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# Circular Dichroism of Cobalt(III) Complexes of the Type *cis*-[$CoN_2O_4$] and *cis*-[$CoN_4O_2$] Containing Acetylacetonate Ion, 2,2′-Bipyridine and 1,10-Phenanthroline

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Two new cobalt(III) complexes, $[Co(acac)(bpy)_2]^{2+}$ and $[Co(acac)(phen)_2]^{2+}$ (acac=acetylacetonate ion, bpy=2,2′-bipyridine and phen=1,10-phenanthroline) were prepared from the reaction of $[Co(CO_3)(bpy)_2]^+$ and $[Co(CO_3)(phen)_2]^+$, respectively, with acetylacetone, and converted to the partially resolved optically active forms using a SP-Sephadex ion-exchange column. $[Co(acac)_2(bpy)]^+$ was also resolved partially with a SP-Sephadex column. $[Co(acac)_2(phen)]^+$ was resolved with a combination of silver dibenzoyl-*d*-tartrate and dibenzoyl-*d*-tartaric acid. The circular dichroism (CD) spectra for these four complexes and for $[Co(acac)_2(en)]^+$ and $[Co(acac)_2(tn)]^+$ (en=ethylenediamine, tn=trimethylenediamine) were measured. A marked solvent effect was observed in the d-d transition region for the CD spectra of the $[Co(acac)_2L]^+$ complexes. The absolute configurations for all these complexes were assigned on the basis of their CD spectra.

The preparation of mixed-ligand cobalt(III) complexes containing ligands which have strong coordinating ability to a cobalt(III) ion, *e.g.*, bipyridine, phenanthroline, acetylacetonate ion and cyanide ion *etc.*, is not easy because of disproportionation to form complexes for which all of the ligands are the same. Archer *et al.*[3,4] found $[Co(acac)_2(NO_2)_2]^-$ to be a good starting material for preparing $[Co(acac)_2(bpy)]^+$ and $[Co(acac)_2(phen)]^+$ complexes. A preliminary report of the mixed acac-bpy and acac-phen complexes has been made.[5] Here the preparation, optical resolution and circular dichroism (CD) of these complexes are reported.

Marked solvent effects were observed for the CD spectra in the d-d transition region for $[Co(acac)_2L]^+$ (L=bpy, phen, en, tn), but not for $[Co(acac)L_2]^{2+}$ (L=bpy, phen).

The assignments of the absolute configurations for these complexes were attempted on the basis of the CD spectra in the region of the d-d transitions and of the exciton bands. Both approaches have been applied to a variety of optically active metal complexes.[6] We assigned the absolute configurations of the $[Co(acac)L_2]^{2+}$ complexes from the CD in the exciton band region, and of the $[Co(acac)_2L]^+$ complexes using the d-d transition region.

## Experimental

*Preparation of Complexes.* *1) Carbonatobis(2,2′-bipyridine)cobalt(III) Chloride Dihydrate*: Cobalt chloride hexahydrate, 4.7 g (0.02 mol) in 10 $cm^3$ of water and 4 $cm^3$ of 30% $H_2O_2$ were mixed in an ice-bath and added dropwise to a slurry of 12.0 g of $KHCO_3$ (0.12 mol) in 12 $cm^3$ of water at 0 °C. After the addition, the mixture was stirred at 0 °C for 30 min. To this solution 6.25 g (0.04 mol) of 2,2′-bipyridine and 2 $cm^3$ of ethanol were added and stirred for 1 h at 20 °C. The temperature was raised to 30—35 °C and stirring was continued for 3 h. Glacial acetic acid 2.4 g (0.04 mol) in 10 $cm^3$ of water was added dropwise to the solution over a period of 15 min. After stirring for an additional 2 h at 50 °C, glacial acetic acid 2.4 g (0.04 mol) in 10 $cm^3$ of water was again added over a period of 15 min. The solution was stirred for an additional 30 min at 50 °C and then cooled in an ice-bath for 2 h. The red crystals were filtered. The filtrate was concentrated to about half volume to obtain a second crop of crystals and then cooled overnight in a refrigerator to obtain another crop of crystals. These crude products were recrystallized from a small amount of hot water (80 °C), then filtered and washed with an acetone-water mixture, then acetone, and dried in air. If the filtrate is concentrated to half volume, more crystals are obtained. Total yield 8.4 g (90%). Found: C, 48.63; H, 4.29; N, 10.58%. Calcd for $[Co(CO_3)(bpy)_2]Cl\cdot 2H_2O$: C, 48.61; H, 3.90; N, 10.79%.

