Table V. Comparison of Calculated and Measured Molar Kerr Constants for Tin Tropolonates

Candidate structure	Symmetry	$10^{24}(b_1 - b_2)$, cm^3	$10^{24}(b_1 - b_3)$, cm^3	$10^{12}{}_mK$(calcd)	$10^{12}{}_mK$(obsd)
trans-$(CH_3)_2Sn(trop)_2$	D_{2h}	24.5	24.5	+279	
cis-$(CH_3)_2Sn(trop)_2$	C_2	−12.2	0	−827	
cis-$(CH_3)_2Sn(trop)_2$	C_{2v}	−11.7	−23.5	−2414	−4270
cis-$Cl_2Sn(trop)_2$	C_2	−12.2	0	−5129	−6990
cis-$Cl_2Sn(trop)_2$	C_{2v}	−11.7	−23.5	−15,856	
trans-$Cl_2Sn(trop)_2$	D_{2h}	24.1	24.1	+273	

tation cannot be taken too far, however, since the highly polar tin complexes may be interacting with benzene molecules to form transient collision complexes through stereospecific associations of the benzene π systems with electron deficient sites in the complexes. Such associations would, for solute molecules of this geometry, tend to lead to apparent molar Kerr constants more negative than those of the "isolated" solute.[25]

Registry No. Tl(trop), 36487-20-4; $(C_6H_5)_2Sn(trop)_2$, 36487-15-7; $(CH_3)_2Sn(trop)_2$, 21844-38-2; $Cl_2Sn(trop)_2$, 36544-14-6; Htrop, 533-75-5.

Acknowledgments. The authors thank Professor R. J. W. Le Fevre, FAA and FRS, Dr. R. S. Armstrong, Dr. K. E. Calderbank, and Dr. R. K. Pierens for advice and assistance given in this work. The award of a grant by the Australian Research Grants Committee is gratefully acknowledged. Travel funds for W. H. N. were provided by the National Science Foundation and Research Corp.

(25) R. J. W. Le Fevre, D. V. Radford, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc. B*, 148 (1968).

Contribution from the Department of Chemistry, Faculty of Science,
Osaka University, Toyonaka, Osaka, Japan

Circular Dichroism of Chromium(III) Complexes. III.[1] Preparation, Optical Resolution, and Ultraviolet Circular Dichroism Spectra of Mixed Complexes Containing α-Diimines or Ethylenediamine and Acetylacetonate or Its 3-Halogeno Derivatives

SUMIO KAIZAKI, JINSAI HIDAKA,* and YOICHI SHIMURA

Received May 11, 1972

Nine new optically active chromium(II) complexes have been characterized by elemental analysis, infrared spectra, and visible and ultraviolet absorption and circular dichroism (CD) spectra; these are $(-)_{589}[(dip)(phen)Cr(OH)_2Cr(dip)(phen)]^{4+}$, $(-)_{589}[Cr(ox)(dip)(phen)]^+$, $(+)_{546}[Cr(acac)(en)_2]^{2+}$, $(+)_{546}[Cr(acac)_2(en)]^+$, and the corresponding 3-chloro- or 3-bromoacetylacetonato complexes (dip = 2,2′-dipyridyl, phen = 1,10-phenanthroline, acac = acetylacetonate). The mixed α-diimine complexes show the theoretically anticipated exciton CD splitting in their long-axis-polarized π–π^* transition region. From the comparison of the ultraviolet absorption and CD spectra for the acetylacetonato and 3-halogenoacetylacetonato complexes, the assignment for six CD bands in the ultraviolet region of the bis-acetylacetonato complex has been attempted. The absolute configuration determined on the basis of the exciton CD bands of the present complexes coincided with that based on the dominant CD component in the first d–d absorption band region.

Introduction

There have been a number of studies on transition metal complexes with the ligands containing unsaturated π-electron systems such as α-diimines[2] or β-diketones.[3] The correlations between the circular dichroism (CD) spectra and the absolute configurations of such complexes have been intensively pursued from a stereochemical and spectroscopical viewpoint.[4-8] The coupling between three or two of the same ligands having a long-axis-polarized π-π^* transition, in a dihedral complex, gives rise to a helical charge displacement and causes zeroth-order intrinsic rotational strengths.[4] On the basis of the exciton model dealing with such dipole–dipole coupling, the absolute configurations of the complexes have been nonempirically determined from the CD splitting in the intraligand π-π^* transition region.[4] The exciton splitting is expected to be observed also in the case of mixed complexes such as $[M(dip)_2(phen)]^{n+}$ or $[M(dip)(phen)_2]^{n+}$ (dip = 2,2′-dipyridyl; phen = 1,10-phenanthroline), because such a dipole–dipole coupling occurs not only between the ligands of one kind but also between the nonidentical ligands.[4,7,8] In fact, the CD spectra of these complexes in the ligand transition

---

(1) Part II: S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, 43, 1100 (1970). In the part II, the symbols $\Delta(C_2)$ and $\Lambda(C_2)$ were used for the absolute configurations of dihedral complexes. But the symbols Δ and Λ used in this paper are opposite in meaning to those in the part II and agree with "Nomenclature of Inorganic Chemistry; Definitive Rules 1970," Butterworths, London, 1971, p 75.

(2) W. R. McWhinnie and J. D. Miller, *Advan. Inorg. Chem. Radiochem.*, 12, 135 (1969).

(3) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, 7, 361 (1966).

(4) B. Bosnich, *Accounts Chem. Res.*, 2, 266 (1969).

(5) I. Hanazaki and S. Nagakura, *Inorg. Chem.*, 8, 654 (1969).

(6) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc. A*, 1428 (1969).

(7) S. F. Mason and B. J. Norman, *Chem. Phys. Lett.*, 2, 22 (1968); S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, 1442 (1969).

(8) B. Bosnich, *Inorg. Chem.*, 7, 2379 (1968).

region follow the theoretically anticipated pattern.[7,8] However, there has been no report[9] about the bis-chelate type complexes containing two nonidentical ligands such as $[M(dip)(phen)X_2]^{n+}$, where X is "spectroscopically neutral" in the spectral region concerned.

In the present paper, the preparation and optical resolution of new chromium(III) complexes containing α-diimines, acetylacetonate (acac), and/or 3-halogenoacetylacetonate (acaX; X = Cl, Br) will be reported. The CD spectra in the ultraviolet region will be discussed on the basis of the exciton model. In particular, the observed six CD bands of the bis-acetylacetonato complexes will be assigned according to the theoretical study[10] on the electronic structure of $[Cr(acac)_3]$. The absolute configuration of the present complexes will be determined on the basis of the ultraviolet CD spectra in accordance with that based on the dominant CD component in the region of the first d–d ligand field transition.

Experimental Section

Preparations and Optical Resolutions. (1) $[(dip)(phen)Cr(OH)_2Cr(dip)(phen)](NO_3)_4 \cdot 6H_2O$. $[CrCl_3(dmf)(dip)]$ (3.78 g) was resolved in 50 ml of water by heating. Then the color of the solution became red. This red species may be $[Cr(OH_2)_4(dip)]^{3+}$. In order to obtain the nitrate, the red solution was poured into the column (450 × 25 mm) containing an anion-exchange resin of NO_3^- type (Amberlite IRA 400). To the resulting nitrate solution was added 7.3 g of 1,10-phenanthrolinium nitrate, phen · HNO_3. The initial pH of the solution was 1.5. A solution (40 ml) of 0.8 g of sodium hydroxide was added dropwise to the red solution during about 8 hr. Then, the final pH of the solution became 4.0 and the color of the solution changed to brown. The brown solution obtained was allowed to stand overnight in a refrigerator. White needles and brown crystals which crystallized were filtered. The desired brown crystals were separated from the mixture by extracting the white needles with methanol and were recrystallized from hot water. *Anal.* Calcd for $C_{44}H_{46}N_{12}O_{20}Cr_2 = [Cr_2(OH)_2(dip)_2(phen)_2](NO_3)_4 \cdot 6H_2O$: C, 45.29; H, 3.97; N, 14.40. Found: C, 45.87; H, 4.09; N, 14.73.

