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The Effects of Electrolytes on Circular Dichroism Curves of Cationic Complex Ions[1]

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The circular dichroism of $[Co(en)_3]Cl_3$ and several structurally related complexes of lower symmetry has been observed in the presence of a variety of electrolytes. The rotational strengths of the observed transitions are quite sensitive to changes in the symmetry of the complex ion as a result of interaction with the anions. In general, two effects can be identified. One effect, of a directional nature reflected as changes in $R(A_2)$, is related to the preferred orientation of the ion pair between the complex and large highly charged oxy anions. The second effect reflected as general increases in R for all transitions is associated with the random interactions with small anions of low charge. The observed changes in circular dichroism although complicated, in some instances, are an aid to the interpretation of the spectra of complex ions.

Introduction

Recent studies have shown that the addition of electrolytes can have a marked influence on the circular dichroism (CD) of optically active $(+)_{589}$-$[Co(en)_3]Cl_3$ in the visible region of the spectrum.[2] These studies have been extended to the charge-transfer region of the spectrum[3] and the effect of replacing N–H bonds in the ligands with N–D bonds has been studied as well.[4] The ion-pairing effects have been shown to be of value in making spectroscopic assignments.[5] A model was proposed[3] for the ion pair between PO_4^{3-} and the $[Co(en)_3]^{3+}$ ions. This report will present in some detail the effects of a variety of anions on the CD of $(+)_{589}$-$[Co(en)_3]^{3+}$ and some structurally related materials in the 600–350-mμ region of the spectrum.

Experimental Section

The method of Broomhead, Dwyer, and Hogarth[6] was used for the preparation and resolution of $[Co(en)_3]Cl_3$. The preparation[7] and resolution[8] of *cis*-$[Co(en)_2(NO_2)_2]Br$ were accomplished using standard procedures. Resolved $(+)_{546}$-$[Co(en)_2gly]I_2$ (gly = glycine) was obtained from Liu of this laboratory, and the preparation and resolution have been reported.[9] Optically active $[Co(en)_2acac]I_2$ (acac = acetylacetone) was obtained from Haines of this laboratory, and the preparation and resolution have been described elsewhere.[10]

CD curves were recorded with a Roussel–Jouan dichrograph at room temperature. Measurements were made on solutions which were 1.6×10^{-3} *M* with complex and the indicated molarity of electrolyte.

Results

For $(+)_{589}$-$[Co(en)_3]Cl_3$ there are two absorption bands in the visible region at 21,500 and 29,000 cm^{-1}. The CD spectrum (curve 1, Figure 1) has three bands in this region. The low-frequency positive band (E_a) and the negative band (A_2) are due to the splitting of the $A_{1g} \rightarrow T_{1g}$ transitions[11] while the positive band at 29,000 cm^{-1} is denoted by (E_b).

Figure 1 shows the effect of Cl^- on the CD of the $(+)_{589}$-$[Co(en)_3]^{3+}$ ion. One observes a gradual increase in the rotational strength (R, proportional to the area of a CD peak) of all three bands with the increase being largest for E_a. The total increase in R is about 10% for 2 *M* Cl^-, and concentrations of Cl^- up to 4 *M* had no greater effect. The effects of Br^- and I^- are similar but weaker. The Br^- ion produces a larger change than I^-. The effect of F^- ion on $R(E_a)$ is about the same as for Cl^-; however, there is a larger increase in $R(A_2)$. Other singly charged anions including NO_3^- and ClO_4^-, but with the notable exception of OH^-, had a similar but weaker effect compared to Cl^-.

The effect of OH^- is shown in Figure 2. One observes that, while the increase in $R(E_a)$ is the same as for Cl^-, the increases in $R(A_1)$ and $R(E_b)$ are considerably larger. The total increase in $R(E_a)$ and $R(A_2)$ is about 20%.

Figure 3 shows the maximum changes observed in the CD of $(+)_{589}$-$[Co(en)_3]Cl_3$ with additions of doubly charged oxy anions. The effect increases for concentrations up to 0.5 *M* and then remains essentially unchanged up to 2.0 *M*. One observes that there is a considerable increase in $R(A_2)$ while $R(E_b)$ increases only slightly and in general $R(E_a)$ decreases. The effects appear larger for the smaller anions.