*2) Carbonatobis(1,10-phenanthroline)cobalt(III) Chloride 4.5-Water*: Cobalt chloride hexahydrate (4.7 g, 0.02 mol) in 10 $cm^3$ of water and 4 $cm^3$ of 30% $H_2O_2$ were mixed in an ice-bath and added dropwise to a slurry of 12.0 g of $KHCO_3$ (0.12 mol) in 12 $cm^3$ of water at 0 °C. After the addition, the mixture was stirred at 0 °C for 30 min. To this solution 10 $cm^3$ of 50% aqueous ethanol and 7.2 g (0.04 mol) of 1,10-phenanthroline were added and the resulting solution was stirred for 1 h at 20 °C. The temperature was raised to 30—35 °C and the stirring was continued for 2 h. After the addition of 10 $cm^3$ of water, the stirring was continued for 1 h at 50 °C. Glacial acetic acid 2.4 g (0.04 mol) in 10 $cm^3$ of water was added dropwise to the solution over a period of 15 min. After stirring for another 2 h at 50 °C, glacial acetic acid 2.4 g (0.04 mol) in 10 $cm^3$ of water was again added over a period of 15 min. The reaction mixture was stirred for 30 min longer at 50 °C and filtered without suction. The filtrate was concentrated to half volume and cooled in a refrigerator overnight. The red crystals were filtered and washed with an acetone-water (small amount) mixture and then with acetone and dried in air. Yield 9.0 g (90%). Found: C, 50.66; H, 4.28; N, 8.83%. Calcd for $[Co(CO_3)(phen)_2]Cl\cdot 4.5H_2O$: C. 50.39; H, 4.22; N, 9.40%.

*3) Acetylacetonatobis(2,2′-bipyridine)cobalt(III) Iodide 1.5 Water*: Acetylacetone (0.6 g in 6 $cm^3$ of water) and 1M HCl 6 $cm^3$ were added to 2.3 g of $[Co(CO_3)(bpy)_2]Cl\cdot 2H_2O$ and the solution was warmed with stirring at 50—55 °C for 5 h. The solution was cooled to room temperature and filtered. Sodium iodide, 1.4 g in 2 $cm^3$ of water, was added to the solution with stirring and the solution was cooled overnight in a refrigerator. The brownish-red product was filtered and washed with 2 $cm^3$ of cold water and then with 4 $cm^3$ of acetone. This crude product was recrystallized from 20 $cm^3$ of hot water (80—85 °C). The red crystals were filtered and washed with a small amount of water-acetone mixture, then with acetone, and dried in air. Yield 0.6 g (17%). Found: C, 41.46; H, 3.20; N, 7.74%. Calcd for $[Co(acac)(bpy)_2]I_2$: C, 41.16; H, 3.10; N, 7.95%.

The perchlorate of the complex was obtained by the addition of $NaClO_4$ to the filtrate from the recrystallization. It was filtered and washed with a small amount of cold water. Yield 0.4 g. Found: C, 42.94; H, 3.80; N, 7.75%. Calcd for $[Co(acac)(bpy)_2](ClO_4)_2 \cdot 1.5H_2O$: C, 43.12; H, 3.76: N, 8.04%.

*4) Acetylacetonatobis(1,10-phenanthroline)cobalt(III) Iodide*: This complex was prepared by using the same method as that for the 2,2′-bipyridine complex except that 2.6 g of $[Co(CO_3)(phen)_2]Cl \cdot 4.5H_2O$ was used. Fifty $cm^3$ of hot water was used for recrystallization. Yield 0.8 g (20%). Found: C, 43.21; H, 3.03; N, 7.24%. Calcd for $[Co(acac)(phen)_2]I_2 \cdot 1.5H_2O$: C, 43.57; H, 3.28; N, 7.14%.

The perchlorate was precipitated by the addition of $NaClO_4$ to the filtrate from the recrystallization. Yield 0.4 g. Found: C, 47.99; H, 3.43; N, 7.55%. Calcd for $[Co(acac)(phen)_2](ClO_4)_2 \cdot 0.5H_2O$: C, 47.95; H, 3.33; N, 7.71%.

*5) Bis(acetylacetonato)(2,2′-bipyridine)cobalt(III) Iodide and Bis(acetylacetonato)(1,10-phenanthroline)cobalt(III) Perchlorate*: These complexes were prepared according to the method reported by Archer *et al.*[3,4]

*Optical Resolution of the Complexes.* *1)* $[Co(acac)(bpy)_2]^{2+}$: A solution of $[Co(acac)(bpy)_2]I_2$ (100—150 mg) was adsorbed on a SP-Sephadex C-25 resin (Pharmacia Fine Chemicals) column (2.5 × 120 cm) and eluted with 0.04 M sodium d-tartrate at a rate of 15—20 $cm^3/h$ over a period of about 1 month. During this time, the red layer did not form separate bands although the band broadened considerably. Each fraction (100—150 $cm^3$) of the effluent was passed through a column of an anion exchange resin (Dowex 1-X8, 100—200 mesh) in $ClO_4^-$ form, then evaporated to a small volume at 30 °C under reduced pressure, and then cooled overnight in a refrigerator. The red crystals of the perchlorate were filtered and washed with a small amount of cold water and dried under vacuum. Fifty mg of the perchlorate of the fast running fractions was again treated on the SP-Sephadex resin in the same way. The perchlorate of the fast running fraction (20 mg) was used for the CD measurement. Found: C, 42.94; H, 3.80; N, 7.75%. Calcd for $[Co(acac)(bpy)_2](ClO_4)_2 \cdot 1.5\,H_2O$: C, 43.12; H, 3.76; N, 8.04%.

