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Solvent Influence on the Circular Dichroism Spectrum of Potassium Ethylenediaminetetraacetatocobaltate(III)

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The circular dichroism (CD) spectrum of optically active potassium ethylenediaminetetraacetatocobaltate(III), (+)-K[Co(edta)]·$2H_2O$, was measured in water and a variety of organic solvents: ethylene glycol, methanol, formamide, ethanol, 2-propanol, chloroform, nitromethane, dichloromethane, dimethyl sulfoxide, acetonitrile, *N,N*-dimethylformamide, benzonitrile, *N,N*-dimethylacetamide, and acetone. The spectra in organic solvents were obtained for the solutions of the complex anion, which were prepared by the addition of a macrobicyclic polyether, cryptand 222. It was found that the peak positions and intensities of the CD bands are markedly influenced by the solvent molecules and this solvent influence on the peak position is linearly correlated to the influence on the corresponding first d-d absorption spectrum. Therefore, the solvent influence on the CD spectrum of this complex is suggested to be caused by the change in the d-d transition energy of this Co(III) complex anion. Furthermore, the positions and intensities of the CD peaks were also correlated with the electrophilic ability (the acceptor number: *AN*) and the bulk polarity (the dielectric constant) of the solvent, respectively. It is proposed that the inherent CD spectrum of $[Co(edta)]^-$ that is not solvated could be estimated on the basis of this correlation.

In the field of coordination chemistry, the circular dichroism (CD) spectra of metal complexes, especially cobalt(III) complexes, have been utilized to determine their absolute configuration around the central metal ions.$^{1)}$ This is because the CD spectra in the d-d transition region are mainly dependent on the configuration of the metal complex, though these are affected to some extent by the conformation of the chelating ligand or the so-called vicinal effect from the ligand asymmetry. However, the CD spectra are sometimes influenced drastically by the outersphere interaction with the counter ion and the solvent molecule. Therefore, one can not obtain any decisive conclusion about the absolute configuration of the complex ion if the influence of the outersphere interaction is not made clear. The influence of the counter ion has so far been investigated for many cobalt(III) complexes:$^{2)}$ $[Co(en)_3]^{3+}$ (en=ethylenediamine) and other cationic Co(III) complexes; the counter ions are oxoacid anions (PO_4^{3-}, SO_4^{2-}, etc.) and some dicarboxylates. As for the influence of the solvent, only a few systematic studies would appear to have been made on the circular dichroism of optically active metal complexes. Concerning the solvent influence on the CD spectra two reasons have so far been proposed. Bosnich and Harrowfield$^{3)}$ reported that the CD spectra of cobalt(III) complexes of *trans*-$[Co(N)_4(X)_2]^+$ are markedly solvent-dependent, where $(N)_4$ refers to chiral quadridentate amines. In their first paper, they suggested that *trans*-(*R,R*)-$[Co(3,2,3\text{-tet})(N_3)_2]ClO_4$(3,2,3-tet=$NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$) changed the sign of the CD peak in the longest wavelength region and this is due to the change of the chelate-ring conformation. By contrast, Hawkins et al.$^{4)}$ investigated the CD and proton NMR spectra of some *trans*-$[Co(R\text{-pn})_2(X)_2]^{n+}$ and related complexes in a variety of solvents (*R*-pn=(*R*)-1,2-propanediamine). They ascribed the solvent dependence of the CD spectra to the stereoselective hydrogen bonding that is formed between the equatorial amino hydrogens of the complex cation and the solvent molecules, leading to the induction of the new asymmetry on the coordinated nitrogens. Thus, in both these two investigations it was proposed that the main factors of this solvent influence on the CD are the change of the chelate-ring conformation and the vicinal effect caused by the asymmetry induction on the coordinated nitrogens.

