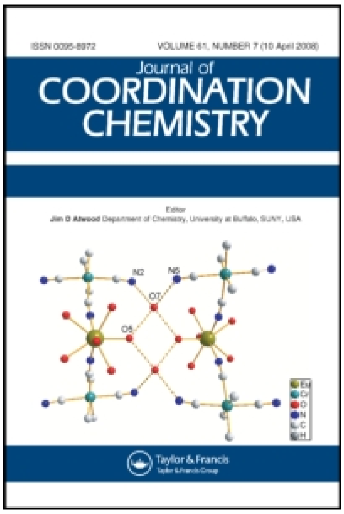

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CIRCULAR DICHROISM OF COBALT(III) COMPLEXES OF THE TYPE [Co(N)$_6$] CONTAINING BIGUANIDE, AND 2,2′-DIPYRIDYL OR 1,10-PHENANTHROLINE

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Biguanide-diamine mixed complexes of the type $[Co(diamine)(Hbg)_2]^{3+}$ and $[Co(diamine)_2(Hbg)]^{3+}$, where the diamines are 1,10-phenanthroline or 2,2′-dipyridyl, have been prepared and resolved. The absorption and circular dichroism (CD) spectra in water, 0.1 M NaOH aqueous solution, and ethanol are reported. Hydroxide ion affects the CD intensity mainly in the first absorption band region. A marked solvent effect of ethanol was also observed for both absorption and CD spectra especially in the first absorption band region. The absolute configurations for all of these complexes are assigned on the basis of their CD spectra.

INTRODUCTION

Biguanide, Hbg = $NH\{C(NH_2)NH\}_2$, forms a variety of metal complexes coordinating with a six-membered planar chelate ring.[2] There have not been many studies, however, concerning the CD spectra of metal complexes of biguanide.[3–6] Michelsen[3] investigated the CD spectra of $(-)_{589}$-$[Co(Hbg)_3]^{3+}$ and $(-)_{589}$-$[Cr(Hbg)_3]^{3+}$ and assigned the same absolute configuration (Λ) to them. Later Brubaker and Webb[4] confirmed the absolute configuration of $(-)_{589}$-$[Cr(Hbg)_3]^{3+}$ to be Λ by X-ray analysis. They suggested, however, that $(-)_{589}$-$[Co(Hbg)_3]^{3+}$ should have the Δ configuration from the comparison of the ultraviolet CD spectra of the cobalt(III) and chromium(III) complexes. In these circumstances Igi *et al.*[5] made an effort to relate the CD data for $(-)_{589}$-$[Co(Hbg)_3]^{3+}$ to those for $(+)_{589}$-$[Co(en)_3]^{3+}$ by studying the mixed complexes $(+)_{589}$-$[Co(en)(Hbg)_2]^{3+}$ and $(+)_{589}$-$[Co(en)_2(Hbg)]^{3+}$ and assigned the Λ absolute configuration to $(-)_{589}$-$[Co(Hbg)_3]^{3+}$. A couple of years later this assignment was proved to be correct by an X-ray technique by Snow.[7] Recently Kawaguchi and Douglas[6] studied biguanide-amino acid complexes of the type $[(Co(am)(Hbg)_2]^{2+}$, where am is the anion of glycine, sarcosine, L-alanine, L-valine, L-isoleucine, or L-proline.

In the present paper, absorption and CD spectra of biguanide-diamine mixed complexes of the type $[Co(diamine)(Hbg)_2]^{3+}$ and $[Co(diamine)_2(Hbg)]^{3+}$, where diamines are 1,10-phenanthroline or 2,2′-dipyridyl, are reported. Special attention is paid to the effect of hydroxide ion and the solvent effect of ethanol on absorption and CD spectra.

EXPERIMENTAL

Preparation and Resolution of Biguanidebis(1,10-phenanthroline)cobalt(III) Chloride, $[Co(Hbg)(phen)_2]Cl_3$. A mixture of $[CoCl_2(phen)_2]Cl\cdot 3H_2O$ (10 g),[8] biguanide (2 g) and activated coconut charcoal (10 g) in 400 ml of absolute methanol was refluxed for two hours. Then the charcoal and a small amount of by-product were filtered. To the filtrate was added 500 ml of diethyl ether while stirring with a glass rod. All at once crystals began to form. The solution containing the crystals was cooled in a refrigerator in order to complete crystallization. Brown-orange fluffy crystals were separated by filtration and washed with ether. The complex was recrystallized from water by the addition of acetone; yield 5.7 g.