(2) $(-)_{589}[Cr_2(OH)_2(dip)_2(phen)_2](NO_3)_4 \cdot 7H_2O$. To 20 ml of a warm aqueous solution containing 0.9 g of $[Cr_2(OH)_2(dip)_2(phen)_2](NO_3)_4 \cdot 6H_2O$ was added 5 ml of an aqueous solution of 1.05 g of $K_2[Sb_2(\text{L-tart})_2] \cdot 3H_2O$. After cooling to room temperature, brown crystals were separated by filtration and were then converted to the nitrate using silver nitrate. The recrystallization was performed in hot water. *Anal.* Calcd for $C_{44}H_{48}N_{12}O_{21}Cr_2 = (-)_{589}[Cr_2(OH)_2(dip)_2(phen)_2](NO_3)_4 \cdot 7H_2O$: C, 44.60; H, 4.08; N, 14.18. Found: C, 44.42; H, 3.98; N, 14.13. $[M]_{589}$ −1030°.

(3) $[Cr(OH)(OH_2)(dip)(phen)](NO_3)_2 \cdot 1.5H_2O$. The mother liquor in section 1 was concentrated to half of its original volume. After cooling in an ice bath, orange-brown crystals were obtained and recrystallized from hot water. *Anal.* Calcd for $C_{22}H_{22}N_6O_{9.5}Cr = [Cr(OH)(OH_2)(dip)(phen)](NO_3)_2 \cdot 1.5H_2O$: C, 46.00; H, 3.85; N, 14.63. Found: C, 46.53; H, 3.89; N, 14.69.

(4) $(-)_{589}[Cr_2(OH)_2(dip)_4]Cl_4 \cdot 9H_2O$ and $(-)_{589}[Cr_2(OH)_2(phen)_4](NO_3)_4 \cdot 7H_2O$. These complexes were prepared by the method of Schaffer, *et al.*,[11] and optically resolved as described above by the method in the literature.[12] The diastereomer of the dip complex was converted to the chloride using barium chloride dihydrate. *Anal.* Calcd for $C_{40}H_{52}N_8O_{11}Cr_2Cl_4 = (-)_{589}[Cr_2(OH)_2(dip)_4]Cl_4 \cdot 9H_2O$: C, 45.04; H, 4.91; N, 10.50. Found: C, 44.90; H, 4.86; N, 10.34. $[M]_{589}$ −7050°. The optical resolution of the corresponding phen complex was made by using the racemic chloride, because the resolution starting from the nitrate was unsuccessful. The diastereomer was converted to the nitrate using silver nitrate. *Anal.* Calcd for $C_{48}H_{48}N_{12}O_{21}Cr_2 = (-)_{589}[Cr_2(OH)_2(phen)_4](NO_3)_4 \cdot 7H_2O$: C, 46.76; H, 3.92; N, 13.63. Found: C, 46.49; H, 3.85; N, 13.26. $[M]_{589}$ −13100°.

(5) $[Cr(ox)(dip)(phen)]Cl$. $[Cr_2(OH)_2(dip)_2(phen)_2](NO_3)_4 \cdot 6H_2O$ (1.0 g) and oxalic acid dihydrate (0.28 g) were dissolved in 10 ml of water. The mixture was heated at 70° for a while and the color of the solution changed from brown to orange. One gram of potassium iodide was added to the orange solution. A brownish yellow precipitate deposited from the cooled solution and was filtered off. The iodide obtained was converted to the chloride using silver chloride. The chloride was recrystallized from hot water. *Anal.* Calcd for $C_{24}H_{16}N_4O_4CrCl = [Cr(ox)(dip)(phen)]Cl$: C, 56.32; H, 3.15; N, 10.95. Found: C, 55.74; H, 3.25; N, 10.69.

(6) $(-)_{589}[Cr(ox)(dip)(phen)]ClO_4 \cdot 2H_2O$. $[Cr(ox)(dip)(phen)]Cl$ (0.8 g) was dissolved in 100 ml of cold water at 3°. To this solution was added a cold solution (14 ml) containing 0.39 g of $(-)_{546}K[Cr(ox)_2(phen)] \cdot 4H_2O$. The mixture was stirred in an ice bath. Then the pink diastereomer deposited and after a few minutes it was filtered. *Anal.* Calcd for $C_{40}H_{31}N_6O_{15.5}Cr_2 = (-)_{589}[Cr(ox)(dip)(phen)](-)_{546}[Cr(ox)_2(phen)] \cdot 3.5H_2O$: C, 50.59; H, 3.29; N, 8.85. Found: C, 50.29; H, 3.43; N, 8.77. The pink diastereomer was suspended in a small amount of cold water and then dissolved in an appropriate amount of cold 70% perchloric acid. By adding cold methanol to this solution, an orange powder was obtained. *Anal.* Calcd for $C_{24}H_{20}N_4O_{10}ClCr = (-)_{589}[Cr(ox)(dip)(phen)]ClO_4 \cdot 2H_2O$: C, 47.11; H, 3.28; N, 9.19. Found: C, 47.35; H, 3.40; N, 8.96. $[M]_{589}$ −2922°.

(7) $(-)_{589}[Cr(ox)(dip)_2]Cl \cdot 4H_2O$ and $(-)_{589}[Cr(ox)(phen)_2]ClO_4 \cdot 2.5H_2O$. These dip and phen complexes were prepared and resolved by the method of Broomhead, *et al.*[13]

(8) $[Cr(acac)(en)_2]Cl_2 \cdot 0.5H_2O$. *cis*-$[CrCl_2(en)_2]Cl \cdot H_2O$ (14 g) was dissolved in 50 ml of an aqueous solution containing 5 g of acetylacetone and 2.1 g of sodium hydroxide. The mixture was heated on a water bath at 70° for a while and the color of the solution changed from red violet to orange. Potassium iodide (20 g) was added to the orange solution. After cooling in an ice bath, orange crystals were precipitated and filtered. The iodide crystals obtained were recrystallized from hot water. *Anal.* Calcd for $C_9H_{23}N_4O_2CrI_2 = [Cr(acac)(en)_2]I_2$: C, 20.59; H, 4.42; N, 10.67. Found: C, 20.75; H, 4.44; N, 10.64. The iodide of this new complex was converted to the chloride with an anion-exchange resin in the chloride form in a batchwise operation. The pure chloride was obtained by recrystallization from methanol (95%) and acetone. *Anal.* Calcd for $C_9H_{24}N_4O_{2.5}Cl_2Cr = [Cr(acac)(en)_2]Cl_2 \cdot 0.5H_2O$: C, 30.78; H, 6.89; N, 15.95. Found: C, 31.28; H, 6.90; N, 16.04.

(9) $(+)_{546}[Cr(acac)(en)_2]Cl_2 \cdot H_2O$. To 50 ml of an aqueous solution containing 7.0 g of $[Cr(acac)(en)_2]Cl_2 \cdot 0.5H_2O$ was added 25 ml of an aqueous solution of 10.4 g of $Na_2[As_2(\text{L-tart})_2] \cdot 2H_2O$ (L-tart = $C_4H_2O_6^{4-}$) and the combined solution was thoroughly mixed. After cooling in an ice bath, orange stick-like crystals were separated and collected. The diastereomer was recrystallized from hot water. *Anal.* Calcd for $C_{17}H_{33}N_4O_{17}CrAs_2 = (+)_{546}[Cr(acac)(en)_2][As_2(\text{L-tart})_2] \cdot 3H_2O$: C, 26.61; H, 4.34; N, 7.30. Found: C, 26.89; H, 4.38; N, 7.35. $[M]_{546}$ +2100°. To the suspension of the diastereomer (*ca.* 5 g) in 0.4 *N* aqueous sodium hydroxide solution was added 3 g of potassium iodide. The orange iodide was precipitated together with white crystals. The iodide was extracted with methanol and the white crystals were removed by filtration. By adding an appropriate amount of ether to the orange methanol solution, the optically active iodide was obtained. This iodide was converted to the chloride with an anion-exchange resin in the chloride form in a batchwise operation. The crude chloride was recrystallized from methanol (95%) and acetone. *Anal.* Calcd for $C_9H_{25}N_4O_3Cl_2Cr = (+)_{546}[Cr(acac)(en)_2]Cl_2 \cdot H_2O$: C, 30.00; H, 7.00; N, 15.55. Found: C, 30.01; H, 7.15; N, 15.32. $[M]_{546}$ +1122°.

