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Directional Ion Association of Optically Active Cobalt(III) Complexes As Inferred from Nuclear Magnetic Resonance and Difference Circular Dichroism Spectra[1]

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Abstract: The mode of ion association between *cis*-bis(ethylenediamine)cobalt(III), *cis*-$[Co(en)_2(X)_2]^+$, and halide anions in dimethyl sulfoxide has been studied by proton NMR and difference circular dichroism spectroscopy under identical conditions, where X = CN^-, NO_2^-, NCS^-, Cl^-, and N_3^-. For complexes with the first four ligands, the former method indicated the association of the anions with the amine hydrogens, which are trans to the X substituent and approximately parallel to the molecular twofold axis of the cation, via hydrogen bonding. In the diazido complex cation, an additional mode of association, wherein the anions hydrogen bond to one of the cis amine hydrogens, has been found to compete with the above mode of association. The corresponding association constants with chloride ions have been determined. The association constants with chloride ions determined by the difference circular dichroism spectra have been found to be wavelength dependent and always larger for the dominant circular dichroism band of the first d–d transition region, irrespective of the ligand field strength of the X substituent. From this result, coupled with the NMR result, it is proposed that the direction of access of an anion toward a complex cation can be inferred from the difference circular dichroism spectrum; the principal effect of ion association upon the circular dichroism spectrum is to alter the rotational strength of that transition which is polarized along the direction of access of the anion toward the cation.

Chiral recognition in solution is a fascinating and yet unexplored field of chemistry. Doubtlessly the first keystep in chiral recognition involving nonlabile metal complexes should be the differential association between the Δ and Λ enantiomers and an optically active substance (resolving agent). Stereochemical features of such ion-associated species have, however, been little clarified. Circular dichroism (CD) spectra might be the most sensitive tool in studying the interaction of optically active substances in solution. Douglas and co-workers[2] have studied the effect of simple electrolytes on the CD spectra of $[Co(en)_3]^{3+}$ (en = ethylenediamine) and structurally related cobalt(III) complexes. They noted substantial changes in the CD spectra due to additives and found two effects. One effect is postulated to arise from the preferred orientation of large highly charged oxyanions with respect to the complex cation and the other is presumed to result from the random interaction with small anions of low charge. Mason and his group[3] made an extensive study on similar systems. They suggested the structure of the ion piar Λ-$[Co(en)_3]^{3+}\cdots PO_4^{3-}$, in which the oxyanion forms a multiple hydrogen bond to the three axial amine hydrogens and the trigonal axis of the complex cation coincides with the threefold axis of the anion. Even for this well-known ion pair, the reason for extracting such a structure from the CD changes does not seem to be well founded, though the X-ray crystal and molecular structure analysis of $[Co(en)_3]_2(HPO_4)_3{\cdot}9H_2O$ by Duesler and Raymond[4] pointed to the relevance of such a structure in solution. Subsequently, Yoneda and co-workers[5] investigated the effect of chiral anions upon the CD spectra of bis- and tris(diamine)cobbalt(III) complexes. Additionally, we can find several important contributions[6,7] to this field, and they are largely confined to the tris(diamine)cobalt(III) cations. In all such works, any unified view connecting the CD change and the ion-pair structure has not been put forward.

Clearly, the main drawback in the tris(diamine) systems lies in small trigonal splittings,[8] rendering difficult the analysis of the effect of ion association upon each rotational strength. Thus, we began our study with *cis*-$[Co(en)_2(X)_2]^+$ ions, in which the crystal field splittings are large enough to make spectroscopic assignments possible and hence the analysis of CD changes should be much easier. The effect of simple anions upon the CD spectra of these complex cations have been investigated very broadly by McCaffery, Mason, and Norman.[9] This paper shows (i) the mode of ion association between *cis*-$[Co(en)_2(X)_2]^+$ and halide ions in dimethyl sulfoxide (Me_2SO) as studied by proton NMR and (ii) a novel finding that the corresponding association constants determined by the difference CD (DCD) spectra are wavelength dependent. From these results, it is proposed that information about the directional ion association can be obtained from the DCD measurements.

For the sake of convenience, we here define the DCD spectrum as the CD spectrum with additives minus the CD spectrum without the additives.

Experimental Section

Materials. The literature methods were used for the preparation and optical resolution of *cis*-$[co(en)_2(X)_2]^+$ complexes, where X = CN^-,[10] NO_2^-,[11] NCS^-,[12] Cl^-,[13] and N_3^-.[14] Each of these complexes was obtained

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(1) This work is part 1 of "Chiral Recognition in Solution" and is taken in part from a Ph.D Thesis of H. Nakazawa, 1981.

(2) (a) Smith, H. L.; Douglas, B. E. *J. Am. Chem. Soc.* **1964**, *86*, 3885–3887. (b) Smith, H. L.; Douglas, B. E. *Inorg. Chem.* **1966**, *5*, 784–788. (c) Russel, R. L.; Douglas, B. E. *Inorg. Chim. Acta* **1969**, *3*, 426–430.

(3) (a) Mason, S. F.; Norman, B. J. *Proc. Chem. Soc., London* **1964**, 339–340. (b) Mason, S. F.; Norman, B. J. *Chem. Commun.* **1965**, 73–75. (c) Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1966**, 307–312.

(4) Duesler, E. N.; Raymond, K. N. *Inorg. Chem.* **1971**, *10*, 1486–1492.

(5) (a) Miyoshi, K.; Oh, C. E.; Nakazawa, H.; Yoneda, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2946–2950. (b) Miyoshi, K.; Oh, C. E.; Yoneda, H. *Ibid.* **1980**, *53*, 2815–2820. (c) Taura, T.; Tamada, H.; Yoneda, H. *Inorg. Chem.* **1978**, *17*, 3127–3129. (d) Taura, T.; Yoneda, H. *Ibid.* **1978**, *1m*, 1495–1498. (e) Taura, T. *J. Am. Chem. Soc.* **1979**, *101*, 4221–4228. (f) Yoneda, H.; Miyoshi, K.; Suzuki, S.; Taura, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1661–1664.

(6) (a) Gollogly, J. R.; Hawkins, C. J. *Chem. Commun.* **1968**, 689–690. (b) Ogino, K.; Saito, U. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 826–829. (c) Norden, B. *Acta Chem. Scand.* **1972**, *26*, 111–126. (d) Fujita, M.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1301–1303. (e) Ogino, K. *Ibid. Chem. Soc. Jpn.* **1969**, *42*, 447–452.

(7) For reviews see: (a) Ciardelli, F.; Salvadori, P., Eds. "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism"; Heyden & Son: London, 1973; Chapter 3.6, pp 196–239, and Chapter 3.8, pp 254–265. (b) Mason, S. F., Ed. "Optical Activity and Chiral Discrimination"; D. Reidel Publishing Co.: Dordrecht, Holland, 1979; Chapter XII, pp 293–318, and Chapter XIII, pp 319–337.

(8) (a) Mason, S. F.; McCaffery, A. J. *Mol. Phys.* **1963**, *6*, 359–371. (b) Kuroda, R.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 433–436. (c) Jensen, H. P.; Galsbøl, F. *Inorg. Chem.* **1977**, *16*, 1294–1297 and references cited therein.

(9) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc.* **1965**, 5094–5107.

