On the Induced Circular Dichroism of *d–d* Transitions of a 14-Membered Macrocyclic Tetra-amine Nickel(II) Complex in β-Cyclodextrin

Nagao Kobayashi,* Xizhang Zao, and Tetsuo Osa*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan
Kazumasa Kato, Kenji Hanabusa, Tomosaku Imoto, and Hirofusa Shirai*
Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan

Induced circular dichroism (i.c.d.) of *d–d* transitions of a 14-membered macrocyclic tetra-amine nickel(II) complex has been recorded in the presence of β-cyclodextrin. I.c.d. intensity appears to depend upon whether or not a band is magnetic dipole allowed, rather than on the direction of polarization of the band.

It is not always easy to obtain detailed information on *d–d* transitions experimentally. In cases of organometallic compounds, for example, *d–d* transitions of nickel in certain Ni^{II} complexes[1–6] and iron in cytochrome c[7,8] and ferrocenes[9–11] have been examined in detail. In this paper, we present the results of the induced circular dichroism (i.c.d.) of a nickel complex observed in the presence of β-cyclodextrin (β-cyd). The cyclodextrins are a series of oligosaccharides produced by the action of, for example, *Bacillius macerans* amylase on starch[12] and have a hydrophobic cavity in their centre capable of including gases, aromatic compounds, alkyl halides, *etc.*, as guest molecules. Accordingly, the c.d. is expected to be induced on the absorption bands of the achiral guest molecules which are included in the cavity of the cyclodextrin. By the accumulation of data, points (*a*)—(*c*) are now theoretically[13] and empirically[14–18] established on the i.c.d. spectra of 1:1 aromatic chromophore guest–cyd complexes. (*a*) Positive i.c.d. signs are produced by transitions parallel to the molecular axis of cyd even if the guest molecules are longer than the depth of the cavity of the cyd and even if their absorption bands are composed of many vibrational bands. (*b*) Negative i.c.d. signs are, on the other hand, produced by the transitions normal to the molecular axis of cyd. (*c*) A seemingly single u.v. absorption band which is actually composed of a superposition of two or more bands polarized perpendicularly to each other can be resolved so long as the oscillator strength of the respective bands are not exceedingly different from each other. (*a*)—(*c*) Should, at least in principle, apply for *d–d* transitions also. However, since some *d–d* transitions are magnetic dipole allowed, we were interested in determining which factor affects the i.c.d. to the greatest degree. Accordingly, we recorded the i.c.d. spectra of a Ni^{II} complex in the presence of β-cyd.

Experimental

Materials.—Since 1:1 [guest:host(= β-cyd)] complex formation was a prerequisite, complex $[Ni(L^1)][NO_3]_2$ (**1**) was prepared as a plausible candidate for the guest molecule.

Ethyl 2-Ethoxycarbonyl-8-hydroxyoctanoate.—This was prepared from 6-bromohexanol and diethyl malonate by the literature procedure[19] in 45% yield. ^1H N.m.r. $[(CD_3)_2SO]$: δ, 1.26 (m, 8 H), 1.28 (t, *J* 7, 6 H), 1.83 (m, 2 H), 3.15 (t, *J* 7, 1 H), 3.37 (m, 3 H), and 4.13 (q, *J* 7 Hz, 4 H). I.r.: $\nu(CO)_{max.}$ at 1 733 and 1 747 cm^{-1}. Mass spectrum (*m*/*e*): 261 (M^+ + 1), 260 (M^+), and 160 ($M^+ - C_6H_{12}O$).

6-(6′-*Hydroxyhexyl*)-5,7-*dioxo*-1,4,8,11-*tetra-azacyclotetradecane*, L^1.—According to the general method for the preparation of 2,4-dioxo-1,5,8,12-tetra-azacyclotetradecane,[20] equimolar amounts of ethyl 2-ethoxycarbonyl-8-hydroxyoctanoate and 1,3-bis[(2′-aminoethyl)amino]propane were refluxed in ethanol for 3 d, and after removal of solvent, the residue was purified through a silica gel column ($CHCl_3$–MeOH 2:1 v/v). Yield: 14% (very hygroscopic prisms) (Found: C, 58.50; H, 9.75; N, 17.30. Calc. for $C_{16}H_{32}N_4O_3$: C, 58.50; H, 9.80; N, 17.05%). ^1H N.m.r. $[(CD_3)_2SO]$: δ, 1.26 (m, 7 H), 1.57 (m, 6 H), 2.57 (m, 8 H), 2.66 (m, 2 H), 2.92 (m, 4 H), 3.36 (m, 3 H), and 7.60 (broad, 2 H). I.r.: $\nu(CO)_{max.}$ at 1 664 cm^{-1}. Mass spectrum (*m*/*e*): 328 (M^+) and 113 ($M^+ - C_9H_{19}N_4O_2$).

