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Redox Behaviors of $[Fe_4S_4(SR)_4]^{2-}$ and $[Mo_2Fe_6S_8X_3(SR)_6]^{3-}$ (R = C_6H_4-*p*-*n*-C_8H_{17}; X = SEt, OMe) in Aqueous Micellar Solutions

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Iron-sulfur and molybdenum-iron-sulfur clusters with *p*-*n*-octylbenzenethiolate as a ligand, $[Fe_4S_4(SR)_4]^{2-}$ (**1**) and $[Mo_2Fe_6S_8X_3(SR)_6]^{3-}$ (R = C_6H_4-*p*-*n*-C_8H_{17}; X = SEt (**2**), OMe (**3**)) have been prepared. The redox potentials of **1**-**3** in nonionic, cationic, and anionic micellar solutions at pH 7.0 fall in the range -0.58 to -0.63 V (vs. SCE), which are very close to those of 4-Fe and 8-Fe ferredoxins in H_2O. Proton concentrations markedly influence the redox potentials of those clusters in the range of pH 4-9, -60 and -30 mV/pH unit for the iron-sulfur and molybdenum-iron-sulfur clusters, respectively, whereas above pH 10 the redox potentials are essentially constant, suggesting the existence of an equilibrium between the protonated and deprotonated clusters in aqueous micellar solutions below pH 10.

Introduction

Iron-sulfur and molybdenum-iron-sulfur proteins have been of much interest in the viewpoints of essential components in biological N_2 fixation; the former containing Fe_4S_4 units is believed to function as an electron-transfer catalyst to the latter, which is known as an active site for the reduction of N_2 to NH_3.[1,2] Although the active site of the molybdenum-iron-sulfur proteins is not still clear, it is believed to contain novel molybdenum-iron-sulfur clusters,[3] which may be placed in a hydrophobic environment of proteins, being similar to the Fe_4S_4 cores of 4-Fe and 8-Fe ferredoxins.[4,5]

Holm et al. and Garner and Christou et al. have developed a series of synthetic methods for iron-sulfur and molybdenum-iron-sulfur clusters with various thiolate ligands as models of active sites of iron-sulfur and molybdenum-iron-sulfur proteins, respectively,[6-11] and the electrochemistry of these synthetic clusters has been extensively studied.[12-18] The redox potentials of synthetic water-soluble Fe_4S_4 clusters in water are fairly positive compared with those of water-insoluble Fe_4S_4 clusters in organic solvents.[12,14,19] The water-soluble Fe_4S_4 clusters, however, exhibit still more negative redox potentials than the 4-Fe and 8-Fe ferredoxins extracted from a variety of organisms.

It has been proposed that the fairly positive redox potentials of the ferredoxins may come from not only the existence of a large hydrophobic moiety of the proteins but also the formation of stable hydrogen bondings between the NH group of peptide chains and the sulfur atom of Fe_4S_4 cores or the terminal cysteine residue of peptide chains.[20-22] In addition, the redox potential of $[Fe_4S_4(SCH_2CH_2COO^-)_4]^{6-}$ in water in the presence of bovine serum albumin or bovine insulin is 170-200 mV more positive than that in its absence. Such a positive shift of the redox potential has been associated not only with a local hydrophobic environment around the Fe_4S_4 core but also with the formation of hydrogen bondings between the amide hydrogen of peptides and the thiolate or bridging sulfur.[23] Recently, we have demonstrated that the redox potentials of synthetic Fe_4S_4 clusters surrounded by hydrophobic substituents vary with the proton concentration in nonionic micellar solutions and the potential at pH 7.0 is close to those of 4-Fe and 8-Fe ferredoxins at the same pH.[24] This paper describes electrochemical behaviors of synthetic molybdenum-iron-sulfur clusters (**2** and **3**) as well as an iron-sulfur cluster (**1**) in aqueous micellar solutions in more detail.

