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Induced Circular Dichroism Spectra of Cobalt(III) Complexes in a Chiral Medium Containing $(+)_{589}$-Diethyl Tartrate

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The induced circular dichroism (CD) spectra of 21 achiral or racemic cobalt(III) complexes have been measured in a chiral medium containing $(+)_{589}$-diethyl tartrate in the region of the first d-d transition bands. The absolute value of the molar circular dichroism ($\Delta\varepsilon$) observed for these complexes is in the range of about 0.04—0.3 $cm^{-1}\ mol^{-1}\ dm^3$. The induced CD spectra of the racemic complexes show a different pattern from the natural CD spectra of their resolved enantiomers. The observed induced CD spectra have been discussed in relation to the stereochemistry of the complexes.

Circular dichroism (CD) is induced for some achiral or racemic compounds when they are dissolved in a chiral medium. Since Mason and Norman[1)] observed this phenomenon, several workers have reported the CD induced for organic[2–6)] and inorganic[2,7–10)] compounds. The mechanism of this phenomenon has been discussed generally in terms of the following effects; (1) the CD may be induced by a direct interaction between a symmetric chromophore and a chiral field produced by chiral solvents, (2) a symmetric chromophore may be solvated by chiral solvents forming a chiral configuration, and (3) one enantiomer in a racemate may be associated with chiral solvents preferentially. It was initially suggested that the hydrogen bonding was the main origin of the phenomenon,[1–4)] but later it was found that such hydrogen bonding was not a prerequisite.[5,6)] Thus the precise mechanism of the phenomenon is still unknown.

In the works on cobalt(III) complexes, so far as we know, the induced CD has been observed for only four chromophores: $[Co(NH_3)_6]^{3+}$,[1)] $[Co(en)_3]^{3+}$,[9)] *trans*-$[CoCl_2(en)_2]^+$,[2)] and *trans-meso*-$[CoCl_2(2,3,2\text{-tet})]^+$.[8)] In the present paper, it will be shown that twenty-one achiral or racemic cobalt(III) complexes also exhibit the induced CD in the region of their first d-d transition bands when the complexes are dissolved in a chiral medium containing $(+)_{589}$-diethyl tartrate, and that the spectral feature of those induced CD is dependent on the properties of ligands.

Experimental

Materials. $(+)_{589}$-Diethyl tartrate was prepared by the method of Sugasawa[11)] and distilled *in vacuo*, bp 123.5—124.5 °C at 2 Torr, $[\alpha]_D$ +7.71 ° (neat). Found: C, 46.57; H, 6.82%. Calcd for $C_8H_{14}O_6$: C, 46.60; H, 6.84%.