(10) (a) Kuroda, K. *Nippon Kagaku Zasshi* **1968**, *89*, 720–721. (b) Chan, S. C.; Tobe, M. L. *J. Chem. Soc.* **1963**, 966–974.

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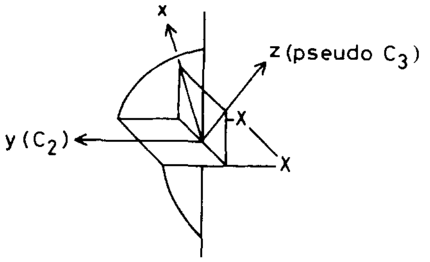

Figure 1. The frame of reference for the *cis*-$[Co(en)_2(X)_2]^+$ ion. Both trans H_A and cis H_A hydrogens point approximately parallel to the C_2 axis.

in the form of chloride, bromide, iodide, and perchlorate. The identity of all the complexes was confirmed by visible absorption, CD, and NMR spectra and by chemical analysis. Cation-exchange chromatography with the SP-Sephadex C-25 resin was used to check the absence of any trans impurities. Dimethyl sulfoxide used for CD measurements was of spectroscopic grade from Katayama Chemical Industries Co., Ltd. (Osaka). Perdeuteriodimethyl sulfoxide (Me_2SO-d_6, 99 atom % D minimum) was purchased from E. Merck (Darmstadt). Other chemicals were of purest grade commercially available and were used without further purification.

Measurements. All the NMR spectra were run at 25 °C on a JEOL PS-100 spectrometer (100 MHz) for Me_2SO-d_6 solutions of the complexes (0.030 mol dm^{-3}). Ionic strength was adjusted to $I = 0.12$ with tetramethylammonium perchlorate (Me_4NClO_4). Chemical shifts were referenced to internal Me_4Si.

Circular dichroism spectra were measured on a JASCO J-40CS recording spectropolarimeter, and the sample cell was kept at 25.0 ± 0.2 °C with a Haake circulator, Model FK. The DCD spectra were obtained by using the data processor compartment operating at 0.2 nm/step of processor resolution. The data processor output was recorded by a terminal recorder on an expanded scale.

Associaltion constants with chloride ions in Me_2SO were determined by proton NMR and DCD methods under identical conditions: solvents (either Me_2SO-d_6 or Me_2SO), temperature (25 °C, ionic strength ($I = 0.12$ with Me_4NClO_4), complex concentration (0.030 mol dm^{-3}), and the chloride source (Me_4NCl) whose concentration ranged from 0.010 to 0.10 mol dm^{-3}. the following method of analysis was used. For the ion-association equilibrium

$$M^+ + X^- \rightleftharpoons MX$$

the initial concentrations of M^+ and X^- are denoted by c_M and c_A, respectively. If the equilibrium concentrations of M^+, X^-, and MX are $(c_M - x)$, $(c_A - x)$, and x, respectively, then the association constant, K, is given by

$$K = x/(c_M - x)(c_A - x) \qquad (1)$$

In the NMR study, we measured the chemical shifts of amine hydrogens of the complex cations as a function of the chloride concentration. The observed chemical shift, ν_{obsd}, is the weighted average of ν_f and ν_{ip}, the chemical shifts of free (not ion-associated) and ion-paired species, respectively.

$$\nu_{obsd} = \nu_f(c_M - x)/c_M + \nu_{ip}x/c_M \qquad (2)$$

Here, ν_f was obtained for the perchlorate salts of the complexes in the absence of Me_4NCl. From eq 1 and 2, we obtain

$$1/(\nu_{obsd} - \nu_f) = 1/(\nu_{ip} - \nu_f) + 1/K(\nu_{ip} - \nu_f)(c_A - x) \qquad (3)$$

In the DCD study, similar equations can be used.

$$D_{obsd} = D_f(c_M - x) + D_{ip}x \qquad (4)$$

$$c_M/(D_{obsd} - D_f) = 1/(D_{ip} - D_f) + 1/K(D_{ip} - D_f)(c_A - x) \qquad (5)$$

where D_{obsd} is the measured CD intensity at some wavelength and D_f and D_{ip} are the CD intensities at the same wavelength for the free and ion-associated species, respectively. The quantity $(D_{obsd} - D_f)$ represents the DCD intensity at that wavelength. To obtain the values of K and ν_{ip} or D_{ip} from eq 3 or 5, we set up a computer program which is based on a nonlinear least-squares method.[15] All the computations were made at the Hiroshima University Computer Center.

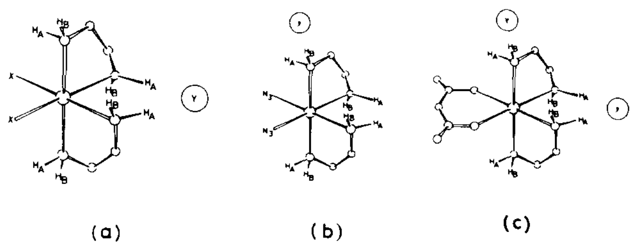

Figure 2. The mode of association between *cis*-$[Co(en)_2(X)_2]^+$ and Y^- in Me_2SO, deduced from NMR.

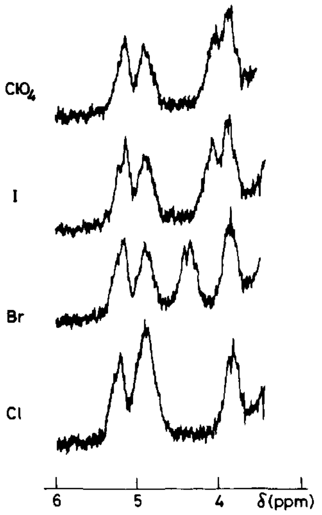

Figure 3. The amine portion of the NMR spectra of *cis*-$[Co(en)_2(N_3)_2]Y$, where Y = ClO_4^-, I^-, Br^-, or Cl^- ($I = 0.12$ with Me_4NClO_4).

Table I. The Chemical Shifts of Amine Hydrogens in Me_2SO-d_6 at 25 °C[a]

Y	NH			
	cis		trans	
	cis-$[Co(en)_2(N_3)_2]Y$			
ClO_4	(520) 512	490 (481)	(408) 400	387 (378)
I	(520) 512	490 (481)	(412) 405	388 (380)
Br	(524) 516	490 (482)	440 433	388 382
Cl	(527) 520	489[b]		388 (380)
	cis-$[Co(en)_2(Cl)_2]Y$			
ClO_4	557[b]		(438) 434	404 (396)
Br	557[b]		(480) 472	400 (392)

[a] For the data of the other complexes, see ref 16. Complex concentration is 0.030 mol dm^{-3} and $I = 0.12$ with Me_4NClO_4. Numbers in parentheses refer to shoulders. [b] Overlapped.

Results and Discussion

Proton NMR Study. The proton NMR spectra of *cis*-$[Co(en)_2(X)_2]^+$ ion in nonaqueous solents consist of a broad, unresolved absorption at about δ 2-3 due to the ethylenic hydrogens of en chelates and two to four absorptions due to amine hydrogens. The *cis*-$[Co(en)_2(X)_2]^+$ cation has the molecular C_2 axis (Figure 1) and so contains four types of amine hydrogens: trans H_A, trans H_B, cis H_A, and cis H_B. Here trans hydrogens are bonded to the nitrogen atoms trans to the substituent X. Both trans H_A and cis H_A are directed approximately parallel to the C_2 axis, while H_B hydrogens are not. In the previous paper,[16] we assigned the amine resonances for the dicyano, dinitro, acetylacetonato, malonato, and oxalato complexes in Me_2SO-d_6 and deuterium oxide. The mode of association for the monovalent complex cations in Me_2SO-d_6 has been

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(11) (a) Springborg, J.; Schäffer, C. E. *Inorg. Synth.* **1973**, *14*, 63-77. (b) Dwyer, F. P.; Garvan, F. L. *Ibid.* **1960**, *6*, 195-197.