(10) $(+)_{546}[Cr(acaBr)(en)_2]Cl_2 \cdot 2.5H_2O$. To an acetic acid solution containing 0.36 g (0.01 mol) of $[Cr(acac)(en)_2]Cl_2 \cdot 0.5H_2O$ was added an acetic acid solution of 0.36 g (0.02 mol) of *N*-bromosuccinimide (NBS). By adding ether to the mixture, a yellow-orange precipitate was obtained. This was recrystallized from methanol (95%) and acetone. *Anal.* Calcd for $C_9H_{22}N_4O_2BrCl_2Cr = [Cr(acaBr)(en)_2]Cl_2$: C, 25.63; H, 5.27; N, 13.31. Found: C, 25.36; H, 5.39; N, 12.84. The optically active isomer of this complex was obtained by the same method as that of the racemic one from $(+)_{546}[Cr(acac)(en)_2]Cl_2 \cdot H_2O$. *Anal.* Calcd for $C_9H_{27}N_4O_{4.5}BrCl_2Cr = (+)_{546}[Cr(acaBr)(en)_2]Cl_2 \cdot 2.5H_2O$: C, 23.19; H, 5.84; N, 12.02. Found: C, 23.20; H, 5.63; N, 11.94. $[M]_{546}$ + 1440°.

---

(9) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, 43, 3024 (1970).

(10) F. Hanazaki, I. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, 50, 276 (1969).

(11) J. Josephsen and C. E. Schaffer, *Acta Chem. Scand.*, 24, 2929 (1970).

(12) S. F. Mason and J. W. Wood, *Chem. Commun.*, 1512 (1968).

(13) J. A. Broomhead, M. Dwyer, and N. A. P. Kane-Maguire, *Inorg. Chem.*, 7, 1388 (1968).

(11) $(+)_{546}[\mathrm{Cr(acaCl)(en)_2}]\mathrm{Cl_2}\cdot1.5\mathrm{H_2O}$. The complex as the chloro-substituted derivative was prepared by a method similar to that for the bromo-substituted complex by using *N*-chlorosuccinimide (NCS) instead of NBS. *Anal.* Calcd for $\mathrm{C_9H_{24}N_4O_3Cl_3Cr} = [\mathrm{Cr(acaCl)(en)_2}]\mathrm{Cl_2}\cdot\mathrm{H_2O}$: C, 27.40; H, 6.13; N, 14.20. Found: C, 27.84; H, 6.30; N, 14.27. *Anal.* Calcd for $\mathrm{C_9H_{25}N_4O_{3.5}Cl_3Cr} = (+)_{546}[\mathrm{Cr(acaCl)(en)_2}]\mathrm{Cl_2}\cdot1.5\mathrm{H_2O}$: C, 26.76; H, 6.24; N, 13.88. Found: C, 27.09; H, 6.27; N, 13.71. $[M]_{546}$ +1544°.

(12) $[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$. To an aqueous solution containing 9.0 g of $[\mathrm{CrCl_2(OH_2)_2(en)}]\mathrm{Cl}$ was added 7.2 g of acetylacetone and 2.8 g of sodium hydroxide. The mixture was warmed with stirring until the color of the solution changed from blue to red. The solution was evaporated as far as possible in a vacuum evaporator. The whole red product obtained was dissolved in a small amount of hot water. Potassium iodide (15 g) was added to this solution. After cooling in an ice bath, red crystals separated were removed by filtration. The crude crystals were recrystallized from hot water. *Anal.* Calcd for $\mathrm{C_{12}H_{24}O_5N_2ICr} = [\mathrm{Cr(acac)_2(en)}]\mathrm{I}\cdot\mathrm{H_2O}$: C, 31.66; H, 5.31; N, 6.15. Found: C, 31.63; H, 5.35; N, 6.17. The chloride of this new complex was obtained by converting the iodide with an anion-exchange resin in the chloride form. The chloride obtained was recrystallized from methanol and ether. *Anal.* Calcd for $\mathrm{C_{12}H_{25}O_{5.5}N_2CrCl} = [\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$: C, 38.66; H, 6.76; N, 7.51. Found: C, 38.65; H, 6.79; N, 7.55.

(13) $(+)_{546}[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$. A solution of 7.6 g of $[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$ in 25 ml of water was mixed with 5.2 g of $\mathrm{Na_2[As_2(L{-}tart)_2]}\cdot2\mathrm{H_2O}$ in 15 ml of water. The combined solution was condensed to 20 ml at room temperature; then a red precipitate was obtained. By adding potassium iodide (2 g) to the suspension of the diastereomer in a small amount of 0.1 *N* aqueous sodium hydroxide solution, the red iodide deposited with a white precipitate. The iodide was extracted with methanol and the white solid was removed by filtration. The red product was obtained from the methanol solution by adding an appropriate amount of ether. This crude optically active isomer was purified by the extraction with chloroform. The iodide which was more soluble in chloroform was obtained as red leaflet crystals by adding ether to the extract. These crystals were found to be optically pure, whereas the less soluble iodide powder was optically impure. The pure iodide crystals were converted to the chloride with an anion-exchange resin in the chloride form in a batchwise operation. *Anal.* Calcd for $\mathrm{C_{12}H_{25}N_2O_{5.5}ClCr} = (+)_{546}[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$: C, 38.66; H, 6.76; N, 7.51. Found: C, 38.53; H, 6.76; N, 7.38. $[M]_{546}$ +7150°. To the filtrate from which the diastereomer was removed, was added 2 g of potassium iodide to deposit the red iodide. By treating this iodide by the same procedure as the case of $(+)_{546}$ isomer, the optically pure $(-)_{546}$ isomer was obtained.

(14) $[\mathrm{Cr(acaBr)_2(en)}]\mathrm{Cl}\cdot2\mathrm{H_2O}$. $[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$ (3.7 g, 0.01 mol) was dissolved in 50 ml of dimethylformamide (DMF) containing 5.34 g (0.03 mol) of NBS. The mixture was allowed to stand for a while. From the resulting brown solution, a brown precipitate was obtained by adding ether and recrystallized from hot water. *Anal.* Calcd for $\mathrm{C_{12}H_{24}N_2O_6Br_2ClCr} = [\mathrm{Cr(acaBr)_2(en)}]\mathrm{Cl}\cdot2\mathrm{H_2O}$: C, 26.71; H, 4.48; N, 5.19. Found: C, 26.78; H, 4.47; N, 5.37.

(15) $(+)_{546}[\mathrm{Cr(acaBr)_2(en)}]_2\mathrm{ClBr}$. This optically active complex was prepared by the same method as that of the corresponding racemic one as described above. The complex obtained was found to be a double salt of chloride and bromide, because the complex showed the liberation of bromine by oxidation with a $\mathrm{KMnO_4{-}H_2SO_4}$ aqueous solution. *Anal.* Calcd for $\mathrm{C_{24}H_{40}N_4O_8Br_5ClCr_2} = (+)_{546}[\mathrm{Cr(acaBr)_2(en)}]_2\mathrm{ClBr}$: C, 27.41; H, 3.83; N, 5.33. Found: C, 27.64; H, 3.84; N, 5.37. $[M]_{546}$ +7500°.

(16) $(+)_{546}[\mathrm{Cr(acaCl)_2(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$. The bis(3-chloroacetylacetonato) complex was prepared by the same method as that of the 3-bromoacetylacetonato complex by using NCS instead of NBS. *Anal.* Calcd for $\mathrm{C_{12}H_{22}N_2O_5Cl_3Cr} = (+)_{546}[\mathrm{Cr(acaCl)_2(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$: C, 33.31; H, 5.23; N, 6.47. Found: C, 33.81; H, 5.03; N, 6.58. $[M]_{546}$ +8050°.