All the cobalt(III) complexes were prepared by well-known methods and identified spectrophotometrically. Many of the complexes were converted into their tetraphenylborate salts by adding the equivalent amount of sodium tetraphenylborate in water to an aqueous solution of the complex ion. Found: C, 70.58; H, 7.32; N, 6.91%. Calcd for $[Co(NH_3)_6](BPh_4)_3\cdot 6H_2O$: C, 70.48; H, 7.39; N, 6.85%. Found: C, 71.87; H, 7.34; N, 7.01%. Calcd for $[Co(NH_3)_4(en)](BPh_4)_3\cdot 5H_2O$: C, 72.03; H, 7.35; N, 6.81%. Found: C, 74.55; H, 7.30; N, 6.51%. Calcd for *cis*-$[Co(NH_3)_2(en)_2](BPh_4)_3\cdot 4H_2O$: C, 73.44; H, 7.30; N, 6.76%. Found: C, 73.52; H, 7.33; N, 6.83%. Calcd for *trans*-$[Co(NH_3)_2(en)_2](BPh_4)_3\cdot 4H_2O$: C, 73.44; H, 7.30; N, 6.76%. Found: C, 71.84; H, 7.34; N, 6.44%. Calcd for $[Co(en)_3](BPh_4)_3\cdot 6H_2O$: C, 71.79; H, 7.42; N, 6.44%. Found: C, 67.01; H, 6.86; N, 9.68%. Calcd for $[Co(NO_2)(NH_3)_5](BPh_4)_2\cdot 2H_2O$: C, 66.68; H, 6.88; N, 9.72%. Found: C, 49.49; H, 6.38; N, 14.33%. Calcd for *cis*-$[Co(NO_2)_2(NH_3)_4](BPh_4)\cdot 2H_2O$: C, 50.19; H, 6.32; N, 14.63%. Found: C, 50.49; H, 6.23; N, 14.76%. Calcd for *trans*-$[Co(NO_2)_2(NH_3)_4](BPh_4)\cdot 2H_2O$: C, 50.19; H, 6.32; N, 14.63%. Found: C, 67.03; H, 6.89; N, 8.16%. Calcd for $[CoF(NH_3)_5[(BPh_4)_2\cdot 2H_2O$: C, 68.83; H, 7.10; N, 8.36%. Found: C, 67.45; H, 6.96; N, 8.17%. Calcd for $[CoCl(NH_3)_5](BPh_4)_2\cdot 2H_2O$: C, 67.50; H, 6.96; N, 8.20%. Found: C, 65.88; H, 6.59; N, 8.05%. Calcd for $[CoBr(NH_3)_5](BPh_4)_2\cdot H_2O$: C, 65.48; H, 6.53; N, 7.95%. Found: C, 55.57; H, 6.22; N, 10.76%. Calcd for *trans*-$[CoCl_2(NH_3)_4](BPh_4)$: C, 55.73; H, 6.24; N, 10.83%. Found: C, 57.38; H, 6.36; N, 10.30%. Calcd for *trans*-$[CoCl_2(NH_3)_2(en)](BPh_4)$: C, 57.49; H, 6.31; N, 10.31%. Found: C, 58.83; H, 6.39; N, 9.78%. Calcd for *trans*-$[CoCl_2(en)_2](BPh_4)$: C, 59.07; H, 6.37; N, 9.84%. Found: C, 67.90; H, 6.98; N, 7.70%. Calcd for $[Co(CH_3COO)(NH_3)_5](BPh_4)_2\cdot 2.5H_2O$: C, 67.73; H, 7.16; N, 7.90%. Found: C, 59.86; H, 6.86; N, 9.48%. Calcd for *cis*-$[Co(CH_3COO)_2(NH_3)_4](BPh_4)\cdot 0.5H_2O$: C, 58.65; H, 6.86; N, 9.77%. Found: C, 59.81; H, 6.87; N, 9.88%. Calcd for *trans*-$[Co(CH_3COO)_2(NH_3)_4](BPh_4)$: C, 59.59; H, 6.79; N, 9.93%. Found: C, 17.57; H, 7.61; N, 20.47%. Calcd for $[Co(en)_3]Cl_3\cdot 3.5H_2O$: C, 17.64; H, 7.65; N, 20.57%. Found: C, 9.32; H, 5.01; N, 22.01%. Calcd for $[Co(ox)(NH_3)_4]Cl\cdot 0.5H_2O$: C, 9.26; H, 5.05; N, 21.59%. Found: C, 22.42; H, 5.67; N, 17.32%. Calcd for $[Co(ox)(en)_2]Cl\cdot H_2O$: C, 22.48; H, 5.66; N, 17.47%. Found: C, 21.33; H, 2.89; N, 8.25%. Calcd for $Na[Co(ox)_2(en)]\cdot H_2O$: C, 21.44; H, 3.00; N, 8.33%. Found: C, 25.90; H, 3.71; N, 7.15%. Calcd for $K[Co(mal)_2(en)]\cdot H_2O$: C, 25.27; H, 3.71; N, 7.37%.

