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CORE STRUCTURES OF IRON-SULFUR COMPLEXES FROM MAGNETIC CIRCULAR DICHROISM

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The magnetic circular dichroism (MCD) spectra were measured for the first time on the rebredoxin model iron-sulfur complexes. The bands at around 390 and 490 nm were assigned to Faraday A terms from curve analysis, which indicated effective T_d symmetries for the complexes. Furthermore the propriety as the rubredoxin model was discussed on the basis of the MCD spectra.

Recently iron-sulfur complexes have been extensively investigated as the model compounds of iron-sulfur proteins.1-3) Structures or physicochemical properties of the active site have been mainly studied from comparison between the model complexes and the proteins. The iron-sulfur proteins have been classified into two types, i.e. one with or without the acid labile sulfur (S^*).4) Especially the latter, called rubredoxin, possesses the simplest FeS_4 core structure with a distorted T_d symmetry.5) Although many kinds of simple thiol- and dithiol-iron(III) complexes generally show the rubredoxin like absorption spectra,6) this does not always guarantee the similarity in the core structure to that of rubredoxin because of broad absorption bands with various kinds of transitions. Actually the 1,2-ethane-dithiol-iron(III) complex7) with an analogous absorption spectrum to that of the rubredoxin was found to have a different core structure from that of rubredoxin on the basis of X-ray studies.5,8,9)

It has been shown repeatedly that the magnetic circular dichroism (MCD) is an elegant technique for resolving overlapping bands.10-14) This is mainly because MCD is composed of three components called Faraday A, B, and C terms. Furthermore MCD spectra vary with the ligand field more sensitively than the conventional absorption spectra. Thus they provide valuable information about the assigments of bands and the electronic structures of the complexes.14-16) Nevertheless, the MCD spectra of iron-sulfur complexes without S^* have not been measured except for rubredoxin.17,20)

The dithiolato complexes used here were prepared by the known method.[6,18,19] Both absorption and MCD spectra were measured under an anaerobic condition. MCD spectra were measured with a JASCO J-20A spectropolarimeter equipped with an electromagnet in field strength of 11.4 kG (10^3 gauss). The magnitudes of the MCD were expressed as $[\theta]_M$ in degree cm^2 gram-ion$(Fe^{3+})^{-1}$ $gauss^{-1}$. Although most of the iron-sulfur complexes used here have a limited stability, large variations of MCD magnitude were not observed under the given conditions.

Recent structural and physicochemical studies have revealed that the rubredoxin has a mononuclear tetrahedral core structure with a high spin ferric ion. The MCD spectrum of the protein in the region from 300 to 650 nm has two dispersion type bands (with crossover points at 382 and 495 nm), and a positive (565 nm) and a negative (357 nm) bell shaped bands.[17,20] Both dispersion type bands were assigned to the Faraday A terms associated with the charge-transfer transitions from the ligand-sulfur orbital to the iron t_2 and e d-orbitals, while the bell shaped bands were assigned to the Faraday B terms.[20,21]

Figures 1-4 show the MCD spectra of iron(III)-sulfur complexes without S^*; 1,2-ethanedithiol-iron (i), 1,4-butanedithiol-iron (ii), 1,6-hexanedithiol-iron (iii) and o-xylyl-α,α'-dithiol-iron (iv) complexes. From the band shape, by analogy with the rubredoxin, the dispersion type MCD band with crossover point at around 380 nm is assigned to the Faraday A term with some contribution of the Faraday B term. The curve analysis of the MCD bands showed that the complexes (ii)-(iv) have the Faraday A terms with crossover points at around 490 nm. The assignments of the Faraday parameters from curve analysis are summarized in Table 1.

The energy difference between two A terms of each complex except for (i) is about 5000 cm^{-1}, which is nearly equal to 10 Dq of iron-sulfur complexes with effective T_d symmetries. Therefore, this fact suggests that the iron core structures of the complexes (ii)-(iv) have approximate T_d symmetries.

The MCD spectrum of (i) is extremely different from that of the rubredoxin as well as from those of the complexes (ii)-(iv), especially in MCD signs of the bands near 600 nm and in Faraday parameters at around 480 nm. The complex (i) has been established to have a binuclear form (Fe_2S_8) with five sulfur atoms coordinated to a ferric ion, and its geometry around the high spin ferric ion is distorted trigonal bipyramidal,[8,9] while the other complexes may have effective T_d symmetries.

