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Magnetic Circular Dichroism Studies on Monomeric and Dimeric Iron–Sulfur Complexes

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Abstract

Magnetic circular dichroism (MCD) spectra were obtained for bis(*o*-xylyl-dithiolato)ferrate(III) ($[Fe(S_2\text{-}o\text{-xylyl})_2]^-$) and bis[*o*-xylyl-dithiolato-μ_2-sulfido-ferrate(III)] ($[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$) ions. The MCD magnitude of the dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion was found to be only one half of that for the monomeric $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ ion. The difference in MCD magnitudes was attributed to the change in the thermal populations of ground state sublevels derived from the magnetic exchange interaction.

Introduction

Monomeric $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ and dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ions** have been synthesized as active site analogues for iron–sulfur proteins without and with labile sulfur, respectively [1–4]. These complexes without or with S* show absorption spectra similar to that for rubredoxin or plant ferredoxin (2Fe–2S*), respectively [1–4]. The monomeric $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ ion has a tetrahedrally coordinated high spin ferric ion, while the dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion is centrosymmetric and has two high spin ferric ions antiferromagnetically coupled [5]. Previously we have reported that the magnitudes of MCD for the dimeric dithiolato-Fe(III) complexes with sulfide ion (S*) are smaller by more than one half as compared with those for the monomeric complexes without S* [1, 2]. A similar trend was seen for the monomeric $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ and the dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion pairs.

Since magnetic circular dichroism (MCD) spectroscopy has been used for exploring the electronic structures of dimeric metal complexes with antiferromagnetic coupling [6–9], we have analyzed the electronic origin for the MCD magnitude difference between the monomeric $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ and the dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ions. The assignment and the detailed analysis of the MCD for $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ ion were discussed previously [9].

Experimental

Monomeric $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ and dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ions were prepared by the methods of Lane *et al.* and Mayerle *et al.*, respectively [3, 4]. MCD spectra were recorded on a Jasco J-500 circular dichroism spectrometer using a Jasco electromagnet with 1.53 T at a sample. Electronic absorption spectra were measured with a Jasco UVIDEC-510 spectrophotometer. Values of molar extinction coefficient ϵ in absorption spectra and magnetic molar ellipticity $[\theta]_M$ in MCD spectra were expressed in units of $dm^3\ mol^{-1}\ cm^{-1}$ and degree $dm^3\ mol^{-1}\ cm^{-1}\ Gauss^{-1}$, respectively.

Results and Discussion

Figures 1 and 2 show MCD and absorption spectra for $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ and $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ions, respectively. It is noted that magnitudes of MCD bands for the $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion are only one half of those for the $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ ion. With lowering temperature the magnitudes of MCD for the $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$ ion increased more than those of the absorption spectra, indicating

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**Abbreviations used: MCD, magnetic circular dichroism; $[Fe(S_2\text{-}o\text{-xylyl})_2]^-$, bis(*o*-xylyl-dithiolato)ferrate(III) ion; $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$, bis[*o*-xylyl-dithiolato-μ_2-sulfido-ferrate(III)] ion; S*, bridged sulfur anion; DMF, dimethylformamide.

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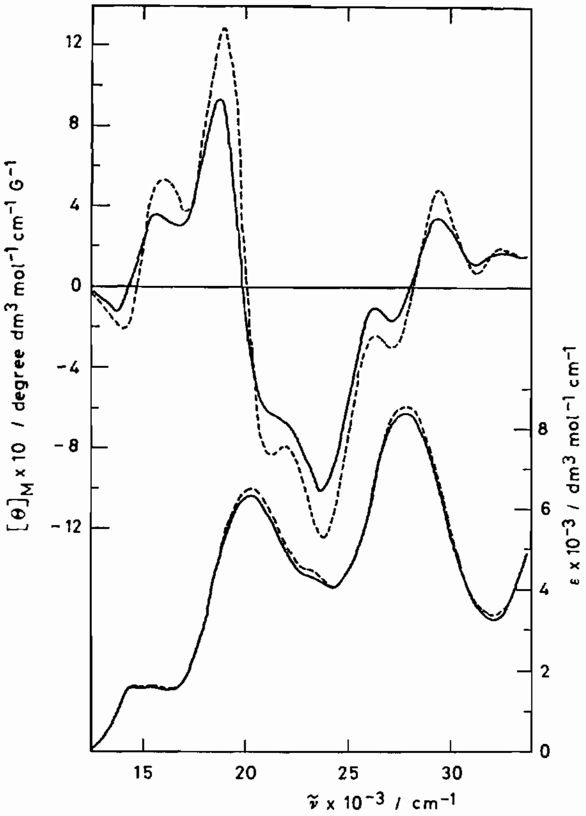

