Preparation and Characterization of $[Fe_4S_4(SFc)_4]^{2-}$ and $[Mo_2Fe_6S_8X_3(SFc)_6]^{3-}$ ($Fc=C_5H_4FeC_5H_5$, X=EtS and MeO), and Their Catalytic Behaviors toward C_2H_2 Reduction

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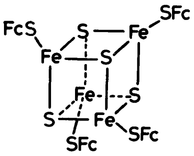
Iron-sulfur and molybdenum-iron-sulfur clusters with ferrocenethiolate, $[Fe_4S_4(SFc)_4]^{2-}$ and $[Mo_2Fe_6S_8X_3(SFc)_6]^{3-}$ ($Fc=C_5H_4FeC_5H_5$, X=EtS and MeO), have been prepared as tetraalkylammonium salts. The reduction potentials of these clusters are more negative than those of the corresponding clusters with benzenethiolate suggesting that the ferrocencethiolate ligand has an electron donor ability stronger than the benzenethiolate ligand. Electronic absorption spectra reveal that the ferrocenethiolate ligand dissociates from the cluster anions in the electrochemically reduced states. The clusters can catalyze the reduction of C_2H_2 in water at pH 7.0 under the controlled potential electrolysis conditions. The rate of the reduction and the selectivity for the C_2H_4 formation are largely dependent on the clusters; the iron-sulfur cluster shows a higher activity than the molybdenum-iron clusters in the C_2H_2 reduction.

Studies of nitrogenase isolated from a variety of microorganisms have revealed that both iron and molybdenum-iron proteins are essential components in biological N_2 fixation.[1,2] The iron protein containing a Fe_4S_4 cluster is believed to function only as an electron-transfer catalyst.[3—5] The molybdenum-iron cofactor (MoFe-co) extracted from nitrogenase involves a novel molybdenum-iron-sulfur cluster,[6] which may be an active center for the reduction of N_2 to NH_3.[7—9] Although the structure of the MoFe-co is still ambiguous, the EXAFS studies suggest that both molybdenum and iron atoms in the MoFe-co are placed in sulfide-rich coordination sphere.[10—13] Most probable atomic ratios of Mo:Fe:S in the MoFe-co are 1:6:8—9, as determined by various chemical and physical techniques.[14] Holm *et al.* have developed a series of synthetic methods for molybdenum-iron single and double cuban clusters with chloride, alkanethiolate, and arenethiolate ligands.[9] The molybdenum-iron clusters prepared so far, however, seem to have still low iron contents relative to molybdenum in comparing with the MoFe-co. The present work was undertaken to incorporate extra iron atoms into the Fe_4S_4 as well as $MoFe_3S_4$ cores, using ferrocenethiolate in place of alkane- or arenethiolate as a ligand. The substitution of the ferrocenethiolate ligand at the cores may result in the increased stability of the cluster toward the oxidation owing to a strong electron-donating property of ferrocene. The stabilization of the cluster to the oxidation, particularly in the $[Fe_4S_4]^{2+}$ core, seem to be important in connection with high potential iron sulfur proteins which exhibit a stable $[Fe_4S_4]^{2+}/[Fe_4S_4]^{3+}$ redox couple.[15]

This paper reports the preparation and characterization of the title clusters I and II, and their catalytic abilities for the reduction of C_2H_2 in aqueous suspension under controlled potential electrolysis conditions.



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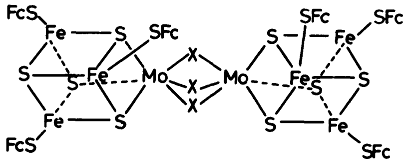

I (X = SEt, OMe)

$Fc = C_5H_4FeC_5H_5$

Experimental

General Procedure and Materials. All manipulations were carried out under N_2 atmosphere. Solvents used for preparations and physical measurements were purified by distillation over dehydration chemicals; CaH_2 for MeCN, magnesium methoxide for MeOH, Na for THF, and CaO for DMF under reduced pressures of N_2. Ferrocenethiol,[16] $(Me_4N)_2[Fe_4S_4(SEt)_4]$,[17] and $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$,[18] were prepared according to the literature methods.