(12) House, D. A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3103-3111.

(13) Bailar, J. C., Jr. *Inorg. Synth.* **1946**, *2*, 222-225.

(14) (a) Staples, P. J.; Tobe, M. L. *J. Chem. Soc.* **1960**, 4812-4820. (b) Yamazaki, K.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3060-3067.

(15) A complete list of this program is available upon requrest to H.Y.

(16) Nakazawa, H.; Sakaguchi, U.; Yoneda, H.; Morimoto, Y. *Inorg. Chem.* **1981**, *20*, 973-979.

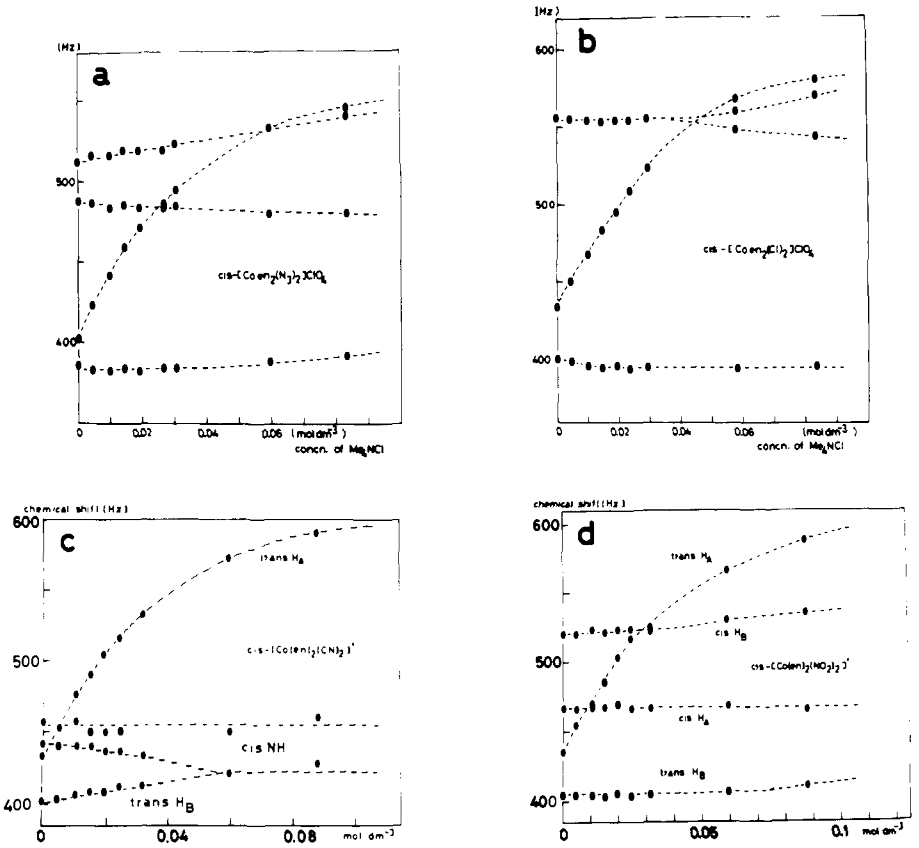

Figure 4. The plots of the chemical shift of amine hydrogens vs. the chloride concentration for the perchlorate salts of the (a) diazido, (b) dichloro, (c) dicyano, and (d) dinitro complexes ($I = 0.12$ with Me_4NClO_4).

shown as depicted in Figure 2a and that for the acetylacetonato complex cation as in Figure 2, where the first association takes place at the trans H_A hydrogens and the second one at the cis H_B hydrogens.

Since the shift behavior of the diazido complex which is investigated here is rather different from that of the other monovalent cations, we briefly describe here the method of assignment. Figure 3 shows the tracings of the amine portion of the proton NMR spectra of the diazido complex, in which the counteranion is varied from perchlorate to iodide, bromide, and chloride. The shift values are summarized in Table I. The amine resonances consist principally of four lines with equal intensities. Of these, we note the presence of one particular hydrogen, whose chemical shift is, among others, susceptible to the couteranions (see Figure 3 and Table I). This is the peak resonating at the second highest magnetic field in perchlorate, iodide, and bromide, and in chloride, it appears as the overlapping peak, the second lowest field peak. The chemical shifts of the other three hydrogens are influenced by counterions to a lesser extent or not at all. Therefore, the identity of this particular hydrogen is evident. the chemical shift of this hydrogen moves to low fields as we go from perchlorate to iodide, bromide, and chloride, in this order. Further, as Figure 4a shows, the chemical shift of this hydrogen is heavily affected, and undergoes a large downfield shift, by the chloride ion concentration. All these behaviors are consistent with the view[16] that the counteranions associate with this hydrogen via hydrogen bonding and cause downfield shifts, because hydrogen bonding is generally known to shift the hydrogen downfield. The ion association constant in dipolar aprotic solvents decreases, generally, in the order: $Cl^- > Br^- > I^- > ClO_4^-$.[17] The perchlorate anion is reported[18] not to be a hydrogen bond acceptor and shown to be completely dissociated in dipolar aprotic solvents. The fact that the hydrogen-bonding ability exactly parallels the above shift order supports the above view. The chemical shift of the dichloro complex and its variation with the chloride ion concentrations are seen from Table I and Figure 4b. From the plots of Figure 4b, it is observed that in the dichloro complex only one type of amine hydrogen associates with chloride ions appreciably. Parts c and d of Figure 4 show analogous plots for the dicyano and dinitro complexes, for which the assignments as indicated in these figures have been made in the previous study.[16] In conformity with the previous work,[16] the hydrogen which undergoes a large downfield shift by chloride ions may be assigned to the trans H_A in both diazido and dichloro complexes.

The assignments of the other hydrogens in the diazido and dichloro complexes are made as follows. A closer look at Figure 3 for the diazido complex reveals that each peak apparently is split into two peaks and the splitting pattern is consistent with the AB-type treatment.[16] Thus, the two lower field peaks and the two higher field peaks of the perchlorate, iodide, and bromide spectra each make an AB-type quartet. This is evidence that the two hydrogens giving rise to the AB pair are spin-spin coupled and hence bonded to the same nitrogen atom. Thus, in the perchlorate spectrum, for example, as the second highest field peak is already assigned to trans H_A, the highest field peak is assigned to trans H_B and the two low field peaks are assigned to two cis amine hydrogens. Of the two cis hydrogens of the diazido complex, the hydrogen giving rise to the lowest field peak undergoes a downfield shift, though small compared with that of trans H_A, from counteranions (see Table I and Figure 4a). This hydrogen may be most probably cis H_B (Figure 2b) in analogy with the second ion association mode of the acetylacetonato complex cation, which is illustrated in Figure 2c. The assignment for the dichloro complex follows similarly from the spin-spin splitting pattern. In perchlorate, the two higher field peaks are assigned to trans hydrogens and the low field overlapping peak to two cis hydrogens. In the monovalent complex cations cis-$[Co(en)_2(X)_2]^+$ with $(X)_2 = (Cl)_2$, $(N_3)_2$, malonate,[16] and oxalate,[16] the trans hydrogens appear at higher magnetic fields than cis ones. This agrees with the prediction based on the effect of the magnetic anisotropy of the central cobalt(III) ion.[16,19] The origin of the shift difference between the two trans hydrogens or the two cis hydrogens is not clear as yet.