On the other hand, it has been found that the peak position of the first d-d absorption band is considerably influenced by solvent molecules when the absorption spectrum of K[Co(edta)]·$2H_2O$ was obtained in several organic solvents;$^{5)}$ the complex is solubilized by the addition of a macrocyclic polyether, 18-crown-6 ether and cryptand 222.$^{6)}$ This phenomenon makes us expect that the CD spectrum of this complex shows a fairly intensive solvent dependence. This complex anion, $[Co(edta)]^-$, has no amino hydrogens in the ligand and seems to have no flexible chelate rings leading to the drastic conformational change. Therefore, this should be a type of complex different from those considered in the above literature.

From this viewpoint, we have observed the CD spectra of optically active potassium ethylenediaminetetraacetatocobaltate(III) in a variety of solvents in order to elucidate how the CD of this complex is influenced by the solvent. The peak positions and intensities in each solvent are examined on the basis of the corresponding peak positions in the d-d absorption spectra, the dielectric constants and the acceptor numbers of solvents; the last parameter was proposed by Mayer et al. as a means of estimating the electrophilic ability of the solvents.$^{7)}$ Thereafter, we have tried to obtain the inherent CD spectrum of

$[Co(edta)]^-$ without the contribution of the outer-sphere interactions.

Experimental

Materials. $K[Co(edta)]\cdot 2H_2O$ was prepared and resolved into two enantiomers $(+)_{546}$- and $(-)_{546}$-$K[Co(edta)]\cdot 2H_2O$[8] by using $(-)$-$[Co(NO_2)_2(en)_2]Br$[9] which was resolved by potassium antimony (*R,R*)-tartrate. The purity of these complexes was checked by spectroscopic methods: 580 nm (−1.72) and 500 nm (+0.77) for (+)-isomer from the less soluble diastereomeric salt [lit,[10] 578 nm (+1.50) and 504 nm (−0.76) for (−)-isomer]. Cryptand 222 was purchased from Merck Co. The organic solvents were of the purest grade commercially available and were used without further purification. The solvents used here are as follows: water, ethylene glycol, methanol, formamide, ethanol, 2-propanol, chloroform, nitromethane, dichloromethane, dimethyl sulfoxide, acetonitrile, *N,N*-dimethylformamide, benzonitrile, *N,N*-dimethylacetamide, and acetone.

Measurements. The circular dichroism (CD) spectra were recorded at ambient temperature[11] on the solutions of $(+)$-$K[Co(edta)]\cdot 2H_2O$ $((1.00-1.50)\times 10^{-3}\ \mathrm{mol\,dm^{-3}})$ for water, and for organic solvents containing cryptand 222 (the 1.5 times concentration). A JASCO J-40CS recording spectropolarimeter with a 1-cm cell was used for the CD measurements. The CD spectra are not influenced by the addition of various amounts of cryptand 222 or by a change of the concentration of the cobalt(III) complex.[12] Furthermore, the slight amount of hydrate water $((2.00-3.00)\times 10^{-3}\ \mathrm{mol\,dm^{-3}})$ were not a problem because the CD spectrum of the anhydrous salt of this complex shows only a minor change (within experimental error) in the solvents of acetonitrile and chloroform.

Results and Discussion

The CD spectra of $(+)_{546}$-$K[Co(edta)]\cdot 2H_2O$ (edta= $^-OOCCH_2(^-OOCCH_2)NCH_2CH_2N(CH_2COO^-)$-$CH_2COO^-$) in water and in chloroform are shown in Fig. 1. It is obvious that these CD spectra are very different from one another in the position and intensity of the peak. In both solvents, the CD spectra of this complex apparently have two components in the first d-d transition region (440—700 nm): a A_2 component of minus sign in the longer wavelength region and a B_2 or B_1 component (overlapped) of plus sign in the shorter wavelength region. (The assignment of the CD peaks has been made for the complex of C_2 symmetry near to the C_{2v} limit by McCaffery et al.[13] and the assignment of $[Co(edta)]^-$ has been carried out by Douglas et al.[10]) The peak positions of both components appear in a longer wavelength region in chloroform than in water. The intensity of the A_2 component is greater in water but that of the B_2 or B_1 component is slightly smaller in water than in chloroform. As the $[Co(edta)]^-$ anion is inert and stable in these solvents, this difference in CD is due to the outersphere interaction between the complex anion and solvent molecules.[14,15]