In Figure 4, curves 2, 3, and 4 show the effects of PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$, respectively. While $R(A_2)$ increases as $R(E_a)$ decreases, it can be seen that the largest fraction of the increase in $R(A_2)$ is between HPO_4^{2-} and PO_4^{3-} (area between curve 2 and 3 compared to that between 3 and 4) whereas the largest decrease in $R(E_a)$ is between $H_2PO_4^-$ and HPO_4^{2-}.

If one reduces the charge on the complex by substituting a glycinate ion for one ethylenediamine, a second (negative A) CD peak appears on addition of electrolytes. This effect has been noted as an aid in

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[1] Taken from a Ph.D. thesis by H. L. Smith, 1965. This work was supported, in part, by a research grant (GM 10829-07) from the Division of General Medical Studies, Public Health Service.

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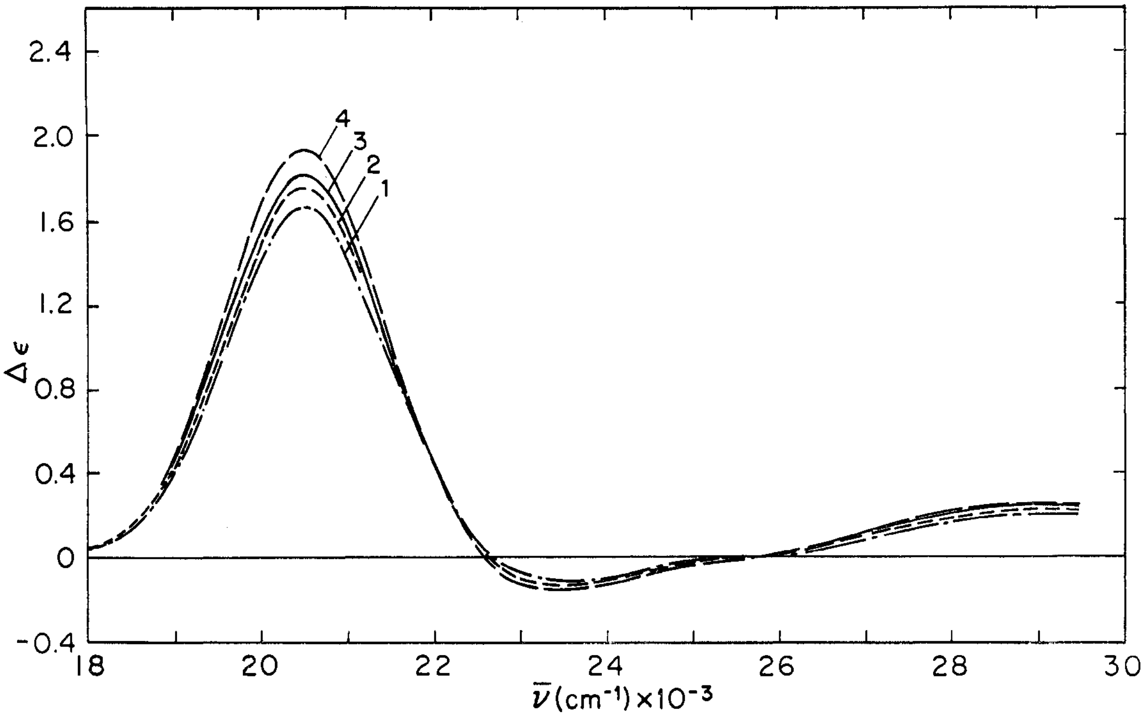

Figure 1.—The effect of NaCl on the circular dichroism of $(+)_{589}$-$[Co(en)_3]Cl_3\cdot H_2O$: (1) no electrolyte added, (2) 0.5 *M* NaCl, (3) 1.0 *M* NaCl, (4) 2.0 *M* NaCl.

