connection with nitrogenase reactions, in which dinitrogen is reduced with eight electrons to afford 2 mol of ammonia as well as 1 mol of dihydrogen (eq 2).¹



In the enzymatic reactions by nitrogenase¹⁵ and hydrogenase,¹⁶ 4-Fe ferredoxins can be replaced by $\text{Na}_2\text{S}_2\text{O}_4$ -reduced methyl viologen radical cation (MV^{2+}) as an electron donor. Synthetic Fe_4S_4 and MoFe_3S_4 clusters, however, exhibit their redox potentials at values more negative than -1.00 V vs SCE in organic solvents unless those clusters are ligated by an arenethiolate with a strong electron-attracting group such as NO_2 .¹⁷ The reduction of water-insoluble synthetic Fe_4S_4 clusters has, therefore, been accomplished by using acenaphthylenide radical anion^{12a} ($E_{1/2} = -1.70$ V vs SCE) or by electrochemical techniques^{12b,13,14} in place of $\text{Na}_2\text{S}_2\text{O}_4$ ($E_m = -0.90$ V vs SCE in H_2O at pH 9.0¹⁸). On the other hand, water-soluble synthetic Fe_4S_4 clusters with a hydrophilic substituent such as $[\text{Fe}_4\text{S}_4(\text{SC}_2\text{H}_4\text{COO}^-)_4]^{6-}$ ($E_{1/2} = -0.83$ V vs SCE)¹⁹ can thermodynamically be reduced with $\text{Na}_2\text{S}_2\text{O}_4$ in water. The reduced species of water-soluble Fe_4S_4 clusters, however, undergoes the hydrolysis reaction of the cluster in water even in the presence of excess amounts of free hydrophilic thiolate ligands.^{19c}

We have recently demonstrated that the redox potential of $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{R})_4]^{2-}$ (R = $n\text{-C}_4\text{H}_9$, $m\text{-C}_8\text{H}_{17}$, and $n\text{-C}_{12}\text{H}_{25}$) solubilized in aqueous micellar solutions fall in the same range as those of various 4-Fe ferredoxins.²⁰ Thus, these synthetic clusters with hydrophobic thiolate ligands are reduced smoothly by $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of methyl viologen dication (MV^{2+}) without a degradation reaction of Fe_4S_4 core. The reduction of an MoFe_3S_4 cluster with the $p\text{-}n$ -octylbenzenethiolate ligand by $\text{Na}_2\text{S}_2\text{O}_4$ also is performed successfully in the presence of MV^{2+} in an aqueous micellar solution. This paper reports the reduction of $n\text{-C}_3\text{H}_7\text{N}_3$ catalyzed by the single cubane Mo-Fe-S and Fe-S clusters $[\text{MoFe}_3\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (1; L = solvent) and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4]^{2-}$ (2) solubilized in aqueous Triton X-100 micellar solutions containing $\text{Na}_2\text{S}_2\text{O}_4$ and MV^{2+} .



Experimental Section

General Procedure and Materials. All manipulations were carried out under N_2 or He atmosphere. Solvents were purified by distillation over dehydration chemicals: calcium hydride for CH_3CN , sodium metal for diethyl ether, and calcium oxide for dimethylformamide (DMF). ($n\text{-Bu}_4\text{N}$)₂[$\text{Fe}_4\text{S}_4(\text{SPh})_4$],²¹ ($n\text{-Bu}_4\text{N}$)₂[$\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4$]²⁰ (2), (Et_4N)₄[$\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2$],⁶ $n\text{-C}_8\text{H}_{17}\text{-}p\text{-C}_6\text{H}_4\text{SH}$,²² and $n\text{-C}_3\text{H}_7\text{N}_3$ ²³ were prepared according to the literature.

Preparation of (Et_4N)₄[$\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2$]. To a CH_3CN solution of (Et_4N)₄[$\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2$] (0.43 g, 0.20 mmol) was added $p\text{-}n\text{-C}_8\text{H}_{17}\text{-C}_6\text{H}_4\text{SH}$ (0.28 cm³, 1.30 mmol), and the mixture was stirred for 1 h at 50 °C, during which time the EtSH

- (5) (a) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. (b) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2354. (c) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455. (d) Holm, R. H.; Simhon, E. D. *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley: New York, 1985; pp 1-87.
- (6) (a) Armstrong, W. H.; Maschark, P. K.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4373. (b) Maschark, P. K.; Armstrong, W. H.; Mizobe, Y.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 475. (c) Palermo, R. E.; Singh, R.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2600.
- (7) Spiro, T. G. Ed. *Iron-Sulfur Proteins*; Wiley: New York, 1982; Vol. IV.
- (8) (a) Dukes, G. R.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 528. (b) Mayerle, I. J.; Denmark, S. E.; Depamphilis, J. A.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032. (c) Cambray, J.; Lane, R. W.; Wedd, A. G.; Johnson, R. W.; Holm, R. H. *Inorg. Chem.* **1977**, *16*, 2565.
- (9) Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1984**, *106*, 4500.
- (10) Johnson, R. E.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7280.
- (11) Kanatzidis, M. G.; Ryan, M.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A. *Inorg. Chem.* **1983**, *22*, 179.
- (12) (a) McMillan, R. S.; Renaud, J.; Reynolds, J. G.; R. H. Holm. *J. Inorg. Biochem.* **1979**, *11*, 213. (b) Tanaka, K.; Tanaka, M.; Tanaka, T. *Chem. Lett.* **1981**, 859. (c) Tanaka, K.; Honjo, M.; Tanaka, T. *J. Inorg. Biochem.* **1984**, *22*, 187.
- (13) Tanaka, K.; Imasaka, Y.; Tanaka, M.; Honjo, M.; Tanaka, T. *J. Am. Chem. Soc.* **1982**, *104*, 4258.
- (14) Hozumi, Y.; Imasaka, Y.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1983**, 897.

