CHEMISTRY LETTERS, pp. 1959-1962, 1982. 1982

DIASTEREOMERS OF ROTAXANE COMPOSED OF LONG-BRIDGED DINUCLEAR COBALT(III) COMPLEX AND α-CYCLODEXTRIN

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Two optically active diastereomers of [2]-[[(en)$_2$Co{NH$_2$(CH$_2$)$_2$-S(CH$_2$)$_{12}$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]Cl$_6$]-[α-cyclodextrin]-rotaxane, [ΔΔ]-[α-CDX] and [ΛΛ]-[α-CDX], were isolated and characterized from their absorption, circular dichroism, and ^{13}C NMR spectra. The yield of ΔΔ isomer is *ca.* 28%, whereas that of ΛΛ isomer only *ca.* 14%.

Recently we reported the preparation of monobridged dinuclear cobalt(III) complexes from the reaction of [Co(NH$_2$CH$_2$CH$_2$S)(en)$_2$](ClO$_4$)$_2$ and α,ω-dibromoalkanes.[1] In the presence of cyclodextrin(CDX), the long-bridged dinuclear complex is expected to form a rotaxane, which has four diastereomers because of the inequality of both openings of CDX as shown in Fig. 1(neglecting the *R* and *S* chiralities of the donor sulfur atoms). The usual synthesis starting from the racemic complex gives a mixture of the diastereomers. Similar rotaxanes of mixed isomers were reported for the system obtained from [CoCl$_2$(en)$_2$]$^+$, α,ω-diaminoalkanes, and CDX.[2] On the other hand, the use of optically active complex Δ- or Λ-[Co(NH$_2$CH$_2$CH$_2$S)(en)$_2$]$^{2+}$ is expected to lead to ΔΔ- or ΛΛ-isomer of the rotaxane, respectively. Here we report the optically active diastereomers of [2]-[[(en)$_2$Co(ddod)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane[3] (1,18-diamino-3,16-dithiaoctadecane NH$_2$(CH$_2$)$_2$S(CH$_2$)$_{12}$S(CH$_2$)$_2$NH$_2$ is hereafter abbreviated as ddod). The isolated two isomers, [ΔΔ]-[α-CDX] and [ΛΛ]-[α-CDX], were characterized from absorption, circular dichroism(CD), and ^{13}C NMR spectra and elemental analysis.

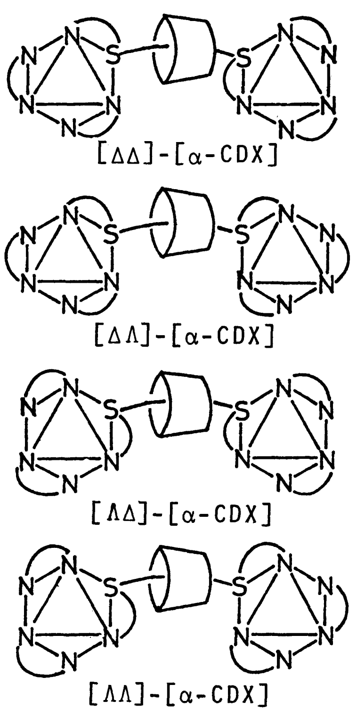

Fig 1. Four possible diastereomers of [2]-[[(en)$_2$Co(ddod)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane.