For the resolution, 4.3 g of $[Co(Hbg)(phen)_2]Cl_3$ was dissolved in 20 ml of warm water. To the solution was added 2.5 g of silver (+)-tartrate and the suspension was warmed at *ca.* 65° for 12 min with stirring. Silver chloride was filtered and washed with 8 ml of warm water. To the combined filtrate and washings was added 40 ml of acetone and this solution was cooled in a refrigerator. The solid diastereomer (2.1 g) was separated by filtration and washed with acetone-water (2:1) mixture and then acetone. Two recrystallizations from water by addition of acetone were necessary to reach a constant CD intensity, $\Delta\epsilon_{487} = -1.79$ (assuming a 1:1 diastereomer, mol wt 703.98). The diastereomer (0.50 g) was dissolved in a small amount of water and passed through an anion-exchange column (Dowex 1–X8, chloride form). The eluate was concentrated under an air stream to dryness. The solid obtained was dissolved in 12 ml of water and 100 ml of acetone was added to it. When the solution was cooled in a refrigerator, a brown-orange precipitate appeared. The precipitate was filtered and washed with acetone; yield 0.30 g; $\Delta\epsilon_{487} = -1.91$ *Anal.* Calcd for $[Co(C_2H_7N_5)(C_{12}H_8N_2)_2]Cl_3{\cdot}4H_2O$: C, 44.68; H, 4.47; N, 18.04. Found: C, 44.37; H, 4.05; N, 18.23.

Preparation and Resolution of Biguanidebis-(2,2'-dipyridyl)-cobalt(III) Chloride, [Co(dipy)$_2$(Hbg)]Cl$_3$. A mixture of $[CoCl_2(dipy)_2]Cl{\cdot}2H_2O$ (15 g),[9] biguanide (3.2 g) and activated coconut charcoal (15 g) in 500 ml of absolute methanol was refluxed for 30 min. After the charcoal and a trace of by-product were filtered, the filtrate was evaporated to dryness under an air stream. Then the solid was dissolved in 150 ml of water, 800 ml of acetone was added to it, and the mixture was cooled in a refrigerator. Red-orange crystals were separated by filtration and washed with acetone. The complex was recrystallized from water by the addition of acetone: yield 8.4 g.

For the resolution, 2 g of $[Co(dipy)_2(Hbg)]Cl_3$ was dissolved in 4 ml of water. To the solution was added 4.1 g of silver di-μ-D-tartrato(4–)-diantimonate(III) and the suspension was warmed at *ca.* 65° for 10 min with stirring. Silver chloride was filtered and washed with a small amount of water. The filtrate and washings were combined and concentrated to dryness under an air stream. The glassy substance obtained was dissolved in 17 ml of water. Then a small amount of light colored substance was precipitated by successive additions of methanol to the solution and cooling in a refrigerator. After the precipitate was filtered, the filtrate was allowed to stand for several days. The diastereomer (1.7 g) which appeared was filtered and recrystallized from hot water three times. Two recrystallizations were enough to reach a constant CD intensity $\Delta\epsilon_{483} = +3.53$ (assuming a 2:3 diastereomer, mol wt 2659.8). The diastereomer (0.5 g) was dissolved in a small amount of water and passed through an anion exchange column (Dowex 1–X8, chloride form). The eluate was concentrated under an air stream to dryness. The solid obtained was dissolved in 7 ml of water and 33 ml of acetone was added to it. When the solution was cooled in a refrigerator, orange-brown crystals appeared. The crystals were filtered and washed with acetone; yield 0.17 g. $\Delta\epsilon_{483} = +4.23$ *Anal.* Calcd for $[Co(C_2H_7N_5)(C_{10}H_8N_2)_2]Cl_3{\cdot}3.5H_2O$: C, 41.17; H, 4.71; N, 19.64. Found: C, 40.75; H, 4.34; N, 19.71. Sometimes the racemate contained a very small amount of disproportionated species, so that purity of the racemate was always checked using SP-Sephadex ion-exchange resin (C-25 sodium form) and elution with 0.2 M NaCl.