- (15) Ware, D. A. *Biochem. J.* **1972**, *130*, 301.
- (16) Daday, A.; Lambert, G. R.; Smith, G. D. *Biochem. J.* **1979**, *127*, 139.
- (17) Depamphilis, B. V.; Averill, B. A.; Herskovitz, T.; Que, Jr., L.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4159.
- (18) Mayhew, S. G. *Eur. J. Biochem.* **1978**, *85*, 535.
- (19) (a) Job, R. C.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 231. (b) Hill, C. L.; Renaud, J.; Holm, R. H.; Mortenson, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 2549. (c) Henderson, R. A.; Sykes, A. G. *Inorg. Chem.* **1980**, *19*, 3103.
- (20) (a) Tanaka, K.; Tanaka, T.; Kawafune, I. *Inorg. Chem.* **1984**, *23*, 516. (b) Tanaka, K.; Moriya, M.; Tanaka, T. *Ibid.* **1986**, *25*, 835.
- (21) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3523.
- (22) Neubert, N. E.; Laskos, S. J.; Griffith, R. F.; Stahl, M. E.; Mauer, J. L. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 221.
- (23) Lieber, E.; Chao, T. S.; Ramachandra, J. *Org. Chem.* **1986**, *22*, 238.

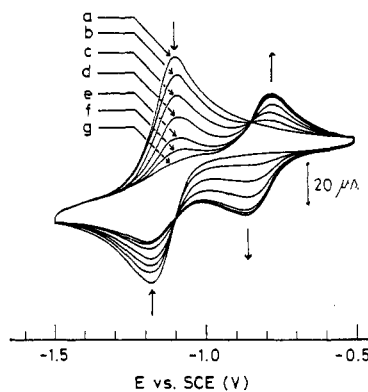


Figure 1. Cyclic voltammograms of $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{4-}$ (3.3×10^{-3} mol/dm³) in the presence of various amounts of $n\text{-C}_5\text{H}_{11}\text{N}_3$: 0 (a), 0.2 (b), 0.4 (c), 0.6 (d), 1.0 (e), 1.6 (f), and 3.4×10^{-3} mol/dm³ (g) in anhydrous DMF. A glassy-carbon electrode was used, with a sweep rate of 100 mV/s.

liberated was removed under reduced pressure every 15 min. After the solvent was removed in vacuo, the resulting oily product was washed with diethyl ether (100 cm³) twice to give a black solid, which was recrystallized from CH_3CN . Anal. Calcd for $\text{C}_{128}\text{H}_{206}\text{Cl}_2\text{Fe}_6\text{Mo}_2\text{N}_4\text{O}_4\text{Si}_4$: C, 49.20; H, 6.64; N, 1.79. Found: C, 48.99; H, 6.72; N, 2.01.

Preparation of Aqueous Micellar Solutions. An acetone or DMF solution (1.0 cm³) of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]$ (3.0 μmol) or $(n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]$ (6.0 μmol) was added to a stirred aqueous Triton X-100 micellar solution (70 mg, 30 cm³) at a given pH adjusted with $\text{H}_3\text{PO}_4\text{-NaOH}$ (0.1 mol/dm³). The resulting dark brown solution was mixed with $n\text{-C}_5\text{H}_{11}\text{N}_3$ (0.60 mmol), followed by vigorous shaking for 1 min.

Reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$. A rubber septum capped reaction flask (35 cm³) was thoroughly flushed with He to remove air. A Triton X-100 micellar solution (10 cm³) containing $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]$ (3.0 μmol) or $(n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]$ (6.0 μmol), $n\text{-C}_5\text{H}_{11}\text{N}_3$, and methyl viologen dibromide ($\text{MVB}r_2$, 2 μmol) was injected into the flask through a septum cap by syringe techniques, and then CH_4 (0.50 cm³) as an internal standard for the analysis of gas evolved in the reaction was introduced into the flask with a pressure-lock syringe (Precision-Sampling). The solution was stirred magnetically in a thermostat maintained at 30 ± 0.1 °C. The reduction was started by injecting an aqueous $\text{Na}_2\text{S}_2\text{O}_4$ solution (1.70 mol/dm³, 0.5 cm³) into the flask. At a fixed time interval, 0.1 cm³ portions of gas were sampled from the gaseous phase in the flask through a septum cap. Quantitative analysis of the gas was performed on a Shimadzu gas chromatograph GC-3BT with a 2-m column filled with molecular sieve 13X at 70 °C with He (40 cm³/min) used as a carrier gas. The analysis of products ($n\text{-C}_5\text{H}_{11}\text{NH}_2$ and NH_3) in the solution was conducted at a fixed time interval as well by sampling 0.1 cm³ portions of the solution from the liquid phase in the flask with syringe techniques. In order to liberate free $n\text{-C}_5\text{H}_{11}\text{NH}_2$ and NH_3 in the solution, 0.1 cm³ of the solution was mixed with an aqueous NaOH solution (ca. 30 wt %, 1.0×10^{-2} cm³) in a sealed tube with a septum cap; the resulting alkaline solution was analyzed with Shimadzu GC-7A and GC-6A gas chromatographs by using a 1.6-m column filled with PEG-HT 5% + KOH 1% Uniport HP 60/80 (for the determination of $n\text{-C}_5\text{H}_{11}\text{NH}_2$) and with a 1.0-m column filled with Chromosorb 103 (for the determination of NH_3), respectively, with N_2 (40 cm³/min) used as a carrier gas. Hydrazine was determined by spectrophotometric titration according to the literature.²⁴