Since the diazido complex cation is monovalent, it is unlikely that two chloride ions associate with the cation simultaneously. Therefore, the ion association of this cation with chloride ions takes place at either trans H_A or cis H_B and the two association modes, given by Figures 2a,b, are

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[17] See, for example: Kay, R. L.; Evans, D. F.; Matesich, M. A. In "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1976; Vol. 2, Chapter 10, pp 105-153.

[18] Millen, W. A.; Watts, D. W. *Aust. J. Chem.* **1966**, *19*, 43-49 and 51-58.

[19] (a) Yoneda, H.; Nakashima, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 669-672. (b) Yoneda, H.; Sakaguchi, U.; Nakashima, Y. *Ibid.* **1975**, *48*, 209-213. (c) Juranic, N.; Celap, M. B.; Vucelic, D.; Malinar, M. J.; Radivojsa, P. N. *Inorg. Chem.* **1980**, *19*, 802-805.

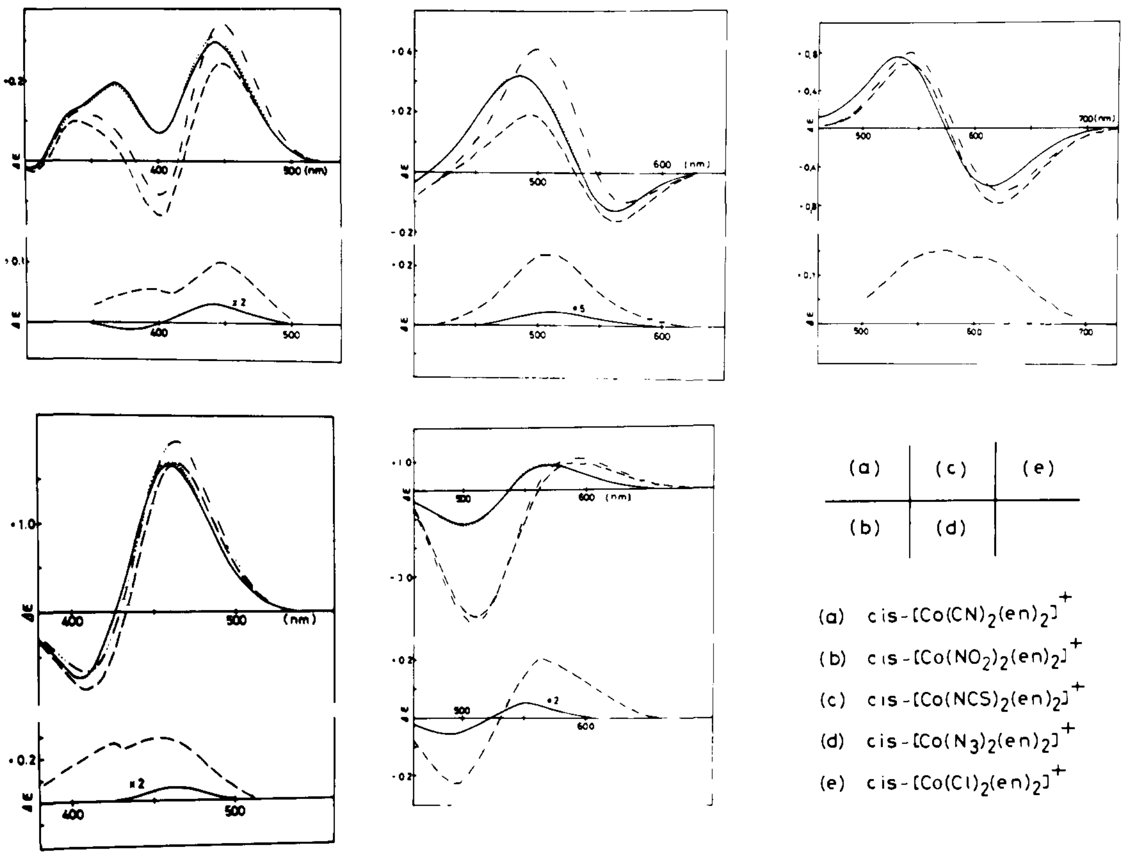

Figure 5. Top: the CD spectra of the Λ enantiomers in aqueous solution (0.01 mol dm^{-3}) containing 0 (—) and 0.1 mol dm^{-3} (⋯) of sodium chloride and in Me_2SO solution (0.03 mol dm^{-3}) containing 0 (—) and 0.03 mol dm^{-3} (-⋯) of sodium chloride. Bottom: their DCD spectra in aqueous solution (—) and Me_2SO solution (---).

competing in Me_2SO solution. The mode of association of *cis*-[$Co(en)_2(N_3)_2$]$^+$ as shown by Figure 2b was proposed previously by Yamazaki and Yoneda[20] for the association with the (*d*-tartrato)antimonate(III) anion.

As seen from Figure 4b, the cis hydrogens of the dichloro complex exhibit a peculiar shift behavior; the cis peak is split symmetrically with increasing chloride concentration. This behavior appears as a secondary effect of ion association at trans H_A, but the true cause is not apparent as yet. In Figure 4c, it is not clear whether the chemical shift of trans H_B of the dicyano complex is really affected by the chloride concentration, because the peaks due to trans H_B and cis hydrogens overlap appreciably.[16]

The association constants with chloride ions have been determined by analyzing the plots of the shifts of trans H_A (and cis H_B for the diazido complex) vs. the chloride concentraion (Figure 4), following the procedure outlined in the Experimental Section. The results are summarized in Table II. The association constant for cis H_B of the diazido complex could not be determined with any certainty owing to relatively small shifts compared with the line width of the NMR peak: see Figures 3 and 4a. The *K* values for trans H_A in Table II corrrelates very well the nephelauextic ratio of the X ligand, β_{35},[21] which is a measure of the covalency of the metal-ligand bonds. This correlation indicates that the acidity of trans amine hydrogens increases as the metal-ligand covalency increases and also supports the view that the association with chloride ions takes place through hydrogen bonding. To sum up the results of the NMR studies, we may envisage the structure of ion pairs in Me_2SO-d_6 as depicted in Figure 2. Figure 2a is the mode of association for monovalent *cis*-[$Co(en)_2(X)_2$]$^+$ ions with $(X)_2$ = $(CN)_2$, $(NO_2)_2$, $(Cl)_2$, oxalate, and malonate. For the diazido complex cation, both modes of association as illustrated in Fiture 2a,b are competing. The degree of association corresponding to these processes may be quantitatively assessed from the association constants.