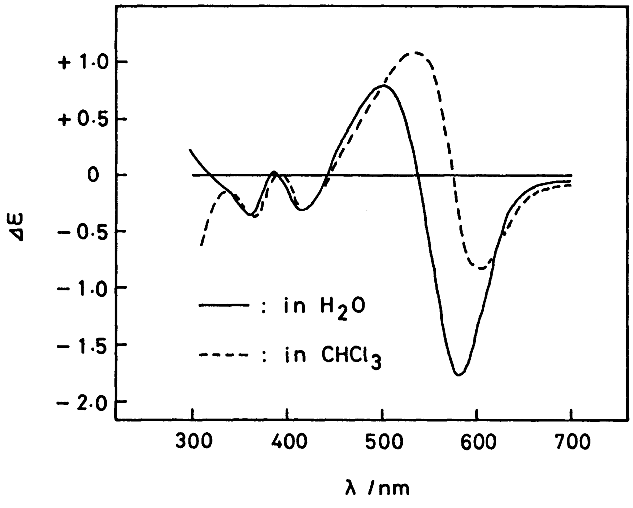

Fig. 1. The CD spectra of $(+)$-$K[Co(edta)]\cdot 2H_2O$ in water (H_2O) and chloroform ($CHCl_3$).

Table 1. The Peak Positions and Intensities of the First d-d Circular Dichroism (CD) Bands of $(+)_{546}$-$K[Co(edta)]\cdot 2H_2O$ in a Variety of Solvents

Solvent	*AN*[a)]	Dielectric constant	λ_1/nm	λ_2/nm	$\Delta\varepsilon_1$	$\Delta\varepsilon_2$
H_2O	54.8	78.5	580	500	−1.72	+0.77
EG		37.7	589	514	−1.57	+1.13
CH_3OH	41.3	32.6	591	517	−1.45	+1.00
FA	39.8	109.5	584	504	−1.91	+0.75
C_2H_5OH	37.1	24.3	593	521	−1.27	+1.14
i-C_3H_7OH	33.5	18.3	598	525	−1.17	+1.33
$CHCl_3$	23.1	4.8	606	535	−0.81	+1.12
CH_3NO_2	20.5	36.7	594	518	−1.44	+0.86
CH_2Cl_2	20.4	8.9	603	528	−0.98	+0.84
Me_2SO	19.3	46.7	596	523	−1.60	+0.99
CH_3CN	18.9	36.0	595	519	−1.43	+0.75
DMF	16.0	36.7	599	528	−1.45	+1.08
C_6H_5CN	15.5	25.2	600	528	−1.32	+0.95
DMA	13.6	37.8	602	532	−1.32	+1.18
Me_2CO	12.5	20.7	602	531	−1.12	+1.00

a) *AN* refers to the acceptor number of the solvent.

All data of the peak positions and intensities of the CD obtained are presented in Table 1 for a variety of solvents: H_2O, ethylene glycol (EG), methanol (CH_3OH), formamide (FA), ethanol (C_2H_5OH), 2-propanol (*i*-C_3H_7OH), chloroform ($CHCl_3$), nitromethane (CH_3NO_2), dichloromethane (CH_2Cl_2), dimethyl sulfoxide (Me_2SO), acetonitrile (CH_3CN), *N,N*-dimethylformamide (DMF), benzonitrile (C_6H_5CN), *N,N*-dimethylacetamide (DMA), and acetone (Me_2CO). This table also includes the acceptor numbers (*AN*) and the dielectric constants of solvents.