Preparation of $(Me_4N)_2[Fe_4S_4(SFc)_4]$ ($Fc=C_5H_4FeC_5H_5$). An MeCN (80 cm^3) solution containing $(Me_4N)_2[Fe_4S_4(SEt)_4]$ (1.01 g, 1.17 mmol) and FcSH (2.04 g, 9.36 mmol) was stirred at 50 °C for 2 h during which time N_2 gas was bubbled into the solution about every 10 min. The resulting solution was evaporated to dryness under reduced pressure. The residual solid was dissolved in MeCN (40 cm^3) and the solution was filtered on warming (35 °C). To the filtrate was added diethyl ether (15 cm^3), and the solution was allowed to stand at 0 °C for 24 h to give black plates, which were collected by filtration,' washed with diethyl ether, and dried *in vacuo*, 25% yield. Anal. Calcd for $C_{48}H_{60}Fe_8N_2S_8$: C, 42.12; H, 4.42; N, 2.04. Found: C, 41.77; H, 4.52; N, 2.07.

Preparation of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_3(SFc)_6]$. An MeCN (30 cm^3) solution containing $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ (0.36 g, 0.21 mmol) and FcSH (0.61 g, 2.78 mmol) was treated by the same procedure as the synthesis of $(Me_4N)_2[Fe_4S_4(SFc)_4]$ to afford black plates, in which only the terminal EtS group has been substituted by the FcS group, 62% yield. Anal. Calcd for $C_{90}H_{129}Fe_{12}Mo_2N_3S_{17}$: C, 40.36; H, 4.89; N, 1.59. Found: C, 40.20; H, 5.00; N, 1.72.

Preparation of $(Bu^n_4N)_3[Mo_2Fe_6S_8(OMe)_3(SFc)_6]$. As an attempt to incorporate the FcS group in the bridging position of Mo-Fe-S double cubane clusters, the following reaction was performed; to an MeOH (20 cm^3) solution containing FcSH (4.31 g, 20 mmol) and MeONa (1.08 g, 20 mmol) was added a filtered MeOH solution (15 cm^3) of $FeCl_3$ (0.81 g, 5.0 mmol), followed by the addition of $(NH_4)_2MoS_4$ (0.44 g, 1.60 mmol). After stirred for 17 h, the solution was diluted with MeOH (10 cm^3) and filtered. To the filtrate was added slowly Bu^n_4NBr (1.61 g, 5.0 mmol) in MeOH (10 cm^3) to give a black precipitate, which was collected by filtration and dissolved in MeCN (20 cm^3) at 50 °C. After slow addition of MeOH (20 cm^3), the solution was cooled to −10 °C to afford black plates of an Mo-Fe-S double cubane cluster with bridging MeO groups, which were collected by filtration, washed with MeOH, and dried *in vacuo*, 20% yield. Anal. Calcd for $C_{111}H_{171}Fe_{12}Mo_2N_3O_3S_{14}$: C, 45.87; H, 5.93; N, 1.45. Found: C, 45.62; H, 5.64; N, 1.44. The presence of three MeO groups in the cluster was confirmed as follows; HNO_3 (0.2 cm^3) was added slowly to a small amount of the product (10 mg) in a test tube with a rubber stopper at 0 °C. The solution was heated at 50 °C to decompose the cluster completely, neutralized with concd aq NaOH at 0 °C, and then diluted with water to 2 cm^3. The solution was analyzed on a gas chromatograph with a 2 m column filled with Gaschropack 54 (Gaschro Kogyo Co. Ltd) at 80 °C, then three moles of MeOH per one mole of the cluster decomposed were detected in the solution.

Reduction of C_2H_2 in Water. The reduction of C_2H_2 was carried out in a C_2H_2-saturated aqueous suspension of the tetraalkylammonium salt of $[Fe_4S_4(SFc)_4]^{2-}$ or $[Mo_2Fe_6S_8X_3(SFc)_6]^{3-}$ (7.0 μ mol, X=SEt, MeO) under the controlled potential electrolysis conditions using an Hg working electrode at −1.30—−1.40 V *vs.* SCF in a cell described in the previous papers.[19,20] pH Values of the suspension were maintained at 7.0±0.2 with an NaOH-H_3PO_4 buffer. Reaction products in the gaseous phase were determined quantitatively on a gas chromatograph with a 2 m column filled with unibeads 1S at 100 °C.