Measurements. The electronic absorption spectra were measured by a Shimadzu spectrophotometer UV-200. The CD spectra were recorded with a Jasco Model J-20 spectropolarimeter with the CD attachment. All measurements were made at room temperature in chiral media in a constant concentration of the complex ion, 0.002 mol dm^{-3}. The chiral media were prepared by mixing $(+)_{589}$-diethyl tartrate (17 cm^3) with water (3 cm^3) for the oxalato and malonato complexes, and with acetone (3 cm^3) for the other complex tetraphenylborates. The concentration of $(+)_{589}$-diethyl tartrate in the chiral media was approximately 4.96 mol dm^{-3}. The CD measurements were confined in the region of the first d-d transition band, because the chiral media showed very strong absorption in the ultraviolet region.

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Results and Discussion

Each of the complexes reported here has an identical electronic absorption spectrum of the first d-d transition band in the chiral media containing diethyl tartrate and in the aqueous solution. This shows that the inner coordination sphere remains unchanged in the chiral media. For the induced CD intensity of the $[Co(NH_3)_6]^{3+}$ complex dissolved in a mixture of acetone and $(+)_{589}$-diethyl tartrate (4.96 mol dm^{-3}), Beer's law holds good over the concentration range 0—7×10^{-3} mol dm^{-3} of the complex. For the same chromophore, the induced CD intensity increases with an increase in the concentration of $(+)_{589}$-diethyl tartrate, steeply in the range of 0—0.1 in its mole fraction, and reaches to a saturation at the mole fraction *ca.* 0.3. The saturated intensity is dependent on the solvent mixed with $(+)_{589}$-diethyl tartrate; the increasing order of intensity is water$<$methanol$<$acetone. This suggests that the association of the complex ion with diethyl tartrate by hydrogen bonding has an important contribution to the induced CD.

Ammine–Ethylenediamine Mixed Complexes (Fig. 1). These $[Co(N)_6]^{3+}$ type complexes show a single negative CD band at or near the position of their first absorption band with an exception of *trans*-diammine complex, which has a small positive CD band at the lower energy side of the dominant negative one. The absolute CD intensity decreases in the following order: $[Co(NH_3)_6]^{3+} > [Co(NH_3)_4(en)]^{3+} > [Co(en)_3]^{3+} >$ *cis*-$[Co(NH_3)_2(en)_2]^{3+} >$ *trans*-$[Co(NH_3)_2(en)_2]^{3+}$. The sequence shows that the ammonia ligand is more effective to the induction of CD than ethylenediamine. This is consistent with the fact that the former ligand has more N–H groups available for hydrogen bonding than the latter. Moreover the N–H groups of the ethylenediamine ligand cannot interact so freely with the chiral solvent molecules as those of ammonia. The tris(ethylenediamine) complex gives somewhat larger induced CD than the diamminebis(ethylenediamine) complexes, and both the racemic tris- and *cis*-bis(ethylenediamine) complexes have a different type of CD pattern from the natural CD of their resolved enantiomers. Such racemic complexes cannot be discussed equally with the achiral complexes. Since the chiral solvent molecules interact with a chiral complex ion in a different way from its enantiomer, the observed induced CD of a racemate comes from the overall effect, and differs from the individual induced CD of the enantiomers. The *trans*-bis(ethylenediamine) complex shows an induced CD pattern analogous to the natural CD of the *trans*-$[Co(NH_3)_2(S\text{-pn})_2\delta\delta]^{3+}$ complex which also has a small positive band at the lower energy side of a dominant negative band.[12] Thus the positive band of the bis(ethylenediamine) complex may be attributed to the ethylenediamine chelate rings which take preferentially the δ-conformation on the interaction with the chiral slovent.