Correlation between the Peak Positions in CD and Absorption Spectra. At first we consider the correlation between the peak positions (λ_{max}(CD)) in the CD spectra and the peak positions (λ_{max}(ABS)) in the first d-d absorption spectra.[16] In Fig. 2, are plotted the λ_{max}(CD) values of the A_2 component against the λ_{max}(ABS) values[5] of the first d-d transition band in the corresponding solvents: H_2O, EG, CH_3OH, FA, C_2H_5OH, *i*-C_3H_7OH, $CHCl_3$, CH_3NO_2, CH_2Cl_2, Me_2SO, CH_3CN, DMF, C_6H_5CN, DMA, and Me_2CO. This figure indicates a linear correlation between these two values. Figure 3, in which the same plot for the B_2 or B_1 component is shown, suggests that the λ_{max}(CD) values are also linearly correlated to the λ_{max}(ABS) values. Therefore, the solvent dependence of the peak position of the CD in the first d-d transition region is completely due to the change in the d-d transition energy of this complex anion.

In the works of Bosnich and Hawkins, it seems that there is no such correlation between the peak positions in CD and absorption spectra. This is because the newly induced ligand asymmetry and the change of the ligand conformation do not influence the absorption spectra in this way. Therefore, this suggests that the solvent influence is not generated from these two factors.

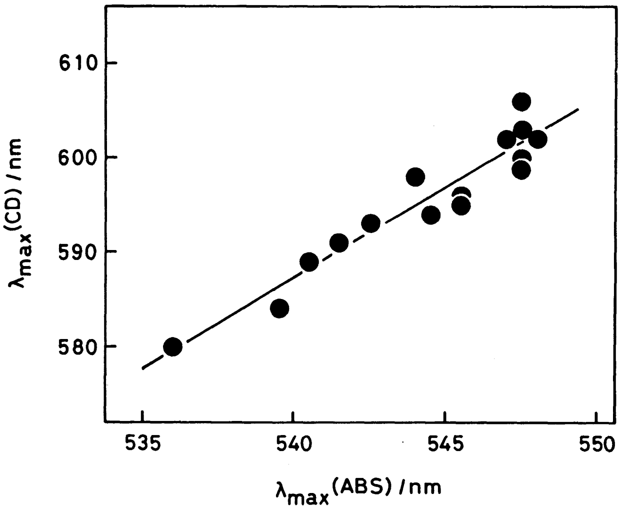

Fig. 2. The correlation between the peak positions (λ_{max}(CD): λ_1 in Table 1) of the A_2 component in the CD spectrum and the peak positions (λ_{max}(ABS)) of the first d-d absorption band in a variety of solvents. The data are plotted for the solvents presented in Table 1; the slope is 1.916 and the correlation coefficient is 0.955. The values of the peak positions of absorption bands are taken from Ref. 5.

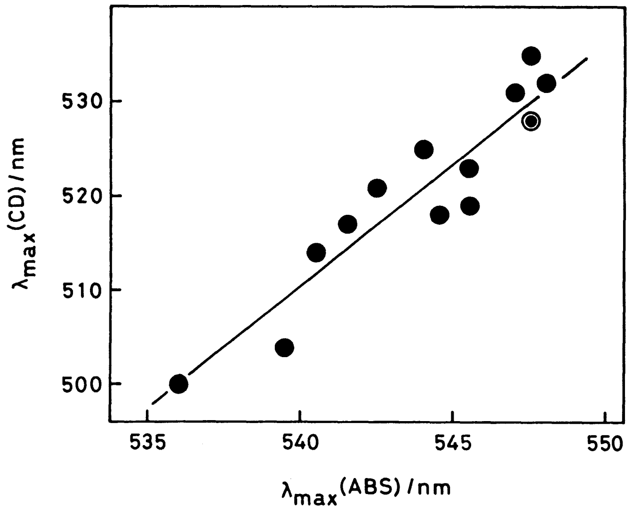

Fig. 3. The correlation between the peak positions (λ_{max}(CD): λ_2 in Table 1) of the B_2 or B_1 component in the CD spectrum and the peak positions (λ_{max}(ABS)) of the first d-d absorption band in a variety of solvents. The data are plotted for the solvents presented in Table 1; the slope is 2.586 and the correlation coefficient is 0.937. The values for absorption bands are from Ref. 5.