Physical Measurements. Electronic absorption and ^{1}H NMR spectra were measured with a Union SM 401 spectrophotometer and a JEOL PS-100 spectrometer, respectively. Cyclic voltammetry measurements were performed on a Hokuto Denko Model HA-301 potentiostat/galvanostat in DMF containing 0.1 mol dm^{-3} $Bu^n_4NClO_4$ as a supporting electrolyte, using a platinum disk-type electrode and a saturated calomel reference electrode (SCE).

Results and Discussion

It is well known that Bu^{t}S group of $[Fe_4S_4(SBu^t)_4]^{2-}$ is labile in solution.[21] Thus, $[Fe_4S_4(SFc)_4]^{2-}$ ($Fc=C_5H_4FeC_5H_5$) has easily been obtained as the tetramethylammonium salt by heating an MeCN solution containing $(Me_4N)_2[Fe_4S_4(SBu^t)_4]$ and excess FcSH at 50 °C with bubbling N_2 into the solution at a fixed time interval to remove Bu^{t}SH liberated. The ^{1}H NMR spectrum of the product in DMSO-d_6 shows three ring proton signals due to FcS at δ 4.60, 4.12, and 4.09 (Fig. 1a); the Bu^t proton signal originally observed in $[Fe_4S_4(SBu^t)_4]$ (δ 2.68)[22] completely disappeared, indicating that Bu^{t}S was substituted by FcS. Two different results have been reported in the substitution reaction of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ with alkanethiols; one is that both the terminal and bridging EtS groups are easily substituted,[23] and the other is that only the terminal EtS groups are active toward the substitution reaction.[24] The ^{1}H NMR spectrum for DMSO-d_6 solution of the product in the reaction of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ with FcSH shows the presence of three Fc-ring proton signals at δ 8.24, 4.16, and 3.85 as well as a S-CH_2 signal of the bridging EtS groups at δ 16.90, whereas the terminal EtS groups whose signals were observed in $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ (S-CH_2-, δ 52.86 and S-CH_2-CH_3, δ 3.37) disappears (Fig. 1b). Similarly, the $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$ cluster exhibits three signals due to Fc-ring protons at δ 8.20, 4.10, and 3.96 (Fig. 1c). No MeO proton signal has, however, been observed because of a large paramagnetic broadening, though the bridging MeO protons of $[Mo_2Fe_6S_8(OMe)_3(SPh)_6]^{3-}$ was reported to appear as a broad signal around δ −3.1 above 50 °C.[18]

Electrochemistry. The cyclic voltammogram of $[Fe_4S_4(SFc)_4]^{2-}$ in DMF gives a pair of cathode and anode peaks (E_c=−1.25 V, E_a=−1.10 V *vs.* SCE) which are a pseudo-reversible (2-/3-) couple (a in Fig. 2). The redox potential approximated by $E_{1/2}$ (Table 1) is about 40 mV negative compared with that of

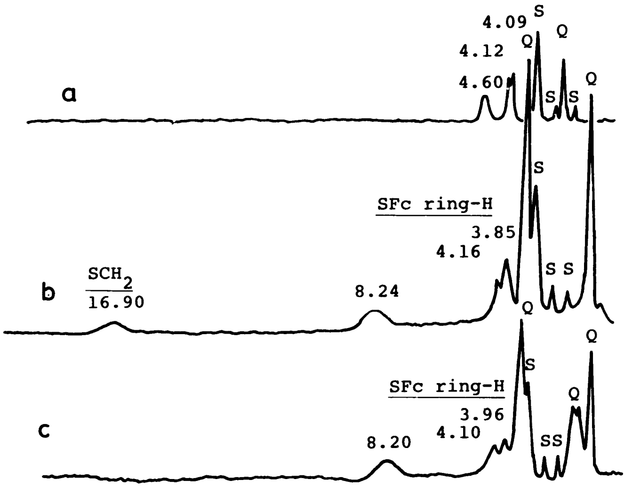

Fig. 1. Proton magnetic resonance spectra of $(Me_4N)_2[Fe_4S_4(SFc)_4]$ (a), $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_3(SFc)_6]$ (b), and $(Bu^n_4N)_3[Mo_2Fe_6S_8(OMe)_3(SFc)_6]$ (c) in $(CD_3)_2SO$ at 298 K. Peaks due to the protons of the quaternary ammonium ion and the solvent are indicated by *Q* and *S*, respectively.

