

Trigonal Splitting of Tris(diamine)cobalt(III) Complexes. An Application of Natural and Magnetic Circular Dichroism

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The absorption, circular dichroism, and magnetically induced circular dichroism spectra are reported for $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(+)\text{(pn)}_3]^{3+}$ in aqueous solution with and without various electrolytes. A method of interpretation of the MCD spectra with respect to the CD spectra is proposed. This interpretation suggests there is considerable trigonal splitting ($\sim 1500 \text{ cm}^{-1}$) in solution, and refutes the possibility that the two bands in the $T_{1g}(\text{O}_h)$ region originate from different conformational isomers in solution.

Introduction

Optical activity in tris-diamine transition metal complexes has been shown to arise from two spatial effects, namely the configuration of the chelate rings and the conformation of each ring about the metal ion. In the case of an optically active ligand, such as 1,2-propanediamine, a third possible source is a vicinal effect arising from the asymmetric center of each ligand. Since the absolute configuration of the ligand determines the preferred ring conformation, it is difficult to distinguish between the conformational and vicinal effects.

Although d-d transitions are electronically forbidden, several theories have been proposed to account for their observed CD dispersions. The origin of optical activity exhibited by the visible absorption bands of transition metal complexes is ascribed in a number of current theories solely to distortions of ligand atoms,^{1,2} or their orbitals,^{3,4} or their charges,⁵ from octahedral dispositions, as well as mixing of d-d with charge transfer transitions.⁶

The assignment of the solution CD bands for $[\text{Co}(\text{en})_3]^{3+}$ has received much attention in the last five years. Woldbye⁷ suggested that the two CD peaks occurring in the $T_{1g}(\text{O}_h)$ region result from the different conformational isomers present in solution. From polarized crystal spectra at 4.2°K Ballhausen and Dingle⁸ estimate the trigonal splitting to be very small ($\sim 10 \text{ cm}^{-1}$). Denning,⁹ on the other hand, using po-

larized crystal and absorption spectra, attributed the two CD peaks in the $T_{1g}(\text{O}_h)$ region (in solution and in the crystal) to Jahn-Teller components instead of trigonal splitting.

Mason and McCaffery,¹⁰ assuming D_3 symmetry, have assigned the two peaks of opposite sign in the $T_{1g}(\text{O}_h)$ region for the solution CD spectra as E_a for the dominant low energy band and A_2 for the weaker high energy band. Using a molecular orbital model, Karipides and Piper¹¹ calculated the trigonal splitting to be approximately 150 cm^{-1} and Schäffer⁴ estimated the trigonal splitting to be about 120 cm^{-1} .

McCaffery *et al.*¹² investigated the solution CD of the lel isomer of $[\text{Co}(\text{pn})_3]^{3+}$ ($\Lambda(+)$ - $[\text{Co}(+)\text{(pn)}_3]^{3+}$)¹³ for which only one conformational isomer with the methyl groups in equatorial positions is present. They found two peaks in the first band region for the lel isomer, but only one band for the ob ($\Lambda(+)$ - $[\text{Co}(-)\text{(pn)}_3]^{3+}$) isomer. The difference in number of peaks was attributed to a shift in the frequency interval between the E_a and the A_2 transitions for the different chelate ring conformations.

Recently Gollogly and Hawkins¹⁴ have shown that the E_a transition has a positive Cotton effect for $\Lambda(+)$ - $[\text{Co}(\text{tm})_3]^{3+}$.¹⁵ This is in contradiction with the prediction by Piper¹⁶ that the sign of the E_a band would be reversed relative to corresponding 1,2-diamine complexes if the angle between the two coordinate bonds is greater than 90° . In the case of $\Lambda(+)$ - $[\text{Co}(\text{tm})_3]^{3+}$ this angle is 94.5° , and the E_a band remains positive. This gives support to the empirical rules which relate the sign of the Cotton effect with the distribution of their chelate rings.^{17,18}

The effect of electrolytes on the solution CD spectra of $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{pn})_3]^{3+}$ and related compounds has been investigated.¹⁹⁻²¹ For certain anions (PO_4^{3-} ,

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(11) A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

(12) A. J. McCaffery, S. F. Mason, B. J. Norman and A. M. Sargesen, *J. Chem. Soc.*, **A**, 1504 (1968).

(13) Λ and Δ refer to the absolute configuration and define the chirality or helicity of the ligands about the metal atom. Λ denotes a right handed helix and Δ a left handed helix, see I.U.P.A.C. Information Bulletin, No. 33, 68 (1968).