Correlation between the Peak Positions in CD and the Acceptor Numbers of Solvents. Furthermore, in order to elucidate the origin of this CD change more clearly, this solvent dependence is examined on the basis of the acceptor numbers (*AN*) that are proposed as a measure of estimating the electrophilic ability of solvents. In Table 1, it is apparent that λ_{max}(CD) (in later sections λ_{max} is used in place of λ_{max}(CD)) values are shifted to the shorter wavelength region as the acceptor number (*AN*) increases. The acceptor number indicates that the solvent bearing the large *AN* value is a strong electron acceptor. Therefore, solvent molecules interact strongly with the anion like $[Co(edta)]^-$ if the solvent bears a large value of the acceptor number. This interaction has already been investigated by the carbon-13 NMR studies.[15] It was reported in this NMR study that protic solvents bearing large *AN* values interact with negatively charged carboxyl groups of $[Co(edta)]^-$ through the hydrogen bonding between solvent hydrogens and carboxyl oxygens of the complex anion. Further, the solvent influence on the carbon-13 NMR chemical shift is rationalized by the electron-withdrawing effect caused by the hydrogen-bond formation. Accordingly, the CD change, which is due to the change of the d-d transition energy, is also supposed to be attributed to this hydrogen-bond formation between solvent molecules and $[Co(edta)]^-$ and to the electron-withdrawing effect. The correlation between this hydrogen bonding and the change in the electronic state of the complex has now been studied by MO calculation.[5b)] Then, the contribution of the solvent interaction to the peak positions of CD will be estimated quantitatively.

In Figs. 4 and 5, are plotted the λ_{max} values of the A_2 and B_2 or B_1 (abbreviated as B later on) components against the acceptor numbers of solvents. These figures indicate that the plots of λ_{max} give straight lines (the correlation coefficients are 0.821 and 0.801, respectively). The linearities of the lines suggest that the λ_{max} values in some solvent can be approximately estimated by using the acceptor number of the solvent. If the complex anion is hypothetically free from the solvation in hexane that bears the *AN* value of zero, the peak positions of the $[Co(edta)]^-$ anion that is not solvated could then be obtained by the extrapolations of these lines. The λ_{max} values of A_2 and B components in the solvent are calculated by the following equations (error bars are for one standard deviation):

$$\lambda_{max}(A_2) = \lambda_{max}{}^{\circ}(A_2) - (0.47 \pm 0.09) \times AN$$

$$\lambda_{max}(B) = \lambda_{max}{}^{\circ}(B) - (0.63 \pm 0.14) \times AN$$

where $\lambda_{max}{}^{\circ}(A_2)$, $\lambda_{max}{}^{\circ}(B)$, and *AN* refer to the peak positions ($\lambda_{max}{}^{\circ}(A_2)=608\pm3$ nm and $\lambda_{max}{}^{\circ}(B)=539\pm4$ nm determined by a linear least-squares analysis) in hexane as a standard solvent (*AN*=0) and the acceptor number of the solvent, respectively. The first terms in these equations could correspond to the inherent peak positions of the A_2 and B components for $[Co(edta)]^-$ that is not solvated and the second terms to the electron-withdrawing effect that is attributed to solvating molecules. Therefore, we could separate the inherent peak positions from the contributions of the solvent molecules.