TABLE 1. ELECTROCHEMICAL AND ELECTRONIC SPECTRAL DATA FOR THE CLUSTERS IN DMF

Cluster	E/V *vs.* SCE			λ_{max}/nm (ε_M/mol^{-1} dm^2)		
	4-/5-	3-/4-	2-/1-			
$[Fe_4S_4(SFc)_4]^{2-}$		−1.18		310 (250000)	430 (140000)	600 (sh) [a]
$[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$	−1.34	−1.13	−0.08	308 (520000)	420 (290000)	580 (sh) [a]
$[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$	−1.37	−1.11	−0.12	308 (580000)	440 (220000)	

a) Shoulder.

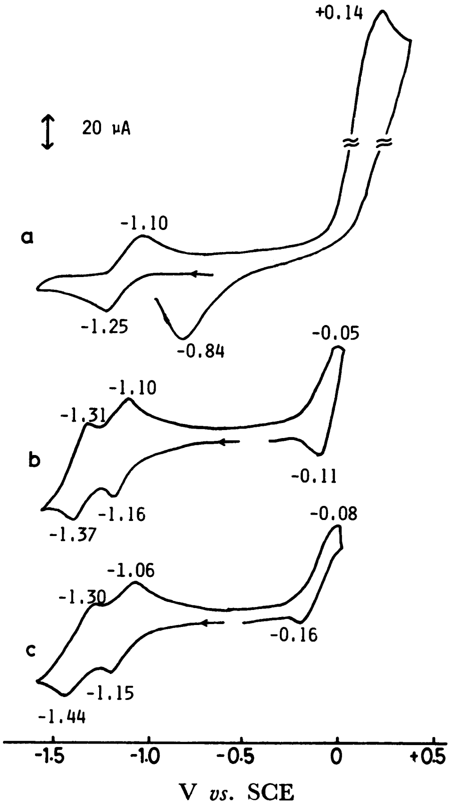

Fig. 2. Cyclic voltammograms of $[Fe_4S_4(SFc)_4]^{2-}$ (a), $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$ (b), and $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$ (c) in DMF containing 0.1 mol dm^{-3} $Bu^n{}_4NClO_4$; the scan rate 0.2 Vs^{-1}.

$[Fe_4S_4(SPh)_4]^{2-}$ in the same solvent.[25] This may be due to a donor ability of FcS stronger than PhS, as suggested for some cubane type clusters in which the more the electron-donating property of substituents is, the more negative shift the redox potential occurs.[26] On sweeping to positive potentials following to the occurrence of the pseudo-reversible couple, a strong anode peak appears at +0.14 V, followed by a cathode one at −0.84 V in the reverse scan (a in Fig. 2). The anode peak current is about 5—6 times larger than the cathode peak current and the potential difference between the these peaks is about 1 V. These results reveal that $[Fe_4S_4(SFc)_4]^{2-}$ is subject to the oxidation not only at the Fe_4S_4 core but also at the Fc moiety at +0.14 V, followed by irreversible chemical reactions. Thus, there has been observed no evidence for the presence of a stable (2-/1-) couple in $[Fe_4S_4(SFc)_4]^{2-}$, which is known to exist in high potential Fe-S proteins.[15]

In contrast to $[Fe_4S_4(SFc)_4]^{2-}$, $[Mo_2Fe_2S_8(SEt)_3(SFc)_6]^{3-}$ exhibits three reversible redox couples (3-/2-), (3-/4-), and (4-/5-) (b in Fig. 2), as confirmed by the observation that the potential difference between the anode and cathode peaks of each couple is 60 mV. The $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$ cluster also displays three redox couples, the anode and cathode peak potentials being close to those of $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$. The potential difference of each couple, however, is larger than 60 mV (c in Fig. 2), suggesting that the redox processes are pseudo-reversible. In addition, the cathode peak current at −0.16 V at sweep rate 0.2 Vs^{-1} is much smaller than that of the corresponding anode peak current at −0.08 V, and the cathode wave almost disappeared at sweep rate 0.02 Vs^{-1}. This result indicates that $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{2-}$ generated by electrochemical oxidation is unstable even in the time scale of cyclic voltammetry. Thus, the Mo-Fe–S double cubane cluster bridged by EtS group may be more stable than that bridged by MeO.