Ammine–Nitro Mixed Complexes (Fig. 2). These

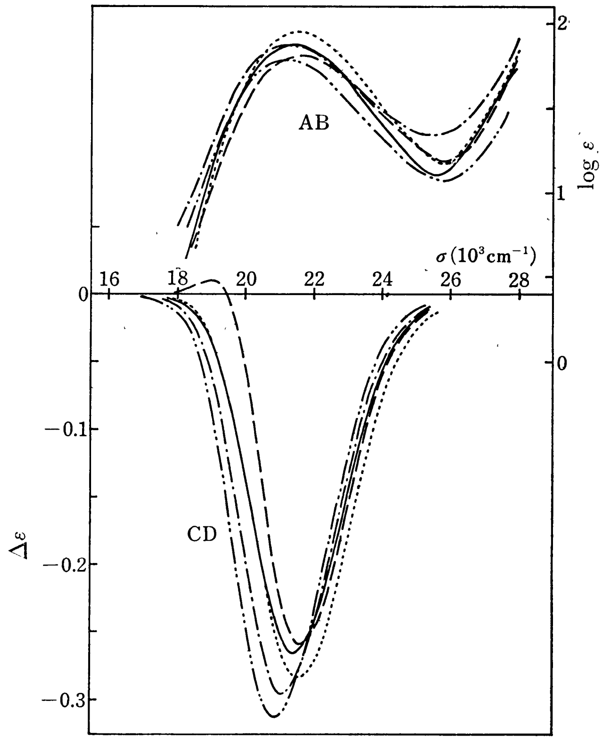

Fig. 1. Absorption (AB) and induced CD spectra of ammine–ethylenediamine mixed complexes in a chiral medium $(+)_{589}$-diethyl tartrate–acetone. $[Co(NH_3)_6]^{3+}$ (–···–), $[Co(NH_3)_4(en)]^{3+}$ (– · –), *rac*-*cis*-$[Co(NH_3)_2(en)_2]^{3+}$ (——), *trans*-$[Co(NH_3)_2(en)_2]^{3+}$ (––––), *rac*-$[Co(en)_3]^{3+}$ (······).

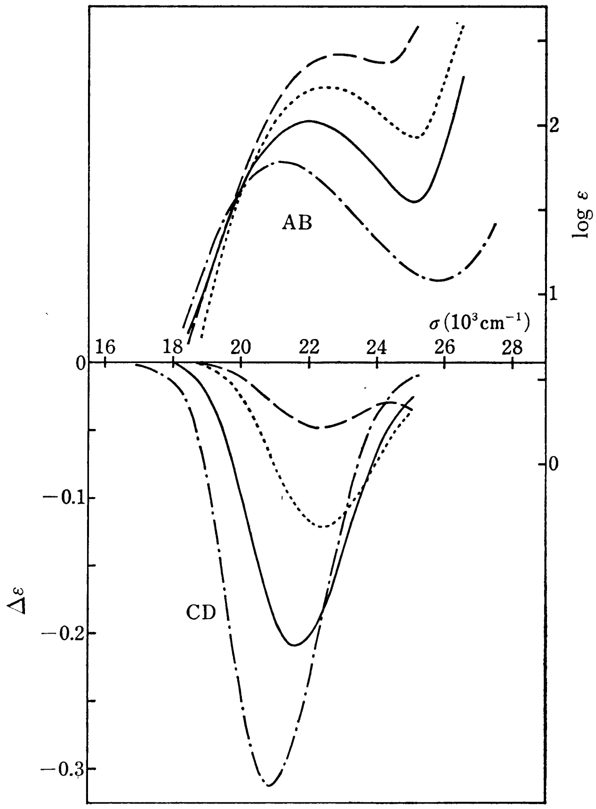

Fig. 2. Absorption (AB) and induced CD spectra of ammine–nitro mixed complexes in a chiral medium $(+)_{589}$-diethyl tartrate–acetone. $[Co(NH_3)_6]^{3+}$ (– · –), $[Co(NO_2)(NH_3)_5]^{2+}$ (——), *cis*-$[Co(NO_2)_2(NH_3)_4]^{+}$ (······), *trans*-$[Co(NO_2)_2(NH_3)_4]^{+}$ (––––).

complexes also show a single negative CD band. The position of the CD peak shifts regularly to the higher energy side by replacing ammine ligands with nitro ones, as in the case of the absorption peak. The CD intensity decreased stepwise with the same replacement, in contrast to absorption. In the dinitro complexes, there is a marked difference between the geometrical isomers, that is, the induced CD of the *trans* isomer is about a half of that of the *cis* isomer.