(14) J. R. Gollogly and C. J. Hawkins, *Chem. Comm.*, 609 (1968).

(15) tm = trimethylenediamine or 1,3-propanediamine.

(16) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(17) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 1969 (1965).

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 (4) C. Schäffer, *Proc. Roy. Soc. A*, **297**, 96 (1967).
 (5) M. Shinada, *J. Phys. Soc. Japan*, **19**, 1607 (1964).
 (6) S. F. Mason and B. J. Norman, *Chem. Comm.*, 48 (1965).
 (7) F. Woldbye, *Rec. Chem. Progr.*, **24**, 197 (1963).
 (8) R. Dingle and C. J. Ballhausen, *Mat. Fys. Medd Dan. Vid. Selsk.*, **35**, 1 (1967).
 (9) R. G. Denning, *Chem. Comm.*, 120 (1967).

SeO_4^{2-} , SeO_3^{2-}) the magnitudes of the E_a and A_2 transitions are decreased and increased, respectively. Mason accounts for this change in intensity by proposing a mixing of the d-d transitions with the charge transfer transition associated with the anion and the complex.

It should be obvious that the interpretation of the solution CD spectrum of $[\text{Co}(\text{en})_3]^{3+}$ is still controversial. More specifically, it is not known to what extent crystal results can be usefully applied to solution spectra. This paper will consider the interpretation of the solution CD spectra in conjunction with the magnetically induced circular dichroism (MCD) spectra of $[\text{Co}(\text{en})_3]^{3+}$.

In the last several years there has been a great resurgence of interest in magnetically induced circular dichroism.²²⁻²⁵ This has been stimulated by the great success of natural circular dichroism as a stereochemical and spectroscopic tool, by the availability of recording instruments and by high field strength superconducting magnets. Magnetically induced circular dichroism has found some useful applications in the field of transition metal chemistry.²⁶⁻³²

Three parameters (A , B , C) are used to describe quantitatively the dispersions found in magnetically induced circular dichroism (MCD). These Faraday parameters depend upon the energy states of the molecule under study. A terms are produced by the Zeeman splitting of the ground or excited states, and hence occur only when at least one of the states is degenerate. The mixing of states caused by the perturbation of the magnetic field gives rise to B terms. Theoretically a B term exists for every electron transition. C terms arise from the repopulation of the ground state sublevels as a result of Zeeman splitting, and hence are present only when the ground state is degenerate. The graphical representation of these parameters in terms of gaussian band shapes are given in Figure 1.

It is the purpose of this work to show how MCD and CD might be interpreted concomitantly to shed some light upon the disputed CD spectral interpretation of $[\text{Co}(\text{en})_3]^{3+}$ in solution.

Experimental Section

The MCD of racemic $[\text{Co}(\text{en})_3]^{3+}$, $(\pm)-[\text{Co}(\pm)-(\text{pn})_3]^{3+}$ and $(\pm)-[\text{Co}(\pm)(\text{pn})_2(\mp)\text{pn}]^{3+}$ and the natural CD of $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ and $\Lambda(+)-[\text{Co}(+)\text{-(pn)}_3]^{3+}$ in water and various aqueous electrolyte solutions were measured. The CD spectra were obtain-

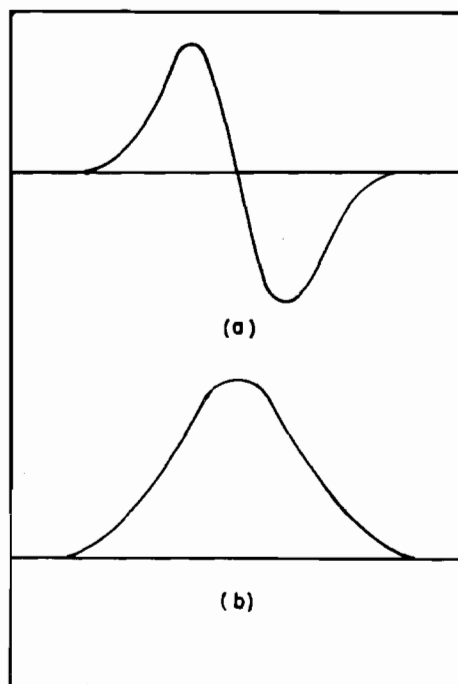


Figure 1. Graphical representations for: (a) A terms, (b) B and C terms, using gaussian band shapes.

ed from a Roussel-Jouan recording dichrograph at room temperature. For all solutions the complex concentration was $2.1 \times 10^{-3} M$ and the total electrolyte concentration was $0.25 M$. The electrolytes that were used were K_3PO_4 , Na_2SeO_4 and Na_2SeO_3 . Spectra were also obtained in $2 M \text{Na}_2\text{SeO}_3$, and both concentrated (99 percent) and $0.01 M$ trifluoroacetic acid.