Physical Measurements. Cyclic voltammograms were recorded on a Hokuto-Denko HA-301 potentiostat, a Hokuto-Denko HB-107A function generator, and a Yokogawa Electric Inc. 3077 X-Y recorder. A hanging mercury drop (Metrohm E-410) or a glassy carbon electrode, a Pt disk electrode, and an SCE were used as working, auxiliary, and reference electrodes, respectively. Electronic absorption spectra were measured with a Union SM 401 spectrophotometer. Spectroelectrochemical experiments were carried out by the use of an optically transparent thin-layer electrode, consisting of a Pt-gauze electrode in a 0.5-mm quartz cuvette, a Pt-wire auxiliary electrode, and an SCE.²⁵

Results and Discussion

Formation of a Single Cubane Cluster $[\text{MoFe}_3\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{2-}$ (**1**; L = DMF) from $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{4-}$ in DMF

(24) Watt, G. W.; Chrisp, J. *Anal. Chem.* **1952**, *24*, 2006.

(25) Lexa, D.; Savent, J. M.; Zickler, J. *J. Am. Chem. Soc.* **1977**, *99*, 2786.

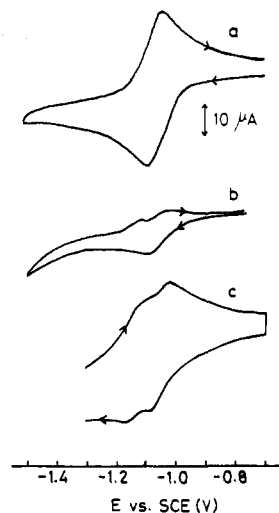


Figure 2. Cyclic voltammograms of $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{2-}$ (2.0×10^{-4} mol/dm³) in the absence (a) and in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (3.6×10^{-3} mol/dm³) (b) and after the application of -1.30 V vs SCE to a glassy-carbon electrode for 3 min in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (3.6×10^{-3} mol/dm³) (c) in DMF. Sweep rates were 100 mV/s for curves a and c, 10 mV/s for curve b.

$n\text{-C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{4-}$ in DMF. The cyclic voltammogram of $(\text{Et}_4\text{N})_4[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]$ in DMF exhibits a pair of cathodic and anodic waves at -1.17 and -1.10 V vs SCE, respectively (curve a in Figure 1), which are close to those of the (2-/3-) redox couple ($E_{pc} = -1.14$ and $E_{pa} = -1.07$ V) of an Mo-Fe-S single cubane cluster ligated with SPH, $[\text{MoFe}_3\text{S}_4(\text{SPh})_3(\text{O}_2\text{C}_6\text{Cl}_4)(\text{DMF})]^{2-}$, formed by solvent-induced bridging bond cleavage of the corresponding double cubane cluster, $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{4-}$, in DMF. This result indicates that the present Mo-Fe-S double cubane cluster $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{4-}$ also may be dissociated into two single cubane clusters **1**, in which solvent DMF is coordinated to the molybdenum atom.⁶ The 30-mV cathodic shift of the 2-/3-redox couple of **1** compared with that of $[\text{MoFe}_3\text{S}_4(\text{SPh})_3(\text{O}_2\text{C}_6\text{Cl}_4)(\text{DMF})]^{2-}$ may be due to the electron-donating ability of the octylbenzene group being larger than that of the phenyl group.¹⁷

Interaction of $[\text{MoFe}_3\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{2-}$ (1**; L = DMF) and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{2-}$ (**2**) with $n\text{-C}_5\text{H}_{11}\text{N}_3$ in DMF.** It has been reported that the solvent molecules coordinated to the molybdenum atom of $[\text{MoFe}_3\text{S}_4(\text{SPh})_3(\text{O}_2\text{C}_6\text{Cl}_4)_2]^{2-}$ (L = Me₂CO, MeCN, DMF) are substituted easily by N_3^- , N_2H_4 , CN^- , and RNC .⁶ In harmony with this, the addition of $n\text{-C}_5\text{H}_{11}\text{N}_3$ to the DMF solution of **1** results in the appearance of a new cathodic and anodic waves at -0.87 and -0.78 V, respectively; the peak currents of these waves increase with increasing the amount of $n\text{-C}_5\text{H}_{11}\text{N}_3$, while those of the original redox couple of **1** are weakened (curves b-g in Figure 1). This result suggests that the DMF of **1** is substituted by $n\text{-C}_5\text{H}_{11}\text{N}_3$ to form $[\text{MoFe}_3\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)(n\text{-C}_5\text{H}_{11}\text{N}_3)]^{2-}$ in solution. It should be noted that the $E_{1/2}$ value ($E_{1/2} = (E_{pc} + E_{pa})/2$) of the $n\text{-C}_5\text{H}_{11}\text{N}_3$ adduct is shifted anodically about by 300 mV compared with that of the DMF adduct, suggesting a decrease of an electron density in the MoFeS₄ core upon replacement of DMF ligated to the molybdenum atom by $n\text{-C}_5\text{H}_{11}\text{N}_3$.