Difference CD Study. Before discussing the DCD spectra, it will be pertinent to recall the spectroscopic assignments for these complexes. The *cis*-[$Co(en)_2(X)_2$]$^+$ ions have the C_2 point symmetry about the central cobalt chromophore. The frame of reference is taken as in Figure 1 after McCaffery et al.[9] The first-excited d-electron manifold is split under the influence of the crystal field of C_2 symmetry into three energy levels of A_2, B_2, and B_1 symmetries. These notations follow those of McCaffery, Mason, and Norman.[9] The A_2 transition is polarized along the unique C_2 axis or the *y* axis of Figure 1, and the B_2 transition along the *x* axis, and the B_1 transition along the pseudo C_3 axis or the *z* axis. It is generally observed that the energy spacing between the A_2 and B_2 states is small and so the observed CD spectra of *cis*-[$Co(en)_2(X)_2$]$^+$ in the first d–d transition region comprise the $A_2 + B_2$ component and the B_1 component. For strong field ligands, e.g., X = CN^- and NO_2^-, the former component appears at longer wavelengths, while the complexes with weak field ligands, e.g., X = NCS^-, Cl^-, and N_3^-, it appears at shorter wavelengths.

Table II. The Association Constant, *K*, of *cis*-[$Co(en)_2(X)_2$]$^+$ with Cl^- in Me_2SO-d_6, Determined by NMR at 25 °C[a]

complex	*K*, mol^{-1} dm^3	D_f, Hz	D_{ip}, Hz	site
cis-[$Co(en)_2(CN)_2$]$^+$	68.0 ± 2.8	433	626 ± 4	trans H_A
cis-[$Co(en)_2(NO_2)_2$]$^+$	41.0 ± 5.9	438	647 ± 20	trans H_A
cis-[$Co(en)_2(N_3)_2$]$^+$	126 ± 12	402 513	563 ± 5	trans H_A cis H_B
cis-[$Co(en)_2(Cl)_2$]$^+$	46.2 ± 4.9	434	635 ± 13	trans H_A

[a] Complex concentration is 0.030 mol dm^{-3} and I = 0.12 with Me_4NClO_4. D_f and D_{ip} are the chemical shifts of trans H_A or cis H_B in free and ion paired species, respectively. [b] See text.

The CD spectra of the Λ enantiomers[9,22] of the complex perchlorates in Me_2SO and water and their changes upon addition of sodium chloride are shown as the top spectra of Figure 5. Note that the sign of the dominant $A_2 + B_2$ band of the Λ enantiomers is plus for all the complexes, except the diazido complex.[22] The bottom spectra of Figure 5

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[20] Yamazaki, S.; Yoneda, H. *J. Chromatogr.* **1979**, *177*, 227–235.

[21] (a) Jørgensen, C. K. *Prog. Inorg. Chem.* **1962**, *4*, 73–124. (b) Jørgensen, C. K. *Discuss. Faraday Soc.* **1958**, *26*, 110–115.

[22] Our recent X-ray structure analysis established that the $(+)_{589}$ enantiomer which forms the less-soluble diastereomer, $(+)_{589}$-*cis*-[$Co(en)_2(N_3)_2$]$_2$[$Sb_2(d\text{-tart})_2$]·$2.5H_2O$, has the Λ absolute configuration, contrary to an earlier assignement based on the CD spectrum,[14b] where [$Sb_2(d\text{-tart})_2$]$^{2-}$ = (*d*-tartrato)antimonate ion. See: Miyanaga, A.; Kushi, Y.; Yoneda, H., manuscript in preparation.

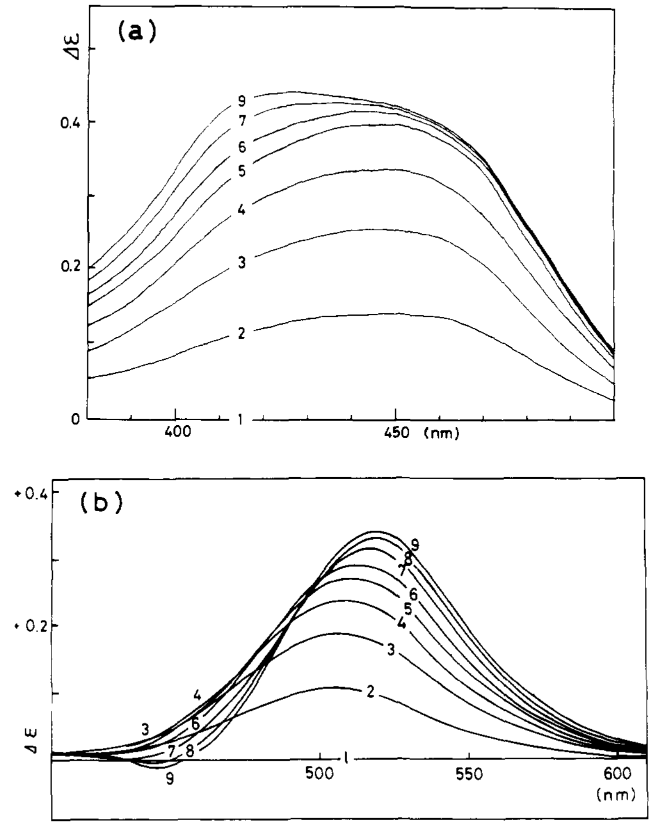

Figure 6. The changes in the DCD spectra of (a) Λ-*cis*-$[Co(en)_2(NO_2)_2]^+$ and (b) Λ-*cis*-$[Co(en)_2(NCS)_2]^+$ in Me_2SO, brought about by addition of increasing amount of Me_4NCl. In both a and b, the chloride concentration is $(n - 1) \times 10^{-2}$ mol dm^{-3} for the spectra numbered as *n*. Complex concentration is 0.030 mol dm^{-3} in both spectra.

illustrate their DCD spectra due to chloride ions. It will be seen that the CD spectra change appreciably with solvents. We have found that in some solvents inversion of the sign of rotational strength occurs, but this aspect will be published elsewhere.[23] The DCD spectra of the dicyano complex obtained in both Me_2SO and water comprise two peaks, corresponding to the $A_2 + B_2$ and the B_1 components of the original CD spectrum. For the dinitro complex, the DCD peak for the $A_2 + B_2$ component is much more prominent in water than that for the B_1 component, while both components appear in Me_2SO. For the diisothiocyanato complex, the DCD spectra in water and Me_2SO show apparently one peak, but it will be shown later that the rotational strength of at least two transitions is affected. It is clear that for the diazido complex both components are affected in both solvents. For the dichloro complex, the DCD spectrum in Me_2SO is composed of two peaks, corresponding to the $A_2 + B_2$ and the B_1 components of the CD spectrum. The DCD spectrum of the dichloro complex in water could not be obtained because of rapid hydrolysis of the complex in this solvent. It is clear from these spectra that both rotational strengths corresponding to the $A_2 + B_2$ and the B_1 components are affected by chloride ions in both solvents. We will consider for the moment the results in Me_2SO, and the results in water will be discussed later.

Surprisingly, the shape of the DCD spectra in Me_2SO of Figure 5 changed with the chloride concentration. This is evidence that each rotational strength changes upon ion association independently and that the association constant, and not the limiting CD spectra (the CD spectra of the ion-associated species), at each transition is different. This will be seen most clearly by the DCD variations of the dinitro and diisothiocyanato complexes with the chloride concentration (Figure 6). For example, the DCD spectrum of the dinitro complex illustrated in Figure 6a indicates clearly that the peak at about 450 nm levels off at higher chloride concentration, while the peak at about 425 nm does not and continues to increase with increasing chloride concentration. The complex variation of the diisothiocyanato spectrum of Figure 6b results presumably from a heavy overlap of the $A_2 + B_2$ and B_1 components. The DCD intensities at several wavelengths were plotted against the chloride concentration and were treated in the same way as for the NMR study. Thus, the association constant was derined at each CD band for each complex cation. The experimental conditions are the same as for the NMR study; at 25 °C, $I = 0.12$ with Me_4NClO_4, 0.030 mol dm^{-3} in complex concentration, and the chloride source (Me_4NCl). The wavelength for the determination of the association constants was chosen so as to minimize the effect of overlap of the $A_2 + B_2$ and the B_1 components. The results are given in Table III.