*2)* $[Co(acac)(phen)_2]^{2+}$: The method was exactly the same as that for the 2,2′-bipyridine complex. Found: C, 47.99; H, 3.43; N, 7.55%. Calcd for $[Co(acac)(phen)_2](ClO_4)_2 \cdot 0.5H_2O$: C, 47.95; H, 3.33; N, 7.71%.

*3)* $[Co(acac)_2(bpy)]^+$: $[Co(acac)_2(bpy)]I$ (100—150 mg) was adsorbed on a SP-Sephadex C-25 column (2.5 × 120 cm) and eluted with 0.01 M sodium d-tartrate at a rate of 10—15 $cm^3/h$ over a period of 2—3 weeks. During this time, the gray-violet layer did not form separate bands although the band broadened considerably. Each fraction (100—150 $cm^3$) of the effluent, to which a small amount of $NaClO_4$ was added, was evaporated to a small volume at 30 °C under reduced pressure. The resulting gray-violet product was filtered, washed with water, and dried under vacuum. Fifty mg of the perchlorate of the fast running fraction was again treated on the SP-Sephadex resin in the same way. The perchlorate of the fast running fraction (20 mg) was used for the CD measurement. Found: C, 46.25; H, 4.49; N, 5.18%. Calcd for $[Co(acac)_2(bpy)]ClO_4 \cdot 0.5H_2O$: C, 46.03; H, 4.44; N, 5.37%.

*4)* $[Co(acac)_2(phen)]^+$: The racemate, $[Co(acac)_2(phen)]ClO_4$ (5 g) and an anion exchange resin (Dowex 1-X8, $Cl^-$ form, 20 g) were combined and stirred for 20 min in 250 $cm^3$ of methanol. The resin was filtered and washed with 20 $cm^3$ of methanol. The combined filtrate and washings were treated with a second portion (6 g) of resin. The resin was filtered and washed with 20 $cm^3$ of methanol. To the combined filtrate and washings were added silver dibenzoyl-*d*-tartrate (2.67 g) and dibenzoyl d-tartaric acid monohydrate (1.75 g) and the mixture was stirred for 10 min at 60 °C. Silver chloride was removed and washed with 30 $cm^3$ of hot methanol. To the combined filtrate and washings was added 90 $cm^3$ of ether and the resulting solution was cooled in a refrigerator. Fraction 1 (4.19 g) was separated by filtration. Fraction 2 (1.66 g) and fraction 3 (0.42 g) were obtained by further addition of ether and subsequent cooling. The filtrate (A) after the separation of the third fraction was used for the isolation of the opposite enantiomer. The solid fraction 1 (4.19 g) was dissolved in 560 $cm^3$ of methanol and 840 $cm^3$ of ether was added and the resulting solution was cooled in a refrigerator. The fraction 1—1 (1.99 g) was separated by filtration and the fractions 1—2 (0.85 g) and 1—3 (0.42 g) were obtained by the same method described above. The filtrate (B) after the separation of fraction 1—3 was also used for the isolation of the opposite enantiomer. Fraction 1—1 (1.99 g) was dissolved in 300 $cm^3$ of methanol and 500 $cm^3$ of ether was added and the resulting solution was cooled in a refrigerator. Two fractions were separated by fractional crystallization. Then, the various fractions with similar $\Delta\varepsilon$ values were combined and purified. Again, fractions of similar $\Delta\varepsilon$ were combined and purified. This kind of purification was repeated many times. Finally, 1.04 g of one diastereomer was obtained. This diastereomer was treated with an anion exchange resin (Dowex 1-X8, $Cl^-$ form) in methanol to obtain the chloride salt. The resin was separated and ether was added to the methanol solution. Two fractions with low $\Delta\varepsilon$ value were separated, and the filtrate was evaporated to dryness under an air stream. The solid obtained by evaporation was purified twice by dissolving in methanol, adding ether and subsequent cooling in a refrigerator. Finally, brownish-violet flaky crystals were separated. Yield 92 mg. $\Delta\varepsilon_{523} = -2.30$ (solvent : water). Found: C, 53.69; H, 4.62; N, 5.24%. Calcd for $[Co(acac)_2(phen)]Cl \cdot H_2O$: C, 53.83; H, 4.93; N, 5.71%.