Preparation and Resolution of Bis(biguanide)-(1,10-phenanthroline)cobalt(III) Chloride, [Co(Hbg)$_2$(phen)]Cl$_3$. This complex was prepared by the method of Dutta and Sarkar.[10] Optical resolution by the method of Dutta and Sarkar could not be reproduced. Therefore the racemate was resolved partially with a SP-Sephadex column.[11] A solution of the racemate (150 mg) was absorbed on a SP-Sephadex C–25 resin column (4.5 x 86 cm) and eluted with 0.15 M sodium (+)-tartrate at a rate of 25 ml per hr over a period of about 20 days. During this time, the orange layer did not form separate bands although the band broadened considerably. The fast running fractions were combined and concentrated in a rotary evaporator at 29°. A large amount of solid sodium (+)-tartrate was removed by filtration. (Here the CD spectrum of the filtrate was measured. The concentration of the filtrate was determined by a comparison of the absorbance of the filtrate with the quantitatively measured absorbance of the racemate at a specific wavelength.) The fast running fractions were concentrated further and desalted repeatedly. The iodide salt of the complex was precipitated by the addition of NaI to the above desalted solution. Then the iodide was changed into the chloride by passing of the aqueous solution of the iodide through the ion-exchange column (Dowex 1-X8 chloride form). Acetone was added to the concentrated eluate and it was cooled in a refrigerator. The slow running fractions were treated in the same way as the fast running fractions. Unfortunately it was found that both supposedly optically active chlorides had racemized significantly during the above procedures. Therefore these samples were used just for checking the sign of optical rotation at the sodium D line. *Anal.* for the racemate, Calcd for $[Co(C_2H_7N_5)_2(C_{12}H_8N_2)]Cl_3{\cdot}1.5H_2O$: C, 33.43; H, 4.38; N, 29.25. Found: C, 32.95; H, 4.62; N, 29.47.

Preparation and Resolution of Bis(biguanide)-(2,2'-dipyridyl)cobalt(III) Chloride, [Co(dipy)(Hbg)₂]Cl₃.

[Co(dipy)(Hbg)$_2$]Cl$_3$. This complex was prepared by the method of Dutta and Sarkar.[10] Optical resolution of the complex was carried out by a modified procedure of the method of Dutta and Sarkar. The racemate, [Co(dipy)(Hbg)$_2$]Cl$_3$, (5.8 g) was dissolved in 600 ml of hot water (70°). To the solution was added 3.6 g of silver (+)-tartrate and the suspension was warmed at 70° for 10 min with stirring. Silver chloride was filtered and washed with 30 ml of water. The filtrate and washings were combined and concentrated to dryness under an air stream. The solid obtained was dissolved in *ca.* 50 ml of hot water and cooled in a refrigerator. The diastereomer (3.2 g) was separated by filtration and washed with a water-acetone (1:1) mixture then with acetone. Two recrystallizations from hot water did not increase the CD intensity. $\Delta\epsilon_{529} = +3.48$ (assuming a 1:1 diastereomer, mol wt 600.89). The diastereomer (2.61 g) was dissolved in 250 ml of water and passed through an anion-exchange column (Dowex 1-X8, chloride form). The eluate was concentrated under an air stream to *ca.* 15 ml. To the solution was added 25 ml of acetone and it was cooled in a refrigerator. Brown-orange crystals were separated and washed with ethanol and then with ether; yield 1.3 g; $\Delta\epsilon_{529} = +3.84$ *Anal.* Calcd for [Co(C$_2$H$_7$N$_5$)$_2$(C$_{10}$H$_8$N$_2$)]Cl$_3$·2H$_2$O: C, 30.04; H, 4.68; N, 30.04. Found: C, 30.10; H, 4.67, N, 30.37.