Experimental Section

General Procedure and Materials. All manipulations were carried out under an N_2 atmosphere. Solvents used for preparations and physical measurements were purified by distillations over dehydration chemicals; magnesium methoxide for MeOH, calcium hydride for MeCN, sodium metal for diethyl ether, and calcium oxide for DMF. $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$[9] and *p*-*n*-octylbenzenethiol[25] were prepared according to the literature.

Preparation of $(n\text{-}Bu_4N)_2[Fe_4S_4(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_4]$ (1). To an MeOH (50 cm^3) solution containing MeONa (2.43 g, 45 mmol) and *p*-octylbenzenethiol (10.0 g, 45 mmol) was added a filtered MeOH (50 cm^3) solution of $FeCl_3$ (2.5 g, 15 mmol), an MeOH (25 cm^3) solution containing MeONa (0.81 g, 15 mmol), and NaSH (0.84 g, 30 mmol) successively. After being stirred for 24 h, the resulting black solution was filtered. To the filtrate was added slowly *n*-Bu_4NBr (4.0 g, 12 mmol) in MeOH (25 cm^3) to give a black precipitate, which was collected by filtration and recrystallized from MeCN; yield 45%. Anal. Calcd for $C_{88}H_{156}Fe_4S_8N_2$: C, 61.38; H, 9.13; N, 1.63. Found: C, 61.19; H, 8.91; N, 1.41.

Preparation of $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_3(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_6]$ (2). A MeCN (60 cm^3) solution containing $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$[9] (1.05 g, 0.61 mmol) and *p*-octylbenzenethiol (1.1 g, 4.9 mmol) was stirred for 2 h at 50 °C, during which time EtSH liberated was removed under re-

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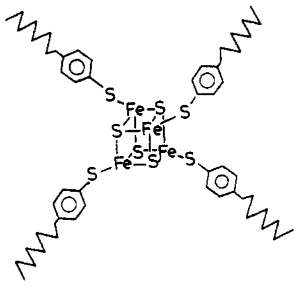

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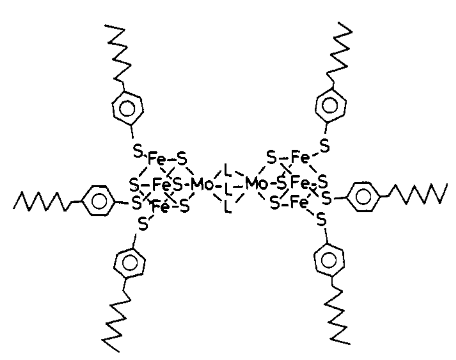

2: L = SEt, 3: L = OMe

duced pressure (~50 mmHg) about every 15 min. After the solvent was removed in vacuo, the resulting oily product was washed with diethyl ether (200 cm^3) three times to give a black powder, which was collected by filtration and recrystallized from MeCN; yield 70%. Anal. Calcd for $C_{114}H_{201}Fe_6Mo_2N_3$: C, 50.98; H, 7.54; N, 1.56. Found: C, 50.91; H, 7.69; N, 1.94.

Preparation of $(n\text{-}Bu_4N)_3[Mo_2Fe_6S_8(OMe)_3(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_6]$ (3). To an MeOH (25 cm^3) solution containing *p*-octylbenzenethiol (11.0 g, 50 mmol) and MeONa (2.8 g, 52 mmol) was added a filtered MeOH (25 cm^3) solution of $FeCl_3$ (2.0 g, 13 mmol), followed by addition of $(NH_4)_2MoS_4$ (1.1 g, 4.1 mmol). After being stirred for 17 h, the solution was diluted with MeOH (10 cm^3) and filtered. To the filtrate was added slowly *n*-Bu_4NBr (4.5 g, 16.0 mmol) in MeOH (20 cm^3) to give a black precipitate, which was collected by filtration and recrystallized from MeCN; yield 60%. Anal. Calcd for $C_{135}H_{243}N_3Fe_6Mo_2S_{14}$: C, 55.31; H, 8.35; N, 1.43. Found: C, 55.31; H, 8.09; N, 1.11.