Electronic Spectra. The electronic spectra of both $[Fe_4S_4(SFc)_4]^{2-}$ and $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$ in DMF show two absorptions around 430 and 600 nm (solid line in Fig. 3), the latter of which has not been evident in the spectrum of $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$ (Table 1). No distinct shoulder around 600 nm has been observed also in the corresponding clusters with PhS, $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$, however, the $[Fe_4S_4X_4]^{2-}$ cluster anions where X=Cl[27] and OPh[28] display a shoulder assignable to a transition within the Fe_4S_4 core in the 600—700 nm range. Thus, the shoulder around 600 nm of the present clusters may be ascribed to transitions within the Fe_4S_4 or $MoFe_3S_4$ cores. Another band around 430 nm of the present clusters is assigned to the charge-transfer transitions from terminal sulfur atoms to metal atoms of the cores on the basis of the close similarity of the spectral features to those of $[Fe_4S_4(SPh)_4]^{2-}$[25] and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$.[29]

The spectra in the course of the reduction of clusters were measured by the use of a OTTLE cell[30] under the controlled potential electrolysis conditions at 0.10—0.25 V more negative than the

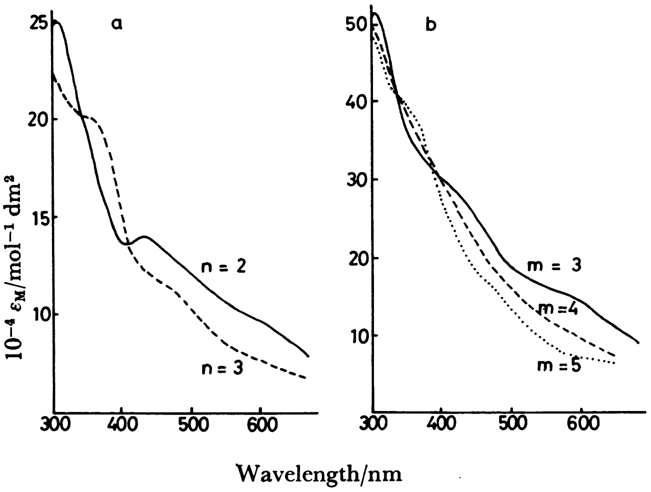

Fig. 3. Absorption spectra of (a) $[Fe_4S_4(SFc)_4]^{n-}$ (n= 2, 3) and (b) $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{m-}$ (m=3, 4, 5) in DMF; the reduced forms with n=3 (a) and m= 4, 5 (b) were generated in an OTTLE cell by applying the potentials −1.50, −1.30, and −1.70 V (*vs.* SCE), respectively.

cathode peak potentials. The reduction of $[Fe_4S_4(SFc)_4]^{2-}$ at −1.50 V (*vs.* SCE) in DMF results in the decrease of absorbances around 430 and 600 nm, instead two new bands around 360 and 480 nm appear as shoulders (a broaken line in Fig. 3). The position of these shoulders are coincidence with those of absorptions appearing in the reduction of FcSH to FcS^- by the controlled potential electrolysis at −1.50 V (*vs.* SCE) in DMF, as shown in Fig. 4. Thus, the reduction of $[Fe_4S_4(SFc)_4]^{2-}$ may result in a partial dissociation of FcS^- as expressed in Eq. 1.

$$[Fe_4S_4(SFc)_4]^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe_4S_4(SFc)_4]^{3-} \rightleftharpoons [Fe_4S_4(SFc)_3]^{2-} + FcS^- \quad (1)$$

The spectral change in the course of reduction was almost ceased in 30 min, except for the 360 nm band whose intensity continued to increase slowly for 1 h. The reoxidation of the resulting solution at −0.90 V (E_a=−1.10 V *vs.* SCE) recovered the 430 nm band up to more than 95%, and the 480 nm shoulder almost disappeared, although the 360 nm band still remained as a shoulder. Further oxidation at −0.50 V for 30 min resulted in complete disappearance of the 360 nm shoulder and the spectrum obtained finally was consistent with that of $[Fe_4S_4(SFc)_4]^{2-}$.