6-(6′-*Hydroxyhexyl*)-5,7-*dioxo*-1,4,8,11-*tetra-azacyclotetradecanenickel*(II) *Nitrate*, (**1**).—L^1 and excess of $Ni(NO_3)_2 \cdot 6H_2O$ were refluxed in distilled ethanol for 1 h. After cooling, the residue was filtered off and the filtrate concentrated and poured into diethyl ether. The resultant pale yellow precipitate was collected (81%). This was soluble in ethanol, methanol, and *NN*-dimethylformamide, but insoluble in diethyl ether and acetone. ^1H N.m.r. $[(CD_3)_2SO]$: δ, 1.26 (m, 7 H), 1.68 (m, 6 H), 2.45 (m, 2 H), 2.97 (m, 8 H), 3.47 (m, 3 H), 4.48 (m, 4 H), and 7.93 (broad, 2 H). I.r.: $\nu(CO)_{max.}$ at 1 640 cm^{-1} (broad). Electronic spectrum (0.05 mol dm^{-3} phosphate buffer, pH 9.2): $\lambda_{max.}$ at 456 nm (ε = 44.8 dm^3 mol^{-1} cm^{-1}).

Measurements.—Absorption and i.c.d. spectra were recorded on a Shimadzu UV-360 spectrophotometer and on a JASCO J-500 spectropolarimeter, respectively. Magnetic circular dichroism (m.c.d.) spectra were measured on the above spectropolarimeter equipped with a JASCO electromagnet to produce longitudinal magnetic fields up to 1.5 T. Each measurement was made with both parallel and antiparallel fields. Pathlengths of the cells used were 5, 10, and 20 mm and the temperature was 20 ± 1 °C. pH Values were determined with a Hitachi-Horiba M-7 pH meter.

Sample Preparation.—Complex (**1**) and β-cyd were directly dissolved in 0.05 mol dm^{-3} H_2SO_4 containing 0.2 mol dm^{-3} Na_2SO_4 or in 0.3 mol dm^{-3} KH_2PO_4 adjusted to pH 9.2 by NaOH.

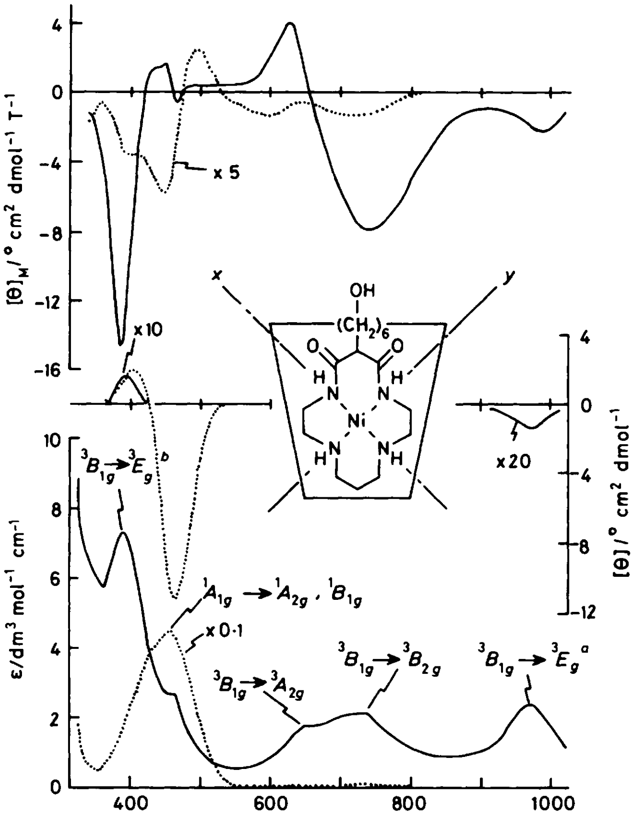

Figure 1. Absorption (bottom), i.c.d. (middle), and m.c.d. (top) spectra of (**1**) in water at pH *ca.* 1 (——) and *ca.* 9.2 (· · · ·). Note the magnification factor. Cell pathlengths used were 5, 10, and 20 mm. The inset shows a (**1**)–β-cyd axial inclusion complex and the directions of *x* and *y* (*z* is normal to the plane containing *x* and *y*). [θ] and [θ]$_M$ are i.c.d. and m.c.d. intensity units, respectively