(17) $[\mathrm{Cr(acac)(acaBr)(en)}]\mathrm{Cl}\cdot2\mathrm{H_2O}$. To 5 ml of DMF solution containing 0.75 g (0.002 mol) of $[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$ was gradually added 0.54 g (0.003 mol) of NBS in 5 ml of DMF. By the addition of ether to the mixture, a brown-red precipitate was obtained. The methanol–water (1:1) solution of the product was poured into a column (300 × 20 mm) of a strong-acid cation-exchange resin (Dowex 50W-X8, 200–400 mesh, lithium form). After the column had been swept with methanol–water (1:1) mixture, the adsorbed band was eluted with 5% lithium chloride solution in methanol–water (1:1). By elution with 5% lithium chloride solution, three colored bands—a red one, a reddish brown one, and a brown one—were eluted in that order. The first and the third eluted band were confirmed, by the measurements of their ultraviolet absorption spectra, to be the starting material, $[\mathrm{Cr(acac)_2(en)}]^+$, and the bis(3-bromoacetylacetonato) complex, $[\mathrm{Cr(acaBr)_2(en)}]^+$, respectively. From the evaporation of the second eluate, the reddish brown complex was isolated. This complex was recrystallized from chloroform and ether. *Anal.* Calcd for $\mathrm{C_{12}H_{25}O_6N_2ClBrCr} = [\mathrm{Cr(acac)(acaBr)(en)}]\mathrm{Cl}\cdot2\mathrm{H_2O}$: C, 31.29; H, 5.47; N, 6.08. Found: C, 31.75; H, 5.53; N, 6.12.

(18) $(+)_{546}[\mathrm{Cr(acac)(acaBr)(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$. The $(+)_{546}$ isomer was obtained from $(+)_{546}[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot1.5\mathrm{H_2O}$ by the same method as for the corresponding racemic one. *Anal.* Calcd for $\mathrm{C_{12}H_{23}O_5N_2ClBrCr} = (+)_{546}[\mathrm{Cr(acac)(acaBr)(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$: C, 32.56; H, 5.24; N, 6.30. Found: C, 32.15; H, 5.43; N, 6.40. $[M]_{546}$ +8060°.

(19) $[\mathrm{CrCl_2(OH_2)_2(en)}]\mathrm{Cl}$. This complex was obtained by the method of House and Garner.[14]

(20) $\mathrm{Na_2[As_2(L\text{-}tart)_2]}\cdot2\mathrm{H_2O}$. This resolving agent was prepared from sodium hydrogen L-tartrate and arsenic trioxide.[15]

Measurements. Absorption spectra were measured by a Beckman DU spectrophotometer. CD spectra were recorded by a Jasco Model J-10 spectropolarimeter with a CD attachment or by a Roussel-Jouan Dichrograph. A Yanagimoto spectropolarimeter, Model 185, was used to check the optical rotation. The infrared spectra were measured with a Jasco DS-402G spectrophotometer with NaCl prism using KBr disks. All measurements were made at room temperature.

Results and Discussion

Mixed α-Diimine Complexes. On the basis of the exciton model, if tris- or bis(α-diimine)metal complexes show a positive and a negative CD band from the lower frequency side in their ligand absorption band region, it may be predicted that the complexes should have a Λ configuration.[4] This prediction coincides with the result of the empirical method based on the major CD component in the first absorption band region[16] and has been recently confirmed by X-ray studies for the absolute configuration of $(-)_{589}[\mathrm{Fe(phen)_3}]^{2+}$ [17] and $(+)_{589}[\mathrm{Ni(phen)_3}]^{2+}$.[18]

The present 2,2′-dipyridyl and 1,10-phenanthroline complexes $(-)_{589}[\mathrm{Cr_2(OH)_2(dip)_4}]^{4+}$, $(-)_{589}[\mathrm{Cr_2(OH)_2(phen)_4}]^{4+}$, $(-)_{589}[\mathrm{Cr(ox)(dip)_2}]^+$, and $(-)_{589}[\mathrm{Cr(ox)(phen)_2}]^+$ give two exciton CD bands, (−) and (+) listing from the lower frequency, in their ligand band region, and a negative major CD component in the first absorption band region (Figures 1 and 2). Accordingly, the absolute configuration of the $(-)_{589}$ isomers of the dip and phen complexes will be assigned to Δ.

In a recent paper by Ferguson, *et al.*,[19] the sign for the exciton splitting was determined experimentally on the basis of the analysis of ligand absorption bands and it was found that the sign for $[\mathrm{Cr(ox)(dip)_2}]^+$ was opposite to that for $[\mathrm{Cr(ox)(phen)_2}]^+$. In consequence, the two $(-)_{589}$ isomers have been assigned to opposite configurations. Taking the metal–ligand and ligand–ligand bonding into consideration, the signs for the exciton splitting are theoretically considered to be affected by the central metal ions and also by the kind of conjugated ligands.[7,16,19] Some ambiguities remain for the adequacy of the absorption band analysis, because of the overlapping of the higher energy ligand band and of the

---

(14) D. A. House and C. S. Garner, *Inorg. Chem.*, 5, 840 (1966).

(15) G. G. Henderson and A. R. Ewing, *J. Chem. Soc.*, 67, 107 (1895).

(16) S. F. Mason, *Inorg. Chim. Acta, Rev.*, 2, 89 (1968).

(17) D. M. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr., Sect. A*, 21, 154 (1966).

(18) K. K. Butler and M. R. Snow, *J. Chem. Soc. A*, 565 (1971).

(19) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, 8, 771 (1969).

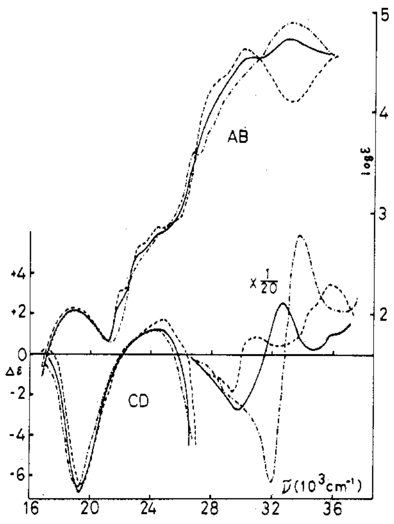

Figure 1. Absorption (AB) and CD curves of $(-)_{589}[Cr_2(OH)_2(dip)_2(phen)_2]^{4+}$ (——), $(-)_{589}[Cr_2(OH)_2(phen)_4]^{4+}$ (– · – · –), and $(-)_{589}[Cr_2(OH)_2(dip)_4]^{4+}$ (- - - - -) in water.

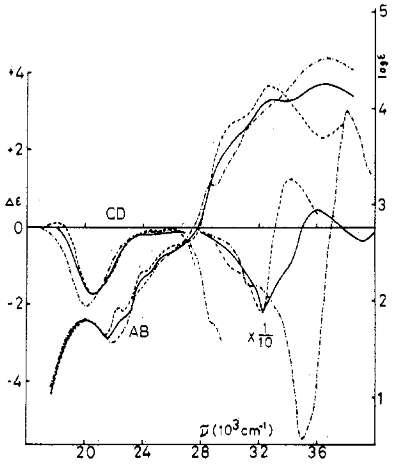

Figure 2. Absorption (AB) and CD curves of $(-)_{589}[Cr(ox)(dip)(phen)]^+$ (——), $(-)_{589}[Cr(ox)(phen)_2]^+$ (– · – · –), and $(-)_{589}[Cr(ox)(dip)_2]^+$ (- - - - -) in water.

lower energy charge-transfer band with the ligand band concerned and because of the association with the vibrational structures. Now, in order to reexamine these exciton interpretations, new mixed complexes, each containing only one of 2,2′-dipyridyl and 1,10-phenanthroline, were prepared and resolved into their optical isomers.