The filtrates (A) and (B) described above were combined and concentrated to 75 $cm^3$ using a rotary evaporator, and 150 $cm^3$ of ether was added. The resulting solution was cooled in a refrigerator. The first fraction (0.63 g) was separated by filtration. The filtrate was concentrated to 50 $cm^3$ with a rotary evaporator, 150 $cm^3$ of ether was added, the resulting solution was cooled in a refrigerator. Fraction 2 (0.34 g) and the fraction 3 (0.34 g) were separated in the same way. Fraction 1 was dissolved in 40 $cm^3$ of methanol, 70 $cm^3$ of ether was added and the resulting solution was kept in a refrigerator. The less active diastereomer (1—1) separated first and was filtered. This filtrate was evaporated to dryness to yield fraction 1—2 (0.19 g). The fractions 2, 3, and 1—2 were combined and treated in the same way as that of the other isomer. Finally, brownish-violet flaky crystals were obtained. Yield 0.28 g. $\Delta\varepsilon_{523} = +2.15$ (solvent : water). Found: C, 50.49; H, 5.55; N, 5.57%. Calcd for $[Co(acac)_2(phen)]Cl \cdot 3H_2O$: C, 50.15; H, 5.35; N, 5.31%.

The increase of $\Delta\varepsilon$ with each purification of the diastereomer was very small. Therefore, many purification steps were necessary.

*5)* $[Co(acac)_2(en)]^+$ *and* $[Co(acac)_2(tn)]^+$: These optical resolutions were carried out according to the methods reported.[7]

*Measurements.* Absorption spectra were obtained with a HITACHI 323 Recording Spectrophotometer and a Cary

14 spectrophotometer. CD spectra were measured with a J-20 Spectropolarimeter of Japan Spectroscopic Company and a Cary 61 recording spectropolarimeter. Optical isomers are identified by the sign of the CD in water at a specified wavelength. PMR spectra were measured with a Varian A-60 Spectrometer in a deuterium oxide solution containing sodium trimethylsilylpropanesulfonate(DSS) as the internal standard.

Ethanol and dimethyl sulfoxide for the measurements of absorption and CD spectra were spectroscopic grade.

## Results and Discussion

*Preparation and Properties.* So far much attention has been paid to the tris-type complexes of cobalt(III) with identical bidentate ligands which have $\pi^* \leftarrow \pi$ ligand transitions, *e.g.*, $[Co(phen)_3]^{3+}$, for CD studies.[6)] The complexes with two different ligands, *e.g.*, $[Co(bpy)_2(phen)]^{3+}$, have not been reported, presumably because of the difficulty of their preparation and optical resolution. Archer *et al.*[3,4)] prepared $[Co(acac)_2(bpy)]^+$ and $[Co(acac)_2(phen)]^+$ by the reaction of bpy and phen, respectively, with $[Co(acac)_2(NO_2)_2]^-$. We attempted to prepare $[Co(acac)(bpy)_2]^{2+}$ and $[Co(acac)(phen)_2]^{2+}$ by the same reaction using increased amounts of bpy and phen, but disproportionation occurred. Then we tried the reactions of $[Co(CO_3)(bpy)_2]^+$ and $[Co(CO_3)(phen)_2]^+$ with acetylacetone instead of acetylacetonate ion. The yields were raised to about 20% by improving the reaction conditions, especially the reaction temperature and the amount of alcohol.

The optical resolution of these four complexes proved to be very difficult. To resolve $[Co(acac)(bpy)_2]I_2$ and $[Co(acac)_2(bpy)]I$, we used six resolving agents unsuccessfully: silver *d*-tartrate, silver dibenzoyl-*d*-tartrate, silver antimonyl *d*-tartrate, silver arsenyl-*d*-tartrate, silver *d*-α-bromocamphor-π-sulfonate and $(+)_{580}$-Ag[Co(edta)] (edta=ethylenediaminetetraacetate ion). For the optical resolution of $[Co(acac)_2(phen)]ClO_4$ five resolving agents were tried: silver *d*-α-bromocamphor-π-sulfonate, $(+)_{580}$-Ag[Co(edta)], $(-)_{564}$-Ag[Co(tmdda)(ox)][8)] (tmdda = trimethylenediamine-*N*,*N'*-diacetate, ox=oxalate), a combination of silver *d*-tartrate and *d*-tartaric acid, and a combination of silver dibenzoyl *d*-tartrate and dibenzoyl *d*-tartaric acid monohydrate. In all trials the racemate was changed into the chloride salt using an anion exchange resin (Dowex 1-X8, $Cl^-$ form) before the addition of resolving agents. The first four resolving agents were not effective at all, even though a mixture of both diastereomers was obtained. The last resolving agent showed the possibility of the separation of diastereomers, but the resolution was very laborious and took a long time. Therefore, the resolutions of the other complexes using these resolving agents were not tried. We attempted to use a SP-Sephadex resin which has been used for the isolation and optical resolution of cobalt(III) complexes.[9)] The optically active forms for the other three complexes were obtained in this way, but complete resolution was not achieved. Low yields were obtained because of the small capacity of the resin. Although we tried to elute the complexes two times as described (Experimental), the increase of $\Delta\varepsilon$ for the complexes the second time was small.

