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USE OF MAGNETIC CIRCULAR DICHROISM IN THE SPIN-FORBIDDEN TRANSITIONS AS A STRUCTURAL PROBE OF CHROMIUM(III) COMPLEXES WITH EDTA ANALOGUES

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Well resolved magnetic circular dichroism spectra have been observed in the spin-forbidden d-d transitions of several Cr(III) complexes with edta analogues at ambient temperature. The positions of the doublet states thus detected have been correlated with the ring size of the chelates in the complexes concerned. From a structural point of view, their positional shifts have been elucidated in terms of the angular overlap model.

It has been revealed that magnetic circular dichroism (MCD) spectra are more potent than absorption and phosphorescence spectra$^{1)}$ as a useful tool for detecting the doublet states of Cr(III) complexes. This advantage of MCD facilitates the study for relating the spin-forbidden transitions to the structures in Cr(III) complexes. In this letter, the MCD spectra in the spin-forbidden transitions are explored for eight Cr(III) complexes and the change of their positions is discussed in connection with nonplanarity of the chelate rings.

Among the present complexes, potassium cis(N)-bis(iminodiacetato)chromate(III), $K[Cr(ida)_2]\cdot 2.5H_2O$;$^{2)}$ sodium trimethylenediaminetetraacetatochromate(III), $Na[Cr(trdta)]\cdot 2H_2O$;$^{2)}$ lithium ethylenediamine-N,N'-diacetato-N,N'-di-3-propionatochromate(III), $Li[Cr(eddda)]\cdot 2.5H_2O$;$^{3)}$ and potassium tetramethylenediaminetetraacetatochromate(III), $K[Cr(tmdta)]\cdot KCl\cdot H_2O$;$^{4)}$ were prepared according to the literature methods. Potassium (±)-2,4-pentanediaminetetraacetatochromate(III), $K[Cr(ptnta)]\cdot H_2O$ and potassium (±)-ethylenediamine-N,N'-disuccinatochromate(III), $K[Cr(edds)]\cdot 2H_2O$ were obtained from racemic H_4ptnta and H_4edds, respectively, by the methods for the corresponding chiral complexes.$^{2,4)}$ Lithium ethylenediaminetetra-3-propionatochromate(III), $Li[Cr(edtp)]\cdot LiCl\cdot 2CH_3OH\cdot 2H_2O$ was prepared by the similar method to that for the corresponding Co(III) complex.$^{6)}$ Lithium ethylenediaminetri-3-propionato-monoacetatochromate(III), $Li[Cr(edtrpa)]\cdot LiCl\cdot 3.5H_2O$ was newly prepared similarly to the edtp complex by using a reaction mixture of ethylenediaminemonoacetic acid and 3-chloropropionic acid with a sodium hydroxide solution. These complexes were confirmed to coordinate the edta analogues as sexadentate ligands by the elemental analyses and infrared spectra as well as the fact that their absorption spectra showed no change with increase in pH. MCD spectra were obtained in a magnetic field of 1.5 T by a Jasco MOE-1 spectropolarimeter in aqueous solutions at room temperature.

As shown in Fig. 1(a), cis(N)-$[Cr(ida)_2]^-$ gives a broad positive MCD band in the