The cyclic voltammograms of the Bu₄N salt of **2** ($E_{pc} = -1.0$, and $E_{pa} = -1.02$ V vs SCE) in DMF (Figure 2a) has not been changed at all even after the addition of about 20 molar equiv excess of $n\text{-C}_5\text{H}_{11}\text{N}_3$ to the solution at the sweep rate 100 mV/s. When the sweep rate is decreased to 10 mV/s in the presence of excess $n\text{-C}_5\text{H}_{11}\text{N}_3$, however, a new anodic wave appears at -1.12 V vs SCE as a shoulder (Figure 2b). In addition, when a potential of -1.30 V is applied to the solution for 3 min, so that all the cluster **2** existing on the electrode surface may be reduced to $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{3-}$, followed by a potential sweep between

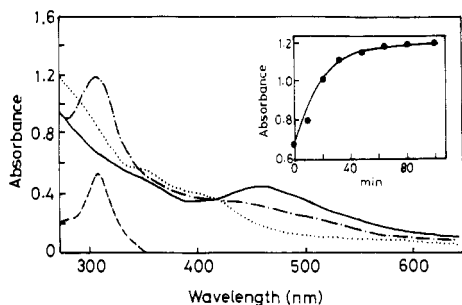


Figure 3. Electronic absorption spectra of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ (5.0×10^{-4} mol/dm³) (—), the reduced species produced at -1.30 V vs SCE in the absence (···) and presence (---) of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (5.0×10^{-3} mol/dm³), and the PhS^- anion (---) formed by the reduction of PhSH (5.0×10^{-4} mol/dm³) at -1.50 V in DMF. Inset: time dependence of the absorbance at 306 nm upon the electrochemical reduction of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (5.0×10^{-3} mol/dm³) at 1.30 V in DMF.

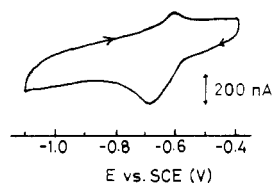


Figure 4. Cyclic voltammogram of $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (**1**; $\text{L} = \text{Me}_2\text{CO}, \text{H}_2\text{O}; 2.0 \times 10^{-4}$ mol/dm³) in an aqueous Triton X-100 micellar solution at pH 7.3. A hanging mercury drop electrode (0.0187 cm^2) was used at 100 mV/s .

-1.30 and -0.70 V at 100 mV/s , a new cathodic wave appears at -1.18 V as a shoulder that may constitute a redox couple with the anodic wave (shoulder) at -1.12 V (Figure 2C). Such a redox couple has been observed more clearly when the sweep rate was increased up to 500 mV/s . These results suggest that the thiolate ligand of $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{2-}$ produced electrochemically is substituted slowly by $n\text{-C}_5\text{H}_{11}\text{N}_3$ and the resulting product (vide infra) exhibits a redox couple at $E_{\text{pa}} = -1.12$ and $E_{\text{pc}} = -1.18$ V vs SCE. Thus, the redox potential of the $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{2-/3-}$ couple is shifted cathodically about by 100 mV upon the substitution of $n\text{-C}_5\text{H}_{11}\text{N}_3$ for the thiolate ligand of **2**.

The assumption that the reduced species of **2** can interact with $n\text{-C}_5\text{H}_{11}\text{N}_3$ in a solution is supported from the electronic absorption spectra of the analogous electrochemically reduced cluster with the benzenethiolate ligand, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$, in the presence and the absence of $n\text{-C}_5\text{H}_{11}\text{N}_3$, as shown in Figure 3. The spectrum of the oxidized species $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ (a solid line in Figure 3) was not changed at all in the presence of a large excess of $n\text{-C}_5\text{H}_{11}\text{N}_3$. On the other hand, the controlled-potential electrolysis of the DMF solution containing $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$, $n\text{-C}_5\text{H}_{11}\text{N}_3$, and $n\text{-Bu}_4\text{NBr}$ at -1.30 V vs SCE results in an appearance of an absorption band centered at 306 nm^{26} assignable to the PhS^- anion. The intensity of the band increases with time and attains a constant value after 1 h (see the dotted broken line and the inset in Figure 3). The final absorptivity of the band suggests that 1 mol of PhS^- (the broken line in Figure 3) is dissociated from 1 mol of the cluster. Such a band does not appear in the same electrolysis in the absence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (a dotted line in Figure 3). Moreover, the reoxidation of the reduced species $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$ in DMF containing $n\text{-C}_5\text{H}_{11}\text{N}_3$ at -0.60 V vs SCE for 1 h almost recovered the spectrum of the oxidized species (a solid line in Figure 3). Such a ligand substitution reaction has been reported for the reduced species of a triply PhS^- bridged double cubane cluster, $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_9]^{4-}$, which also affords the 1:1 adduct with CH_3N_3 , liberating a terminal PhS^- ligand in DMF.²⁷ Thus, $n\text{-C}_5\text{H}_{11}\text{N}_3$ coordinates to the molybdenum of the MoFe_3S_4 core²⁸

(26) The oxidized cluster $(\text{Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]$ in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ in DMF exhibited no absorption band at 306 nm .

(27) (a) Kuwabata, S.; Hozumi, Y.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1985**, 401. (b) Kuwabata, S.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1986**, 25, 1691.