Reaction of $[Cr(OH_2)_4(dip)]^{3+}$ with 1,10-phenanthroline gave two kinds of products, the one brown and the other orange-brown, which are assigned to a μ-diol binuclear and a hydroxoaquo mononuclear complex, respectively, from the following considerations. From the elemental analyses and the ultraviolet absorption spectra, it was revealed that these complexes contain both 2,2′-dipyridyl and 1,10-phenanthroline. The first d-d absorption band of the brown complex in water approximately coincides with those of $[Cr_2(OH)_2(dip)_4]^{4+}$ and $[Cr_2(OH)_2(phen)_4]^{4+}$, whereas that of the orange-brown complex in water shows some blue shift. When the complexes were dissolved in 0.1 *N* HNO_3, the color of the former brown complex changed negligibly, as in the case of $[Cr_2(OH)_2(dip)_4]^{4+}$ and $[Cr_2(OH)_2(phen)_4]^{4+}$, but that of the latter orange-brown complex instantaneously changed to orange. The first absorption band of the orange solution agrees with that of $[Cr(OH_2)_2(dip)_2]^{3+}$ or $[Cr(OH_2)_2(phen)_2]^{3+}$. Therefore, the orange-brown complex is characterized as a mononuclear hydroxoaquo complex, $[Cr(OH)(OH_2)(dip)(phen)](NO_3)_2 \cdot 1.5H_2O$. It may be considered that the brown complex is an equimolar mixture of $[Cr_2(OH)_2(dip)_4]^{4+}$ and $[Cr_2(OH)_2(phen)_4]^{4+}$. However, judging from the facts that the $(dip)_4$ complex is more soluble than the $(phen)_4$ complex and that the ultraviolet absorption spectra of the brown complex were unchanged by recrystallization, the brown complex can be identified as having the formula of $[(dip)(phen)Cr(OH)_2Cr(dip)(phen)](NO_3)_4 \cdot 6H_2O$, in which each chromium(III) ion takes only one 2,2′-dipyridyl and one 1,10-phenanthroline. Since the meso type of μ-diol $(dip)_4$ or $(phen)_4$ complex is considered to be formed with difficulty owing to the steric hindrance,[11,12] only the racemic $[(dip)(phen)Cr(OH)_2Cr(dip)(phen)]^{4+}$ may be obtained. Although two geometrical isomers, in which two dip or phen lie at the same or opposite sides with respect to the plane containing $Cr(OH)_2Cr$, are possible for $[(dip)(phen)Cr(OH)_2Cr(dip)(phen)]^{4+}$, it could not be revealed which isomer was isolated.

As is seen in Figures 1 and 2, the ultraviolet absorption spectra of the μ-diol and the oxalato complexes $[Cr_2(OH)_2(dip)_2(phen)_2]^{4+}$ and $[Cr(ox)(dip)(phen)]^+$ have common bands as in the case of the μ-diol $(dip)_4$ and $(phen)_4$ complexes $[Cr_2(OH)_2(dip)_4]^{4+}$ or $[Cr_2(OH)_2(phen)_4]^{4+}$ and the oxalato $(dip)_2$ and $(phen)_2$ complexes $[Cr(ox)(dip)_2]^+$ or $[Cr(ox)(phen)_2]^+$. The CD spectra in the ligand absorption band region of the present new $(-)_{589}$ complexes show a typical exciton CD pattern similar to those of $(-)_{589}$ $(dip)_4$ and $(phen)_4$ binuclear complexes and of $(-)_{589}$ $(dip)_2$ and $(phen)_2$ mononuclear oxalato complexes. That is, an intense negative lower frequency band and a positive higher frequency CD band are observed near the long-axis-polarized π-π^* transitions of dip (32 kK) and phen (36 kK), respectively, as is predicted by the exciton model.[4] If there were no interaction between the dip and phen transitions in the present complexes, the CD bands at 32 and 36 kK would have same signs for the same tris-chelate configurations as in the case of L-tartrato-α-diiminechromium(III) complexes.[20] This is the first example of the exciton CD spectra due to the dipole-dipole interaction between only two nonidentical π-π^* transitions, and the present observation supports that the exciton interpretation based on the simple electrostatic treatment is applicable to the CD spectra of both the dip and phen complexes of Cr(III). From the behavior of the exciton CD bands at 32-36 kK, $(-)_{589}$ isomers of the new mixed complexes are assigned to a Δ absolute configuration. This assignment agrees with the empirical one on the basis of the dominant CD band in the region of the first ligand field band.

Acetylacetonato and 3-Halogenoacetylacetonato Complexes. (a) Identifications. The new acetylacetonato complexes $(+)_{546}[Cr(acac)(en)_2]Cl_2$ and $(+)_{546}[Cr(acac)_2(en)]Cl$ were prepared and optically resolved into their enantiomers using $Na_2[As_2(L\text{-}tart)_2] \cdot 2H_2O$. Their optical characteristics are summarized in Tables I-III. The halogenation to the 3 position of acetylacetonato ligands of these $(+)_{546}$ complexes was carried out by the same method as that for the tris(acetylacetonato)chromium(III) complex.[21] The reaction products of the mono- and bis-

---

(20) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, 42, 988 (1969).

(21) J. P. Collman, R. A. Moss, H. Matz, and C. C. Heidel, *J. Amer. Chem. Soc.*, 83, 531 (1961).

Table I. Infrared Absorption Data for Acetylacetonato and 3-Halogenoacetylacetonato Complexes (cm^{-1})

$[Cr(acac)_3]$	$[Cr(acac)_2(en)]Cl$	$[Cr(acac)(en)_2]Cl_2$
683	690	684
931	935	945
1275	1283	1284
1520	1522	1522
1570	1560	1568
$[Cr(acaCl)_3]$	$[Cr(acaCl)_2(en)]Cl$	$[Cr(acaCl)(en)_2]Cl_2$
706	710	707
925	924	926
1297	1294	1296
1565	1564	1560
$[Cr(acaBr)_3]$	$[Cr(acaBr)_2(en)]Cl$	$[Cr(acaBr)(en)_2]Cl_2$
702	708	710
922	924	924
1287	1290	1297
1550	1555	1553
	$[Cr(acac)(acaBr)(en)]Cl$	
	606, *ca.* 706 sh	
	924, *ca.* 935 sh	
	1285	
	1525	
	1550	

acetylacetonato complexes with *N*-halogenosuccinimide are identified as the mono- and bis(3-halogenoacetylacetonato) complexes by their elemental analysis, infrared spectra, and ultraviolet absorption spectra. The mono- and bis(3-halogenoacetylacetonato) complexes show ir patterns similar to tris(3-halogenoacetylacetonato) complexes (Table I). $[Cr(acac)(acaBr)(en)]Cl$ shows ir bands common with both $[Cr(acac)_2(en)]Cl$ and $[Cr(acaBr)_2(en)]Cl$. The ultraviolet absorption spectra of acetylacetonato complexes show two or three bands around 30-39 kK (Figure 3). By means of 3-halogeno substitution, these absorption bands shift to lower frequencies by about 2000 cm^{-1} (Figures 4-7 and Tables II, III). The ultraviolet absorption spectra of $[Cr(acac)(acaBr)(en)]Cl$ have common bands with both $[Cr(acac)_2(en)]Cl$ and $[Cr(acaBr)_2(en)]Cl$.

Table III. Absorption (AB) and CD Data for $(+)_{546}[Cr(L)(en)_2]Cl_2$ Type Complexes (Wave Numbers in 10^3 cm^{-1})

L	AB (log ϵ_{max})	CD ($\Delta\epsilon_{ext}$)
acac	20.2 (1.96)	21.1 (+2.75)
	24.0 (*ca.* 2.05)	
	25.0 (*ca.* 2.30)	
	30.3 (3.81)	30.0 (−4.80)
		35.3 (+0.42)
	39.0 (3.73)	39.3 (−5.15)
acaCl	20.0 (*ca.* 2.05)	21.1 (+2.62)
	22.3 (2.24)	
	28.7 (3.72)	28.4 (−2.80)
		33.3 (+0.61)
	37.5 (3.68)	38.5 (−1.97)
acaBr	20.0 (*ca.* 1.95)	21.2 (+2.38)
	22.5 (2.19)	
	28.3 (3.64)	28.3 (−2.48)
		34.3 (+0.47)
	37.2 (3.61)	38.7 (−1.63)

It has been revealed from the CD intensities in the first spin-allowed d-d absorption band region that the chirality (optical activity) of these $(+)_{546}$ complexes is retained

Table II. Absorption (AB) and CD Data for $(+)_{546}[Cr(L)_2(en)]Cl$ Type Complexes (Wave Numbers in 10^3 cm^{-1})