The spectral change during the electrochemical redox cycle of $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$ in DMF is similar to that of $[Fe_4S_4(SFc)_4]^{2-}$; the reduction of $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$ at −1.30 V (*vs.* SCE) results

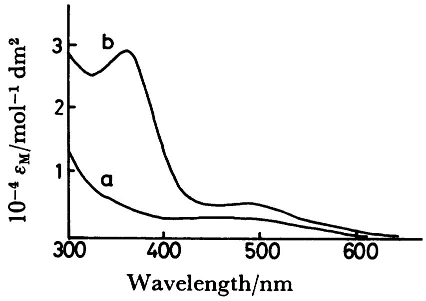

Fig. 4. Absorption spectra of FcSH (a) and FcS^- (b) in DMF ; the latter was generated in an OTTLE cell by applying the potential −1.50 V (*vs.* SCE) to a solution of the $Bu^n{}_4$ N salt.

in weakening of the shoulder at 420 and 580 nm, and the appearance of a shoulder at 360 nm (a broken line in Fig. 3b). Further reduction at −1.70 V (*vs.* SCE) to produce $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{5-}$ strengthens the absorbance at 480 nm as a shoulder as well as 360 nm (a broaken line in Fig. 3b). Further reduction at −1.70 V (*vs.* SCE) to produce $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{5-}$ strengthens the absorbance at 480 nm as a shoulder as well as 360 nm (a dotted line in Fig. 3b). The absorbance at 360 nm attained to a constant value in about 30 min, which is much longer than the time required for the disappearance of the 420 nm band. The reoxidation at −0.50 V (*vs.* SCE) of the resulting solution also required more time for the disappearance of the 360 nm band than for the recovery of the intensity of the 420 nm band; the final spectrum of the solution was consistent with that of $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$. Similar spectral changes were observed in the reduction (−1.30 and −1.70 V *vs.* SCE) and oxidation (−0.50 V *vs.* SCE) cycle of $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$ in DMF, while no distinct shoulder appeared at 480 nm in the electrolysis at −1.70 V (*vs.* SCE). The reduction of $[Mo_2Fe_6S_8X_3(SFc)_6]^{3-}$ (X=SEt and OMe), therefore, also results in a partial dissociation of FcS^- in DMF as expressed in Eq. 2.

$$[Mo_2Fe_6S_8X_3(SFc)_6]^{z-} \rightleftharpoons [Mo_2Fe_6S_8X_3(SFc)_5]^{(z-1)-} + FcS^- \quad (2)$$

z=4 and 5; X=SEt and OMe

Reduction of C_2H_2 *by Clusters.* It has been reported that $[Fe_4S_4(SPh)_4]^{3-}$ can reduce C_2H_2 in an aprotic solvent in the presence of CH_3COOH to give C_2H_4 selectively in a 60% yield,[31] and both $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ catalyze the reduction of C_2H_2 to C_2H_4 in MeOH/THF under the controlled potential electrolysis conditions.[19] These results may be similar to the reduction of C_2H_2 by nitrogenase, where only C_2H_4 is produced with-

TABLE 2. CONDITIONS FOR THE REDUCTION OF C_2H_2 AND THE PRODUCTS DISTRIBUTION IN H_2O (pH 7.0)

Catalyst[a]	Potential V *vs.* SCE	C_2H_4/H_2	C_2H_4/C_2H_6	TN[b]
$[Fe_4S_4(SFc)_4]^{2-}$	−1.30	0.79	11.1	1.65
$[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$	−1.40	0.29	11.1	1.38
$[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$	−1.40	0.22	10.0	0.63

a) 7 μmol. b) Turnover number; C_2H_4 mol/(cluster mol h).