Table III. The Association Constant, *K*, of *cis*-$[Co(en)_2(X)_2]^+$ with Cl^- in Me_2SO, Determined by DCD at 25 °C[a]

X	λ nm	*K*, mol^{-1} dm^3	$\Delta\epsilon_{MA}$	$\Delta\epsilon_M$	assignt[9,21]
CN^-	454	126 ± 9	+0.410 ± 0.002	+0.259	$A_2 + B_2$
	376	59.0 ± 1.9	+0.092 ± 0.001	−0.010	B_1
NO_2^-	470	295 ± 64	+1.95 ± 0.01	+1.59	$A_2 + B_2$
	405	28.6 ± 0.6	+0.211 ± 0.011	−0.830	B_1
N_3^-	485	37.2 ± 4.2	−3.50 ± 0.03	−2.99	$A_2 + B_2$
	585	28.7 ± 1.1	+2.93 ± 0.04	+0.898	B_1
NCS^-	540	27.9 ± 3.9	+0.276 ± 0.025	−0.082	B_1
Cl^-	535	426 ± 144	+0.823 ± 0.006	+0.660	$A_2 + B_2$
	625	113 ± 38	−0.514 ± 0.021	−0.766	B_1

[a] Conditions are the the same as in Table II. $\Delta\epsilon_M$ and $\Delta\epsilon_{MA}$ are the molar Δε values, at the wavelength specified, of the free and ion paired species, respectively.

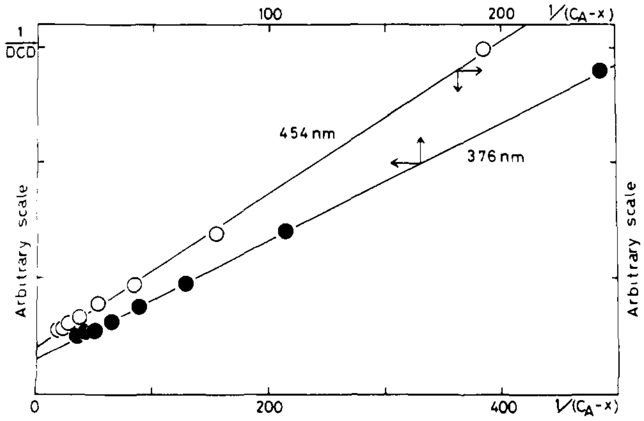

Figure 7. The plots of 1/(DCD intensity) vs. $1/(c_A - x)$, eq 5, for the dicyano complex. The arrows indicate the coordinates to be referred to.

The most noteworthy features in Table III are (i) that the association constants determined for the $A_2 + B_2$ component are indeed different from and uniformly larger than those determined for the B_1 component, regardless of the ligand field strength of the X substituent, and their differences are also rather large, well beyond the experimental uncertainties, and (ii) that the association constants determined by the DCD method for the $A_2 + B_2$ component are substantially larger, except for the diazido complex, than those determined by the NMR method. Since the CD band at the $A_2 + B_2$ component is composed of two contributions from the two rotational strengths, the DCD band at this component might be expected to show a complex variation with the chloride concentration. However, the plots of eq 5 were almost linear for the data in Table III, which indicates that the variation is dominated by a change in only one rotational strength, presumably that of the A_2 transition (see below). The plots of eq 5 for the dicyano complex are shown in Figure 7. The linearity of the plots of eq 5 is evidence that both the $A_2 + B_2$ and the B_1 components change independently and the DCD change at the $A_2 + B_2$ component is brought about by a change in one rotational strength. These observations seem to lend credence to our treatment. Though the association constant of the dichloro complex at 535 nm involves rather large errors, its value (K = 425 mol^{-1} dm^3) compares fairly well with that determined by the conductance method (K = 367 ± 10 mol^{-1} dm^3 at 25 °C in Me_2SO[24]).

The finding that the association constants differ drastically from one CD band to another was at first surprising because no such resulats were reported.[25] One can understand, however, the reason for the absence of the data of such characteristics, if one note the following. The con-

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(23) Sakaguchi, U.; Nakazawa, H.; Sakai, K.; Yoneda, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1862–1868.

(24) Millen, W. A.; Watts, D. W. *J. Am. Chem. Soc.* **1967**, *89*, 6858–6864.

(25) Wavelength-dependent association constants can be found in early papers on charge-transfer complexes. But the results were questioned and the problems involved were discussed critically by Person: Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167–170.

ventional means to obtain association constants have been the conductance or spectrophotometric measurements.[25,26] The first method gives, of course, no information about the directional nature of ion association. In the latter method, one has usually determined the association constant either at one wavelength or at several closely spaced wavelengths. The second and the most iomportant point is that in almost all cases the change in the unpolarized absorption spectrum is due to one and only one charge-transfer (CT) transition, between the metal and the associating anion, which newly appears upon ion association usually in the ultraviolet region. Therefore, even if one measured spectral changes in totally separated absorption bands, only one association constant resulted because the origin of the changes is the same (CT transition). In contrast, the CD spectrum of a metal complex in the visible region has long been known to change by ion association even in the absence of any CT contribution (vide infra). Furthermore, the inherent drawback in the unpolarized absorption spectrum is that the one apparent band is merely an overlap of several component bands corresponding to each electronic transition. As often pointed out, the CD spectrum is much more well resolved than the unpolarized absorption spectrum. For example, the unpolarized absorption spectrum of the dinitro complex exhibits only one band in the $^1A_{1g}$ to $^1T_{1g}$ (Oh parentage) transition region, whereas the CD spectrum shows two peaks of opposite signs in this region (Figure 5b). Of course, the intrinsic electronic mechanisms are different; the absorption spectrum depends on only electric transition dipole moments, while the CD spectrum depends on both electric and magnetic transition moments. Therefore, the DCD spectrum may detect the change in each rotational strength, which is otherwise impractical.

Since the association constants in Tables II and III were obtained under identical conditions, their values can be compared directly, with the possible reservation that the entity recognized as the ion-paired species by both methods will not necessarily be identical.[27] The NMR method employed here sees only those ion pairs which are formed between the amine hydrogens of a complex cation and chloride ions via hydrogen bonding.[16] This type of ion pair may be called a contact or tight ion pair. The DCD spectra may detect, in addition to contact ion pairs, more weakly interacting species whose spatial extension should be much larger than that of contact ion pairs. This seems to be the implication of point ii noted above. Only one NMR signal could be seen for one type of N–H hydrogen, which means that our systems are fast-exchange cases. Therefore, the observed NMR spectra are the averages of the spectra of the free and ion-paired species, weighted according to their population.