Results and Discussion

Figure 1 shows the electronic absorption, i.c.d., and m.c.d. spectra of (**1**) in the presence of β-cyd at pH 1 and 9.2. For dioxo tetra-amine (L) nickel^{II} complexes, it is well known[21–25] that they exist in aqueous solution as an equilibrium mixture of a blue, octahedral, high-spin species and a yellow, planar, low-spin species according to equation (1). Also, the dioxo tetra-amine framework itself is more planar than usual tetra-amine ligands because of the presence of two oxo groups.[25] In the present case, the spectra at pH 1 can be assigned to a blue, high-spin species[4,5,24] and those at pH 9.2 to a yellow, low-spin species[6,21,24,25] mixed with a small percentage of a high-spin complex, from the shape of the characteristic absorption spectra. The composition ratio of the (**1**)–β-cyd inclusion complex was, on the other hand, 1 : 1 at pH 9.2 as indicated by the continuous variation plots in Figure 2. The ratio at pH 1 could not be obtained because the i.c.d. intensity at this pH was too low. However, since the Corey–Pauling–Koltum molecular model effectively eliminates the possibility of inclusion of more than one molecule of (**1**), the ratio at pH 1 is also considered to be 1 : 1. The type of inclusion of (**1**) in β-cyd is then considered to be an axial inclusion (in which the long axes of arenes are parallel to the axis of the cyd cavity), since (**1**) is almost the same size as pyrene and pyrene is known to be one of the best sized molecules for an axial inclusion in β-cyd.[18] Also, the Corey–Pauling–Koltum model reasonably suggests an axial inclusion.

$$\underset{\substack{\text{blue}\\\text{high-spin}}}{[\mathrm{NiL(H_2O)_2}]^{2+}} \rightleftharpoons \underset{\substack{\text{yellow}\\\text{low-spin}}}{[\mathrm{NiL}]^{2+}} + 2\mathrm{H_2O} \qquad (1)$$

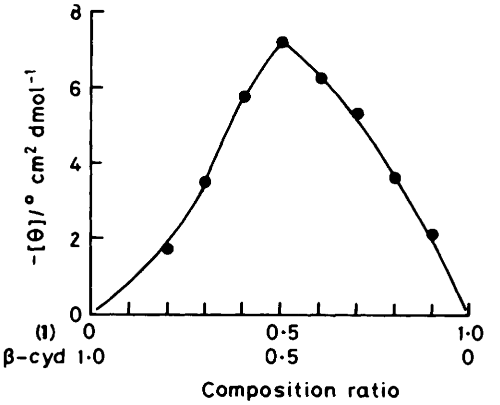

Figure 2. Continuous variation plots for the (**1**)–β-cyd system at pH 9.2 (i.c.d. intensity at 463 nm was used). [(**1**)] = [β-cyd] = 0.01 mol dm^{-3}

At pH 1, m.c.d. showed positive or negative signs corresponding to all the absorption peaks. In contrast, i.c.d. was observed only in the range 370—420 nm and above *ca.* 900 nm. Corresponding to the absorption peak of the former band ($^2B_{1g} \longrightarrow {}^3E_g{}^b$), a tiny positive i.c.d. appeared, whereas a negative i.c.d. was recognized above 900 nm. Based on the analysis of the polarized single-crystal spectrum of [Ni(L^2)Cl$_2$] (L^2 = 1,4,8,11-tetra-azacyclotetradecane),[4] where the vibronic intensity mechanism in conjunction with the usual symmetry consideration was taken into account, electronic transitions $^3B_{1g} \longrightarrow {}^3E_g{}^a$ and $^3B_{1g} \longrightarrow {}^3E_g{}^b$ are polarized not only along the *z* axis but also in the *xy* plane.* Bearing the above information on the polarization in mind, we can now ascertain whether or not points (*a*)—(*c*) established on cyd–aromatic guest 1 : 1 inclusion complexes hold.