Measurements

The electronic absorption spectra were recorded on a Cary 14 spectrophotometer and a UVIDEC-I spectrophotometer of Japan Spectroscopic Company. The CD spectra were recorded on a Cary 61 spectropolarimeter and a J-20C spectropolarimeter of Japan Spectroscopic Company. The racemate was used for the absorption spectrum of [Co(Hbg)$_2$(phen)]$^{3+}$, while active forms were used for the other complexes. For the CD spectrum of [Co(Hbg)$_2$(phen)]$^{3+}$, the fast running fraction on the ion-exchange column (SP-Sephadex) was used. No racemization was observed during the spectral measurements for any of the complexes. The sign of optical rotation at the sodium D line was checked with an automatic digital polarimeter OR-50D of UNION GIKEN. Optical isomers are identified by this sign of rotation. The partially racemized chloride mentioned above was used for checking the sign of optical rotation of [Co(Hbg)$_2$(phen)]$^{3+}$.

RESULTS AND DISCUSSION

Electronic Absorption and CD Spectra

The absorption and CD spectra of (+)$_{589}$-[Co(Hbg)$_2$-(phen)]$^{3+}$ in water are shown in Figure 1. The first *d-d* absorption band appears at 21.1 kK and the band at 36.5 kK is derived from the intraligand transition of phenanthroline.[12] The shoulders between the above two peaks arise probably from charge transfer transitions. The intraligand transitions of biguanide are considered to be located above 40 kK. The CD curve shows two peaks of opposite sign at 18.6 and 21.1 kK in the first absorption band region, the typical pattern for tris(bidentate) complexes of cobalt(III). Two CD peaks of opposite sign are also observed in the intraligand transition region at 35.6 and 38.2 kK. However the π-π* exciton bands,[4,5,7] which should be caused by the interaction of two biguanide ligands, are probably located above 40 kK. The origin of the peak at 33.1 kK may be a charge transfer transition.

The absorption and CD spectra of (+)$_{589}$-[Co-(dipy)(Hbg)$_2$]$^{3+}$ in water and in 0.1 M NaOH aqueous solution are shown in Figure 2. The first absorption band (21.4 kK) in water is located at

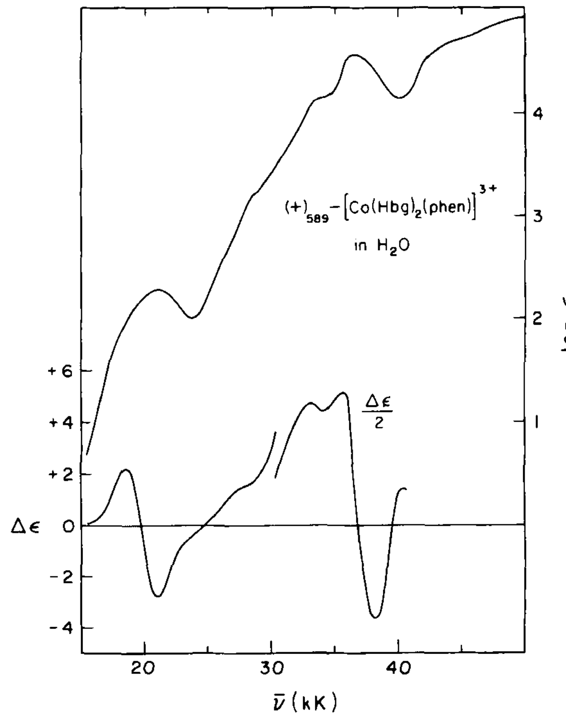

FIGURE 1 Absorption and CD spectra for (+)$_{589}$-[Co-(Hbg)$_2$(phen)]$^{3+}$ in water.