Preparation of Aqueous Micellar Solutions. A DMF (1.0 cm^3) solution of **1**, **2**, or **3** (12 μmol) was added to a stirred aqueous solution (40 cm^3, pH 4–11) containing $NaOH\text{-}H_3PO_4$ (0.1–0.2 mol dm^{-3}) and Triton X-100, potassium *p*-octylbenzenesulfonate, or dodecyltrimethylammonium chloride (0.024–0.48 mol dm^{-3}). The resulting dark brown solution was filtered to prepare an aqueous micellar solution.

Physical Measurements. ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer. Cyclic voltammetry measurements were performed with a Hokuto Denko HA-301 potential galvanostat using a mercury-drop electrode both in aqueous micellar solutions and in DMF containing $NaOH\text{-}H_3PO_4$ and *n*-Bu_4NBr as supporting electrolytes, respectively. A saturated calomel electrode (SCE) was used as a reference.

Results and Discussion

Figure 1 shows the ^{1}H NMR spectra of **1**–**3** in $Me_2SO\text{-}d_6$. Although each spectrum is rather complicated, two signals at δ 5.19 and 7.80 observed in **1** (Figure 1a) are tentatively assigned to ortho and meta ring protons, respectively, from the comparison of the ^{1}H NMR spectrum of $[Fe_4S_4(SPh)_4]^{2-}$ in the same solvent.[7] The spectrum of **2** shows ortho and meta ring proton signals of the terminal ligand at δ −3.30 and 13.51, respectively, as well as a CH_2 proton signal of the bridging SEt group at δ 16.48, whereas the CH_2 proton signal (δ 55.4)[10] of the terminal SEt groups observed in $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ disappears (Figure 1b), indicating that the only terminal SEt group of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ is substituted by octylbenzenethiol. Another double cubane cluster **3** prepared by the standard assembly reaction in MeOH exhibits the ortho and meta ring proton signals at δ −1.13 and 14.82, respectively, as well as a bridging OCH_3 proton signal at δ −1.40 (Figure 1c), as assigned from the comparison with the ^{1}H NMR spectrum of $[Mo_2Fe_6S_8(OCH_3)_3(SPh)_6]^{3-}$ in the same solvent.[10,18]

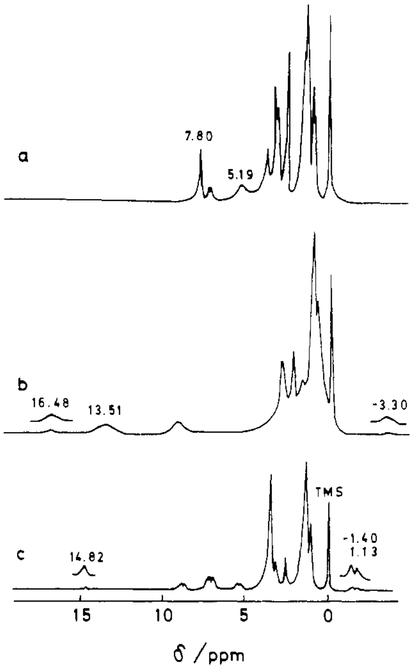

Figure 1. ^{1}H NMR spectra of (a) $(Bu_4N)_2[Fe_4S_4(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_4]$, (b) $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_3(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_6]$, and (c) $(Bu_4N)_3[Mo_2Fe_6S_8(OMe)_3(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_6]$ in $Me_2SO\text{-}d_6$ at 298 K.