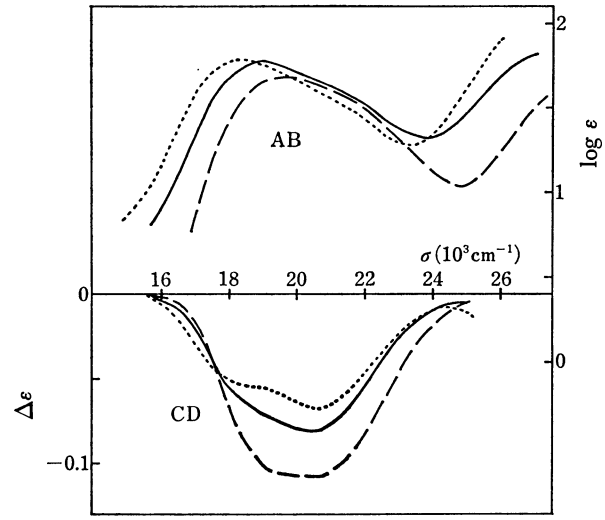

Fig. 3. Absorption (AB) and induced CD spectra of three pentaamminehalogeno complexes in a chiral medium $(+)_{589}$-diethyl tartrate–acetone. $[CoF(NH_3)_5]^{2+}$ (----), $[CoCl(NH_3)_5]^{2+}$ (——), $[CoBr(NH_3)_5]^{2+}$(······).

Pentaamminehalogeno Complexes (Fig. 3). The first absorption band of these complexes splits clearly into the A_2 and E components of C_{4v} symmetry. The induced CD spectra also show splitting into the two components with a negative sign. The A_2 non-degenerate component is dominant contrary to the absorption spectrum, and as expected from Yamatera's rule,[13] the A_2 component with higher energy remains at about the same position as that of the T_{1g} transition of the $[Co(NH_3)_6]^{3+}$ chromophore, irrespective of the kinds of halogens. On the other hand, the E component, which appears as a shoulder at the lower energy side of the dominant A_2 component, shifts according to the spectrochemical series of halogens. As for the CD intensity, the smaller the atomic number of halogens, the stronger the CD intensity. It is evident that the halogeno ligands have an important contribution to the induced CD.

trans-*Tetraamminedichloro Type Complexes (Fig. 4).* The induced CD of the *trans*-$[CoCl_2(N)_4]^+$ chromophores also shows a marked splitting for the first absorption band region. If we adopt the representation of D_{4h} symmetry for these complexes, their CD peaks correspond to the A_{2g} (higher energy) and E_g (lower energy) components. The induced CD of the E_g component increases proportionally with the number of ethylenediamine rings, but that of the A_{2g} component shows a tendency to decrease. The induced CD of the tetraamminedichloro complex does not contain any contribution from the chiral ring conformation, whereas the induced CD of the other two complexes having one or two puckered ethylenediamine rings would contain some contribution from the chelate ring conformation. The conformational contribution in these two complexes would be approximated by the CD difference from the tetraamminedichloro complex. On the E_g component, it is really found that the ratio of the differences is about 1:2 for the mono(ethylenediamine) to the bis(ethylenediamine) complex. Hawkins and his coworkers[14] reported that the natural CD spectra of the analogous chromophore having one or two (*R*)-propylenediamine chelate rings of λ-conformation instead of ethylenediamine rings showed a positive sign for the E_g component, and that the rotational strength of the bis(propylenediamine) complex was approximately twice that of the mono(propylenediamine) complex. From the analogy with this, it is suggested that the ethylenediamine chelate rings of the present complexes are partially fixed to a preferable δ-conformation because of the interaction with the chiral solvent. In the A_{2g} region, the propylenediamine complexes gave a negative natural CD band, whose sign is opposite to the induced CD of the present ethylenediamine complexes. This result, however, is not in conflict with the above discussion, because Bosnich and Harrowfield[15] showed that the natural CD displayed in such a region for several *trans*-$[CoCl_2(N)_4]^+$ chromophores is markedly dependent on solvents.