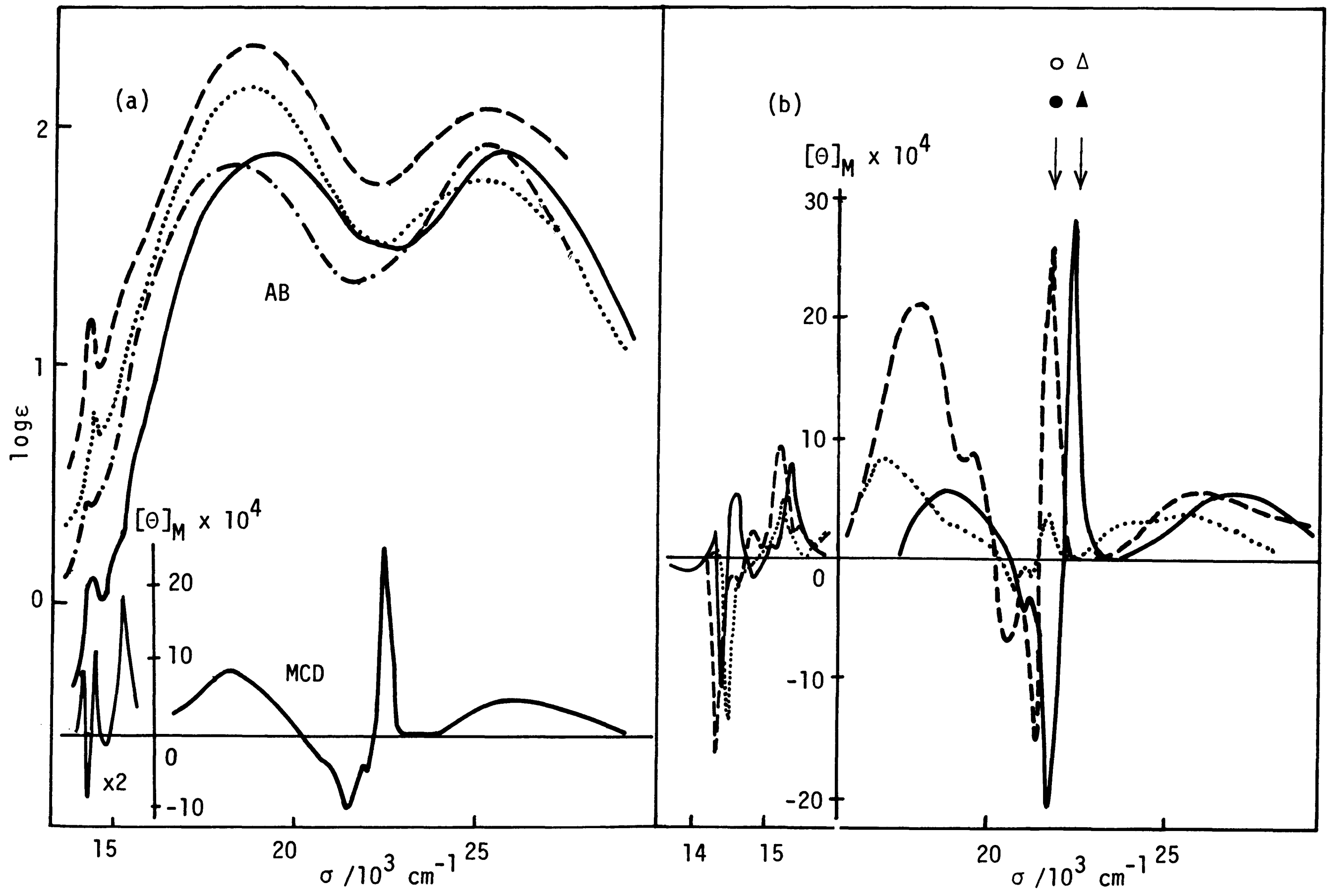

Fig. 1(a) Absorption(AB) curves of cis(N)-$[Cr(ida)_2]^-$(——), $[Cr(tmdta)]^-$(—•—), $[Cr(edtp)]^-$(••••), and $[Cr(edtrpa)]^-$(----); and MCD curve of cis(N)-$[Cr(ida)_2]^-$. (b) MCD curves of $[Cr(ptnta)]^-$(——), $[Cr(edtp)]^-$(••••), and $[Cr(edtrpa)]^-$(----); the marks at the arrows show the highest energy MCD peaks of $[Cr(eddda)]^-$(O), $[Cr(edds)]^-$(●), $[Cr(trdta)]^-$(Δ), and $[Cr(tmdta)]^-$(▲).