Fig. 1. MCD (upper) and absorption (bottom) spectra for $[Fe_2(S_2\text{-}o\text{-xylyl})_2]^-$ ion in DMF: 300 K (——); 214 K (- - - -).

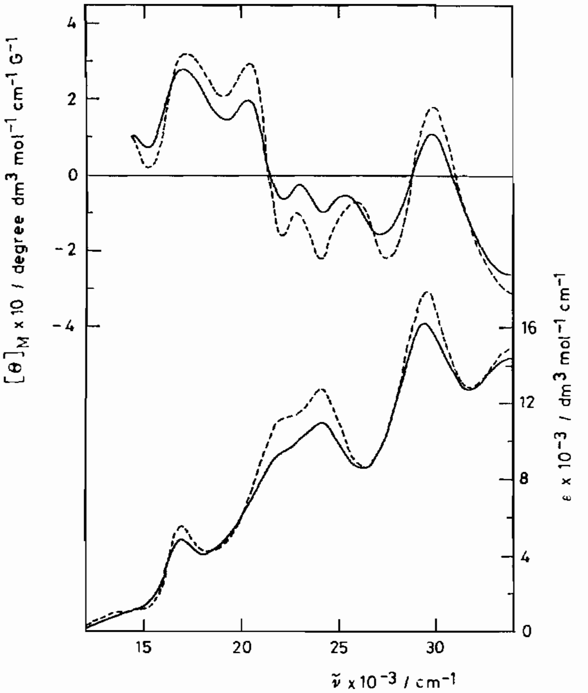

Fig. 2. MCD (upper) and absorption (bottom) spectra for $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion in DMF: 300 K (——); 213 K (- - - -).

that the MCD spectra consist of Faraday C terms. The result is consistent with the theoretical prediction that transitions from the spin degenerate ground state give rise to Faraday C term MCD [11–14]. The Faraday C term for the transition $j \leftarrow a$ is expressed as follows [11]

$$C = (3/d_a)\sum_i \langle a|\mu_z|a\rangle \mathrm{Im}\langle a|m_x|j\rangle\langle j|m_y|a\rangle \qquad (1)$$

where d_a is the degeneracy of the ground state, and μ_z and m_γ ($\gamma = x$ or y) are the components of magnetic and electric transition moment operators, respectively. Im means an imaginary part. The magnitudes of the MCD for the $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion also increased at lower temperature. However the intensities of absorption spectra increased in proportion to those of the MCD spectra. In order to estimate intrinsic MCD magnitudes (*IM*) for the $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion, the relative magnitude of MCD to absorption ($IM = \int_{\mathrm{band}}[\theta]_M d\nu / \int_{\mathrm{band}}\varepsilon\, d\nu$) was calculated. The *IM* values were calculated to be 0.16 and 0.18 at 300 and 213 K, respectively. Although the difference in the intrinsic MCD magnitudes between 300 and 213 K is not so large, there exists *ca.* 10% increase in the intrinsic MCD magnitude at 213 K as compared with that at 300 K. The dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion has two high spin ferric ions bridged by two sulfide ions, and the coordination structure at each site has a somewhat distorted tetrahedral symmetry [4]. The ground state of a high spin ferric ion is an orbitally non-degenerate $^6A_1$ [9, 10].