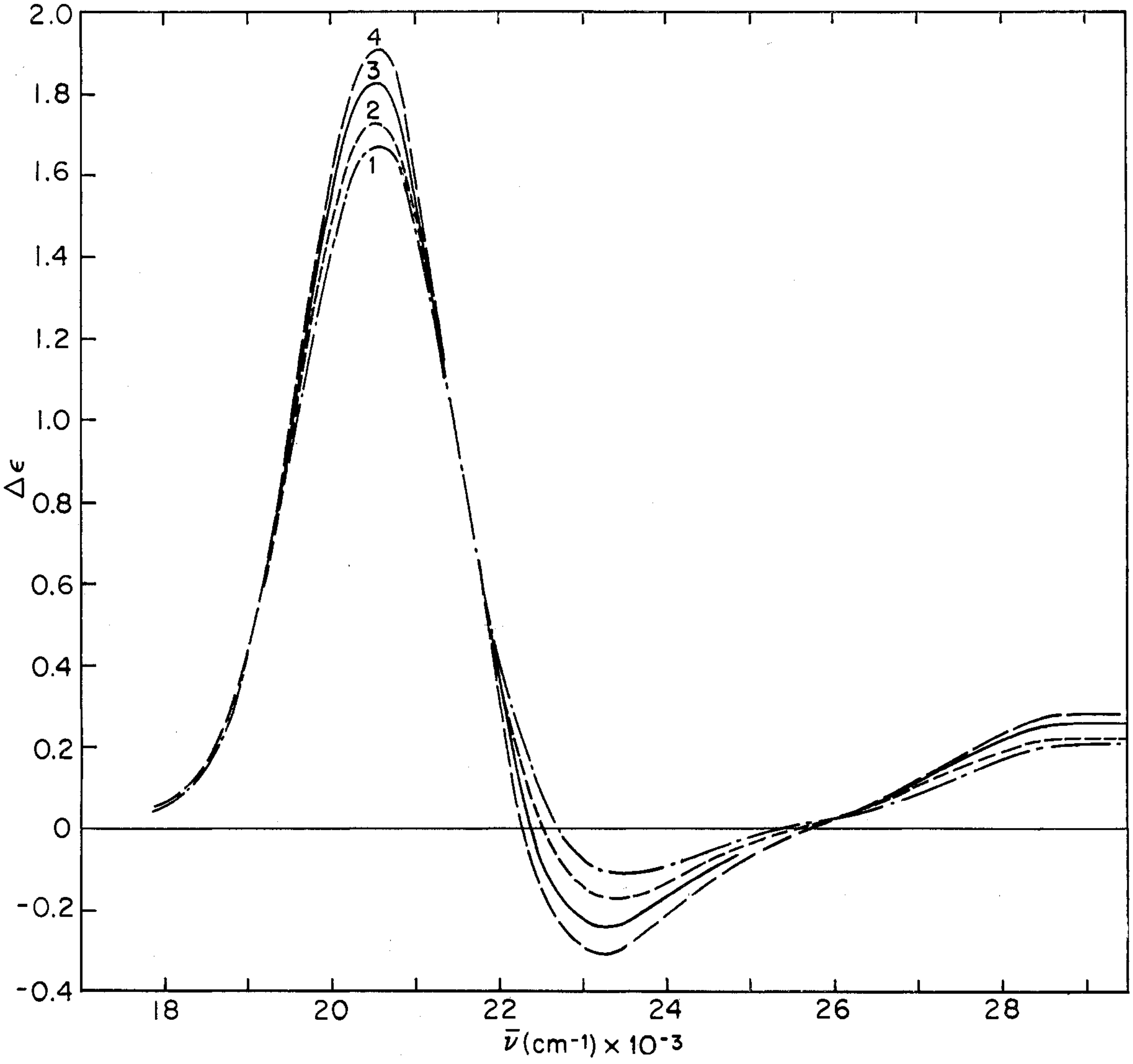

Figure 2.—The effect of NaOH on the circular dichroism of $(+)_{589}$-$[Co(en)_3]Cl_3\cdot H_2O$: (1) no electrolyte added, (2) 0.1 *M* NaOH, (3) 1.0 *M* NaOH, (4) 3.0 *M* NaOH.