	In water		In methanol		
$(L)_2$	AB (log ϵ_{max})	CD ($\Delta\epsilon_{ext}$)	AB (log ϵ_{max})	CD ($\Delta\epsilon_{ext}$)	Assignment[a]
$(acac)_2$	19.0 (1.95)	17.7 (−0.84)	18.9 (1.94)	17.3 (−0.29)	
		20.1 (+4.00)		20.0 (+3.30)	
	26.3 (2.57)	25.3 (−1.02)	26.3 (2.62)	25.3 (−1.13)	
		29.1 (−4.36)		29.1 (−12.8)	$V_2(E)$
	30.1 (4.08)	30.7 (+17.4)	30.0 (4.06)	31.2 (+18.6)	$V_4(E)$
		34.7 (−14.5)		34.3 (−16.6)	$V_2(A_1)$
	39.0 (3.97)	38.3 (+3.66)	39.0 (3.94)		$V_7(E)$
		40.7 (−7.00)		40.2 (−7.35)	$V_5(A_1)$
		44.7 (−14.0)		44.3 (−15.2)	$V_8(E)$
(acac)(acaBr)	19.0 (1.95)	17.7 (−0.84)	18.7 (1.96)	17.2 (−0.22)	
		20.1 (+3.59)		20.0 (+3.35)	
		25.3 (−1.06)		25.7 (−1.66)	
	28.3 sh	28.0 (*ca.* −0.5)		28.1 (−3.97)	$V_2(E)$
	29.9 (3.97)	30.0 (+11.6)	29.7 (3.93)	29.9 (+20.9)	$V_4(E)$
		33.7 (−11.8)		33.6 (−14.5)	$V_2(A_1)$
	38.3 (3.89)	38.0 (+2.56)	38.3 (3.90)	38.0 (+1.59)	$V_7(E)$
		40.3 (−4.10)		40.2 (−4.70)	$V_5(A_1)$
		45.0 (−8.80)		44.3 (−9.37)	$V_8(E)$
$(acaBr)_2$	19.0 (2.02)	17.3 (−0.88)	18.7 (2.00)	17.7 (−0.13)	
		20.2 (+4.40)		20.2 (+4.13)	
		26.9 (−2.70)		27.0 (−6.00)	$V_2(E)$
	28.3 (3.97)	28.9 (+11.4)	28.2 (3.95)	28.7 (+22.4)	$V_4(E)$
		32.2 (−11.8)		32.0 (−14.2)	$V_2(A_1)$
	37.3 (3.88)	36.7 (+3.54)	36.7 (3.88)	36.7 (+3.20)	$V_7(E)$
		39.8 (−1.96)		39.5 (−2.00)	$V_5(A_1)$
		44.7 (−6.80)		44.4 (−8.36)	$V_8(E)$
$(acaCl)_2$	18.9 (2.00)	17.7 (−0.86)	18.7 (1.98)	17.3 (−0.17)	
		20.2 (+4.21)		20.2 (+3.94)	
		25.7 (−1.73)			
		26.8 (−2.70)		27.0 (−5.40)	$V_2(E)$
	28.4 (4.00)	28.8 (+15.6)	28.2 (3.95)	28.9 (+19.1)	$V_4(E)$
		32.2 (−12.2)		32.2 (−14.8)	$V_2(A_1)$
	37.0 (3.90)	36.5 (+3.22)	37.0 (3.89)	37.0 (+2.10)	$V_7(E)$
		40.0 (−2.42)		39.5 (−4.03)	$V_5(A_1)$
		44.7 (−5.76)		44.4 (−8.07)	$V_8(E)$

[a] The trigonal notation is used according to Hanazaki, *et al.*[10]

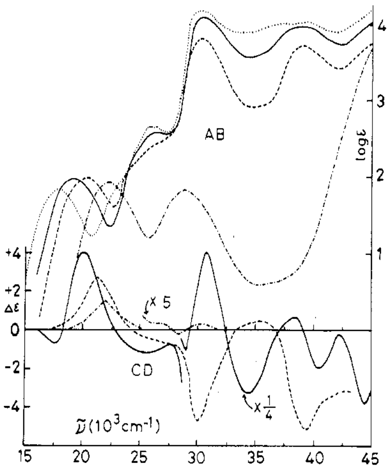

Figure 3. Absorption (AB) and CD curves of $(+)_{546}[\mathrm{Cr(en)_3}]^{3+}$ (—·—·—), $(+)_{546}[\mathrm{Cr(acac)(en)_2}]^{2+}$ (-----), and $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^{+}$ (——) in water and the AB curve of $[\mathrm{Cr(acac)_3}]$ (· · · ·) in methanol.

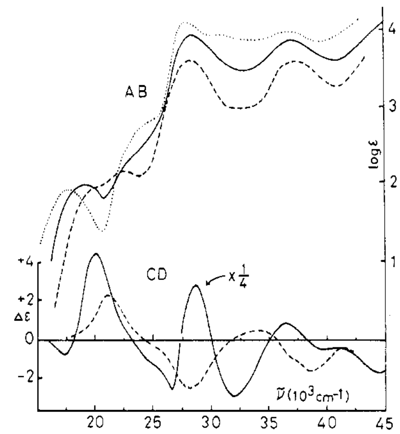

Figure 4. Absorption (AB) and CD curves of $(+)_{546}[\mathrm{Cr(acaBr)(en)_2}]^{2+}$ (-----) and $(+)_{546}[\mathrm{Cr(acaBr)_2(en)}]^{+}$ (——) in water and the AB curve of $[\mathrm{Cr(acaBr)_3}]$ (· · · ·) in chloroform.

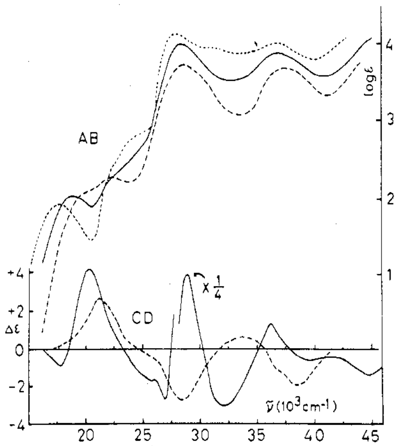

Figure 5. Absorption (AB) and CD curves of $(+)_{546}[\mathrm{Cr(acaCl)(en)_2}]^{2+}$ (-----) and $(+)_{546}[\mathrm{Cr(acaCl)_2(en)}]^{+}$ (——) in water and the AB curve of $[\mathrm{Cr(acaCl)_3}]$ (· · · ·) in chloroform.

throughout the halogenation. Such optical retention during the halogenation reaction was also observed in the case of partially resolved tris-acetylacetonato complexes.[22]

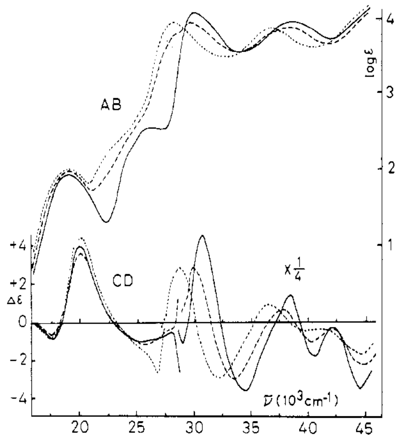

Figure 6. Absorption (AB) and CD curves of $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^{+}$ (——), $(+)_{546}[\mathrm{Cr(acac)(acaBr)(en)}]^{+}$ (-----), and $(+)_{546}[\mathrm{Cr(acaBr)_2(en)}]^{+}$ (· · · ·) in water.

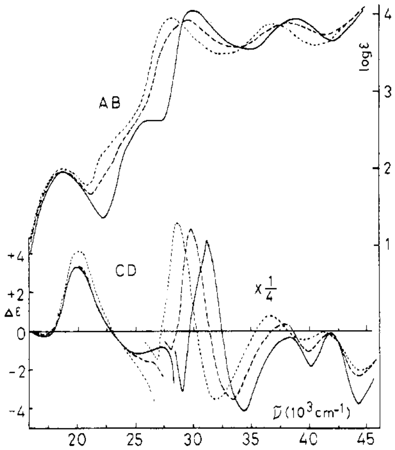

Figure 7. Absorption (AB) and CD curves of $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^{+}$ (——), $(+)_{546}[\mathrm{Cr(acac)(acaBr)(en)}]^{+}$ (-----), and $(+)_{546}[\mathrm{Cr(acaBr)_2(en)}]^{+}$ (· · · ·) in methanol.