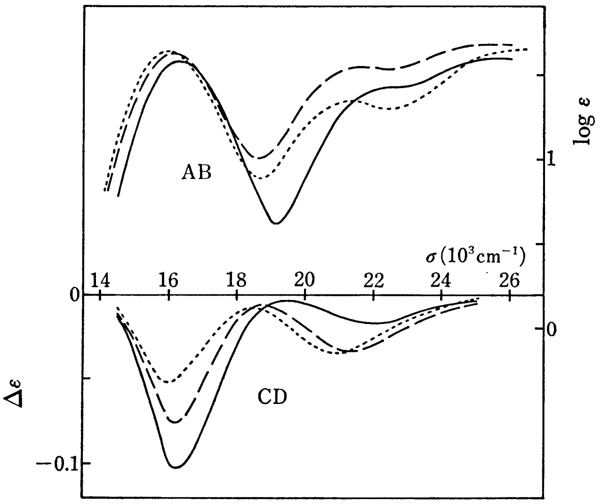

Fig. 4. Absorption (AB) and induced CD spectra of *trans*-tetraamminedichloro type complexes in a chiral medium $(+)_{589}$-diethyl tartrate–acetone. *trans*-$[CoCl_2(NH_3)_4]^+$ (······), *trans*-$[CoCl_2(NH_3)_2(en)]^+$(----), *trans*-$[CoCl_2(en)_2]^+$ (——).

Acetato–Ammine Mixed Complexes (Fig. 5). Three complexes in this group show induced CD spectra quite different from each other. The monoacetato complex exhibits a single negative CD band in its A_2 region, *i.e.* in the region of T_{1g} band of the $[Co(N)_6]^{3+}$ chromophore. The *trans* diacetato complex shows a positive and a negative CD band of comparable intensities which correspond to the E_g (lower energy) and A_{2g} (higher energy) components, respectively. The *cis* diacetato complex shows a dominant positive and a small negative CD band in the order of increasing energy; the former corresponds to the B_1 component and the latter to the

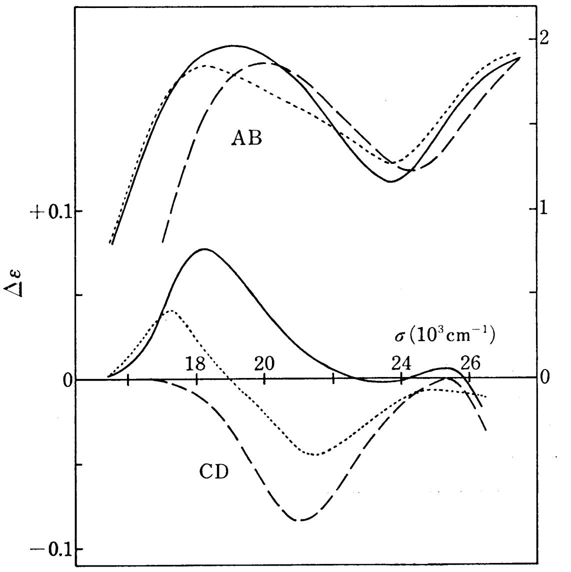

Fig. 5. Absorption (AB) and induced CD spectra of acetato–ammine mixed complexes in a chiral medium $(+)_{589}$-diethyl tartrate–acetone. $[Co(CH_3COO)(NH_3)_5]^{2+}$ (----), *cis*-$[Co(CH_3COO)_2(NH_3)_4]^+$ (——), *trans*-$[Co(CH_3COO)_2(NH_3)_4]^+$ (······).