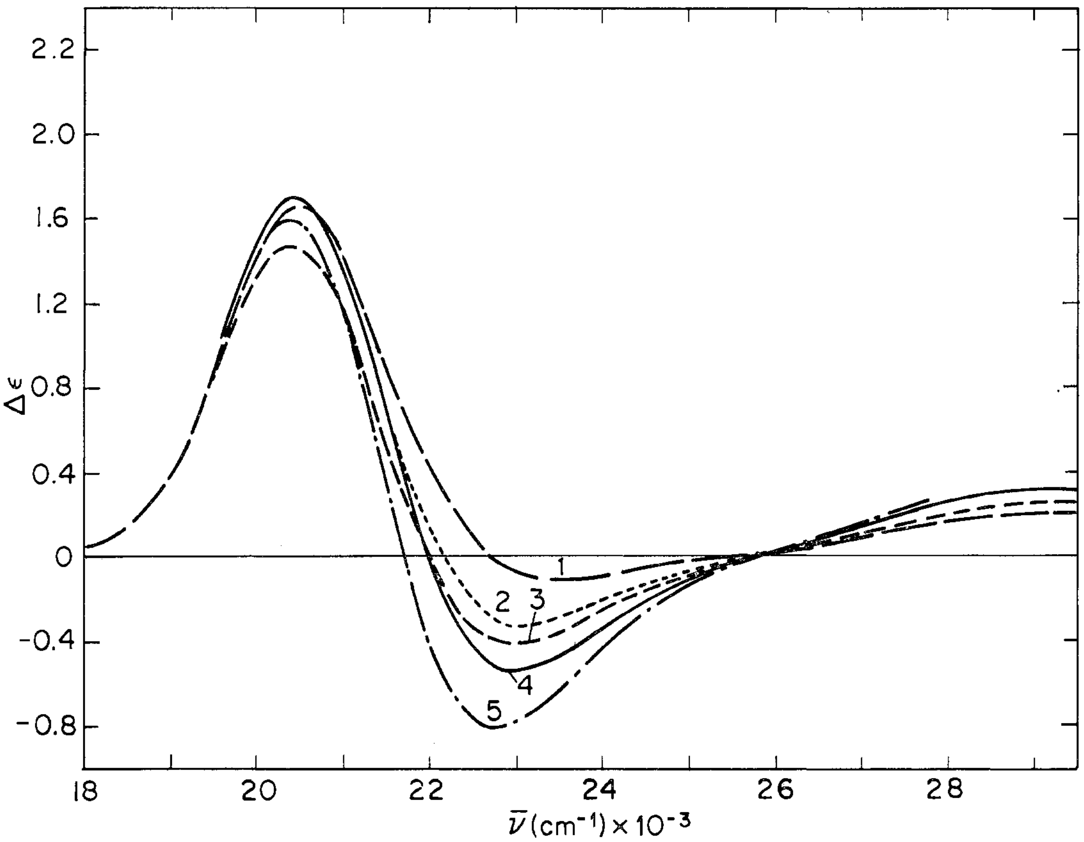

Figure 3.—Effects of some doubly charged anions on the circular dichroism of $(+)_{589}$-$[Co(en)_3]Cl_3\cdot H_2O$: (1) no electrolyte added, (2) 0.5 *M* Na_2SO_4, (3) 0.5 *M* $Na_2S_2O_3$, (4) 0.5 *M* Na_2SO_3, (5) 0.5 *M* Na_2CO_3.

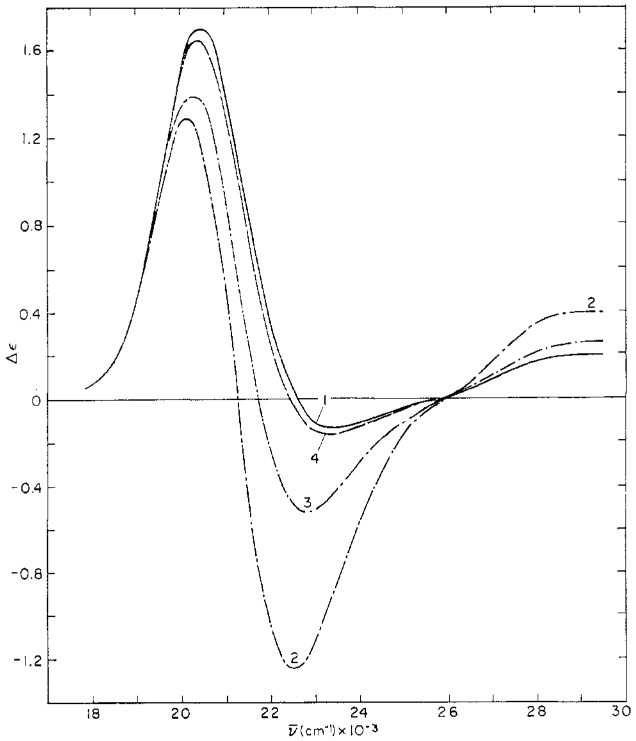

Figure 4. Effects of phosphate ions on the circular dichroism of $(+)_{589}$-$[Co(en)_3]Cl_3\cdot H_2O$: (1) no electrolyte added, (2) 0.05 *M* Na_3PO_4, (3) 0.05 *M* Na_2HPO_4, (4) 0.05 *M* NaH_2PO_4.

the interpretation of CD curves where the peaks are poorly resolved.[5,9] The effects of the various ions are qualitatively the same as for the tris(ethylenediamine) compound although they are greatly reduced (Figure 5).