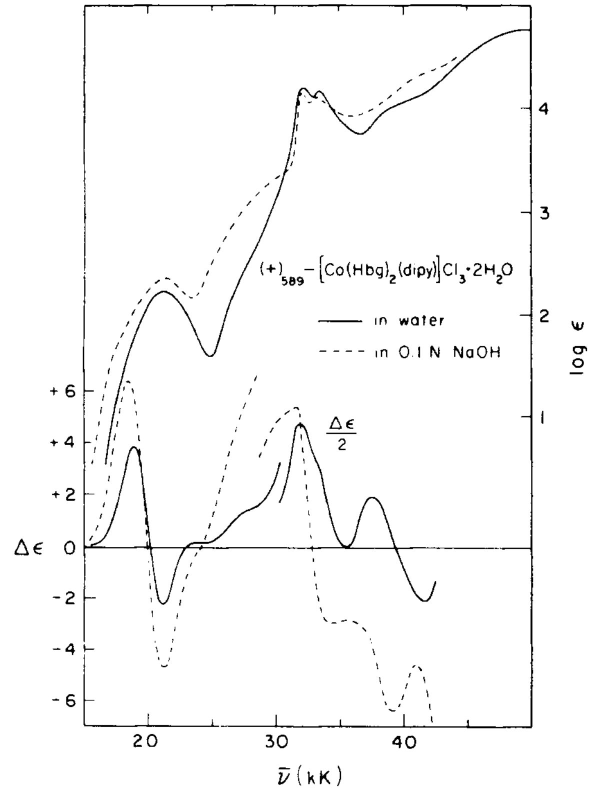

FIGURE 2 Absorption and CD spectra for $(+)_{589}$-[Co(dipy)(Hbg)$_2$]$^{3+}$ in water, and in 0.1 M NaOH.

nearly the same position as in 0.1 M NaOH solution, although the intensity is a little higher in 0.1 M NaOH solution. Probably the first absorption band is overlapped by the charge transfer band in the case of the spectrum in 01. M NaOH solution. The bands located at 32.2 and 33.5 kK in the spectrum of the neutral solution originate from the intraligand transition of dipyridyl.[12] The CD curves in both water and 0.1 M NaOH solution show two peaks of opposite sign (at 18.9 and 21.2 kK in water and at 18.5 and 21.3 kK in 0.1 M NaOH solution). Both CD peaks in 0.1 M NaOH solution are much more intense than those in water in the first absorption band region. A similar phenomenon was also observed in the other complexes investigated, as will be mentioned later. The CD pattern in water differs from that in 0.1 M NaOH aqueous solution in the ultraviolet region. The π-π^* exciton bands,[4,5,7] which should be caused by the interaction of two biguanide ligands, are considered to be located beyond 40 kK.

The absorption and CD spectra of $(+)_{589}$-[Co(Hbg)(phen)$_2$]$^{3+}$ in water, 0.1 M NaOH aqueous solution, and ethanol are shown in Figure 3. The absorption spectra in the three solvents do not differ very much except in the first absorption band region. The first absorption maximum in water is located at 20.0 kK and that in 0.1 M NaOH aqueous solution is shifted to the lower energy side and the intensity of it is a little higher than that in water. The positions of the first absorption maximum in water and in 0.1 M NaOH aqueous solution reflect clearly that Hbg has a stronger ligand field than bg$^-$, as Hbg of $(+)_{589}$-[Co(Hbg)(phen)$_2$]$^{3+}$ in the alkaline solution is considered to be deprotonated.[5] In ethanol the first absorption band has a shoulder on the higher energy side. The CD spectra in all three solvents show three bands of alternating sign, (+)(−)(+), in the first absorption band region. In the CD curve in 0.1 M NaOH aqueous solution, the first and second peaks are shifted to the lower energy side compared with those in water, which is consistent with the shift of the first absorption band in the corresponding absorption spectrum. Further it is to be noted that the CD intensities in 0.1 M NaOH aqueous solution

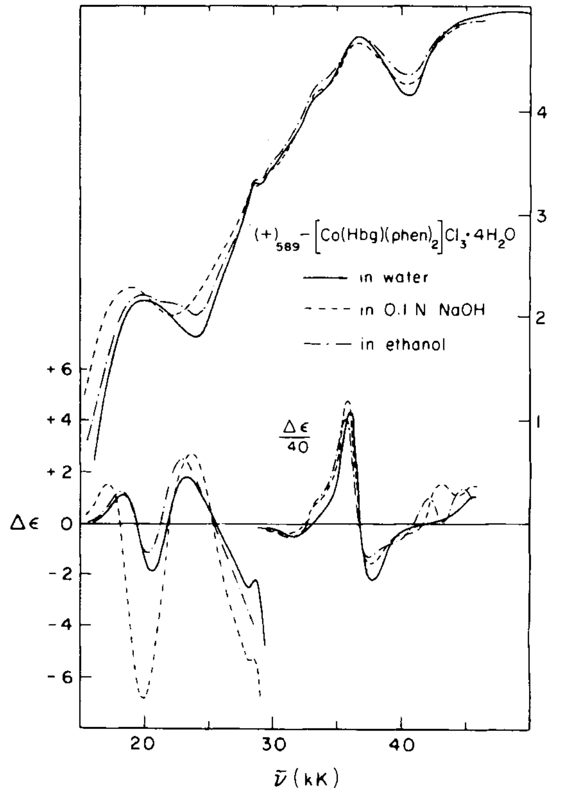

FIGURE 3 Absorption and CD spectra for $(+)_{589}$-[Co(Ilbg)(phen)$_2$]$^{3+}$ in water, in 0.1 M NaCH, and in ethanol.