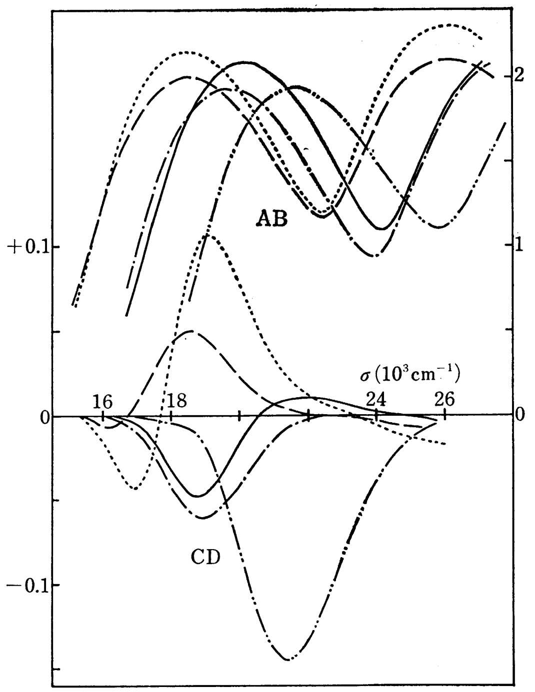

Fig. 6. Absorption (AB) and induced CD spectra of oxalato and malonato complexes in a chiral medium $(+)_{589}$-diethyl tartrate–water. *rac*-$[Co(en)_3]^{3+}$ (-···-), $[Co(ox)(NH_3)_4]^+$ (- · · -), *rac*-$[Co(ox)(en)_2]^+$ (——), *rac*-$[Co(ox)_2(en)]^-$ (······), *rac*-$[Co(mal)_2(en)]^-$ (----).

A_2+B_2 component. The monoacetato complex has the induced CD intensity of the same order as the natural CD intensity of the (α-amino carboxylato)-pentaamminecobalt(III) complexes,[16] which also belong to the chromophore $[Co(O)(N)_5]^{2+}$, its natural CD being contributed by the so-called vicinal effect of the coordinated chiral amino carboxylate ligand. In this respect, the induced CD of these three acetato–ammine complexes may be recognized as a kind of vicinal effect of the chiral solvent molecules.

Oxalato and Malonato Complexes (Fig. 6). Figure 6 shows the absorption and induced CD spectra of these four complexes measured in a chiral medium $(+)_{589}$-diethyl tartrate–water. The induced CD spectra of the $[Co(en)_3]^{3+}$ and $[Co(ox)(en)_2]^+$ complexes in this medium showed essentially the same pattern as in the $(+)_{589}$-diethyl tartrate–acetone medium, except that the intensity in the aqueous medium is reduced to about one-half of that in the acetone medium.

The $[Co(ox)(en)_2]^+$ complex has a dominant negative and a small positive induced CD band in the order of increasing energy. The $[Co(ox)(NH_3)_4]^+$ complex gives a single negative band at the position of the dominant band of the bis(ethylenediamine) complex. The tetraammine complex has a slightly more intense induced CD than the ethylenediamine complex. The $[Co(ox)_2(en)]^-$ and $[Co(mal)_2(en)]^-$ complexes of the *cis*-$[Co(O)_4(N)_2]^-$ chromophore also show a negative and a positive induced CD band in the order of increasing energy. The band at the higher energy side is dominant in contrast to the above *cis*-$[Co(O)_2(N)_4]^+$ chromophore; thus it is common to both kinds of chromophores that the dominant band appears in the region of the non-degenerate component. Although the induced CD patterns are alike in the oxalato and malonato complex anions, the intensity for the latter complex is about one-half of that for the former. As has been noted in one of the preceding sections, the induced CD spectra of the racemic complexes of this group have quite a different pattern from the natural CD spectra of their enantiomers.[17,18]

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