Even with the above reservations in mind, both results should be interpreted consistently, being obtained under identical conditions. It seems most reasonable to postulate that the larger association constants obtained by the DCD method for the $A_2 + B_2$ component than for the B_1 component reflect the dominance of the association of chloride ions from the C_2 axis of the complex cations. This type of access of chloride ions is revealed by the present NMR study and also quite reasonable on electrostatic grounds; since the X ligand carries a negative charge, the anion will approach the complex cation along the C_2 axis from the side opposite the X ligands. The access of an anion along the x axis appears unlikely for steric reasons, because the ethylenediamine chelates protrude around this axis. Thus, it is highly likely that the direction of ion association is reflected in the DCD spectrum, in such a fashion that if an anion approaches the cation along the C_2 axis, for example, then the transition moment (electric and/or magnetic) polarized along the C_2 axis is subjected to a change in magnitude and hence a change in the rotational strength corresponding to the C_2 axis polarized transition (the A_2 transition). This postulate bears some resemblance to the polarization of CT spectra.[28] The fact that larger association constants were obtained uniformly for the $A_2 + B_2$ components irrespective of the ligand field strength of the X substituent strongly supports the above postulate.

A support to the above postulate is provided by the example of the diazido complex. The NMR study has shown that the diazido complex cation adopts the cis association (Figure 2b) in addition to the trans association (Figure 2a), unlike the other monovalent cations. This unique behavior of the diazido complex appears to be nicely reproduced in the association constants determined by the DCD method being similar in magnitude for both components; according to our postulate, the cis association tends to increase the association constant for the B_1 or B_2 transition rather than for the A_2 transition. In the other monovalent complexes, the difference in association constants for the two components are quite large. If we generalize our postulate and apply to the $[Co(N)_6]^{3+}$ complexes of D_3 symmetry, the recent results of Mason and co-workers also seem to support our postulate. They noted that the effect of N-alkyl substitution on the d-electron optical activity of Λ-$[Co(en)_3]^{3+}$ is similar to that of polarizable oxyanions such as PO_4^{3-} or SeO_3^{2-}.[29] Also, the stepwise covalent capping along the C_3 axis of Λ-$[Co(en)_3]^{3+}$, yielding Λ-$[Co(sen)]^{3+}$ and Λ-$[Co(sep)]^{3+}$, was shown[30,31] theoretically to enhance $R(A_2)$ (A_2 rotational strength) at the expense of $R(E_a)$, where sen = 1,1,1-tris((2-aminoethyl)aminomethyl)ethane[32] and sep = (S)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.[33] These results suggested that the addition of atoms or groups, whether covalent, ionic, or hydrogen bonded, to the D_3 polar region of the $[Co(N)_6]^{3+}$ complexes enhances generally $R(A_2)$. This is in keeping with our posltulate; since the A_2 transition is polarized along the C_3 axis, the D_3 polar perturbations are expected to alter $R(A_2)$ rather than $R(E_a)$ in our model. Therefore, our postulate seems to be substantiated; the effect of ion association upon the CD spectra of metal complexes is to alter the rotational strength of that transition which is polarized along the direction of access of the anion. If our posltulate is valid, then the DCD spectra is Figure 5 tell that the chloride ions approach the complex cations not only from the C_2 axis but also from the other axes or also from between these axes.

At present, we can find no general trend in the direction of the CD change, enhancement or reduction of the rotational strength, due to ion association. The DCD spectra obtained in water are in most cases rather similar in shape to those in Me_2SO, though small in magnitude owing to smaller association constants in water. In the dicyano complex, the signs of the DCD band at about 375 nm are opposite in both solvents. The K values for the $A_2 + B_2$ components in Table III follow the order $Cl^- > NO_2^- > CN^- > N_3^-$, which appears to be the opposite to the order of the K values found by NMR. But we can not give any explanation to it.

Origin of CD Change due to Ion Association. We briefly discuss the origin of the CD change due to ion association. Several mechanisms have been put forward to explain the CD changes observed to date and these include the following: (i) creation of new asymmetric center(s) at N–H by stereospecific hydrogen bonding to amine hydrogen(s),[32] (ii) displacement from the equilibrium population of the conformation (δ and λ) of coordinated en rings,[34] (iii) intensity borrowing of CT transition which newly appears in the near-ultraviolet region of the spectrum upon ion pairing.[35] If the first mechanism makes a dominant contribution to the CD changes obtained in this work, it is expected that the association constants determined by the NMR method should be similar in magnitude to those determined by the DCD method. This is because the former method detects directly the number of the species which are interacting through the mechanism i. As seen from Tables II and III, this expectation was not fulfilled. Thus, the first mechanism appear to have a minor contribution, if any. If the second mechanism plays a dominant role, then the chemical shift of all the four kinds of amine hydrogens of the complex cations are expected to undergo appreciable changes. This is because a substantial change in the relative population of en ring conformations should bring all amine hydrogens into different magnetic environments from those at equilibrium population. Previously, we have shown[16] that such a shift can really be obsered for the system $[Co(en)_2(acac)]^{2+}\cdots$malonate^{2-} in aqueous solution, where acac = 2,4-pentanedionate. In the present system, no such shifts were observed and a change in the chemical shift of only trans H_A (plus cis H_B in the case of the diazido complex) was observed even in Me_2SO. Since the degree of ion association should be less extensive in water with dielectric constant of about 80 than in Me_2SO with dielectric constant of about 47, mechanism ii should be even less likely in aqueous solution. Likewise, the observation[32] that the CD change of the system $(-)_{589}$-$[Co$-$(-)$-$(chxn)_3]^{3+}\cdots PO_4^{3-}$ is very similar to that of the system Λ-$[Co(en)_3]^{3+}\cdots PO_4^{3-}$ disfavors the possibility of (ii), where chxn is $trans$-1,2-diaminocyclohexane. The chxn chelate is conformationally fixed.[32] The third mechanism appears also unlikely, as pointed out by Sarneski and Ur-

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(26) (a) Beck, M. T. *Coord. Chem. Rev.* **1968**, *3*, 91–115. (b) Pethybridge, A. D.; Spiers, D. J. *J. Chem. Soc., Dalton Trans.* **1976**, 64–72, 73–78. (c) Palmer, D. A.; Watts, D. W. *Inorg. Chem.* **1971**, *10*, 281–286. (d) Watts, D. W. *Pure Appl. Chem.* **1979**, *51*, 1713–1724.

(27) Discussions are given on the differences of results obtained by different physical methods in: (a) Schneider, H. In "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; Vol. 2 Chapter 11, pp 155–228. (b) Reference 25.

(28) See, for example: Kuroda, H.; Kunii, T.; Hiroma, S.; Akamatsu, H. *J. Mol. Spectrosc.* **1967**, *22*, 60–75.

(29) Hearson, J. A.; Mason, S. F.; Seal, R. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1026–1034.

(30) Drake, A. F.; Kuroda, R.; Mason, S. F. *J. Chem. Soc., Dalton Trans.* **1979**, 1095–1100.

(31) Mason, S. F. *Acc. Chem. Res.* **1979**, *12*, 55–61.

(32) Sarneski, J. E.; Urbach, F. L. *J. Am. Chem. Soc.* **1971**, *93*, 884–888.

(33) Creaser, I. I.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181–3182.

(34) Sargeson, A. M. *Transition Met. Chem. (N.Y.)* **1966**, *3*, 303–343.