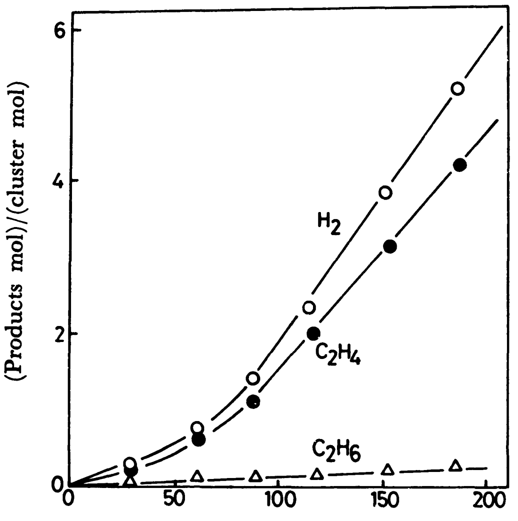

Fig. 5. Reduction of C_2H_2 catalyzed by $[Fe_4S_4(SFc)_4]^{2-}$ under the controlled potential electrolysis at −1.30 V (*vs.* SCE) in H_2O at pH 7.0.

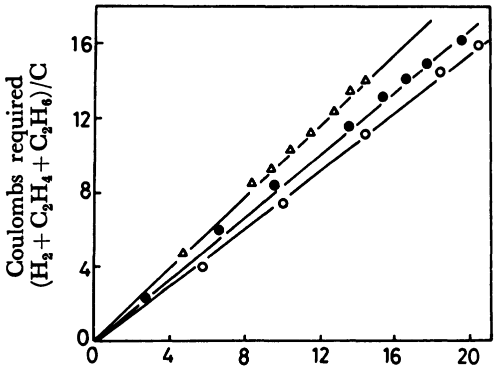

Fig. 6. Plots of the total number of coulombs required for the formation of all the products ($H_2+C_2H_4+C_2H_6$) *vs.* coulomb consumed in the reduction of C_2H_2 catalzed by $[Fe_4S_4(SFc)_4]^{2-}$ (○), $[Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-}$ (●), and $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-}$ (△) under the controlled potential electrolysis conditions in H_2O at pH 7.0.

out evolving C_2H_6 nor H_2.[32] Thus, the reduction of C_2H_2 by the reduced species of the present clusters may be of interest in comparing with that by nitrogenase. Since the present clusters are sparingly soluble in water, they were dispersed in water; a DMSO solution (1.0 cm³) of $[Fe_4S_4(SFc)_4]^{2-}$ (7 μmol) was injected into C_2H_2-saturated water (20 cm³) containing Triton X-100 (0.01 cm³) as a surfactant and a supporting electrolyte. The controlled potential electrolysis of the solution at −1.30 V *vs.* SCE evolves C_2H_4 together with a small amount of C_2H_6 and a considerable amount of H_2, as shown in Fig. 5; the total mole of C_2H_4 and C_2H_6 produced in about 60 min exceeds the number of moles of the cluster used, confirming that the reduction of C_2H_2 proceeds catalytically. Similar catalytic reduction of C_2H_2 have occurred in water involving dispersed $[Mo_2Fe_6S_8X_3(SFc)_6]^{3-}$ (X=EtS, MeO) under the electrolysis at −1.40 V *vs.* SCE. The total numbers of coulombs required for the formation of all the products are related linearly with those consumed in the electrolysis conditions, as shown in Fig. 6, which indicates that the current efficiency for the C_2H_4, C_2H_6, and H_2 formation is essentially constant during the reaction. In addition, the electronic spectrum of the propylene carbonate extract of an aqueous suspension of either cluster in the working electrode cell after the electrolysis was identical in appearance with that in the same solvent, suggesting that most of the cluster used as a catalyst for the reduction of C_2H_2 has not been decomposed during the reaction.