The magnetic circular dichroism was obtained from a Jasco recording ORD-CD spectrophotometer in conjunction with a superconducting magnet obtained from Gardner Cryogenics. All spectra were recorded at a constant magnetic field strength of 65,000 gauss and at room temperature. For all solutions the complex concentration was $2 \times 10^{-2} M$ and the total electrolyte concentration was $0.25 M$. Since the concentration of electrolyte chosen was that observed to have a limiting effect,^{19,20} the higher concentration of complex for MCD should have a much smaller effect than would a significant further increase in electrolyte concentration.

The MCD of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ($4.6 \times 10^{-2} M$) was obtained at room temperature. All absorption spectra were recorded on a Cary 14 recording spectrophotometer. Representative absorption, CD and MCD spectra are given in Figure 2. All dispersions are reported in terms of $\Delta\epsilon = (\epsilon_l - \epsilon_r)$ which has the units $\text{cm}^{-1} \text{moles}^{-1} \times 1$ for CD and $\text{cm}^{-1} \text{moles}^{-1} \times 1 \times \text{gauss}^{-1}$ for MCD. For racemic, lel, and mixed $[\text{Co}(\text{pn})_3]^{3+}$ and $\Lambda(+)-[\text{Co}(+)\text{-(pn)}_3]^{3+}$ the concentrations of complex and electrolytes are the same as those for $[\text{Co}(\text{en})_3]^{3+}$.

The $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ were prepared by standard methods.^{33,34} Racemic, lel and mixed

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

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(28) P. J. Stephens, A. J. McCaffery, and P. N. Schatz, *Inorg. Chem.*, **7**, 1923 (1968).

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(30) S. Lin and H. Eyring, *J. Chem. Phys.*, **42**, 1780 (1965).

(31) P. J. Stephens, *Inorg. Chem.*, **4**, 1690 (1965).

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(33) J. B. Work, *Inorg. Syn.*, **2**, 222.

(34) J. Bjerrum and I. R. McReynolds, *Ibid.*, **2**, 217.

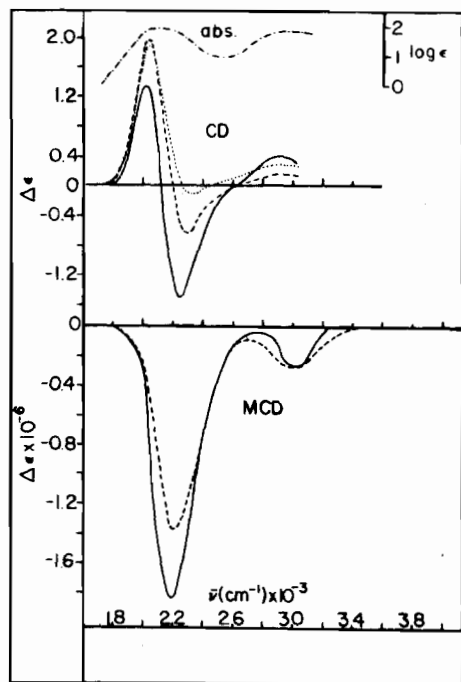


Figure 2. (—) represents the absorption spectrum for $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$, (---) the CD for $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ in water, (—) CD for $\Lambda(+)-[\text{Co}(\text{pn})_3]^{3+}$ in 0.25 M K_3PO_4 , (---) CD of $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ in water. In the lower figure are the MCD spectra for, (—) $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ and (---) $(\pm)-[\text{Co}(\text{en})_3]^{3+}$.

$[\text{Co}(\text{pn})_3]^{3+}$ and $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ were obtained from L. Froebe in this laboratory. $\Lambda(+)-[\text{Co}(\text{pn})_3]^{3+}$ was resolved by a standard procedure.³⁵ Absorption coefficients and nitrogen analyses were checked for all compounds as chloride salts to assure purity.

A Dupont 310 Curve Analyzer was used with gaussian band shapes to resolve all the curves reported.