(35) Larsson, R.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1966**, 301–307.

bach.[32] They observed that the CD spectrum of $[Co(sen)]^{3+}$ and its change with phosphate ions is similar to the Λ-$[Co(en)_3]^{3+}$ case. However, there was no interionic CT transition in the former system, unlike in the latter. Thus, it appears that the CT transition is not essential to the production of CD changes. We can find several other systems which show substantial CD changes due to additives but show no CT transition. These include Λ-$[Co(en)_3]^{3+}\cdots d$-tartrate^{2-} or sulfate.[3c,6e]

Conclusion

The finding that the association constants are different from one CD band to another has led us to postulate that detailed stereochemical information about ion pairs can be extracted from DCD studies. Though any detailed electronic mechanism leading to rotational strength changes could not be presented, we believe that the present finding should give an impetus to further works. Our own works aimed at the experimental demonstration of the validity of our postulate are in progress.

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Registry No, *cis*-$[Co(en)_2(N_3)_2]ClO_4$, 14877-87-3; *cis*-$[Co(en)_2(N_3)_2]I$, 79270-30-7; *cis*-$[Co(en)_2(N_3)_2]Br$, 15275-20-4; *cis*-$[Co(en)_2(N_3)_2]Cl$, 68265-39-4; *cis*-$[Co(en)_2(Cl)_2]ClO_4$, 23791-80-2; *cis*-$[Co(en)_2(Cl)_2]Br$, 79270-31-8; *cis*-$[Co(en)_2(CN)_2]ClO_4$, 21861-61-0; *cis*-$[Co(en)_2(NO_2)_2]ClO_4$, 14781-32-9; *cis*-$[Co(en)_2(NCS)_2]^+$, 21169-85-7; Λ-*cis*-$[Co(en)_2(CN)_2]^+$, 18660-79-2; Λ-*cis*-$[Co(en)_2(NO_2)_2]^+$, 18660-78-1; Λ-*cis*-$[Co(en)_2(NCS)_2]^+$, 50762-67-9; Λ-*cis*-$[Co(en)_2(N_3)_2]^+$, 56906-68-4; Λ-*cis*-$[Co(en)_2(Cl)_2]^+$, 18660-62-3; Cl^-, 16887-00-6.

(Trimethylphosphine)cobalt(I) Complexes. 1. Reactivity with Ethylene and Crystal Structure of $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4{\cdot}MeCN$

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Abstract: The reaction of $Co^IBr(PMe_3)_3$ with ethylene in various solvents was investigated at −80 and 35 °C by $^{31}P\{^1H\}$ NMR spectroscopy. In toluene, acetone, and methanol, ethylene adds reversibly to the paramagnetic tetrahedral d^8 Co^I complex to give the diamagnetic $CoBr(C_2H_4)(PMe_3)_3$ species with C_2H_4 and Br in equatorial positions. Adding acetonitrile (1:1) to acetone or methanol leads to a mixture of two pentacoordinate diamagnetic compounds: $[Co(L)(C_2H_4)(PMe_3)_3]Br$ (where L = C_2H_4 or MeCN) and $[Co(MeCN)(C_2H_4)(PMe_3)_3]Br$. In the former, L cannot be unambiguously identified, but both L and C_2H_4 have to be equatorial. In the latter species, the ligand distribution is the same as found in the crystals of the corresponding BPh_4^- salt, i.e., C_2H_4 equatorial and MeCN axial. The same spectrum was obtained with $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4{\cdot}MeCN$, which confirms that Br has been expelled from the coordination sphere of cobalt. The affinity of MeCN for Co^I in this system is evidenced by the formation of the trigonal-bipyramidal (TBP) adducts $[Co(MeCN)_2(PMe_3)_3]^+$ and $[Co(MeCN)(PMe_3)_4]^+$ in acetonitrile solutions of $CoBr(PMe_3)_3$ and $[Co(PMe_3)_4]BPh_4$, respectively, at −80 °C. The reaction of ethylene with $[Co(PMe_3)_4]BPh_4$ yields a TBP adduct $[Co(C_2H_4)(PMe_3)_4]BPh_4$ with equatorial C_2H_4. The crystals of $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4$, MeCN belong to space group $P2_1/c$ with a = 12.738 Å, b = 28.52 Å, c = 11.891 Å, and β = 106.85°. The structure contains a distorted TBP $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ cation in which MeCN and PMe_3 are axial, whereas C_2H_4 and two PMe_3 ligands are equatorial. The ethylene double bond lies on the equatorial plane, and it undergoes the usual structural changes upon coordination. The distortions in the TBP are related to the individual steric requirements of each type of ligand.

The d^8 $RhCl(PPh_3)_3$ complex is well-known for its ability to react with ethylene, giving rise to monomeric and dimeric molecular or cationic ethylene complexes. Its catalytic properties toward olefin isomerization and hydrogenation have been well investigated.[2]

The corresponding cobalt(I) compound $CoCl(PPh_3)_3$ is less reactive,[3] although recently, ethylene dimerization has been reported to be catalyzed by $CoBr(PPh_3)_3$ in presence of BF_3 as cocatalyst.[4] The type of phosphorus ligand has an influence, since $CoX(PR_3)_3$ complexes with $P(OEt)_3$, $P(OPh)_3$, and $P(OMe)_3$ have shown catalytic properties in the hydrogenation and isomerization of olefins.[5] However, up to now, few cobalt(I)–ethylene complexes with monodentate phosphorus ligands have been isolated. The synthesis of the first examples $CoR(C_2H_4)(PMe_3)_3$ (where R = Me, Ph, H), and $[Co(C_2H_4)(P(OMe_3)_3)_4]^+$ has been carried out recently by Klein et al.[6,7] and by Muetterties and Watson,[8] respectively. The alkyl and aryl complexes have been synthesized by adding methyl or phenyl lithium to a tetrahydrofuran solution of $CoCl(PMe_3)_3$ under 1 atm of ethylene at low temperature. The formation of an ethylene adduct of $CoCl(PMe_3)_3$ as an inter-

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(1) (a) Laboratoire de Chimie de Coordination du CNRS. (b) Université de Montréal. (c) Technische Universität München.

(2) (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711–1732. Herberhold, M. "Metal π-complexes"; Elsevier: Amsterdam, 1972; Vol. II. Meakin, P.; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 3240–3242. Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *Ibid.* **1974**, *96*, 2762–2774. Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629–630. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134–2143, 2143–2147, 4450–4455.

(3) Aresta, M.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1969**, *3*, 227–231.

(4) Kawakami, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn* **1978**, *51*, 21–24.

(5) (a) Vol'pin, M. E.; Kolomnikov, I. S. *Dokl. Akad. Nauk SSSR* **1966**, *170*, 1321–1324. (b) Gosser, L. W.; Parshall, G. W. *Inorg. Chem.* **1974**, *13*, 1947–1950. Gosser, L. W. *Ibid.* **1975**, *14*, 1453–1456; **1977**, *16*, 427–429, 430–434. (c) Rakowski, M. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 739–743.

(6) Klein, H. F.; Hammer, R.; Wenninger, J., Gross, J. "Catalysis in Chemistry and Biochemistry"; Pullman, B., Ed.; D. Reidel Publishing Co.: Amsterdam, 1979; p 285.

(7) Klein, H. F.; Hammer, R.; Gross, J.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *18*, 809–810.

(8) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1976**, *98*, 4665–4667; **1978**, *100*, 6978–6989.

0002-7863/82/1504-3891$01.25/0