are larger on the whole than that in water in the first absorption band region. In particular the second peak from the lower energy side is more than 3.5 times larger than that in water. The CD curve in ethanol does not differ drastically from that in water. The second peak from the lower energy side, however, is decreased in intensity and the third peak is increased in intensity. It is worthwhile to note that the solvent effect on the third peak in the CD curve is also prominent in the absorption spectrum, showing a new shoulder at the corresponding position, as mentioned above. The absorption band at 36.8 kK in water arises from the intraligand transition of phenanthroline.[12] The CD curve in water shows plus and minus peaks at 36.0 and 37.7 kK, respectively, in the intraligand transition region, these are the so-called π-π^* exciton bands.[13-15] The CD spectra in 0.1 M NaOH aqueous solution and in ethanol show a similar pattern to that in water in this region.

The absorption and CD spectra of $(+)_{589}$-$[\mathrm{Co}(\mathrm{dipy})_2(\mathrm{Hbg})]^{3+}$ in water, 0.1 M NaOH aqueous solution, and ethanol are shown in Figure 4. The first absorption maximum in water is located at 20.2 kK, and that in 0.1 M NaOH aqueous solution is shifted to the lower energy side and the intensity of it is a little higher than in water. A similar phenomenon was also observed in the absorption spectrum of the corresponding phenanthroline complex. In ethanol the trough located at the higher energy side of the first absorption band is much more shallow than that in water. In the case of the corresponding phenanthroline complex the first absorption band had a shoulder on the higher energy side as mentioned above. The CD spectra in all three solvents show three bands of alternating sign, (–)(+)(–), in the first absorption band region. It is to be noted that the CD intensity in 0.1 M NaOH aqueous solution is higher than that in water over the whole region. The corresponding phenanthroline complex in 0.1 M NaOH aqueous solution had higher CD intensity mainly in the first absorption band region. The CD curve in ethanol does not differ very much from that in water. Minor solvent effects, however, are observed as for the absorption spectrum. The first and second CD peaks from the lower energy side decrease their intensities and the third peak increases its intensity. The absorption band at 33.1 kK in water arises from the intraligand transition of dipyridyl. The CD curve in water shows a positive and a negative π-π^* exciton band[13-15] in this region. The CD spectrum in ethanol shows a similar pattern to that in water, while that in 0.1 M NaOH aqueous soultion shows a different trend in this region. The latter is probably caused by overlap with other transitions, for example, charge transfer transitions related to biguanide.

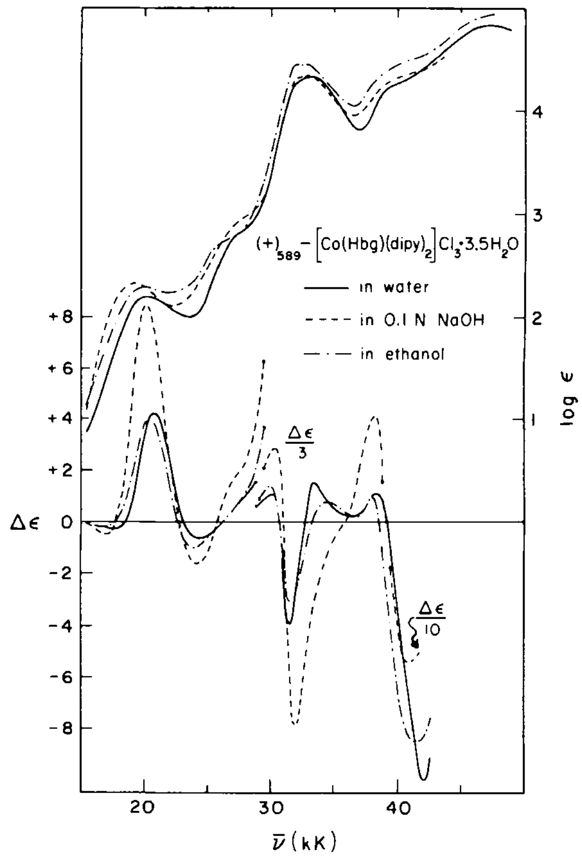

FIGURE 4 Absorption and CD spectra for $(+)_{589}$-$[\mathrm{Co}(\mathrm{dipy})_2(\mathrm{Hbg})]^{3+}$ in water, in 0.1 M NaOH, and in ethanol.