Results and Discussion

Recently Stephens *et al.*²⁸ reported the MCD spectra of $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ in aqueous solution. From the general similarity of band shapes it was proposed that the $[\text{Co}(\text{en})_3]^{3+}$ spectrum relied primarily upon a vibronic mechanism, as in the case of $[\text{Co}(\text{NH}_3)_6]^{3+}$. Little mention was made of the fact that the intensities of the $[\text{Co}(\text{en})_3]^{3+}$ peaks were twice those of $[\text{Co}(\text{NH}_3)_6]^{3+}$. Upon close reexamination of these spectra in this laboratory an alternate interpretation is proposed.

In the visible region two electronic transitions ($A_{1g} \rightarrow T_{1g}$ and $A_{1g} \rightarrow T_{2g}$) are seen for $[\text{Co}(\text{NH}_3)_6]^{3+}$. Transitions of this type should show both *A* and *B* Faraday dispersions. A possible resolution of this spectrum into its *A* and *B* components for each $A \rightarrow T$ transition is shown in Figure 3. It is noteworthy that the $\Delta\epsilon_{\text{max}}$ for the *B* term and the inflection point for the *A* term occur at $21,000 \text{ cm}^{-1}$, which is the

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maximum for the absorption spectrum. A similar analysis was carried out for the band at $29,500 \text{ cm}^{-1}$. Thus the experimental MCD maxima ($21,600 \text{ cm}^{-1}$ and $29,100 \text{ cm}^{-1}$) do not correspond with the absorption maxima ($21,000 \text{ cm}^{-1}$ and $29,500 \text{ cm}^{-1}$) for a one electron transition. The inclusion of both *A* and *B* terms brings the positions of the transitions for CD and MCD into coincidence. The *A* term dispersion was neglected earlier.²⁸

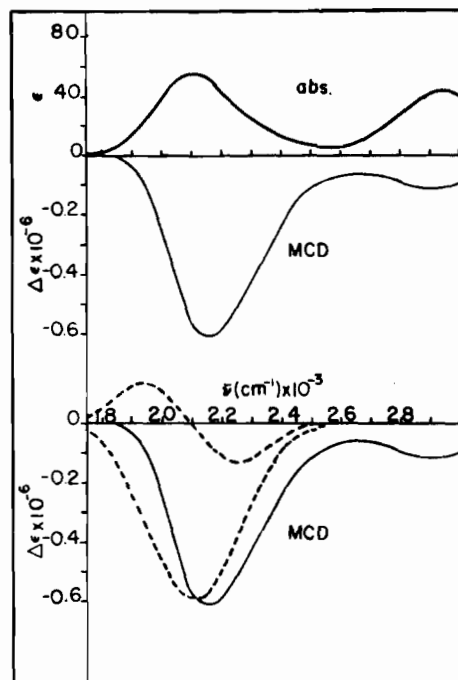


Figure 3. Above are the absorption and MCD spectra for $[\text{Co}(\text{NH}_3)_6]^{3+}$ in water. Below is the MCD interpretation in terms of an *A* and a *B* term at $21,000 \text{ cm}^{-1}$.

By replacing the ammonias in $[\text{Co}(\text{NH}_3)_6]^{3+}$ by ethylenediamines (*en*), the symmetry of the complex is lowered from O_h to D_3 . This D_3 perturbation causes the T_{1g} level to split into an E_a and an A_2 component, and the T_{2g} level to split into an E_b and an A_1 level. The MCD spectrum of $[\text{Co}(\text{en})_3]^{3+}$ is found to undergo no change in band shape or band position upon addition of various electrolytes. Likewise, the MCD spectra of racemic $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ and $(\pm)-[\text{Co}(\pm)(\text{pn})_2(\mp)\text{pn}]^{3+}$ are identically the same in water and upon addition of various electrolytes.

One should expect a close correspondence in the curve analysis for absorption, natural CD, and MCD, since the same electronic transitions are involved. To illustrate, consider the MCD of $[\text{Co}(\text{en})_3]^{3+}$ in water (Figure 2). Here the band maximum in the first band region occurs at $22,000 \text{ cm}^{-1}$, while the two CD peaks occur at $20,300 \text{ cm}^{-1}$ and $23,400 \text{ cm}^{-1}$, and the absorption maximum occurs at $21,400 \text{ cm}^{-1}$. The higher energy position of the first MCD band (relative to the CD and absorption), and its slight tail toward higher energy make it difficult to interpret without including a second band in the higher energy region. If Mason's

value¹⁰ for the position of the E_a band ($21,050\text{ cm}^{-1}$) is used as the E_a band position, and if the trigonal splitting is considered to be very small ($<150\text{ cm}^{-1}$), then it is not possible to account for the MCD band position and width in terms of the sum of individual A and B band shapes. The spectra of the propylenediamine complexes greatly resemble the ethylenediamine complexes, and cannot be resolved in terms of a small trigonal splitting.