The second terms in these equations are slightly different from each other (the coefficients are −0.47 for $\lambda_{max}(A_2)$ and −0.63 λ_{max} (B), respectively). Though the origin of this slight difference is not clear, these terms should be in principle the same because stereoselective solvation does not exist in this system, as has been shown in the carbon-13 NMR study.[15)] The solvent molecules interact equivalently with the four (axial and equatorial) carboxyl oxygens.

Correlation between the Intensities in CD and the Dielectric Constants of Solvents. One of the most interesting results in this work is the correlation between the intensities in CD and the dielectric constants of the solvents. The intensities of the CD peaks are varied from one solvent to another in Table

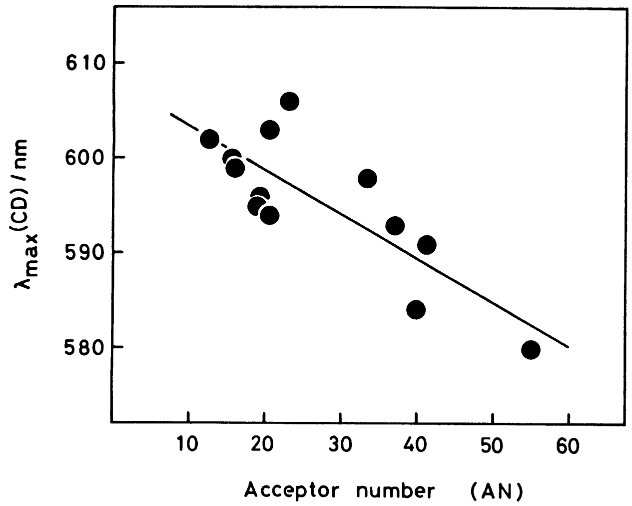

Fig. 4. The correlation between the peak positions (λ_{max}(CD): λ_1 in Table 1) of the A_2 component and the acceptor numbers (*AN*) of the solvents. The data are plotted for the solvents except for ethylene glycol (EG) presented in Table 1.

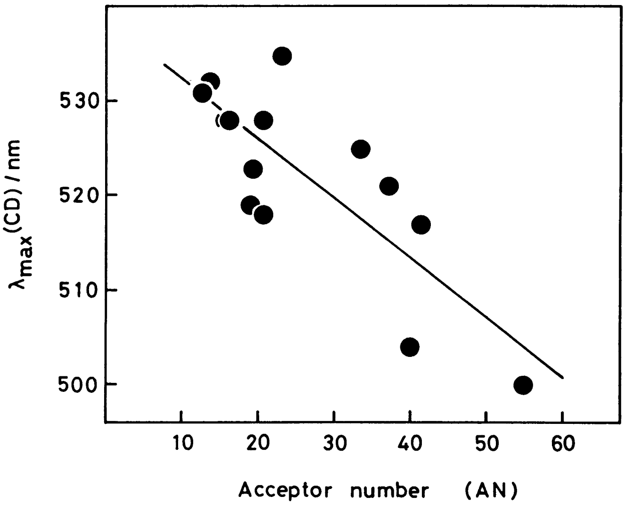

Fig. 5. The correlation between the peak positions (λ_{max}(CD): λ_2 in Table 1) of the B_2 or B_1 component and the acceptor numbers (*AN*) of the solvents. The data are plotted for the solvents except for ethylene glycol (EG) presented in Table 1.

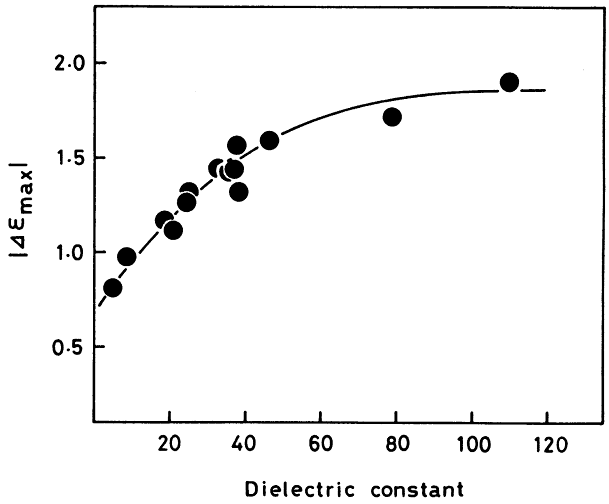

Fig. 6. The correlation between the intensities ($|\Delta\varepsilon_{max}|$: the absolute values of $\Delta\varepsilon_1$ in Table 1) of the A_2 component and the dielectric constants of the solvents.