Though the MCD spectra of the dithiol-iron(III) complexes (ii)-(iv) in the region from 400 to 650 nm have the same Faraday parameters, the MCD signs at around

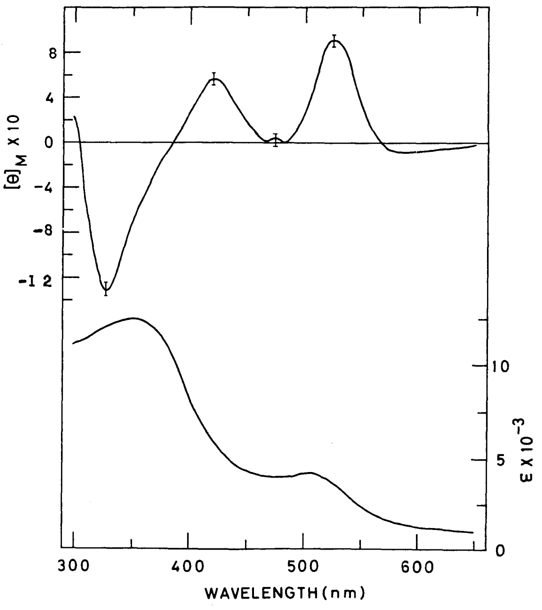

Fig. 1. MCD and absorption spectra of 1,2-ethanedithiol-iron(III). This data was obtained by mixing the ligand and ferric chloride in the molar ratio of 100:1 in 80% (v/v) ethanol solution containing borate buffer (pH 9.0).

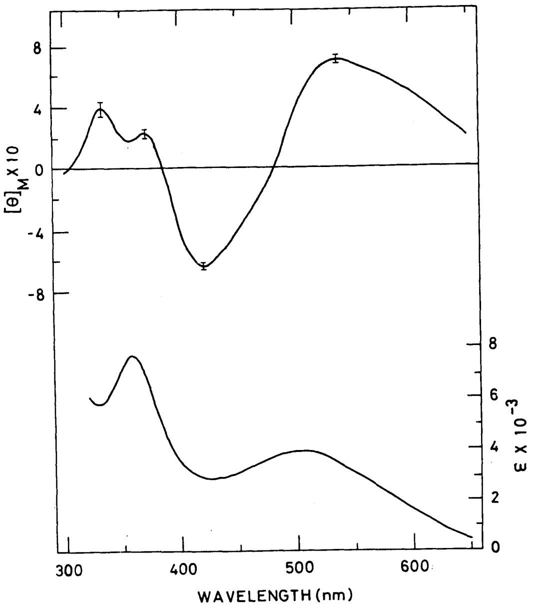

Fig. 2. MCD and absorption spectra of 1,4-butanedithiol-iron(III). The experimental condition was similar to that for Fig. 1.

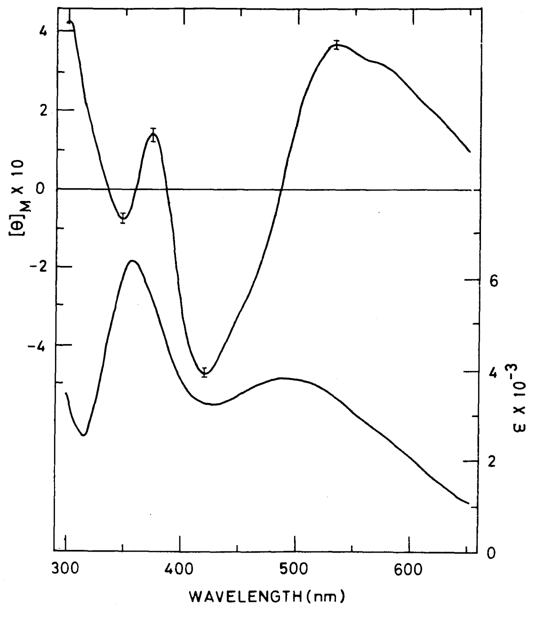

Fig. 3. MCD and absorption spectra of 1,6-hexanedithiol-iron(III). The experimental condition was similar to that for Fig. 1.