(b) CD Spectra in the Ultraviolet Region. From Figure 3, it is evident that the ultraviolet absorption spectra of mono- and bis-acetylacetonato complexes are similar on the whole to that of the tris-acetylacetonato complex, although the intensities become weaker in the order of tris, bis, and mono complexes. That is, it may be seen that the coordinated ethylenediamine is "spectroscopically neutral" in this region. The 30- and 40-kK bands of the acetylacetonato complexes become sharper and simpler in shape in the order of tris, bis, and mono complexes (Figures 3-5). The variation in shape of the absorption bands for the mono- and bis-acetylacetonato complexes may reflect the characteristics in the CD spectra in the corresponding region, because the contrast between the CD spectra of mono and bis complexes is remarkable in the ultraviolet region; the CD spectra of the bis complexes are more complicated than those of the mono complexes (Figures 3-5); *i.e.*, six CD bands for bis complexes and three bands for mono complexes are observed in the ultraviolet region. From these absorption and CD spectra, it is suggested that the splitting of the energy state in the ultraviolet region is due to the presence of two acetylacetonate ligands.

Four of six observed CD bands of the bis complexes may be differentiated from the other two bands in terms of the substitution effect and the solvent effect. Upon 3-

---

(22) J. P. Collman, R. P. Blair, A. L. Slade, and R. L. Marshall, *Inorg. Chem.*, 2, 576 (1963).

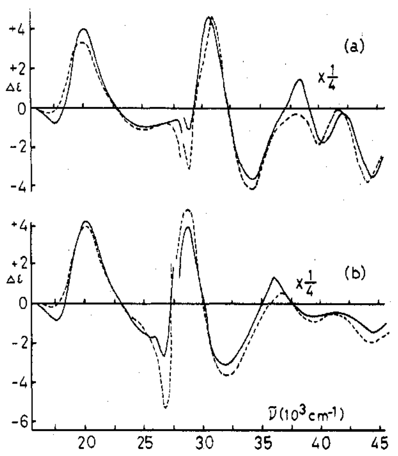

Figure 8. CD curves of $(+)_{546}[Cr(acac)_2(en)]^+$ (a) and $(+)_{546}[Cr(acaCl)_2(en)]^+$ (b) in water (——) and in methanol (- - - - -).

halogeno substitution into the $(+)_{546}$-bis(acetylacetonato) complex, the highest frequency CD band near 45 kK is unaffected in position, but the other five bands shift by about 1000-2000 cm^{-1} to lower frequencies (Figures 6 and 7). A negative CD band near 29 kK of $(+)_{546}[Cr(acac)_2(en)]^+$ is narrower and weaker than the other higher frequency CD bands (Figure 3). The intensities of the sharp CD bands near 27-29 kK for the bis complexes in methanol are found to be approximately 2-3 times as strong as those in water, even 10 times for $(+)_{546}[Cr(acac)(acaBr)(en)]^+$, whereas those of the other remaining five CD bands remained little changed (Figures 7-9 and Table II). Accordingly, four of the six CD bands, (+) at 30.5 kK, (−) at 34.5 kK, (+) at 38.5 kK, and (−) at 40.5 kK, of $(+)_{546}[Cr(acac)_2(en)]^+$, which show common behavior with both the substitution and solvent change, are assumed to be due to like origins. Further, the four CD bands may be classified into two groups on the basis of the intensities; the one includes a negative band at 30.5 kK and a positive band at 34.5 kK, which have approximately equal area, and the other includes a negative band at 38.5 kK and a positive band at 40.5 kK, which also have approximately equal area.

In general, two absorption bands are observed in the ultraviolet region of transition metal-tris(acetylacetonato) complexes, and the lower frequency weaker and the higher frequency stronger band are assigned to the charge transfer and the intraligand transition, respectively.[23,24] In the case of $[Cr(acac)_3]$, the ultraviolet spectrum is anomalous in its complexity and stronger intensity of the lower frequency band. According to a simple Huckel LCAO-MO calculation,[24] the 30-kK band of $[Cr(acac)_3]$ was assigned to the charge-transfer transition from 3dπ to ligand π^*, and the 40-kK band to a π-π^* transition. From the comparison of the absorption spectra of chromium(III) complexes containing various types of β-diketones and on the basis of the SCF-MO method, DeArmond and Forster[25] proposed that the 30-kK band was ascribed to a π-π^* transition but did not always reject the possibility of a charge-transfer transition. From the recent calculation on the basis of the composite or "molecules in molecule" method by Hanazaki, *et al.*,[10] it is revealed that the 30-kK bands are due to three excited states, $V_2(E)$, $V_4(E)$, and $V_2(A_1)$ from the lower frequency, which are mainly composed of the long-axis-polarized charge-transfer and singlet-triplet π-π^* excitations; the last two, $V_4(E)$ and $V_2(A_1)$, are mixed with the singlet-singlet π-π^* excitation of the same polarization by 10-16% of the dipole strength. The absorption bands near 40 kK were assigned to three excited states, $V_7(E)$, $V_5(A_1)$, and $V_8(E)$ from the lower frequency, of which the first two, $V_7(E)$ and $V_5(A_1)$, are predominantly of the long-axis-polarized singlet-singlet π-π^* excitation and the latter one is composed of the charge-transfer and singlet-triplet π-π^* excitations. Of the three kinds of excitations, the long-axis-polarized singlet-singlet π-π^* excitation only contributes to the exciton CD splitting. Therefore, the six states expected in the ultraviolet region may be classified into three pairs; *e.g.*, two of them are the $V_4(E)$ and $V_2(A_1)$ and the $V_7(E)$ and $V_5(A_1)$ states, for each of which the rotational strengths of the two bands may be expected to be of opposite signs, the remaining one being the $V_2(E)$ and $V_8(E)$ states in the lowest and the highest frequency, respectively.

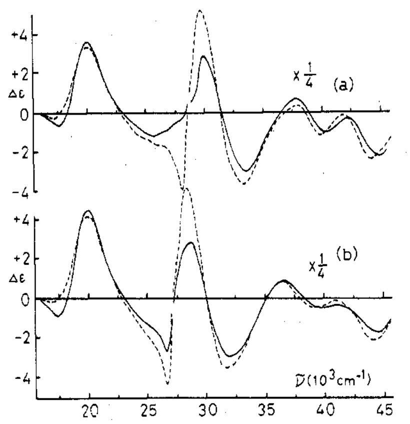

Figure 9. CD curves of $(+)_{546}[Cr(acac)(acaBr)(en)]^+$ (a) and $(+)_{546}$-$[Cr(acaBr)_2(en)]^+$ (b) in water (——) and in methanol (- - - - -).

Judging from the similarity of the absorption and CD bands of the bis-acetylacetonato complex in the ultraviolet region to those of $[Cr(acac)_3]$ and $(+)_{589}$-tris((+)-3-acetylcamphorato)chromium(III), $[Cr((+)atc)_3]$,[26] the ultraviolet CD spectrum of the bis complex will be discussed on the basis of the theoretically studied electronic structure of $[Cr(acac)_3]$. In fact, the experimental classification of the ultraviolet CD bands of the bis complex mentioned before shows a fairly good correspondence to that expected from the theoretical study. That is, of the two CD pairs of $(+)_{546}$-$[Cr(acac)_2(en)]^+$, the higher frequency pair, (+) at 38.5 kK and (−) at 40.5 kK, corresponds to the long-axis-polarized singlet-singlet π-π^* transitions; thus these are due to the exciton splitting and assigned to $V_7(E)$ and $V_5(A_1)$ from the lower frequency side, respectively. The remaining pair, (+) at 30.5 kK and (−) at 34.5 kK, may be assigned to $V_4(E)$ and $V_2(A_1)$ from the lower frequency side, respectively. Just as is proposed by Mason, *et al.*,[6,16] for visible charge-transfer CD spectra of tris(α-diimine)-iron group metal complexes, it may be possible to take into account the mixing of the long-axis-polarized charge-transfer excitation with the singlet-singlet π-π^* excitation of the same polarization. Thus, it may be suggested that the CD bands of $(+)_{546}$-$[Cr(acac)_2(en)]^+$ in the region of 30-35 kK take the characteris-

---

(23) R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).

(24) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(25) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963).