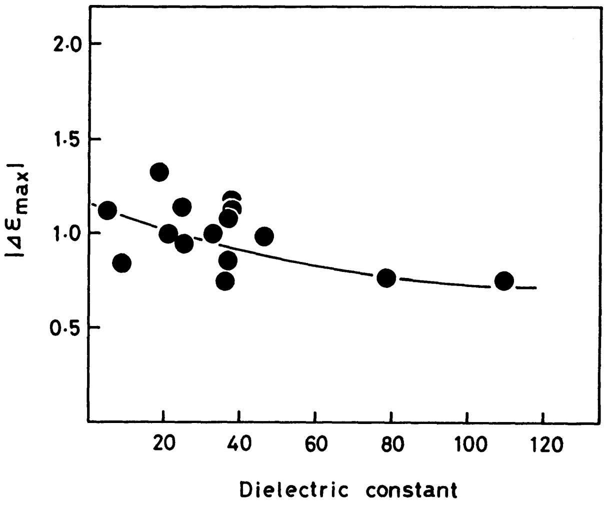

Fig. 7. The correlation between the intensities (|Δε$_{max}$|: the absolute values of Δε$_2$ in Table 1) of the B$_2$ or B$_1$ component and the dielectric constants of the solvents.

1. This variation is found to be correlated to the polarities of solvents, indicated by the dielectric constant. In Figs. 6 and 7, the intensities of the A$_2$ and B components are plotted against the dielectric constants of the solvents. The intensity of the B component does not drastically vary in this series of solvents. (The larger deviation of the plot in Fig. 7 is probably because this CD band contains two components B$_2$ and B$_1$.) In contrast to this component, the CD intensity of the A$_2$ component increases markedly and continuously as the dielectric constant of the solvent increases (Fig. 6). This A$_2$ component of the CD of [Co(edta)]$^-$ is assigned by McCaffery et al. and Douglas et al. The transition for the A$_2$ component is polarized along the C$_2$ axis of the complex, which is illustrated in Fig. 8. The electric dipole moment of this complex also extends along the C$_2$ direction, and so the polarization of the complex along this direction could increase more because of the polar environment of a large dielectric constant around the complex anion. Though a theoretical interpretation for the change of the rotational strength according to the dielectric constant of the solvent could not be suggested, it is probable that the rotational strength of the transition component A$_2$ polarized along the direction of the dipole increases as the polarization of the complex along this direction increases.

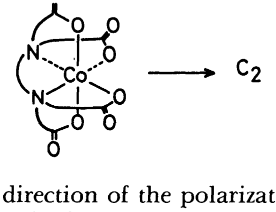

Fig. 8. The direction of the polarization for the A$_2$ transition and of the electric dipole moment of [Co(edta)]$^-$. The absolute configuration corresponds to the (+)$_{546}$-isomer that is used in this work.

We can confirm this result by considering the datum for formamide. This is one of the solvents bearing a dielectric constant larger than that of water. The dielectric constant of formamide (109.5) is much greater than that of water (78.5). In Fig. 6 one can clearly observe that the intensity of the A$_2$ component in formamide is much greater than the intensity in water.

It can be concluded that the intensity of the A$_2$ component which appears in the longest wavelength region increases as the dielectric constant corresponding to the bulk polarity of the solvent increases though the correlation is not linear.