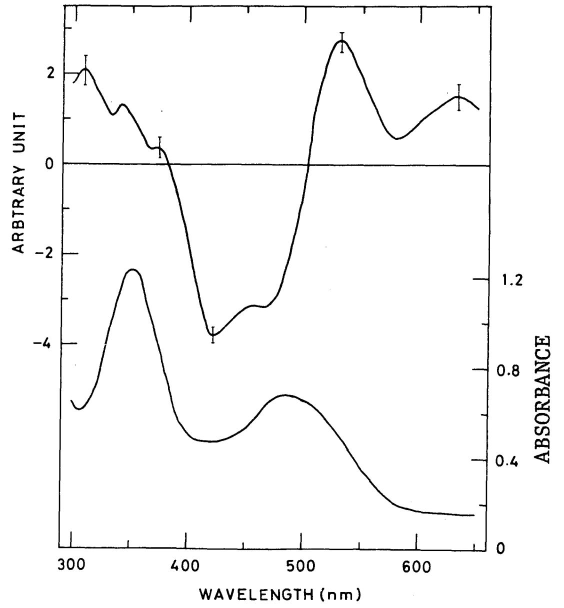

Fig. 4. MCD absorption spectra of o-xylyl-α,α'-dithiol-iron(III). This data was obtained by mixing the ligand, sodiummethoxide and ferric chloride in DMF in molar ratio of 10:10:1.

Table 1. Summary of Results and Assignment of Faraday Parameters.
$(\lambda_{nm}([\theta]_M \times 10 \text{ degree cm}^2 \text{ gram-ion}(\mathrm{Fe}^{3+})^{-1} \text{ gauss}^{-1}))$

(i)	326(-13.3) B	384(-∿5.0, 5.5) A	472(0.2) B	525(9.0) B	590(-0.8) B
(ii)	335(3.9) B	387(2.3,-6.4) A	483(- , 6.9) A		∿600(+) B
(iii)	346(-0.8) B	386(1.3,-4.8) A	487(- , 3.8) A		∿570(3.2) B
(iv)[a]	344(+) B	388(+ , -) A	504(- , +) A		634(+) B
rubredoxin[b]	357(-0.3) B	382(0.8,-2.8) A	495(-2.2,2.5) A		565(1.7) B

a) The MCD magnitude for o-xylyl-α,α'-dithiol-iron complex could not be determined due to the lack of its exact concentration.

b) Data from reference 16.

350 nm of the complex (iii) is different from those of the complexes (ii) and (iv). Since the complexes (ii) and (iv) would form seven membered chelates different from the complex (iii) which might make nine membered chelate, it may suggest that the MCD spectra of the dithiol-iron(III) complexes at around 350 nm reflect sensitively the chelate rign size.

Though the MCD band shape of the complex (iii) appears to be somewhat different from that of the rubredoxin, the Faraday parameters, crossover points and maxima of B terms are in excellent agreement with those of the protein in all region (Table 1). Therefore the core structure of complex (iii) is expected to be similar to that of the rubredoxin. Recently the complex (ii) was reported to have a rubredoxin like core structure with a high spin ferric ion from an EPR study.22) The Faraday parameters and their signs for complexes (ii) and (iv) agree with those of the rubredoxin in the region from 400 to 650 nm, however, the signs of Faraday parameters at around 350 nm are opposite to those of the rubredoxin. This difference might come from the excellent sensitivity of MCD on the electronic structures of the complex in the excited states as compared with EPR.

In conclusion, the sensitivity of the MCD spectra on the differences in core structures was exemplified for iron-sulfur compounds. Thus, it was clarified that complexes (iii) has a similar core structure to that of the rebredoxin. Hence, the MCD spectroscopy can be pointed out to be a potential method to determine the approximate core structures of metal complexes, particularly for those not isolated. Although our experiment for the complex (i) was carried out in an aqueous solution without isolation, it may be considered from the MCD results that the complex (i) has not a mononuclear form. This is in agreement with the results of X-ray analysis in a solid state.[5,8,9)]

References and Notes

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