As mentioned above, an axial inclusion is the one and only inclusion inferred. Then, the i.c.d. intensities in the transitions which have polarization directions along *x* and *y* (45° from the direction of the long axis, see inset in Figure 1) become small due to the theory[13] as developed in ref. 14. Accordingly, i.c.d. in the 550—850 nm region was not observed. Also, the transitions along *x* and *y* in the 370—420 and 900—1 000 nm regions did not show any i.c.d. by the same arguments. If the transitions along *z* are to be observed, a negative i.c.d. should be detected based on point (*b*). This is the case in the 900—1 000 nm region. For the same reason we expected a negative i.c.d. peak in the 370—420 nm region. However, a positive i.c.d. was detected. Thus, if we try to explain the observed i.c.d. from the standpoint of the direction of polarization, rationalization of this region is difficult. An alternative approach for the interpretation of i.c.d. spectra is to determine whether or not the band corresponds to a magnetic allowed transition. Under D_{4h} symmetry, $B_{1g} \longrightarrow E_g$ transitions are strongly magnetic dipole allowed, while a $B_{1g} \longrightarrow B_{2g}$ transition has no first-order magnetic dipole moment. Accordingly, in this respect, it appears reasonable that an i.c.d. was observed in the 370—420 and 920—1 020 nm regions and that no i.c.d. was detected in the 600—800 nm region.

At pH 9.2, a relatively intense absorption band, which can be

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* The absorption spectrum of (**1**) at pH 1 is very similar to that of [Ni(L^2)Cl$_2$] or [Ni(L^2)Br$_2$] (Figure 4 of ref. 4), while that at pH 9 has the characteristics of a low-spin square-planar Ni complex (ref. 25). The spectra of these complexes have all been interpreted on the approximation of D_{4h} symmetry. Accordingly, we adopted D_{4h} symmetry to interpret the spectra of (**1**). Although (**1**) has C_{2v} symmetry at alkaline pH, we have considered only the close vicinity of the nickel atom.

assigned to $^1A_{1g} \longrightarrow {}^1A_{2g}$ and/or $^1A_{1g} \longrightarrow {}^1B_{1g}$ transition(s)[6] in diamagnetic tetragonal Ni chelates, appeared at 456 nm. The presence of a trace amount of a high-spin component could also be recognized from the spectra in the 370—420 and 550—800 nm regions. As expected from (*b*), a negative i.c.d. appeared corresponding to this band. Of $^1A_{1g} \longrightarrow {}^1A_{2g}$ and $^1A_{1g} \longrightarrow {}^1B_{1g}$ transitions, the contribution of the latter transition might be reflected, since these transitions are from d_{xy} to $d_{x^2-y^2}$ orbitals and from d_{z^2} to $d_{x^2-y^2}$ orbitals, respectively. On the other hand, from the standpoint of magnetic dipole moment, $^1A_{1g} \longrightarrow {}^1A_{2g}$ and $^1A_{1g} \longrightarrow {}^1B_{1g}$ transitions are allowed and forbidden transitions, respectively. Accordingly the opposite result is suggested. That is, a negative i.c.d. in the 430—530 nm region appears to be the $^1A_{1g} \longrightarrow {}^1A_{2g}$ transition. Of the two conflicting possibilities, the latter may be greater considering that the spectrum at pH 1 was more reasonably understood based on the magnetic dipole moment.

As mentioned above, the i.c.d. of (**1**) in β-cyd may be interpreted with the aid of knowledge of i.c.d. on 1 : 1 aromatic guest–cyd complexes. However, the above results suggest that i.c.d. intensity depends rather more sensitively on whether or not the band is magnetic dipole allowed. Although this study is only the first step, we believe the present method is attractive for the study of *d–d* transitions because (*i*) cyclodextrins of various sizes are now available depending on the size of metal complex and (*ii*) sample preparation is very simple. (If the compounds are not water-soluble, a supernatant solution can be used after stirring the compounds in water containing the cyclodextrin. Also, solvents such as *NN*-dimethylformamide and dimethyl sulphoxide might be employed, since cyclodextrins can form inclusion complexes with arenes in these solvents.[26]) I.c.d. measurements appear, at least, to be useful in resolving overlapping bands (as shown for the band at 350—550 nm at pH 9.2).

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