PMR spectra of $[Co(acac)(bpy)_2]Cl_2 \cdot 6H_2O$ and $[Co(acac)(phen)_2]Cl_2 \cdot 4.5H_2O$ were measured. The chloride salts, which are more soluble than the perchlorates, were obtained using anion exchange columns. The former complex shows a methyl resonance at 2.28 ppm and a methine resonance at 6.11 ppm (δ relative to DSS). The latter complex shows a methyl resonance at 2.55 ppm and a methine resonance at 6.47 ppm. These signals show significant downfield shifts, especially for the methine resonances, compared to $[Co(acac)(en)_2]I_2$ (a methyl resonance at 2.17 ppm and a methine resonance at 5.78 ppm in $D_2O$ solution[10)]). This may be a consequence of the magnetic aniostropy of bpy and phen. The resonances of the bpy and phen ligands were observed at 7.7—9.7 ppm although these regions were not analyzed. The spectral pattern of $[Co(acac)(phen)_2]^{2+}$ in the region of the phenanthroline ligand is slightly different from that of $[Co(en)(phen)_2]^{3+}$.[11)]

*Circular Dichroism and Absolute Configuration.* Figures 1 and 2 show the CD spectra and visible and ultraviolet absorption spectra in water and in ethanol for $[Co(acac)(bpy)_2](ClO_4)_2 \cdot 1.5H_2O$ and $[Co(acac)(phen)_2](ClO_4)_2 \cdot 0.5H_2O$, respectively, in the first eluates from a Sephadex column. For the absorption spectrum of $[Co(acac)(bpy)_2]^{2+}$, the first d-d band (~20000 cm$^{-1}$) and $\pi^* \leftarrow \pi$ ligand bands (33000—34000 cm$^{-1}$) are evident. The split exciton CD bands at about 34000 cm$^{-1}$ are positive and then negative from lower energy, indicating a Λ configuration.[12)] The positions of the exciton CD bands are similar to those of $[Co(bpy)_3]^{3+}$ (at 32500 cm$^{-1}$ ) and $[Co(bpy)_2(ox)]^+$ (at 33000 cm$^{-1}$).[13)] The corresponding $\pi^* \leftarrow \pi$ absorption peaks for the

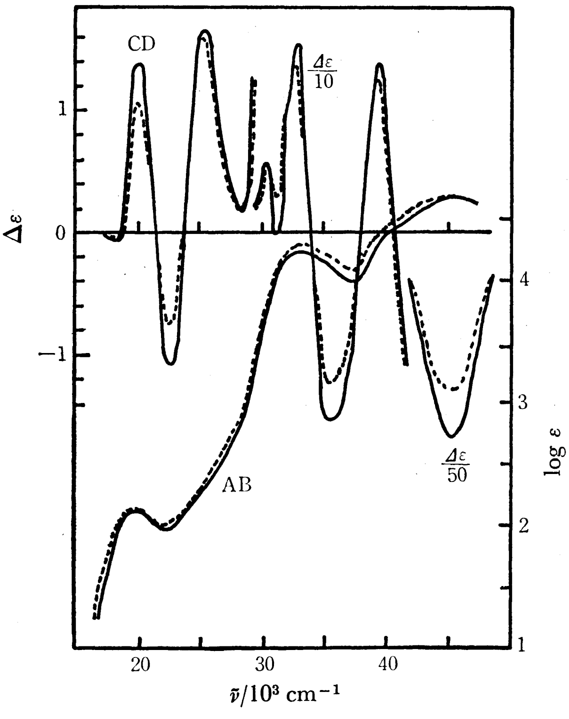

Fig. 1. Absorption (AB) and CD spectra of $(+)_{495}$-$[Co(acac)(bpy)_2]^{2+}$, in water (—) and in ethanol (---).

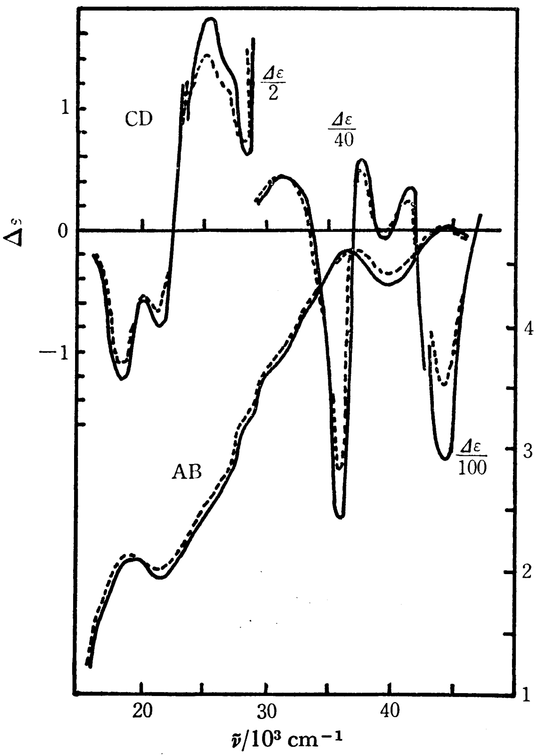

Fig. 2. Absorption (AB) and CD spectra of $(-)_{543}$-$[Co(acac)(phen)_2]^{2+}$, in water(—) and in ethanol(---).