The results of the reduction of C_2H_2 by the present clusters under the electrolysis conditions are collected in Table 2. Although the mole ratio C_2H_4/C_2H_6 evolved is nearly the same irrespective of the nature of the clusters used, the concomitant H_2 evolution in the reduction of C_2H_2 largely depends on the clusters; the mole ratio C_2H_4/H_2 increases in the order $[Mo_2Fe_6S_8(OMe)_3(SFc)_6]^{3-} < [Mo_2Fe_6S_8(SEt)_3(SFc)_6]^{3-} < [Fe_4S_4(SFc)_4]^{2-}$, and the rate of the C_2H_4 formation increased also in the same order. Thus, the Fe–S cluster may be concluded to exhibit not only a higher activity but also a better selectivity for the C_2H_2 reduction than the Mo–Fe–S clusters in the present reaction conditions, while the latter involves a skeltal more or less similar to MoFe-co as suggested by the EXAFS technique.[10,13]

References

1) W. E. Orme-Johnson and L. C. Davis, "Iron-Sulfur

Proteins," Vol. III, Ed. W. E. Lovenberg, Academic Press, New York (1977), p. 16.

2) L. E. Mortenson and R. N. F. Thorneley, *Ann. Rev. Biochem.*, **48**, 387 (1979).

3) B. E. Smith, D. J. Lowe, and R. C. Bray, *Biochem. J.*, **130**, 641 (1972).

4) B. E. Smith, D. J. Lowe, and R. C. Bray, *Biochem. J.*, **135**, 331 (1973).

5) B. E. Smith and G. Lang, *Biochem. J.*, **137**, 169 (1974).

6) V. K. Shah and W. J. Brill, *Proc. Natl. Acad. Sci., U. S. A.*, **78**, 348 (1981).

7) V. K. Shah, J. R. Chisnell, and W. J. Brill, *J. Biochem. Biophys. Res. Commun.*, **81**, 232 (1978).

8) H. Berndt, D. J. Lowe, and M. J. Yates, *Eur. J. Biochem.*, **86**, 133 (1978).

9) R. H. Holm, *Chem. Soc. Rev.*, **10**, 455 (1981).

10) S. P. Cramer, W. O. Gillum, K. O. Hodgeson, L. E. Mortenson, E. I. Stiefel, J. R. Chisnell, W. J. Brill, and V. K. Shah, *J. Am. Chem. Soc.*, **100**, 3814 (1978).

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

12) B. Teo and B. A. Averill, *Biochem. Biophys. Res. Commun.*, **88**, 1454 (1979).

13) M. A. Antonio, B. Teo, W. H. Orme-Johnson, M. J. Nelson, S. E. Groh, P. A. Lindahl, S. M. Kanzlarich, and B. A. Averill, *J. Am. Chem. Soc.*, **104**, 4703 (1982).

14) M. J. Nelson, M. A. Lery, and W. H. Orme-Johnson, *Proc. Natl. Acad. Sci., U. S. A.*, **80**, 147 (1983).

15) C. D. Stout. "Iron-Sulfur Proteins," Vol. IV, Ed. T. G. Spiro, Academic Press, New York (1982), p. 99.

16) G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, **1958**, 692.

17) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973).

18) G. Christou and C. D. Garner, *J. Chem. Soc., Dalton*, **1980**, 2354.

19) K. Tanaka, M. Tanaka, and T. Tanaka, *Chem. Lett.*, **1981**, 895.

20) K. Tanaka, Y. Imasaka, M. Tanaka, M. Honjo, and T. Tanaka, *J. Am. Chem. Soc.*, **104**, 4258 (1982).

21) L. Que, Jr, M. A. Bobrik, J. A. Iberse, and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 4168 (1974).

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

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

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

25) B. V. Depamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr, and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 4159 (1974).

26) M. A. Bobrik, E. J. Laskowski, R. W. Johnson, W. O. Gillum, J. M. Berg, and R. H. Holm, *Inorg. Chem.*, **17**, 1402 (1978).

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

28) W. E. Cleland, D. A. Holtman, M. Sabat, J. A. Ibers, G. C. DeFotis, and B. A. Averill, *J. Am. Chem. Soc.*, **105**, 6021 (1983).

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

30) D. Lexa, J. M. Saveant, and J. Zickler, *J. Am. Chem. Soc.*, **99**, 2786 (1977).

31) R. S. McMillan, J. Renaud, J. G. Reynold, and R. H. Holm, *J. Inorg. Biochem.*, **11**, 213 (1979).

32) R. W. F. Hardy, R. H. Holsten, J. K. Jackson, and R. C. Burns, *Plant Physiol*, **43**, 1185 (1968).