first and the second spin-allowed band region, while in the region corresponding to the lower energy spin-forbidden band five sharp but rather intense MCD peaks with alternate signs are observed. The lowest doublet state of $[Cr(ida)_2]^-$ which has been observed and assigned to one of the splitting components of the $^2T_{1g}$ state by Flint and Matthews[7)] can not be detected by the present MCD measurements. Between the first and the second bands of this complex, a strong negative and a positive MCD peaks are observed from the lower energy side together with weak negative components as in Fig. 1. The MCD spectra of the other edta type complexes behave similarly to that of the ida complex(Fig. 1). The difference in the positions of the lower energy MCD peaks near 15000 cm^{-1} is found to be small for the present complexes(Fig. 1(b)); all the present complexes have almost the same interelectronic repulsion energies. On the other hand, the MCD positions near 22000 cm^{-1} vary from one group of the complexes to the other. That is, for the ida, trdta, ptnta, and tmdta complexes which are classified as A group, the highest energy MCD peaks locate from 22200 cm^{-1} to 22400 cm^{-1}, and those for the eddda, edds, and edtrpa complexes which are classified as B group lie from 21600 cm^{-1} to 21700 cm^{-1} as in Fig. 1(b). It appears that such a large difference in the MCD positions is not responsible for the

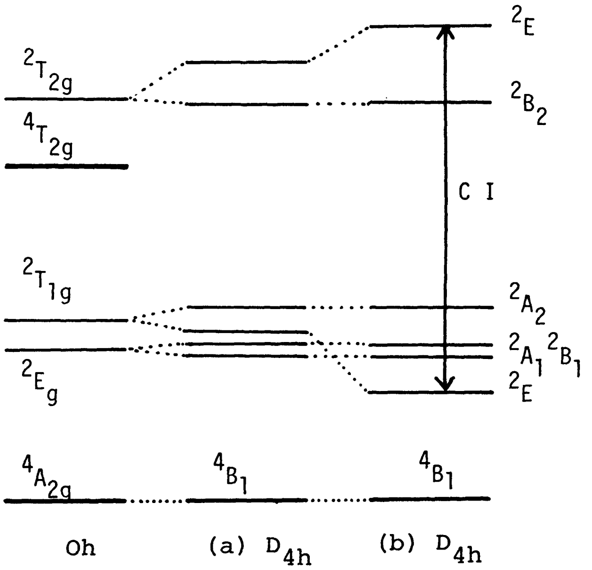

Fig. 2. Energy levels in a tetragonal field with weak(a) and strong(b) configurational interaction (CI) between the ^2E states of Cr(III) ions. (The subscript g omitted for D_{4h})

nephelauxetic effect.$^{8)}$ This classification of the complexes into two groups coincides with that based on the chelate ring size in the in-plane O-N-N-O girdle ring(G ring). The eddda and edds complexes have been determined to take a trans(O_5) geometrical structure with two in-plane six-membered rings by the X-ray analysis$^{9)}$ and the CD spectra,$^{3)}$ respectively. For the edtrpa complex, the most favorable structure seems to be a trans(O_5,O_6) one owing to the preferential coordination of six-membered chelates in the G ring. On this basis, the A group complexes have two five-membered glycinate chelates in the G ring, while the B group complexes have two in-plane β-alaninate chelates. Therefore, it is apparent that the positions of the highest energy MCD peaks are closely related to the structures in the complexes of this type. This may be elucidated by the following consideration.

In tetragonal(D_{4h}) holohedrized symmetry for cis-[Cr(N)$_2$(O)$_4$] type complexes, the configurational interaction results in the stabilization of the lower $^2E(^2T_{1g})$ state and the destabilization of the higher $^2E(^2T_{2g})$ state by the amount given in the following equation as shown in Fig. 2.

$$\Delta(t_{2g})^2/(6B + 2C),$$

where $\Delta(t_{2g})$ is the energy interval between the tetragonal splitting (e_g and b_{2g}) within the t_{2g} shell(Fig. 3), and B and C are the Racah interelectronic repulsion parameters. Since the B and C are almost the same for the present complexes, the shift of the ^2E states is much susceptible to the change of the $\Delta(t_{2g})$ value, which may arise mainly from the anisotropic Cr-O π interactions with respect to the chelate planes. A simple approach of the angular overlap model(AOM)$^{10)}$ predicts that the $\Delta(t_{2g})$ for $[Cr(ida)_2]^-$ is two times that for $[Cr(ox)_2(en)]^-$ on the assumption of the predominant Cr-O π interaction vertical to the chelate planes($e_{\pi\perp} \gg e_{\pi/\!/}$) and by using the same values for the AOM $e_{\pi\perp}$ parameter of the oxalate and amino carboxylate oxygen as in Fig. 3(a) and (b). This difference in the $\Delta(t_{2g})$ values gives rise to the shifts of the $^2E(^2T_{1g})$ state for these complexes: the lowest doublet state of the ida complex has been observed at the lower energy side by about 1000 cm^{-1} than that of the oxalato complex.$^{7,11)}$ Taking into account of this strong configurational interaction between the ^2E states of $[Cr(ida)_2]^-$, the highest energy positive MCD peak of the ida complex and the other edta type complexes is certainly assigned to the $^2E(^2T_{2g})$ state. It is also predicted that the $\Delta(t_{2g})$ value of $[Cr(ida)_2]^-$ decreases with increasing an angle α of rotations of the coordinated oxygen p orbitals in the xy plane about Cr-O bonds owing to the mismatch of d-p_π orbital overlaps(Fig. 3(c)), while the inclination of two oxygen p orbitals on the z-axis at the