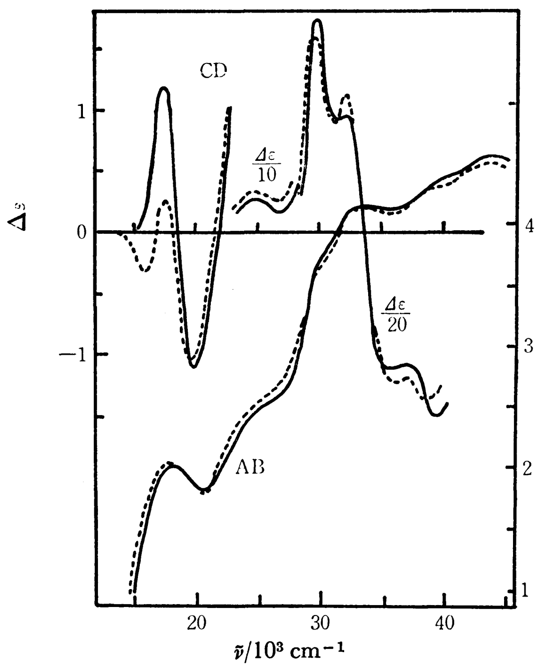

Fig. 3. Absorption (AB) and CD spectra of $(-)_{505}$-$[Co(acac)_2(bpy)]^+$, in water(—) and in ethanol(---).

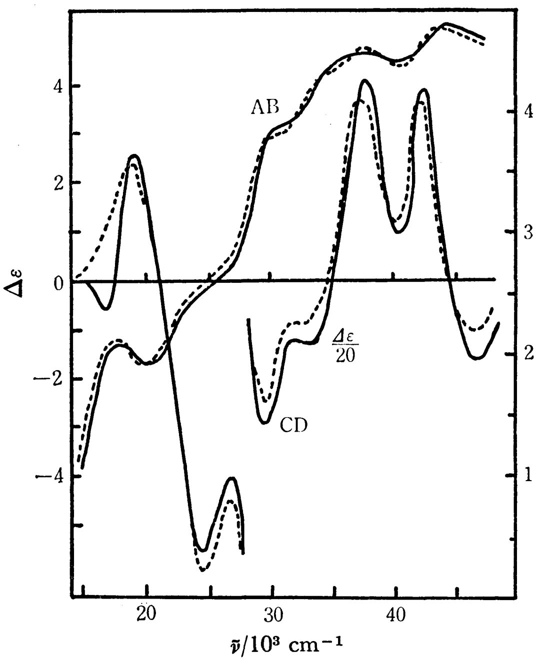

Fig. 4. Absorption (AB) and CD spectra of $(+)_{523}$-$[Co(acac)_2(phen)]^+$, in water (—) and in ethanol(---).

$[Co(acac)(phen)_2]^{2+}$ ion are observed at 36600 $cm^{-1}$, where the CD spectrum gives a negative and a positive band from lower energy, indicating the opposite or $\Lambda$ configuration. The split exciton CD bands at about 37000 $cm^{-1}$ correspond to those of $[Co(phen)_3]^{3+}$ (at 36300 $cm^{-1}$) and $[Co(phen)_2(ox)]^+$ (at 36800 $cm^{-1}$).[13] The CD curves in the visible region are quite different for the bpy and phen complexes. In each case one CD peak appears near the trough between the first d-d absorption band $[T_{1g}(O_h)]$ and the shoulder at higher energy, where the $T_{2g}(O_h)$ band is expected. Although assignments of the individual CD components cannot be made, the signs of the dominant CD peak (or the net rotational strength) in the $T_{1g}$ region are consistent with the $\Lambda$ configuration for $[Co(acac)(bpy)_2]^{2+}$ (Fig. 1, net positive) and $\Delta$ for $[Co(acac)(phen)_2]^{2+}$ (Fig. 2, net negative). The absorption spectra for $[Co(acac)(bpy)_2]^{2+}$ and $[Co(acac)(phen)_2]^{2+}$ in ethanol show slight red shifts relative to those in water. The CD spectral patterns in these solvents are almost the same, although the intensities of the peaks are slightly different.