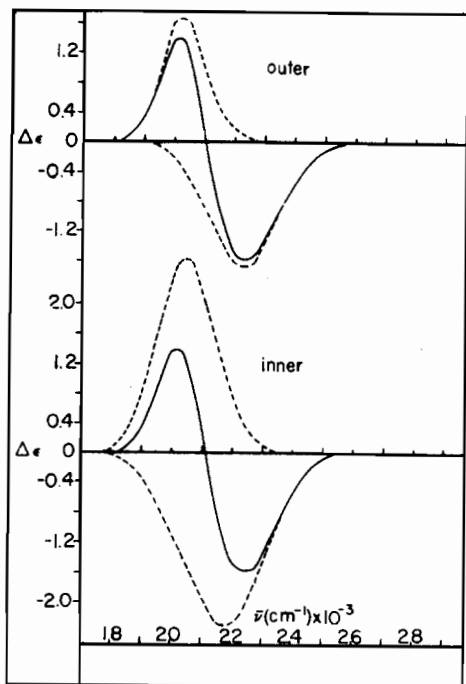


Figure 4. The graphical representation of the outer ($20,300\text{ cm}^{-1}$ and $22,450\text{ cm}^{-1}$) and inner ($20,500\text{ cm}^{-1}$ and $21,750\text{ cm}^{-1}$) limits for the CD spectrum of $\Lambda(+)-[\text{Co}(+)(\text{pn})_3]^{3+}$ in $0.25\text{ M K}_3\text{PO}_4$.

By the use of a Dupont 310 curve analyzer it was found that another band was necessary in the $21,000\text{--}23,000\text{ cm}^{-1}$ region to account for the experimentally observed MCD band shape. This empirical evidence for a second band seems to support a greater trigonal splitting in solution than in the crystal. Earlier estimates of the splitting^{4,8-11} have been based upon crystal spectra almost entirely. The much larger peak separation observed for solution CD of $[\text{Co}(\text{en})_3]^{3+}$ has been rationalized as the result of extensive cancellation of the peaks of opposite sign.^{10,11} The results of the present study also argue against the possibility of the second CD band in the $T_{1g}(\text{O}_h)$ region as arising from different conformational isomers. This second conclusion can be made since the MCD spectra of $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ and $(\pm)-[\text{Co}(\pm)(\text{pn})_2(\mp)\text{pn}]^{3+}$, where only one conformational isomer is present in solution, are identically the same. Thus, conformational effects seem to have little effect upon MCD spectra. Therefore, the necessity of a second band of higher energy in the first band region requires that this band originates from the $A_1 \rightarrow A_2$ transition, not from a conformational isomer.

In order to make empirical analyses of these MCD spectra, it is necessary to reexamine the solution CD spectra of $\Lambda(+)-[\text{Co}(+)(\text{pn})_3]^{3+}$ in water and in different electrolytes to establish certain energy boundaries for the E_a and A_2 transitions under which all the CD and MCD spectra can be interpreted. The problem of establishing limits for the E_a and A_2 transitions for the CD spectra of $\Lambda(+)-[\text{Co}(+)(\text{pn})_3]^{3+}$ can be most easily seen for the spectrum in $0.25\text{ M K}_3\text{PO}_4$. Here both the E_a and the A_2 bands have comparable intensities, which makes the curve fitting somewhat more restrictive. Assuming the curve to be a composite of overlapping E_a (positive, lower energy) and A_2 (negative, higher energy) transitions with gaussian band shapes, all possible combinations which gave satisfactory fits were recorded (Figure 4). Lower and upper limits as indicated in the figure were established for the E_a and A_2 bands. The E_a band was found to vary from $20,500$ to $20,300\text{ cm}^{-1}$ and the A_2 band from $22,450$ to $21,750\text{ cm}^{-1}$. These limits are felt to be significant since the observed splitting is about $58\text{ m}\mu$, which is nearly twice that considered by Wellman and Djerassi.³⁶ Representative values of $20,400\text{ cm}^{-1}$ for the E_a and $22,150\text{ cm}^{-1}$ for the A_2 were found to fit all the CD curves regardless of the electrolyte present, by changing the individual peak intensities. Although the values used to fit these curves are only empirical approximations, they do provide evidence for substantial trigonal splitting in solution.