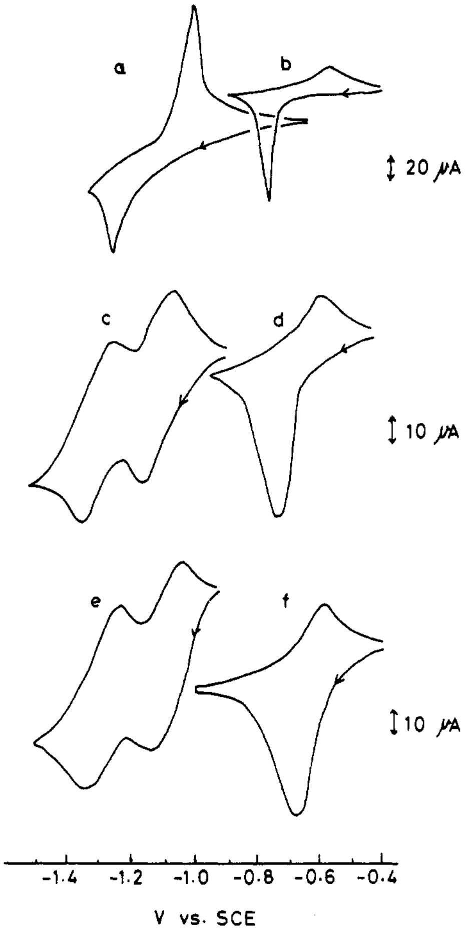

Figure 2. Cyclic voltammograms of **1**, **2**, and **3** in DMF (a, c, e) and in aqueous Triton X-100 solutions (b, d, f) (scan rate 0.2 V s^{-1}).

Figure 2 shows the cyclic voltammograms of **1**–**3** in DMF and in aqueous Triton X-100 micellar solutions at pH 7.0. Somewhat unusual shapes of an anodic wave (Figure 2a) and a cathodic wave (Figure 2b) observed in cluster **1** may be due to a weak adsorption of the reduced form of **1** in DMF and the oxidized form of **1** in

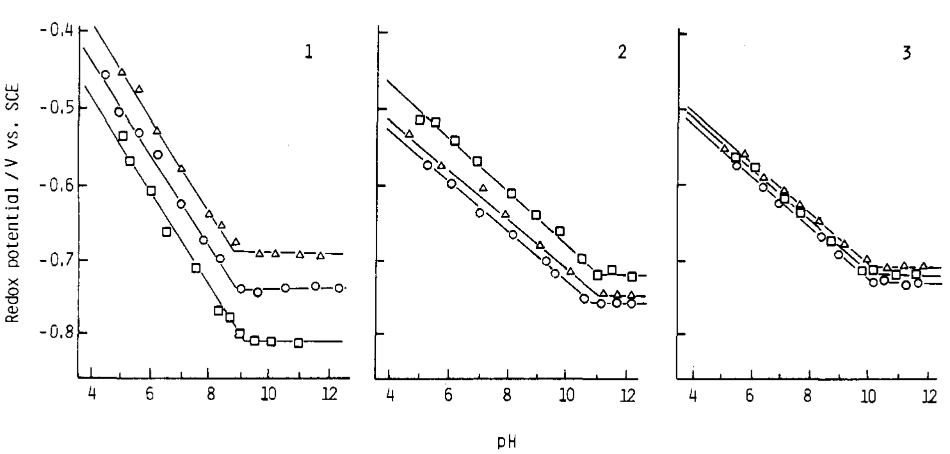

Figure 3. Plots of the $E_{1/2}$ values of **1**–**3** in aqueous Triton X-100 (○), potassium *p*-octylbenzenesulfonate (□), and dodecyltrimethylammonium chloride (△) solutions vs. pH at 20 °C.