As mentioned above, solvent effects in ethanol were observed for $(+)_{589}$-$[\mathrm{Co(Hbg)(phen)_2}]^{3+}$ and $(+)_{589}$-$[\mathrm{Co}(\mathrm{dipy})_2(\mathrm{Hbg})]^{3+}$ (Figure 3 and 4). Similar solvent effects were observed for $[\mathrm{Co(acac)_2L}]^+$ complexes (L = dipy, phen, en, or tn)[11] and also for $[\mathrm{Cr(acac)_2(en)}]^+$ and the corresponding 3-chloro or 3-bromoacetylacetonato complexes.[16] It is to be noted, however, that solvent effects are observed in both absorption and CD spectra for the present complexes, whereas solvent effects were observed mainly in CD spectra for the complexes investigated previously.

If the CD intensities in the intraligand absorption band region of the diamine are compared between $(+)_{589}$-$[\mathrm{Co(Hbg)_2(phen)}]^{3+}$ and $(+)_{589}$-$[\mathrm{Co(Hbg)(phen)_2}]^{3+}$ (Figures 1 and 3), and between

$(+)_{589}$-[Co(dipy)(Hbg)$_2$]$^{3+}$ and $(+)_{589}$-[Co(dipy)$_2$-(Hbg)]$^{3+}$ (Figures 2 and 4), the bis(diamine) complex has higher intensities for each pair. In the bis-(diamine) complexes there is an interaction of long-axis-polarized ligand transitions, causing high intensity π-π^* resonance splitting,[13-15] which is the reason for the above phenomenon. When π-π^* exciton CD bands are compared between active [Co(phen)$_3$]$^{3+}$ and [Co(Hbg)(phen)$_2$]$^{3+}$, the former[15] has higher intensity. In the case of a comparison between active [Co(dipy)]$^{3+}$ and [Co(dipy)$_2$(Hbg)]$^{3+}$, the former has much higher intensity. This is due to the increase of the number of diamine ligands which interact with each other to cause π-π^* exciton CD bands.

Absolute Configuration

The bisbiguanide complexes, $(+)_{589}$-[Co(Hbg)$_2$-(phen)]$^{3+}$ and $(+)_{589}$-[Co(dipy)(Hbg)$_2$]$^{3+}$, have similar CD patterns showing a plus peak and a minus peak listing from the lower energy side in the first absorption band region in all solvents (Figures 1 and 2). This fact suggests that both complexes have the same absolute configuration. The CD curve[5] of $(-)_{589}$-[Co(Hbg)$_3$]$^{3+}$, of which absolute configuration has been determined to be Λ by X-ray analysis,[7] is the reverse of those of the above two complexes, showing a minus peak and a plus peak from the lower energy side in the first absorption band region. On this basis, the absolute configuration of $(+)_{589}$-[Co(Hbg)$_2$(phen)]$^{3+}$ and $(+)_{589}$-[Co(dipy)(Hbg)$_2$]$^{3+}$ may be assigned to be Δ.

