Exciton Circular Dichroism of Chromium(III) Complexes Containing Two Nonidentical α-Diimines

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Application of the exciton theory to the circular dichroism (CD) spectra of tris- or bis-α-diimine metal complexes has been carried out intensively.[1-4] The exciton interaction between the nonidentical long-axis π-π* transitions of the coordinated 2,2′-dipyridyl (dip) and 1,10-phenanthroline (phen) has been reported in the cases of the CD spectra of $[M(dip)_2(phen)]^{n+}$ and $[M(dip)(phen)_2]^{n+}$ complexes.[1,3] In order to confirm the interaction of this kind, it is most desirable to investigate the simpler mixed complex, $[M(dip)(phen)L_2]^{n+}$, which contains only one each of the nonidentical α-diimines.

A new binuclear μ-diol chromium(III) complex of this kind was prepared by the reaction of $[CrCl_3(dmf)(dip)]$ with $phen\cdot HNO_3$ in water at 70°C. Found: C, 45.87; H, 4.09; N, 14.73%. Calcd for $C_{44}H_{46}N_{12}O_{20}Cr_2=[(dip)(phen)Cr(OH)_2Cr(dip)(phen)](NO_3)_4\cdot 6H_2O$: C, 45.29; H, 3.97; N, 14.40%. Another new mononuclear oxalato complex was obtained by heating the aqueous solution of the μ-diol complex with oxalic acid. Found: C, 49.25; H, 3.61; N, 11.66%. Calcd for $C_{24}H_{21}N_5O_{9.5}Cr=[Cr(ox)(dip)(phen)]NO_3\cdot 2.5H_2O$: C, 49.41; H, 3.63; N, 12.00%. The μ-diol and oxalato complexes were optically resolved by using resolving agents, potassium di-μ-L-tartrato(4-)diantimonate(III) trihydrate and $(-)_{589}$-$K[Cr(ox)_2(phen)]\cdot 4H_2O$, respectively. The $(-)_{589}$-isomers were isolated and characterized as a nitrate heptahydrate (μ-diol complex) and a perchlorate dihydrate (oxalato complex). As seen in Fig. 1, the absorption spectra of the present μ-diol and oxalato complexes have common bands with μ-diol tetra-dip or -phen complex and oxalato bis-dip or -phen complex, respectively.[3,4] The CD spectra in the ligand absorption band region of the present $(-)_{589}$ complexes show a typical exciton band pattern as in those of $(-)_{589}$-tetra-dip or -phen binuclear complex and of $(-)_{589}$-bis-dip or -phen mononuclear complex.[3,4] That is, from the longer wavelength side, an intense negative and a positive CD band are observed near the long-axis π-π* transitions of the dip (310 mμ) and phen (275 mμ), respectively. If there were no interaction between the dip and phen transitions in the present complexes, the CD bands at 310 and 275 mμ would have the same sign for the same tris-chelate configuration as in the case of L-tartrato α-diimine chromium(III) complexes.[5] Thus, the present observation confirms the existence of the exciton interaction between the nonidentical π-π* transitions of the dip and phen in a complex. From the behavior of the exciton CD bands at 310 and 275 mμ, the $(-)_{589}$-isomers of the present complexes are assigned to the $\Delta(C_2)$ configuration.[1,2] This assignment agrees with the empirical one on the basis of a major CD band in the first d-d absorption band region.

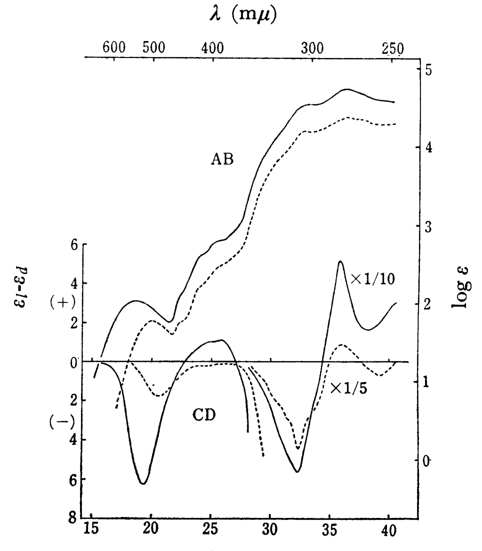

Fig. 1. Absorption (AB) and CD curves of $(-)_{589}$-$[(dip)(phen)Cr(OH)_2Cr(dip)(phen)](NO_3)_4\cdot 7H_2O$ (——) and $(-)_{589}$-$[Cr(ox)(dip)(phen)]ClO_4\cdot 2H_2O$ (----) in water.

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