When the symmetry and charge of the complex are lowered further, the effect of electrolytes is quite small. This is demonstrated with the $(+)_{589}$-*cis*-$[Co(en)_2(NO_2)_2]Br$ complex in Figure 6. The effects are very small for the ions used with $(+)_{589}$-$[Co(en)_3]Cl_3$ other than those shown. Electrolytes had no effect on the CD of the $(+)_{589}$-$[Co(en)_2acac]I_2$ which contains one unsaturated ligand.

Discussion

Mason and Norman[3] have demonstrated that hydrogen bonding plays an important role in the ion-pair formation between PO_4^{3-} and $[Co(en)_3]^{3+}$ or $(+)$-$[Co(+\text{-}pn)_3]^{3+}$. In their model, three of the phosphate oxygen atoms are hydrogen bonded to the hydrogen atoms whose N–H bonds parallel the C_3 axis of the complex. They propose that the charge-transfer transition of the ion pair having E symmetry mixes with the E transition so that E_b borrows rotational strength from E_a and A_2 increases because of the removal of the overlapping E_a. This assumption accounts for the equal changes in $R(E_a)$ and $R(A_2)$.

Hydrogen bonding could occur in a similar way between PO_4^{3-} and the amine groups on one octahedral face of $[Co(en)_2gly]^{2+}$. It is reasonable that the effect is reduced (Figure 5) because of the lower charge and the fact that only one face is available for this type of interaction. With *cis*-$[Co(en)_2(NO_2)_2]^+$ the interaction with PO_4^{3-} cannot be of this same type and might