In the case of the complexes containing two acetylacetonate ligands, the absorption spectra are very similar in water and in ethanol (Figs. 3, 4, 6. and 7). The CD spectra are also affected only to a small extent except in the region of the first absorption band. The CD spectrum of $[Co(acac)_2(bpy)]^+$ (Fig. 3, the isomer shown is from the first eluate from a Sephadex column) in ethanol shows three well-defined peaks of alternating signs in the first absorption band region, while in water there are only two peaks. For $[Co(acac)_2(phen)]^+$ (the enantiomer shown in Fig. 4 is from the more soluble diastereoisomer with hydrogen dibenzoyl *d*-tartrate) only one CD peak appears in ethanol in this spectral region, while two peaks appear in water. Note that the CD spectra throughout the d-d absorption region (Figure 5) are similar for $[Co(acac)_2(phen)]^+$ in dimethyl sulfoxide and in a KBr disc to that in ethanol. The solvent effects appear to be more remarkable in the case of $[Co(acac)_2(en)]^+$ and $[Co(acac)_2(tn)]^+$ (Figs. 6 and 7). In both cases there are two CD peaks in the first absorption band region for each solvent, but the lowest energy peak appears to change sign. It

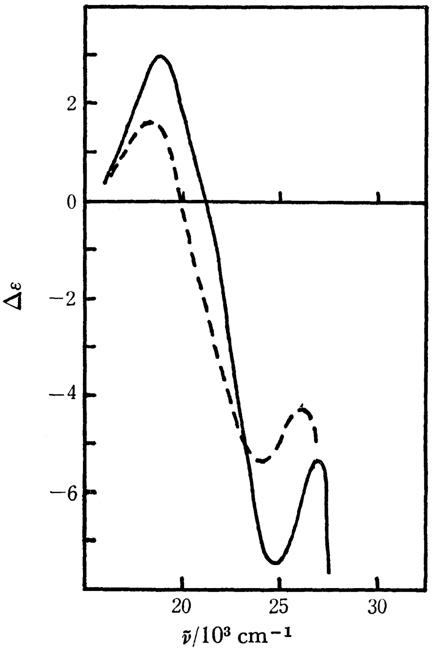

Fig. 5. CD spectra of $(+)_{523}$-[Co(acac)$_2$(phen)]$^+$, in dimethyl sulfoxide (—) and KBr disc(---) (arbitrary scale).

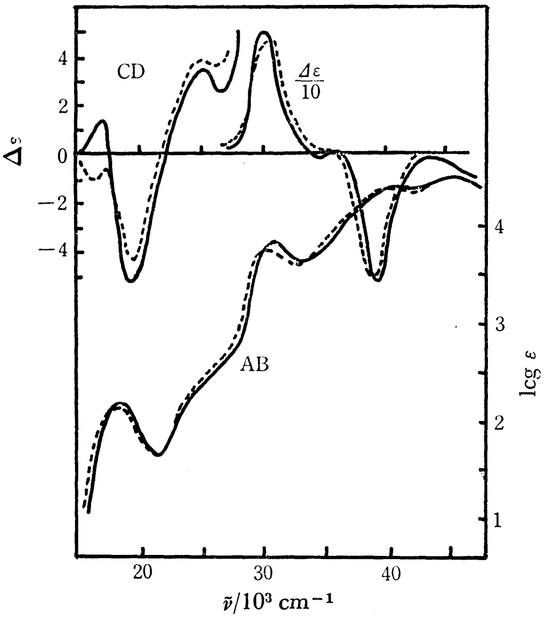

Fig. 6. Absorption (AB) and CD spectra of $(-)_{510}$-[Co(acac)$_2$(en)]$^+$, in water (—) and in ethanol(---).

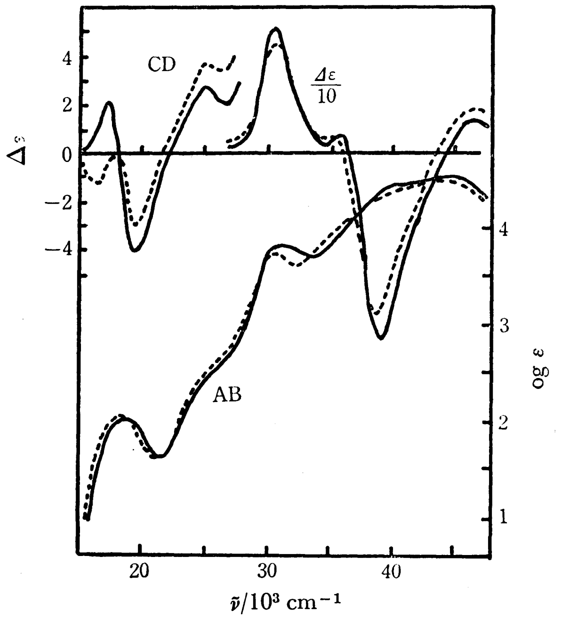

Fig. 7. Absorption (AB) and CD spectra of $(-)_{512}$-[Co(acac)$_2$(tn)]$^+$, in water (—) and in ethanol(---).

should be noted that for both complexes the lowest energy (negative) CD peak is at lower energy in ethanol than the lowest energy (positive) peak in water.