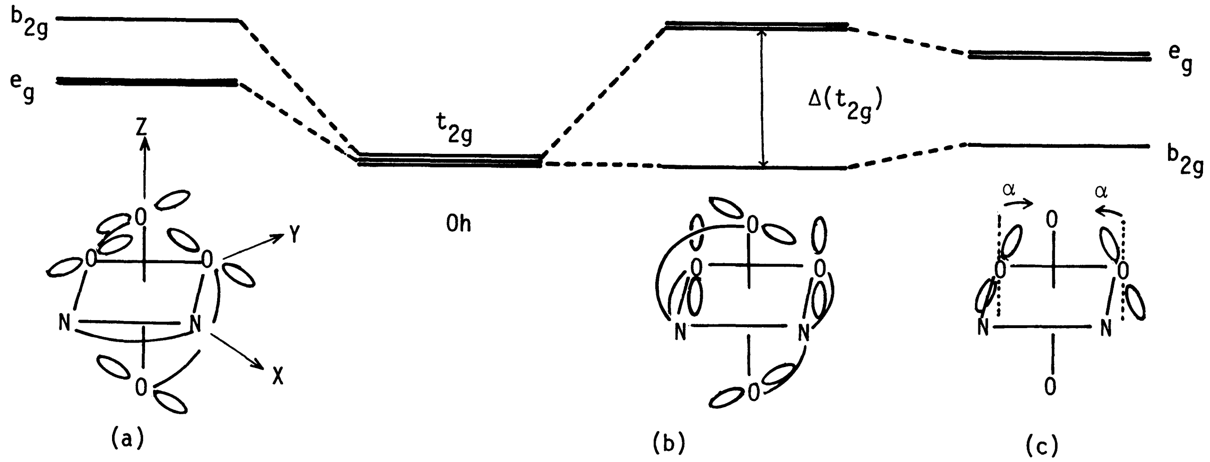

Fig. 3. Orbital splittings within the t_{2g} shell due to the π interaction between metal d orbitals (omitted for clarity in the lower half of the figure) and coordinated oxygen p orbitals (depicted by lobes) vertical to the chelate planes: (a) $[Cr(ox)_2(en)]^-$, (b) $[Cr(ida)_2]^-$, and (c) the reduced splitting due to the rotation of the oxygen p orbitals about Cr-O bonds in the G ring of $[Cr(ida)_2]^-$.

same angle about Cr-O bonds does not affect the d orbital splitting. Consequently, it is probable that the shift of the ^2E states is sensitive to the conformational change of the chelates in the G ring of the edta type complexes. Since six-membered chelate rings are more subject to distortion than five-membered ones, the coordinated oxygen p orbitals vertical to β-alaninate chelate planes in the edta type complexes tend to incline at a larger angle than those vertical to glycinate ones; then the $\Delta(t_{2g})$ for the former complexes becomes smaller than that for the latter ones. Therefore, it is most probable as a result of the decrease in the configurational interaction between the ^2E states that the B group complexes with β-alaninate chelates in the G ring give the $^2E(^2T_{2g})$ state at the lower energy side than the A group complexes with in-plane glycinate chelates as observed by the present MCD measurements. From this consideration, it is confirmed that the edtrpa complex is a trans(O_5,O_6) isomer. The preliminary calculations involving all configurational interactions for the d^3 configuration in terms of the AOM support the present qualitative treatment.

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