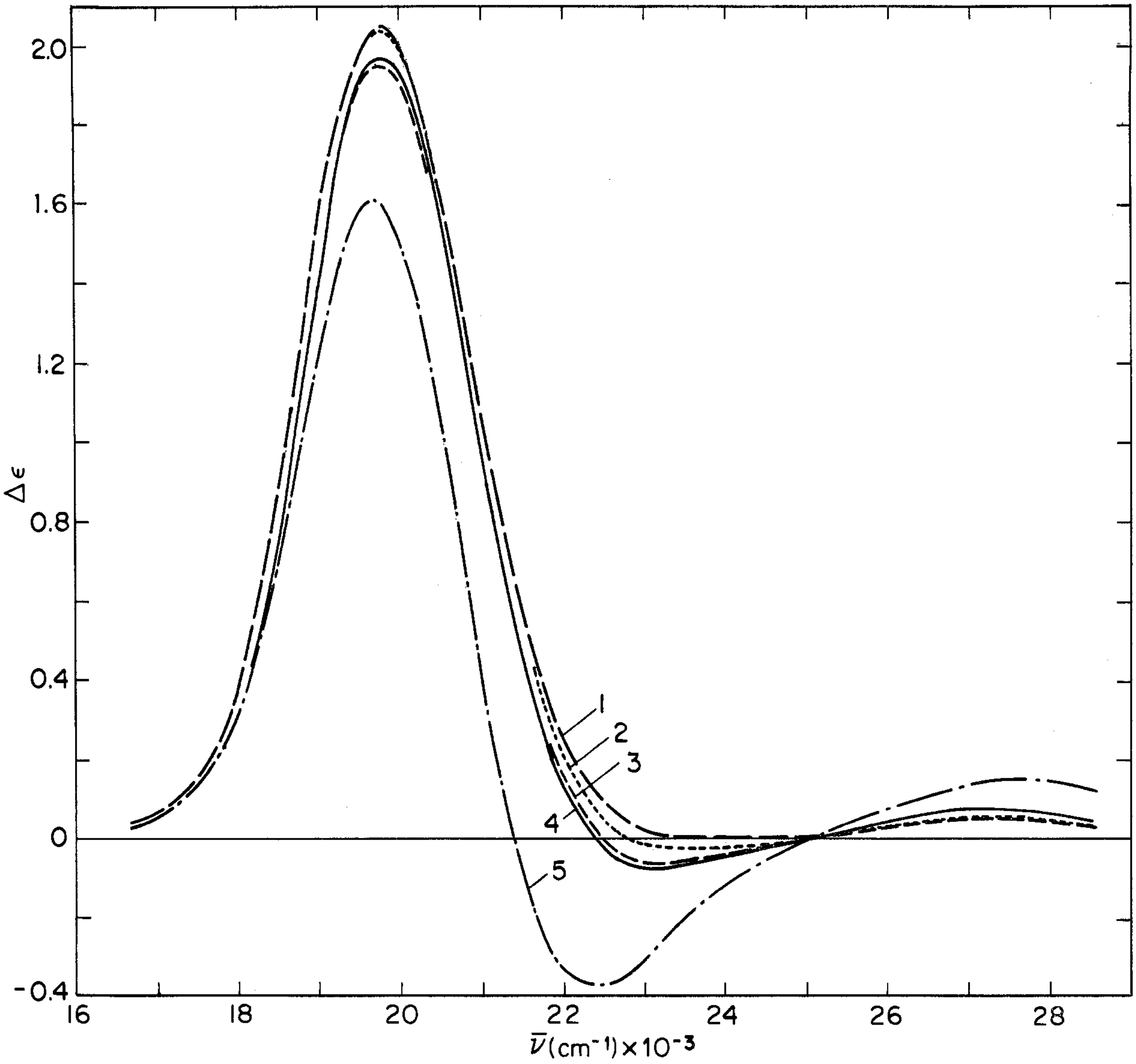

Figure 5.—Effects of electrolytes on the circular dichroism of $(+)_{589}$-$[Co(en)_2gly]I_2$: (1) no electrolyte added, (2) 2.0 *M* NaCl, (3) 0.5 *M* Na_2SO_4, (4) 0.5 *M* Na_2CO_3, (5) 0.5 *M* Na_3PO_4.

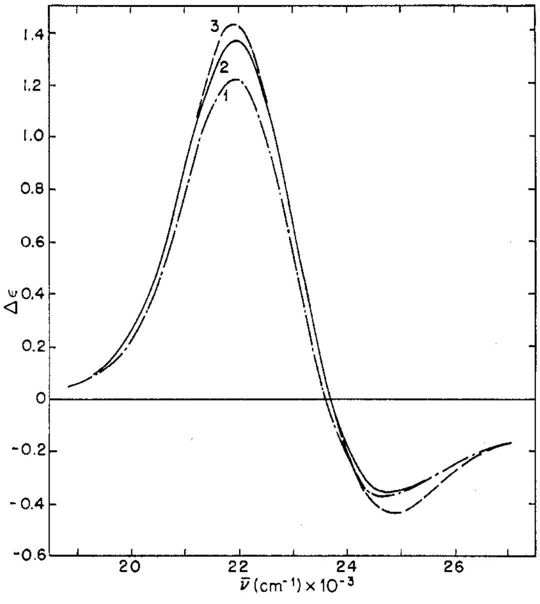

Figure 6.—Effects of Na_3PO_4 and Na_2CO_3 on the circular dichroism of $(+)_{589}$-$[Co(en)_2(NO_2)_2]Br$: (1) no electrolyte added, (2) 0.05 *M* Na_2CO_3, (3) 0.05 *M* Na_3PO_4.

be expected to be weaker (Figure 6). The effects of PO_4^{3-} might also be expected to be less highly directional for *cis*-$[Co(en)_2NO_2)_2]^+$ and the CD peaks with E_a and A_2 parentage are seen not to be affected to the same extents.

The protonation of PO_4^{3-} might be expected to interfere with the symmetrical interaction suggested by Mason. This and the lower charge on the anion would account for the smaller effect observed (Figure 4).