The magnetic exchange interaction between a pair of ferric ions can be described by a Heisenberg–Dirac–Van Vleck (HDVV) type Hamiltonian [16–20]

$$\mathcal{H}_{\mathrm{HDVV}} = -2JS_AS_B \qquad (2)$$

where A and B refer to respective ions, S is the spin quantum number of each ferric ion, J is the antiferromagnetic interaction constant. This Hamiltonian is sufficient for an orbitally non-degenerate system. However, because a spin angular moment couples with an orbital angular moment, the Hamiltonian is not enough for a system with an orbital degeneracy. Considering the symmetry over a pair of ions [21–24], we constructed the energy levels of the $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion using the method proposed by Herber [22]. Figure 3 shows the energy diagram of the ground and the excited states resulting from a single electron excitation. The energy separation in the ground state sublevels between $S = 0$ and $S = 1$ for the $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ ion is predicted to be $2J$ within the HDVV approximation [25]. The magnetic exchange interaction constant, J, for $[Fe_2S^*_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$ has been estimated to be -148 cm^{-1} by Gillum *et al.* [5]. Since the energy separation between $S = 0$ and $S = 1$ sublevels

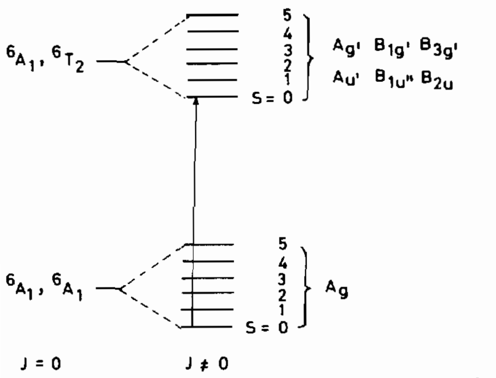

Fig. 3. The energy diagrams for dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ ion.

is not so large as compared with kT (k and T are the Boltzmann constant and the absolute temperature). The thermal population of the $S = 1$ sublevel is important to analyze the optical spectra. The populations (P_i) of each sublevel at various temperatures are derived from the eqn. (3) [18], and shown with respect to T in Fig. 4,

$$P_i = (2S_i + 1) \exp(-E_i/kT) \Bigg/ \sum_{i=0}^{5} (2S_i + 1) \exp(-E_i/kT) \qquad (3)$$

where S_i is the spin quantum number. The energy of each sublevel E_i is calculated from eqn. (4).

$$E_i = J[(35/2) - S_i(S_i + 1)] \qquad (4)$$

Figure 4 shows that the $S = 1$ sublevel has a very small population difference in the temperature range between 300 and 213 K, while the $S = 0$ level at 213 K is populated more than that at room temperature by *ca.* 10%. The absorption spectrum of the dimeric ion, $[Fe_2S^*_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$, from 13500 to 34000 cm^{-1} at 213 K increased by 6% in integrated intensity as compared with that at 300 K, which is nearly equal to the increment of the population of the $S = 0$ sublevel. Because Faraday C terms are derived only from the degenerate ground state, we conclude that the population of $S = 1$ sublevel gives rise to the small temperature dependence of MCD for the $[Fe_2S^*_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ ion. The thermal population of the $S = 1$ sublevel for the $[Fe_2S^*_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ is theoretically predicted to be 0.46 at 300 K, which is about one half of the population of the ground sextet state for the monomeric $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ ion (see Fig. 4). The reduction of the populations of the spin degenerate sublevel leads to the small magnitudes of MCD bands for the dimeric ion in comparison with that for the monomeric ion.

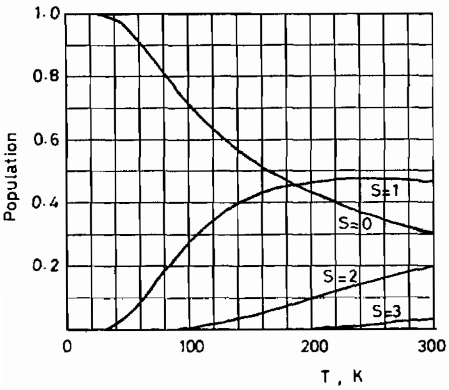

Fig. 4. Thermal populations for each multiplet level in the ground state calculated with $J = -148$ cm^{-1}.

In conclusion, the reduction of MCD magnitudes for the dimeric $[Fe_2S^*_2(S_2\text{-}o\text{-}xylyl)_2]^{2-}$ ion as compared with the monomeric $[Fe(S_2\text{-}o\text{-}xylyl)_2]^-$ ion is attributed to the decrease of Faraday C term contribution, which is determined by the populations of the spin degenerate sublevels.

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