Table I. Electrochemical Parameters and p*K* Values of the Clusters in Aqueous Micellar Solutions

cluster	micelle	$E_{1/2}$[a]	$dE_{1/2}/d(\mathrm{pH})$	p*K*
1	nonionic[b]	−0.63	−0.059	9.1
	anionic[c]	−0.68	−0.062	9.0
	cationic[d]	−0.58	−0.062	8.8
2	nonionic[b]	−0.63	−0.032	10.8
	anionic[c]	−0.58	−0.034	10.9
	cationic[d]	−0.62	−0.032	11.0
3	nonionic[b]	−0.62	−0.034	10.1
	anionic[c]	−0.61	−0.032	10.0
	cationic[d]	−0.61	−0.033	10.3

[a] V vs. SCE at pH 7.0. [b] Triton X-100. [c] Potassium *p*-octylbenzenesulfonate. [d] Dodecyltrimethylammoniium chloride.

the aqueous micellar solution on an Hg electrode, respectively. The enhancement of these peak currents may arise from an electron transfer involving the adsorbed clusters at nearly the same potential as the normal electron transfer.[26] The redox potential, approximated by $E_{1/2}$, of **1** in DMF is −1.10 V vs. SCE, which is almost consistent with that of $[\mathrm{Fe_4S_4(SPh)_4}]^{2-/3-}$ in the same solvent. However, **1** in aqueous micellar solution, nonionic, anionic, or cationic, exhibits $E_{1/2}$ in the range −0.58 to −0.68 V vs. SCE at pH 7.0, as listed in Table I, which indicates that the $E_{1/2}$ value is not affected so much by the nature of surface-active agents. It should be noted that the redox potentials of **1** in aqueous micellar solutions are very close to those of 4-Fe (−0.52 to −0.67 V vs. SCE) and 8-Fe (−0.65 to −0.73 V vs. SCE) ferredoxins in water.[12] This may partly be associated with a hydrophobic environment of the $\mathrm{Fe_4S_4}$ core of **1**.

The cyclic voltammogram of **2** in DMF (Figure 2c) shows two successive pseudoreversible single-electron transfers at $E_{1/2} = -1.07$ and −1.28 V vs. SCE, which are assigned to the redox couples of 3−/4− and 4−/5−, respectively, from the comparison with the $E_{1/2}$ values of $[\mathrm{Mo_2Fe_6S_8(SPh)_9}]^{3-}$ in the same solvent ($E_{1/2} = -1.02$ and −1.23 V vs. SCE). In nonionic, cationic, and anionic micellar solutions at pH 7.0, however, **2** exhibits only one redox couple around −0.6 V vs. SCE (Figure 2d and Table I), suggesting that **2** in aqueous micellar solutions undergoes two-electron reduction at the same potential (vide infra). Thus, $E_{1/2}$ of **2** in aqueous micellar solutions is shifted to positive potentials by 0.4–0.6 V compared with that in DMF. A similar positive shift is observed for the $E_{1/2}$ value of **3** in aqueous micellar solutions compared with $E_{1/2}$ in DMF (Figure 2e,f and Table I).

Although the $E_{1/2}$ values of **1**–**3** in aqueous micellar solutions have remained unchanged irrespective of the concentration of surface-active agents (0.024–0.48 mol dm^{-3}), they are shifted to more positive potentials with an increase of the proton concentration. Plots of the $E_{1/2}$ values of **1**–**3** in aqueous micellar solutions against pH (4–11) are depicted in Figure 3, which reveals that the $E_{1/2}$ values of these clusters are not affected so much by the nature of surface-active agents but controlled by proton concentrations.

The shifts of $E_{1/2}$ for the iron–sulfur cluster **1** and molybdenum–iron–sulfur clusters **2** and **3** are nearly −60 and −30 mV/pH unit in the pH 4–10 range, respectively, while the redox potentials are almost constant for pH higher than 10. Such a change of the redox potentials with pH may be explained by the participation of protons in the redox reaction of the clusters; if one assumes that *m* protons interact with the oxidized cluster Ox with an equilibrium constant *K* in aqueous micellar solutions (eq 1), the

$$\mathrm{Ox}(m\mathrm{H}^+) \overset{K}{\rightleftharpoons} \mathrm{Ox} + m\mathrm{H}^+ \tag{1}$$