From this correlation, we can tentatively estimate the intensities of the A$_2$ and B$_2$ or B$_1$(B) components in the hypothetical environment of the dielectric constant zero. These values are −0.70 (±10% error) for the A$_2$ and +1.15 (±20% error) for the B, which are evaluated by the extrapolation of the plots in Figs. 6 and 7. It is certain that, generally speaking, the solvent influence on the CD intensity depends not only on the dielectric constant but also on other solvent properties, ex. refractive indices. In this case the CD-intensity variation seems to depend mainly on the dielectric constants of the solvents.

Conclusion

The solvent influence on the circular dichroism spectrum of [Co(edta)]$^-$ has been rationalized by examining the correlation between the peak positions of the CD spectra and the acceptor numbers, and the correlation between the intensities of the CD bands and the dielectric constants of the solvents. Based on this rationalization, the CD spectrum was divided into the inherent CD and the contribution of the solvent influence. Eventually, the inherent CD spectrum of optically active [Co(edta)]$^-$ that is not solvated could be proposed. The peak positions and intensities for (+)$_{546}$-isomer are 608±3 nm (−0.70) and 539±4 nm (+1.15) [obsd.: 580 nm (−1.72) and 500 nm (+0.77) in water].

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References

1) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley Interscience, New York (1971), Chap. 5.

2) S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, **1966**, 307; H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966); A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966); J. E. Sarneski and F. L. Urbach, *J. Am. Chem. Soc.*, **93**, 884 (1971); T. Taura and H. Yoneda, *Inorg. Chem.*, **17**, 1495 (1978); T. Taura, *J. Am. Chem. Soc.*, **101**, 4221 (1979).

3) B. Bosnich and J. M. Harrowfield, *J. Am. Chem. Soc.*, **94**, 989 (1972); B. Bosnich and J. M. Harrowfield, *Inorg. Chem.*, **14**, 828, 847, 861 (1975).

4) C. J. Hawkins, G. A. Lawrance, and R. M. Peachey, *Aust. J. Chem.*, **30**, 2115 (1977); C. J. Hawkins and M. L. McEniery, *Aust. J. Chem.*, **32**, 1433 (1979); C. J. Hawkins and J. Martin, *Inorg. Chem.*, **21**, 1074 (1982).

5) a) T. Taura, *Chem. Lett.*, **1984**, 2011; b) T. Taura, unpublished results.

6) T. Taura, *Inorg. Chim. Acta*, **98**, L15 (1985); T. Taura, presented at the 50th Annual Meeting of the Chemical Society of Japan, April 1985 (Abstract I, 1K18).

7) U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).

8) F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955); F. P. Dwyer and F. L. Garvan, *Inorg. Synth.*, **6**, 192 (1960).

9) F. P. Dwyer and F. L. Garvan, *Inorg. Synth.*, **6**, 195 (1960).

10) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

11) The temperature for the measurement is 23—25 °C. The CD spectrum was measured more than twice. The peak position was the same within experimental error (±1 nm) and the intensity was reproduced within ±3% of random errors. Therefore, the CD spectrum is not dependent on the temperature under the conditions used here.

12) It seems that there is no influence of the ion association with K^+ or the $K^+ \cdot C222$ complex on the CD spectra of the $[Co(edta)]^-$ anion, where C222 refers to cryptand 222.

13) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

14) The absorption and CD spectra in the solvents did not show the time dependence during the measurements.

15) T. Taura, *Inorg. Chem.*, **27**, 2845 (1988).

16) The plot of the wavenumbers (cm^{-1}) of the peak positions against the acceptor number also gives the straight line. The intercepts and correlation coefficients are quite similar to those obtained from the plots of the wavelengths (nm). The intercept and correlation coefficient are 16440±80 cm^{-1} (608 nm) and 0.820 for the A_2 component and 18550±150 cm^{-1} (539 nm) and 0.801 for the B component, respectively.