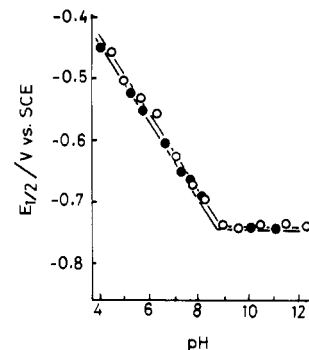


Figure 5. $E_{1/2}$ values of the $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-/3-}$ ($\text{L} = \text{Me}_2\text{CO}, \text{H}_2\text{O}$) (●) and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{2-/3-}$ (○) redox couples at various pH values in aqueous micellar solutions at 30°C .

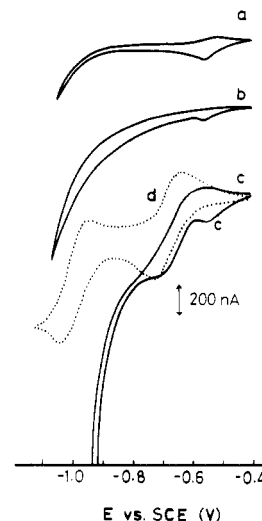


Figure 6. Cyclic voltammograms of $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (**1**; $\text{L} = \text{Me}_2\text{CO}, \text{H}_2\text{O}; 2.0 \times 10^{-4}$ mol/dm³) in the absence (a) and in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (2.0×10^{-2} mol/dm³) (b), a mixture of **1**, MVBr_2 (2.0×10^{-4} mol/dm³), and $n\text{-C}_5\text{H}_{11}\text{N}_3$ (c), and MVBr_2 (d) in aqueous Triton X-100 micellar solutions at pH 6.0. $dE/dt = 10 \text{ mV/s}$.

and to an iron of the Fe_4S_4 core of **1** and **2**, respectively.

Redox Behaviors of $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (1**; $\text{L} = \text{Me}_2\text{CO}, \text{H}_2\text{O}$) and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-}\text{C}_8\text{H}_{17})_4]^{2-}$ (**2**) in an Aqueous Micellar Solution.** The cyclic voltammogram of **1** in an aqueous Triton X-100 micellar solution at pH 7.3 exhibits a pair of cathodic and anodic waves at -0.68 and -0.60 V vs SCE, respectively, as shown in Figure 4. The strong cathodic wave compared with the anodic one may result from weak adsorption of the oxidized cluster on an Hg electrode.^{20,29,30} The $E_{1/2}$ value has hardly been influenced by the amount of Triton X-100 in the range of $0.60\text{--}2.50 \text{ g dm}^{-3}$ but is largely dependent on the proton concentration as shown in Figure 5, which indicates that the $E_{1/2}$ value is shifted by about -57 mV/pH unit in the pH value 4–9,

(28) The coordination of $n\text{-C}_5\text{H}_{11}\text{N}_3$ to the Fe atom of the MoFe_3S_4 core of **1** may take place only in the case of a prolonged electrochemical reduction of **1** in the presence of a large excess of $n\text{-C}_5\text{H}_{11}\text{N}_3$, since the controlled-potential electrolysis of a DMF solution containing $[\text{MoFe}_3\text{S}_4(\text{SPh})_3(\text{O}_2\text{C}_6\text{Cl}_4)(\text{DMF})]^{2-}$ (1.5×10^{-4} mol/dm³), $n\text{-C}_5\text{H}_{11}\text{N}_3$ (3.0×10^{-4} mol/dm³), and $n\text{-Bu}_4\text{NBr}$ (1.0×10^{-1} mol/dm³) at -1.30 V vs SCE showed no electronic absorption band assignable to PhS^- (306 nm), while the electrolysis in the presence of a large excess of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (1.5×10^{-3} mol/dm³) under otherwise similar conditions resulted in an appearance of the 306-nm band as a weak shoulder after 45 min. Then, the intensity slowly increased with time, and 1 mol of PhS^- was dissociated from 1 mol of the cluster for 3 h.

(29) No redox couple of the present clusters in aqueous micellar solutions has been observed at all when a glassy-carbon electrode was used in place of an Hg electrode.

(30) (a) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, 39, 1514. (b) Tanaka, K.; Masanaga, M.; Tanaka, T. *J. Am. Chem. Soc.* **1986**, 108, 5448.

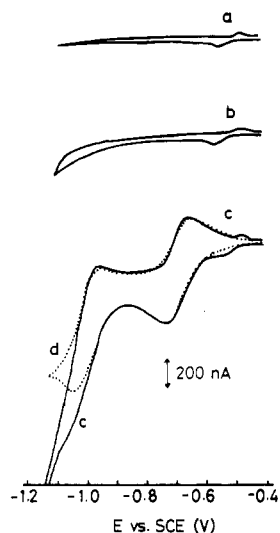


Figure 7. Cyclic voltammograms of $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4]^{2-}$ (**2**; 2.0×10^{-4} mol/dm³) in the absence (a) and in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (2.0×10^{-2} mol/dm³) (b), a mixture of **2**, MVBr_2 (2.0×10^{-4} mol/dm³), and $n\text{-C}_5\text{H}_{11}\text{N}_3$ (c), and MVBr_2 (d) in aqueous Triton X-100 micellar solutions at pH 6.0. $dE/dt = 10$ mV/s.

while the value is almost constant at pH higher than 9. This is suggestive of the participation of a single proton in the redox reaction of **1** in the pH range lower than 9. Such a pH dependence of $E_{1/2}$ is observed for **2** in a Triton X-100 micellar solution²⁰ (Figure 5). Thus, not only the redox potential but also the pK_a values of both clusters are essentially identical with each other in aqueous micellar solutions.