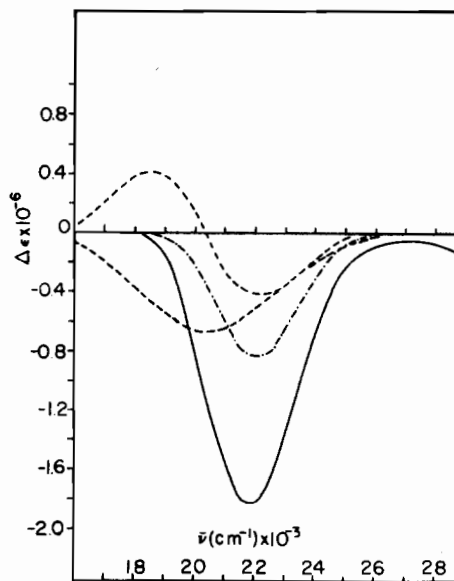


Figure 5. The MCD interpretation of $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ in water, in terms of A and B terms at $20,400\text{ cm}^{-1}$ (E_a) and a B term at $22,150\text{ cm}^{-1}$ (A_2).

Using these empirically established positions for the E_a and A_2 transitions, the MCD spectrum of $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ in water was interpreted as shown in Figure 5. The combination of the A and the B terms

(36) K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscovitz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 66 (1965).

(expected for an A_1-E_a transition) account for the rather sharp low energy side of the first band. The single B term expected for the A_1-A_2 transition accounts nicely for the broad high energy side of the band. Identical analyses of the MCD spectra of $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ in the various electrolytes were also carried out with the same splitting parameters. A similar interpretation of the second band region ($T_{2g}(O_h)$) was made in terms of the difference between the CD maximum at $28,800\text{ cm}^{-1}$ (E_b) and the MCD maximum at $30,300\text{ cm}^{-1}$ (the A_1 band is forbidden in CD). It was found that a second band (A_1) was needed at $30,500\text{ cm}^{-1}$ to account for the MCD maximum, however this interpretation carries less significance due to the low intensity of the MCD band. Corresponding limits for the CD spectra of $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ in water and various electrolytes were found to be $20,550\text{ cm}^{-1}$ and $22,150\text{ cm}^{-1}$. Using this trigonal splitting the MCD spectra were easily resolved, as for $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$.

Conclusions

The above results can be summarized and accounted for in the following way. The CD spectra for $\Lambda(+)-[\text{Co}(+)(\text{pn})_3]^{3+}$ in water and in various electrolytes are all resolvable in terms of the same splitting parameters and positions, as was also true for $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$. The changes in intensity needed to fit the experimental curves can be accounted for in the following ways. First, Mason²⁰ has suggested that ion-pairing favors the $1e_1$ conformation in $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$, therefore, ion-pairing increases the number of molecules with D_3 symmetry and thus a change in the peak intensities would be expected. Second, the change in intensity might be due to borrowing from the charge transfer band associated with the ion pair as suggested by Mason.¹⁹ In either case it would seem likely that the energy of the electron transitions should remain the same.

After establishing empirical limits, by curve fitting, for the E_a and A_2 transitions from CD spectra, these values were used for the interpretation of the MCD spectra. Good fits were obtained for all the MCD curves reported. Conformational effects should not affect MCD spectra, as evidenced by the similar spectra for $(\pm)-[\text{Co}(\pm)(\text{pn})_3]^{3+}$ and $(\pm)-[\text{Co}(\pm)(\text{pn})_2(\mp)\text{pn}]^{3+}$ where different conformational isomers are present. The necessity of a second band in the $T_{1g}(O_h)$ region requires that this band arise from an electronic transition ($A_1 \rightarrow A_2$) rather than from a conformational isomer. It is proposed in light of the MCD band shape and position for the complex in solution that there is a trigonal A_2 component some 1500 cm^{-1} above the E_a component.

It is realized that this interpretation is empirical and very qualitative, and that the error of the MCD measurements is about 10%. Nevertheless, the band positions and shapes are very reproducible and the noise level is somewhat smaller than previously reported.²⁸

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