Mason's model might be adapted to describe the interaction between $[Co(en)_3]^{3+}$ or $[Co(en)_2gly]^{2+}$ and SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$. However, for these anions, CO_3^{2-}, and the singly charged anions, the effects are not only smaller compared to PO_4^{3-}, as expected because of the lower charge, but the E_a and A_2 bands are not affected to the same extent as noted by Mason for PO_4^{3-}. The predominant effects of the doubly charged anions appear to increase $R(A_2)$, suggesting that there is still a directional effect (Figure 3). However, there must also be nondirectional interactions since there is not a corresponding decrease in

$R(E_a)$. The nondirectional effects could arise from different orientations as ion pairs or from the association of additional anions with an ion pair oriented as described by Mason. The charge on $[Co(en)_3]^{3+}$ is neutralized in an ion pair formed with PO_4^{3-}, but not with anions of lower charge.

The singly charged anions show no evidence of preferred orientation of anions about the complex cation (Figures 1 and 2) as all the bands show some increase in R. Random orientation of the anions might be expected to increase R because of polarization effects and/or slight lowering of the symmetry.

The effects of electrolytes must be due to several factors. Mason's model for the interaction between $[Co(en)_3]^{3+}$ and PO_4^{3-} can account for the major effect in this case which is the most favorable one for such preferred orientation. In other cases, the other factors become increasingly important until the effect of such preferred orientation disappears for the singly charged anions.

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Proton Magnetic Resonance Studies of the Solvation of Cations in N,N-Dimethylformamide Solutions of Cobalt(II) and Nickel(II) Perchlorates and the Direct Determination of the Solvation Number of Cobalt(II)[1]

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At temperatures below −38° the proton nmr signals of N,N-dimethylformamide (DMF) in the first coordination sphere of Co(II) in DMF solutions can be distinguished. From the relative intensities of these signals, a primary solvation number of six was calculated for Co(II). The relative widths of these signals below −55° require that DMF should be coordinated to Co(II) *via* the oxygen atom and that the Co–O–C angle be bent. Above −55° the widths of the signals are dominated by the rate of exchange of DMF between the primary solvation sphere and the bulk solvent. Throughout a wide temperature range, the width of the *bulk* solvent formyl proton signal of DMF solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ is dependent on the rate of exchange of DMF between the bulk solvent and the species $M(DMF)_6^{2+}$. From the line width data the exchange parameters k_1 (sec^{-1} at 25°), ΔH^* (kcal), and ΔS^* (eu) were calculated for $Ni(DMF)_6^{2+}$ and $Co(DMF)_6^{2+}$, respectively: 3.8×10^3, $+15.0 \pm 0.5$, 8 ± 2; and 3.9×10^5, $+13.6 \pm 0.5$, 12.6 ± 2. For the Co(II) system, the exchange parameters obtained from the bulk solvent line broadening are in excellent agreement with those calculated from the widths of the proton signals of $Co(DMF)_6^{2+}$. Both the Co(II) and Ni(II) systems exhibit large proton contact chemical shifts from which the scalar coupling constants were calculated. Some comparisons are made between these data and those obtained for other Co(II) and Ni(II) systems.

Introduction

Recently nuclear magnetic resonance (nmr) spectroscopy has been applied to the study of a number of rapid substitution reactions involving metal ions in solution.[2-6] Of particular interest is that, under the proper conditions, nmr signals of the solvent molecules in the first coordination sphere of a metal ion can be detected. Thus, Jackson, Lemons, and Taube[7] have shown that it is possible to distinguish separate ^{17}O nmr signals arising from water in the first coordination sphere of selected diamagnetic cations and from that in the bulk solvent. Connick and Fiat,[8] using water enriched in ^{17}O, obtained the primary solvation numbers of Al(III) and Be(II) (six and four, respectively) by comparing the integrated intensities of the two ^{17}O signals. By lowering the temperature of methanol–water solutions of $Mg(ClO_4)_2$, Swinehart and Taube[9] were able to increase the mean lifetime of the solvent molecules in the first coordination sphere of Mg(II) sufficiently to allow the direct observation of the proton (OH) nmr signals of aquo–methanol complexes. Luz and Meiboom[10] have shown that, even with the paramagnetic ions Co(II) and Ni(II) in methanol–water solutions at low temperatures, the proton nmr signals of methanol and water in the first coordination sphere can be detected, and the rate of exchange of solvent molecules between the bulk solvent and the coordination sphere can be calculated from the widths of the signals. The exchange rates obtained in this manner were used to elucidate the relaxation mechanisms which contribute to the line widths of the nmr signals of the *bulk* solvent protons over a wide range of temperatures.[11]

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