Role of MV^{2+} in the Reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ Catalyzed by $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (1**; $\text{L} = \text{Me}_2\text{CO}$, DMF, H_2O) and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4]^{2-}$ (**2**) in Aqueous Micellar Solutions.** The cyclic voltammograms of **1** in aqueous Triton X-100 micellar solutions at pH 6.0 in the absence and the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ are depicted by curves a and b in Figure 6. The cathodic current at potentials more negative than the cathodic wave of **1** (-0.55 V vs SCE) is much increased in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (Figure 6b) compared with that in the absence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (Figure 6a), suggesting that $n\text{-C}_5\text{H}_{11}\text{N}_3$ is reduced by the reduced species of **1**, since $n\text{-C}_5\text{H}_{11}\text{N}_3$ is not reduced with an Hg electrode under the present experimental conditions. The reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ may take place in lipophilic spheres in micelles, since both **1** and $n\text{-C}_5\text{H}_{11}\text{N}_3$ are hardly soluble in water. It is well-known that surface-active agents are adsorbed on an Hg electrode to strongly interfere with the redox reaction of an electroactive species on the electrode.³¹ The electron transfer from the electrode to the clusters solubilized in a lipid sphere of an micelle may, therefore, more or less be disturbed compared with that in homogeneous systems. In order to mediate an electron transfer from the electrode to the clusters in a micelle, MV^{2+} was added to an aqueous micellar solution containing **1** and $n\text{-C}_5\text{H}_{11}\text{N}_3$. Then, the cathodic current due to the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ was further increased (Figure 6c). It should be noted that the threshold potential of the cathodic current is almost consistent with the cathode peak potential (-0.68 V vs SCE) of the $\text{MV}^{2+/+}$ redox couple (Figure 6d), suggesting that MV^{2+} functions as an electron mediator in the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$.

The reduced species of **2** also has the ability to reduce $n\text{-C}_5\text{H}_{11}\text{N}_3$, as confirmed by the increase of the cathodic current at more negative potentials than the (2-/3-) redox couple of **2** in the presence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (Figure 7b) compared with that in the absence of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (Figure 7a), though the cathodic current

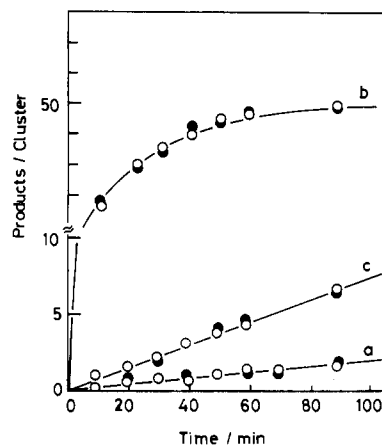


Figure 8. Amounts of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ (O) and N_2 (●) formed in the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (2.0×10^{-2} mol/dm³) by $\text{Na}_2\text{S}_2\text{O}_4$ (8.0×10^{-2} mol/dm³) in aqueous Triton X-100 micellar solutions (10 cm³ at pH 10.0) containing $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4]^{2-}$ (**2**) in the absence (a) and in the presence of (b) of MVBr_2 and $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (**1**) in the absence of MVBr_2 (c) at 30 °C. $[\text{1}], [\text{2}],$ and $[\text{MBBr}_2] = 2.0 \times 10^{-4}$ mol/dm³.

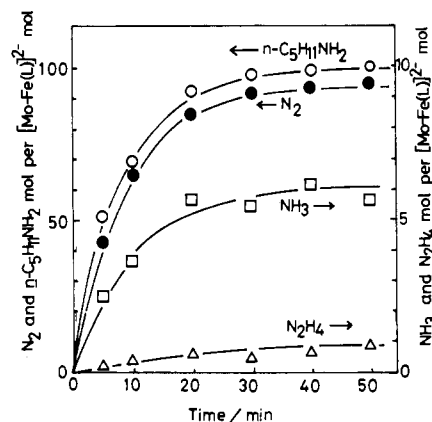
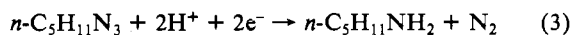


Figure 9. Amounts of products formed in the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (2.0×10^{-2} mol/dm³) by $\text{Na}_2\text{S}_2\text{O}_4$ (8.0×10^{-2} mol/dm³) in an aqueous Triton X-100 micellar solution (10 cm³ at pH 10.0) containing $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (**1**; $\text{L} = \text{Me}_2\text{CO}$, H_2O ; 2.0×10^{-4} mol/dm³) and MVBr_2 (2.0×10^{-4} mol/dm³) at 30 °C.

due to the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ is much weaker than that when **1** was used as catalyst (compare Figure 7b with Figure 6b). Moreover, the threshold potential of the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ in the presence of MV^{2+} (Figure 7c) is almost identical with that of the second cathode peak of the $\text{MV}^{2+/0}$ couple ($E_{1/2} = -1.03$ V vs SCE) (Figure 7d). Thus, MV^0 mediates the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ in the presence of **2**. The fact that MV^{2+} and MV^0 function as electron carriers in the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by **1** and **2**, respectively, indicates that $n\text{-C}_5\text{H}_{11}\text{N}_3$ coordinated to the molybdenum atom in the MoFe_3S_4 core is reduced easily more than that coordinated to the iron atom in the Fe_4S_4 core.

Reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ by $\text{Na}_2\text{S}_2\text{O}_4$ in the Presence of $[\text{MoFe}_3(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (1**; $\text{L} = \text{Me}_2\text{CO}$, DMF, H_2O) and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4]^{2-}$ (**2**) in Aqueous Micellar Solutions.** As described in the previous section, the $E_{1/2}$ values of **1** and **2**²⁰ in aqueous Triton X-100 micellar solutions are shifted cathodically with decreasing the proton concentration until the pH value of the solution reaches to ca. 9. The redox potentials of both clusters in aqueous Triton X-100 micellar solutions, however, are positive more than the midpoint potential of $\text{S}_2\text{O}_4^{2-}$ ($E_m = -0.90$ V vs SCE at pH 9.0¹⁸) even at pH values larger than 9. In fact, the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ with $\text{Na}_2\text{S}_2\text{O}_4$ is catalyzed by **1** and **2** in Triton X-100 micellar solutions at pH 10.0 to afford equal amounts of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ and N_2 (eq 3),³² as shown by lines



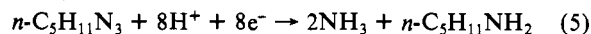
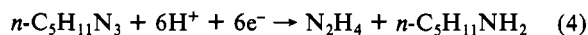
(31) (a) Zatic, V.; Plese, T.; Yomaic, J.; Legovic, T. *Mol. Cryst. Liq. Cryst.* **1984**, *113*, 131. (b) Kozarac, Z.; Cosovic, B. *Bioelectrochem. Bioenerg.* **1984**, *12*, 353. (c) Cosovic, B.; Batina, N.; Kozarac, Z. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *113*, 239. (d) Pospisil, L.; Kuta, J.; Muller, E.; Dorfler, H. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *106*, 359. (e) Muller, E.; Emons, H.; Dorfler, H. D. *Bioelectrochem. Bioenerg.* **1983**, *10*, 279.

Table I. Reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (2.0×10^{-2} mol/dm³) by $\text{Na}_2\text{S}_2\text{O}_4$ (8.0×10^{-2} mol/dm³) in Aqueous Triton X-100 Micellar Solutions Containing $[\text{MoFe}_3\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_3(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}]^{2-}$ (1; L = Me₂CO, H₂O, DMF) or $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{-}p\text{-}n\text{-C}_8\text{H}_{17})_4]^{2-}$ (2) (2.0×10^{-4} mol/dm³) and in the Absence and in the Presence of MV^{2+} (2.0×10^{-4} mol/dm³) at 30 °C for 1 h

entry	cluster	pH ^a	solvent ^b for solubilization	mol of products/ mol of cluster			
				$n\text{-C}_5\text{H}_{11}\text{-}$			
In the Absence of MVBr_2							
				N ₂	NH ₂	N ₂ H ₄	NH ₃
1	1	6.0	acetone	5.4	5.6	0	0
2	1	8.0	acetone	4.8	5.0	0	0
3	1	10.0	acetone	4.3	4.2	0	0
4	2	6.0	acetone	0.2	0.1	0	0
5	2	8.0	acetone	1.1	1.3	0	0
6	2	10.0	acetone	0.9	1.0	0	0
In the Presence of MVBr_2							
7	1	6.0	acetone	90.1	75.0	0.5	20.3
8	1	8.0	acetone	90.0	83.1	0.4	12.5
9	1	10.0	acetone	93.4	96.2	0.4	5.3
10	1	6.0	DMF	41.8	50.5	0.5	12.4
11	2	6.0	acetone	16.8	16.1	0	0
12	2	8.0	acetone	56.0	56.8	0	0
13	2	10.0	acetone	47.5	46.9	0	0

^a H₃PO₄-NaOH buffer (0.1 mol/dm³). ^b A total of 0.33 cm³ was used to solubilize the cluster into aqueous micellar solutions (10 cm³).

c and a in Figure 8, respectively, which reveal that the amounts of products formed in the reduction catalyzed by 1 are about 5 times larger than those formed by 2, suggesting that the cluster 1 is more active than cluster 2 toward the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$. Moreover, the initial rate of the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ by $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of MV^{2+} and 2 is about 20 times faster than that in the absence of MV^{2+} , as can be seen from comparing line b with line a in Figure 8. On the other hand, the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 1 is much more accelerated and is almost completed in 30 min as shown in Figure 9, where considerable amounts of NH₃ and N₂H₄ as well as N₂ and $n\text{-C}_5\text{H}_{11}\text{NH}_2$ are produced. Thus, 1 catalyzes not only two-electron reduction but also six- and eight-electron reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ (eq 4 and 5, respectively). This result is in contrast to the reduction

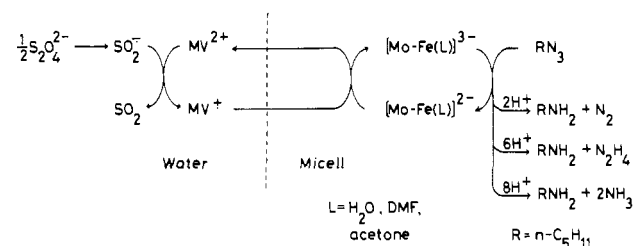


of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 2, which gives only two-electron products (eq 3) and is almost stopped in 60 min when a fair amount of $n\text{-C}_5\text{H}_{11}\text{N}_3$ still remained unreacted (line b in Figure 8). A further addition of MV^{2+} and 2 to the reaction mixture after the reduction process leveled off had no effect on the reduction. This result indicates that neither MV^{2+} nor 2 is decomposed in the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$. On the other hand, when the reduction was conducted in the presence of a large excess of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ (1.0×10^{-2} mol/dm³), the rate of the formation of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ and N₂ was decreased to 1/4 compared with that in the absence of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ (line b in Figure 8). Thus, the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 2 is depressed by the accumulation of the reaction product, $n\text{-C}_5\text{H}_{11}\text{NH}_2$, in micelles.