(26) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).

tics of the singlet-singlet π-π^* transition and reproduce the exciton CD pattern, for the following reasons. First, the CD behaviors are consistent with the theoretically anticipated pattern; that is, two CD bands in the charge-transfer region reproduce the exciton CD splitting in the long-axis-polarized π-π^* transition region. Second, the CD spectrum of $(+)_{546}[\mathrm{Cr(acac)(acaBr)(en)}]^+$ is similar to those of $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^+$ and $(+)_{546}[\mathrm{Cr(acaBr)_2(en)}]^+$ in both the charge-transfer and the π-π^* transition regions. Third, two CD pairs of $(+)_{546}[\mathrm{Cr(acac)(acaBr)(en)}]^+$ are found to be at the intermediate position between $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^+$ and $(+)_{546}[\mathrm{Cr(acaBr)_2(en)}]^+$ as may be predicted by the exciton model[4] (Table II and Figures 6 and 7). Fourth, if the CD bands (+) at 30.5 kK and (−) at 34.5 kK originate from the charge-transfer transition, the mono- and bis-acetylacetonato complexes may show similar CD patterns in this region. This is not the finding.

The remaining two CD bands at the lowest and the highest frequency for $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^+$, (−) at 29.1 kK and (−) at 44.7 kK, may be ascribed to $\mathrm{V_2(E)}$ and $\mathrm{V_8(E)}$, respectively, from the lower frequency side.

The assignment for the ultraviolet CD bands of the 3-halogenoacetylacetonato complexes may be made similarly to those of the bis-acetylacetonato complex as is seen in Table II.

On the basis of the signs of two CD pairs due to the exciton splitting, the absolute configuration of $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^+$ and its 3-halogeno derivatives is determined to be Λ in accordance with the dominance of positive CD in the first ligand field band region. This assignment is also consistent with that of Λ-$(+)_{589}[\mathrm{Cr((+)atc)_3}]$, which shows visible and ultraviolet CD spectra[26] similar to those of $(+)_{546}[\mathrm{Cr(acac)_2(en)}]^+$ and its 3-halogeno derivatives and whose absolute configuration has been determined by means of an X-ray method.[27]

Registry No. $[\mathrm{(dip)(phen)Cr(OH)_2Cr(dip)(phen)}](\mathrm{NO_3})_4\cdot 6\mathrm{H_2O}$, 36537-23-2; $(-)$-$[\mathrm{Cr_2(OH)_2(dip)_2(phen)_2}](\mathrm{NO_3})_4\cdot 7\mathrm{H_2O}$, 36537-24-3; $[\mathrm{Cr(OH)(OH_2)(dip)(phen)}](\mathrm{NO_3})_2\cdot 1.5\mathrm{H_2O}$, 36487-19-1; $(-)$-$[\mathrm{Cr_2(OH)_2(dip)_4}]\mathrm{Cl_4}\cdot 9\mathrm{H_2O}$, 36544-33-9; $(-)$-$[\mathrm{Cr_2(OH)_2(phen)_4}](\mathrm{NO_3})_4\cdot 7\mathrm{H_2O}$, 36544-34-0; $[\mathrm{Cr(ox)(dip)(phen)}]\mathrm{Cl}$, 36544-35-1; $(-)$-$[\mathrm{Cr(ox)(dip)(phen)}]\mathrm{ClO_4}\cdot 2\mathrm{H_2O}$, 36538-29-1; $(-)$-$[\mathrm{Cr(ox)(dip)(phen)}][\mathrm{Cr(ox)_2(phen)}]\cdot 3\mathrm{H_2O}$, 12769-30-1; $(-)$-$[\mathrm{Cr(ox)(dip)_2}]\mathrm{Cl}\cdot 4\mathrm{H_2O}$, 23539-88-0; $(-)$-$[\mathrm{Cr(ox)(phen)_2}]\mathrm{ClO_4}\cdot 2.5\mathrm{H_2O}$, 36544-37-3; $[\mathrm{Cr(acac)(en)_2}]\mathrm{Cl_2}\cdot 5\mathrm{H_2O}$, 36544-31-7; $[\mathrm{Cr(acac)(en)_2}]\mathrm{I_2}$, 36544-32-8; $(+)$-$[\mathrm{Cr(acac)(en)_2}]\mathrm{Cl_2}\cdot\mathrm{H_2O}$, 36544-02-2; $(+)$-$[\mathrm{Cr(acac)(en)_2}][\mathrm{As_2(L\text{-}tart)_2}]\cdot 3\mathrm{H_2O}$, 12769-26-5; $(+)$-$[\mathrm{Cr(acaBr)(en)_2}]\mathrm{Cl_2}\cdot 2.5\mathrm{H_2O}$, 36544-03-3; $(+)$-$[\mathrm{Cr(acac)(en)_2}]\mathrm{Cl_2}\cdot\mathrm{H_2O}$, 36544-02-2; $(+)$-$[\mathrm{Cr(acaCl)(en)_2}]\mathrm{Cl_2}\cdot 1.5\mathrm{H_2O}$, 36544-05-5; $[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot 1.5\mathrm{H_2O}$, 36544-06-6; $[\mathrm{Cr(acac)_2(en)}]\mathrm{I}\cdot\mathrm{H_2O}$, 36544-07-7; $(+)$-$[\mathrm{Cr(acac)_2(en)}]\mathrm{Cl}\cdot 6.5\mathrm{H_2O}$, 36544-08-8; $[\mathrm{Cr(acaBr)_2(en)}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$, 36544-09-9; $(+)$-$[\mathrm{Cr(acaBr)_2(en)}]_2\mathrm{ClBr}$, 12769-27-6; $(+)$-$[\mathrm{Cr(acaCl)_2(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$, 36544-10-2; $[\mathrm{Cr(acac)(acaBr)(en)}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$, 36544-11-3; $(+)$-$[\mathrm{Cr(acac)(acaBr)(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$, 36544-12-4.

[27] W. D. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, 92, 7620 (1970).

Contribution from the Department of Chemistry, Faculty of Science,
Osaka University, Toyonaka, Osaka, Japan

Circular Dichroism of Chromium(III) Complexes. IV.[1] Elucidation of Circular Dichroism in the Spin-Forbidden Transitions

SUMIO KAIZAKI, JINSAI HIDAKA,* and YOICHI SHIMURA

Received May 11, 1972

Circular dichroism (CD) spectra of 19 optically active chromium(III) complexes have been measured in the spin-forbidden and the spin-allowed d–d transition region. It has been revealed that the rotational strengths for the spin-forbidden transitions are theoretically related to those for the spin-allowed transitions. On the basis of this relationship, the CD peaks in the spin-forbidden transition region have been assigned to the zero-field splitting components of the doublet state in connection with the CD bands in the first spin-allowed transition region and also with the absolute configurations of the complexes.

Introduction

The absorption spectra of most chromium(III) complexes show in the visible region two broad but moderately intense bands associated with the d–d Laporte-forbidden but quartet–quartet spin-allowed transitions and in the near-infrared region weak but sharp bands associated with the doublet–quartet spin-forbidden transitions. There have been a number of investigations[2] concerning the latter spin-forbidden transitions for various types of chromium(III) complexes. The spin-forbidden absorption bands are notoriously difficult to observe in solution, because these bands are not only of very low intensity but are also obscured by the strong high-frequency spin-allowed absorption bands. As to the position of the 0–0 band of the spin-forbidden transitions, the phosphorescence measurement[3,4] is a useful technique, but other higher energy components of the doublet states cannot be detected by means of this method. McCaffery, Stephens, and Schatz[5] reported that the magnetic circular dichroism (MCD) in the spin-forbidden transitions of chromium(III) complexes was much more intense than in the spin-allowed transitions. They stated that MCD can greatly aid in the detection and assignments of the spin-forbidden transitions. However, since the observed MCD curves may consist of the dispersion

[1] Part III: S. Kaizaki, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, 12, 135 (1973).

[2] L. S. Forster, *Transition Metal Chem.*, 5, 1 (1969).

[3] G. B. Porter and H. L. Schlafer, *Z. Phys. Chem. (Frankfurt am Main)*, 38, 227 (1963).

[4] G. B. Porter and H. L. Schlafer, *Z. Phys. Chem. (Frankfurt am Main)*, 40, 280 (1964).

[5] A. J. McCaffery, P. J. Stephens, and P. N. Schatz, *Inorg. Chem.*, 6, 1614 (1967).