Nernst equation for the redox potential (E) of the protonated cluster $\mathrm{Ox}(m\mathrm{H}^+)$ (eq 2) can be written as eq 3, where $E^{\circ\prime}$, n, and

$$\mathrm{Ox}(m\mathrm{H}^+) + ne^- \rightleftharpoons \mathrm{Red}(m\mathrm{H}^+) \tag{2}$$

$$E = E^{\circ\prime} + \frac{RT}{nF}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Red}(m\mathrm{H}^+)]} - \frac{RT}{nF}(m(\mathrm{pH}) - \mathrm{p}K) \tag{3}$$

F are the formal potential of the electrode, the number of electrons, and Faraday constant, respectively. The differentiation of eq 3 by pH gives $dE/d(\mathrm{pH}) = -0.059(m/n)$ at 25 °C as a theoretical value for the slope of the E vs. pH plots. The theoretical value thus obtained is in good agreement with the experimental value for **1**, −60 mV/pH unit, indicating that the stoichiometry for the redox reaction (eq 2) of **1** requires a single electron per proton ($m = n = 1$). Similar dependence of the redox potential on pH is known for some iron–sulfur proteins,[27,28] such as Reiske iron–sulfur proteins in mitochondria site II, whose midpoint reduction potential, E_{m}, is shifted by −60 mV/pH unit. Such a shift of E_{m} with pH has been suggested to reflect the function of the iron–sulfur protein as proton carrier coupled with electron transfer.[29] The involvement of protons in analogous redox reactions has been reported for the synthetic iron–sulfur cluster $[\mathrm{Fe_4S_4(SCH_2CH_2COO^-)_4}]^{6-}$ in an aqueous bovine serum albumin solution, where $dE_{1/2}/d(\mathrm{pH}) = -63$ mV in the pH 5.0–8.0 range, which may be explained in terms of accessiblity of water to the $\mathrm{Fe_4S_4}$ cores placed in the protein.[23] Thus, not only iron–sulfur proteins but also synthetic iron–sulfur clusters may be subjected to a protonation reaction in an appropriate pH range in water.[30]

On the other hand, the experimental values for **2** and **3**, −30 mV/pH unit, are consistent with the stoichiometry of two electrons per proton ($n = 2$, $m = 1$) (eq 2) for the redox reactions of **2** and **3**. This result suggests not only that each cluster undergoes the two-electron reduction at the same potential but also that the

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(30) **1** in Triton X-100 micellar solutions at pH 7 has undergone no hydrolysis reaction under anaerobic conditions, as confirmed from no change of the visible spectra for 10 h.

protonated and deprotonated species coexist as equilibrium mixtures (eq 1) in aqueous micellar solutions at pH lower than 10. The equilibrium of eq 1, however, lies far to the right at pH higher than 10, resulting in the redox potential being almost constant. The p*K* values of the clusters obtained from the redox potential nature of the surface-active agents used to form micellar solutions have little effect on the p*K* values of the clusters. The p*K* values of the clusters may reflect not only the hydrophobicity of the environment of the cluster but also the basicity of the Fe_4S_4 cores.[31] The present clusters have p*K* values somewhat larger than those of iron–sulfur proteins reported so far (p*K* = 6.5–8.9).[28,31-33] A most possible site for the protonation of **1**, **2**, or **3** is a terminal[34] or a bridged sulfur atom, since both atoms in some high-potential iron–sulfur proteins are basic enough to form stable hydrogen bondings with the NH proton of polypeptide chains.[20-22]

Registry No. **1**, 88510-46-7; **2**, 100165-84-2; **3**, 100165-86-4; $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$, 72895-02-4; HSC_6H_4-*p*-*n*-C_8H_{17}, 4527-48-4; Triton X-100, 9002-93-1; potassium *p*-octylbenzenesulfonate, 73948-22-8; dodecyltrimethylammonium chloride, 112-00-5.