In the case of monobiguanide complexes, $(+)_{589}$-[Co(Hbg)(phen)$_2$]$^{3+}$ and $(+)_{589}$-[Co(dipy)$_2$-(Hbg)]$^{3+}$, the CD pattern in all solvents is very similar but signs are reversed in the first absorption band region (Figures 3 and 4). The CD spectrum of $(+)_{589}$-[Co(Hbg)(phen)$_2$]$^{3+}$ shows (+)(−)(+) peaks and that of $(+)_{589}$-[Co(dipy)$_2$(Hbg)]$^{3+}$ shows (−)(+)(−) peaks listing from the lower energy side. Therefore these two complexes should have the opposite absolute configuration. When the CD spectra of $(+)_{589}$-[Co(Hbg)$_2$(phen)]$^{3+}$ and $(+)_{589}$-[Co(Hbg)(phen)$_2$]$^{3+}$ (Figures 1 and 3) are compared, it seems that two peaks at the lowest energy side correspond well showing a positive peak and a negative peak from the lower energy side. The fact that both second negative peaks from the lower energy side are located nearly at the same position as the corresponding first absorption maximum, respectively, supports this consideration. Furthermore the third peak from the lower energy side in the CD spectrum of $(+)_{589}$-[Co(Hbg)-(phen)$_2$]$^{3+}$ is affected rather drastically by ethanol, and the absorption component at that approximate position is also affected by ethanol. These facts indicate that the third peak is not reliable for the determination of absolute configuration. Accordingly the absolute configuration of $(+)_{589}$-[Co(Hbg)-(phen)$_2$]$^{3+}$ would be assigned to be Δ as for $(+)_{589}$-[Co(Hbg)$_2$(phen)]$^{3+}$. Consequently $(+)_{589}$-[Co(dipy)$_2$(Hbg)]$^{3+}$ should have the Λ absolute configuration.

It has often been assumed that the π-π^* exciton splitting should be (+) and (−) from the lower energy side if the complex has the Λ absolute configuration.[14] This consideration was derived from the dipole-dipole approximation. Hawkins,[12] however, objects to the simple rule, and emphasizes that great care must be taken in the correct assignment of the π-π^* exciton splitting components, because in most cases the interactions leading to the exciton resonance splitting cannot be simplified to dipole-dipole interactions. Ferguson *et al.*[15] assigned the Δ absolute configuration for d-[Co(phen)$_3$]$^{3+}$ which shows (+) and (−) π-π^* exciton splitting from the lower energy side and also Λ for ℓ-[Co(dipy)$_3$]$^{3+}$ which shows (−) and (+) π-π^* exciton splitting from the lower energy side. In the present cases $(+)_{589}$-[Co(Hbg)(phen)$_2$]$^{3+}$, which was assigned to be Δ, has (+) and (−) splitting components from the lower energy side. Moreover $(+)_{589}$-[Co(dipy)$_2$(Hbg)]$^{3+}$, which was assigned to be Λ, has (−) and (+) splitting components from the lower energy side. These patterns correspond well with Ferguson's assignment of the absolute configuration for d-[Co(phen)$_3$]$^{3+}$ and ℓ-[Co-(dipy)$_3$]$^{3+}$. These considerations support Hawkin's stand[12] that the exciton resonance splitting cannot be explained by the simple dipole-dipole approximation.

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REFERENCES

1. Present Address: The Department of Chemistry, University of Tsukuba, Ibaraki, 300–31 Japan.
2. P. Ray, *Chem. Rev.*, **61**, 313 (1961).
3. K. Michelsen, *Acta Chem. Scand.*, **19**, 1175 (1965).
4. G. R. Brubaker and L. E. Webb, *J. Am. Chem. Soc.*, 91, 7199 (1969).
5. K. Igi, T. Yasui, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, **44**, 426 (1971).

6. H. Kawaguchi and B. E. Douglas, *J. Coord. Chem.*, **5**, 115 (1976).
7. M. R. Snow, *Acta Cryst.*, **B30**, 1850 (1974).
8. A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).
9. F. M. Jaeger and J. A. van Dijk, *Z. Anorg. Chem.*, **227**, 305 (1936).
10. R. L. Dutta and S. Sarkar, *J. Indian Chem. Soc.*, **44**, 832 (1967).
11. K. Kashiwabara, K. Igi and B. E. Douglas, *Bull. Chem. Soc. Japan*, **49**, 1573 (1976).
12. C. J. Hawkins, *Absolute Configuration of Metal Complexes*, Wiley-Interscience, N. Y. (1971).
13. S. F. Mason, *Inorg. Chim. Acta Rev.*, **2**, 89 (1968).
14. B. Bosnich, *Acc. Chem. Res.*, **2**, 266 (1969).
15. J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire and H. Lip, *Inorg. Chem.*, **8**, 771 (1969).
16. S. Kaizaki, J. Hidaka and Y. Shimura, *Inorg. Chem.*, **12**, 142 (1973).