The patterns of the CD spectra in the region of the first absorption band (Figs. 3, 4, 6, and 7) are not so erratic as might appear at first. For each of the four complexes, two CD peaks of opposite sign appear in water. The number of peaks and their signs vary in ethanol, except that the curves are similar for [Co(acac)$_2$(en)]$^+$ and [Co(acac)$_2$(tn)]$^+$. The variations are more comprehensible if one considers the actual symmetry of the complexes, $C_2$. Three CD components are expected in the first absorption band region for $C_2$ symmetry, although often fewer components appear because of overlap resulting from small splittings. Three CD peaks actually appear for [Co(acac)$_2$(bpy)]$^+$ in ethanol. If one considers that there are actually three closely spaced components of alternating signs in each case, all of the spectra can be understood. It is expected that solvent changes or the addition of electrolytes will affect the relative intensities of the component and, to a lesser extent, their energies. The dominant component at highest energy in the first absorption band region, however, shows very slight solvent effect. For [Co(acac)$_2$(bpy)]$^+$ a lowering of the intensity of the lowest energy (negative) CD peak, or an increase of the intensity of the center (positive) CD peak, in going from ethanol to water would result in the two CD peaks observed in water (Fig. 3). The slight shift in the position of the positive peak toward lower energy in water would result from less cancellation by the lower energy negative peak. In the case of [Co(acac)$_2$(phen)]$^+$ (Fig. 4), the dominant CD peak in the first absorption band is positive, opposite in sign to that of [Co(acac)$_2$(bpy)]$^+$. In ethanol it would appear that the lowest energy component (also positive) for [Co(acac)$_2$(phen)]$^+$ completely cancels the middle (negative) component, resulting is a single positive CD peak. The middle (negative) peak shows up in water, because of lowering of intensity of the lowest energy component (or increase in intensity of the middle component). The CD curves for both [Co(acac)$_2$(en)]$^+$ and [Co(acac)$_2$(tn)]$^+$ (Figs. 6 and 7) in the first absorption band show two peaks of the same sign in ethanol, presumably the lowest and highest energy components, with the middle positive component being cancelled completely. For these complexes, two peaks of opposite sign appear in water, with the lowest energy (negative) peak being cancelled completely.

The similarity of the CD patterns in the first band region in water for all complexes and the sign of the solvent insensitive intense peak on the higher energy side of the first absorption band provide a basis of relating the absolute configurations of the complexes. The sign of this peak is the same as the sign of the net rotational strength for the first absorption band region in each case. The CD spectral pattern for $(+)_{510}$-$[Co(acac)_2(en)]^+$ (the enantiomer of the isomer in Fig. 6) in water is strikingly similar up to 40000 $cm^{-1}$ to that of $\Lambda$-$[Co(acac)_3]$, whose absolute configuration was determined by X-ray analysis.[14] Accordingly, $(+)_{510}$-$[Co(acac)_2(en)]^+$ should have the $\Lambda$ configuration, as also assigned by Boucher[15] based on the sign of the dominant CD peak in the first band region. The enantiomers $(-)_{510}$-$[Co(acac)_2(en)]^+$ (Figure 6), $(-)_{512}$-$[Co(acac)_2(tn)]^+$ (Fig. 7), and $(-)_{505}$-$[Co(acac)_2(bpy)]^+$ (Fig. 3) have the $\Delta$ configuration and $(+)_{523}$-$[Co(acac)_2(phen)]^+$ (Fig. 4) has the $\Lambda$ configuration. These assignments, based on the spectral sign pattern of $\Lambda$-$[Co(acac)_3]$, agree with those made based on the sign of the net rotational strength or of the intense solvent insensitive CD peaks in the first absorption band region.

The ultraviolet CD curves for $[Co(acac)_2(bpy)]^+$ and $[Co(acac)_2(phen)]^+$ are not very helpful in confirming the assignment of absolute configurations. The CD peaks for $[Co(acac)_2(bpy)]^+$ in the 32000—35000 $cm^{-1}$ region (Fig. 3) overlap other peaks, so one cannot make reliable distinctions between charge transfer and possible exciton bands in this region. The $\pi^*\leftarrow\pi$ excition CD bands for other bis(acac) complexes have been observed at 40000 $cm^{-1}$ or higher energy.[15] The characteristic split exciton CD bands require the coupling of two or more ligands with $\pi$-electron systems. No splitting of the $\pi^*\leftarrow\pi$ CD band occurs for $[Co(en)_2(phen)]^{3+}$ where there is only one ligand with a $\pi$-electron system.[17] The $\pi^*\leftarrow\pi$ transitions differ in energy for acac and bpy and it appears that such coupling between these ligands is not effective. If the absorption peak for $[Co(acac)_2(phen)]^+$ at *ca.* 43000 $cm^{-1}$ corresponds to the $\pi^*\leftarrow\pi$ transition for acac, then the two CD peaks in this region, positive (at lower energy) and negative, could be the split exciton bands. This sign pattern is consistent [16] with the $\Lambda$ configurations assigned from the first d-d band.

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