The results of the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ by $\text{Na}_2\text{S}_2\text{O}_4$ in aqueous micellar solutions at three different pH are summarized in Table I, which confirms that the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 2 gave almost equal amounts of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ and N₂; neither NH₃ nor N₂H₄ was formed at the present pH values, irrespective of the absence or the presence of MV^{2+} (entries 4–6 and 11–13 in Table I). Similar results are obtained for the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 1 in the absence of MV^{2+} (entries 1–3). On the other hand, 1 catalyzed the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ to afford not only $n\text{-C}_5\text{H}_{11}\text{NH}_2$ and N₂ but also NH₃

(32) Irrespective of either presence or absence of MV^{2+} , $n\text{-C}_5\text{H}_{11}\text{N}_3$ is not reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in an aqueous Triton X-100 micellar solution.

Scheme I



and N₂H₄, the latter two of which increase with decreasing pH value of the solution (entries 7–9). In the view of the facts that the (2-/3-) redox potential of 1 is shifted by -57 mV/pH (Figure 5), while that of the $\text{MV}^{2+}/\text{MV}^+$ couple is virtually invariant with the change of proton concentrations,³³ an increase of the proton concentration may result in enhancement of the electron transfer from MV^{2+} to 1. Thus, not only high proton concentrations but also fast electron flow to the cluster seem to be essential factors for the multielectron reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ to proceed, affording N₂H₄ and NH₃.

It should be mentioned that the amounts of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ formed in the reduction catalyzed by 1 at pH 6.0 and 8.0 in the presence of MV^{2+} are less than the total amounts of N₂, N₂H₄, and NH₃ (entries 7 and 8 in Table I). Furthermore, the amounts of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ gradually decreased even after the reduction has been completed when (CH₃)₂CO was used as a solvent to solubilize the cluster into micelles (see Experimental Section). These results may be due to the reaction of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ with (CH₃)₂CO taking place. This assumption is consistent with the fact that the amount of $n\text{-C}_5\text{H}_{11}\text{NH}_2$ formed in the reduction catalyzed by 1 solubilized into a micelle by using DMF in place of (CH₃)₂CO is essentially equal to the total amounts of N₂, N₂H₄, and NH₃ (entry 10 in Table I), though the rate of the reduction is decreased compared with that catalyzed by 1 solubilized into a micelle by using (CH₃)₂CO (compare entry 9 with entry 10 in Table I). A coordination ability of DMF stronger than (CH₃)₂CO or water to the molybdenum atom in the MoFe₃S₄ core, therefore, is suggested to result in a weak inhibitory effect on the coordination of $n\text{-C}_5\text{H}_{11}\text{N}_3$ to the cluster.

Pathway of the Reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$. Sodium dithionite and MV^{2+} have widely been used as a reducing agent and an electron-transfer mediator, respectively, in biochemical studies, where MV^{2+} formed by the reduction with $\text{S}_2\text{O}_4^{2-}$ functions as an efficient electron donor to hydrogenase¹⁵ and nitrogenase¹⁶ in their enzymatic reactions. The active species of methyl viologen functioning as a mediator for the electron transfer from $\text{S}_2\text{O}_4^{2-}$ to those enzymes in water is usually considered to be MV^{2+} , since $\text{S}_2\text{O}_4^{2-}$ in water is dissociated partially into two SO_2^- radical anion which can reduce MV^{2+} with a single electron to produce MV^{+} selectively.³⁴ Thus, the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 1 may be mediated by MV^{+} , as represented in Scheme I.³⁵ In the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 2, however, neutral methyl viologen MV^0 may function as an electron-transfer mediator (Figure 7). The amount of MV^0 formed by the disproportionation reaction of MV^{+} (eq 6) in an aqueous phase may be too small



to mediate the electron required for the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$, since the equilibrium constant (*K*) calculated from eq 7³⁶ is as

$$E_{1/2}^1 - E_{1/2}^2 = (RT/F) \ln K \quad (7)$$

(33) (a) Mueller, O. H. *Ann. N.Y. Acad. Sci.* **1940**, *40*, 9. (b) Elofson, R. M.; Edsberg, R. L. *Can. J. Chem.* **1957**, *35*, 646.

(34) (a) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632. (b) Mayhew, S. G. *Eur. J. Biochem.* **1978**, *85*, 535.

(35) Most of $n\text{-C}_5\text{H}_{11}\text{N}_3$ may be reduced at the Mo atom of the MoFe₃S₄ core, since the replacement of SC₆H₄-*p*-*n*-C₈H₁₇ ligated to the Fe atom of the MoFe₃S₄ core by $n\text{-C}_5\text{H}_{11}\text{N}_3$ is a slow reaction,²³ while the reduction of $n\text{-C}_5\text{H}_{11}\text{N}_3$ catalyzed by 1 is almost completed in 30 min (Figure 9).

(36) Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49.