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[34] The p*K* value of HSC_6H_4-*p*-*n*-C_8H_{17} determined by potentiometric titration in an aqueous Triton X-100 solution at 30 °C is 10.87.

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Optical Spectra of Exchange-Coupled Manganese(II) Pairs in Cadmium Chloride and Cadmium Bromide

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The high-resolution optical absorption spectra of $Cd_{0.92}Mn_{0.08}Cl_2$ and $Cd_{0.85}Mn_{0.15}Br_2$ show clear evidence of manganese(II) pair exchange interactions in the $^4A_1{}^4E(G)$, $^4T_2(D)$, and $^4E(D)$ regions of the spectra. From the variation of band intensities between 1.4 and 3.0 K, values of J = 1.43 and 1.33 cm^{-1} were determined for the ground-state exchange parameter in $Mn_2Cl_{10}{}^{6-}$ and $Mn_2Br_{10}{}^{6-}$, respectively. These values provide a good estimate of nearest-neighbor exchange interactions in pure manganese(II) chloride and manganese(II) bromide. The effective exchange parameter in the excited $^4A_1(G)$ state is approximately 30% larger than J in both dimers.

Introduction

The study of excited states of coupled dimers provides deeper insight into the nature and mechanisms of exchange interactions than the study of ground-state properties alone.[2] Recent optical[3] and inelastic neutron-scattering[4] work on the chain compounds $CsMg_{1-x}Mn_xBr_3$ shows that the interaction in isolated $Mn_2Br_9{}^{5-}$ dimers is a very good measure of the nearest-neighbor exchange in pure $CsMnBr_3$. Mn(II) compounds with layer structures, such as manganese(II) chloride and manganese(II) bromide, are not as well characterized. Transitions to very complicated 3D magnetically ordered phases were observed at 1.96 and 1.81 K for manganese(II) chloride and at 2.30 K for manganese(II) bromide.[5,6] For these compounds, however, no estimates of nearest-neighbor exchange constants are available. Detailed spectroscopic and magneto-optical studies have been reported for the pure compounds, manganese(II) chloride[6] and manganese(II) bromide.[7,8] Dominant effects due to the magnetic coupling were observed at low temperatures. Very little, on the other hand, has been reported on the analogous diluted systems. While some evidence for dimer absorptions in $Cd_{0.85}Mn_{0.15}Cl_2$ was noted by Trutia et al.,[9] they made no thorough study down to very low temperatures, where the magnetic effects are expected to become dominant. We therefore decided to study the diluted systems $Cd_{1-x}Mn_xCl_2$ and $Cd_{1-x}Mn_xBr_2$ in order to determine exchange splittings and exchange parameters in the $Mn_2Cl_{10}{}^{6-}$ and $Mn_2Br_{10}{}^{6-}$ dimers.

Experimental Section

Crystal Preparation. The Bridgman technique was used to prepare cadmium chloride and cadmium bromide doped with 8 and 15 mol % manganese. Two of the four crystals prepared were of superior optical quality and were used almost exclusively for the spectroscopic investigations.

Crystal Structures. Cadmium chloride, cadmium bromide, and manganese(II) chloride are isomorphous and belong to space group $D_{3d}^5(R\bar{3}m)$.[10] The structures contain a cubic close packing of the anions.[11] Manganese(II) bromide belongs to space group $D_{3d}^3(P\bar{3}m1)$ and has hexagonal close-packed layers.[12] Since all these structures contain sheets of edge-sharing MX_6 octahedra, the crystals cleave very readily perpendicular to the threefold axis to yield samples that can be used without further polishing to obtain axial spectra. For the σ ($E \perp c$) and π ($E \parallel c$) spectra the crystals must be cut and polished parallel to the unique axis, a somewhat more troublesome procedure.

Spectroscopic Measurements. Some absorption spectra were obtained on a Cary 17 spectrophotometer equipped with an Air Products closed-cycle cryogenic refrigerator. With this apparatus spectra were recorded

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