4.4 mmol of Δ- or Λ-[Co(NH$_2$CH$_2$CH$_2$S)(en)$_2$]-

$(ClO_4)_2$ and 2.6 mmol of 1,12-dibromododecane(20% excess) were dissolved in 10 ml of dimethyl sulfoxide containing 5 g of α-CDX. The mixture was kept for 10 days at 30°C, leading to deep red solution. During this period, white crystals appeared gradually in the bottom of reaction vessel, which were identified with the inclusion compound of $(CH_2)_{12}Br_2$ and α-CDX. The unreacted dibromoalkane was extracted into diethyl ether for several times. The resulting dark red oil was dissolved in water, adsorbed on an SP-Sephadex C-25 cation exchange column(Na^+ form), and eluted with a 0.8 mol dm^{-3} NaCl solution. Six colored bands, f1-f6, were eluted. The species, f2 (dark brown), f3(orange), f5(orange), and f6(orange), were characterized as $[Co(NH_2CH_2CH_2S)(en)_2]^{2+}$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}OH\}]^{3+}$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}]^{3+}$, and $[(en)_2Co(ddod)Co(en)_2]^{6+}$(bridged complex), respectively. Orange band f1 was evaporated to a small volume and to give the chloride salt, whose composition agreed with $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}]Cl_3 \cdot 2(\alpha\text{-CDX})$. Orange band f4 was also evaporated to a small volume and, after repeated removal of NaCl deposited out, the solution was treated with a large amount of ethanol to give the orange precipitate of the desired rotaxane. The yield of [ΔΔ]-[α-CDX] isomer was *ca.* 28%, whereas that of [ΛΛ]-[α-CDX] isomer only *ca.* 14%.[4)] Found: C, 36.74; H, 7.48; N, 6.60%. Calcd for [2]-[ΔΔ-$[(en)_2Co(ddod)Co(en)_2]Cl_6$]-[α-CDX]-rotaxane·$2.5C_2H_5OH \cdot 8H_2O$ = $C_{65}H_{159}N_{10}O_{40.5}S_2Cl_6Co_2$: C, 36.76; H, 7.55; N, 6.60%. Found: C, 37.14; H, 7.45; N, 6.57%. Calcd for [2]-[ΛΛ-$[(en)_2Co(ddod)Co(en)_2]Cl_6$]-[α-CDX]-rotaxane·$3C_2H_5OH \cdot 7H_2O$ = $C_{66}H_{160}N_{10}O_{40}S_2Cl_6Co_2$: C, 37.24; H, 7.58; N, 6.58%.

Figure 2 shows the absorption and CD spectra. The absorption spectra of both isomers are characteristic of the $[Co(N)_5(S)]$ chromophore containing a

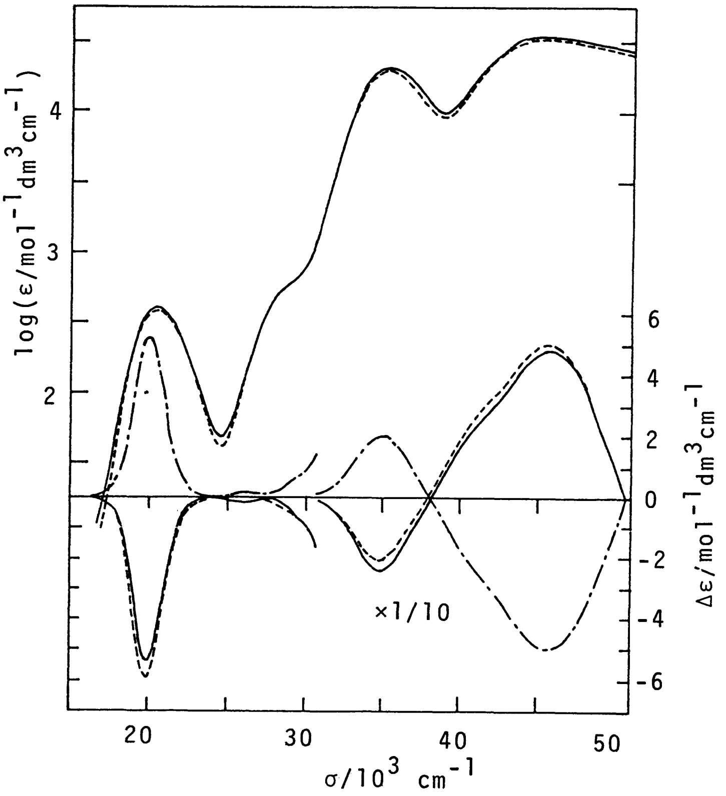

Fig 2. Absorption and CD spectra of [2]-[ΔΔ-$[(en)_2Co(ddod)Co(en)_2]Cl_6$]-[α-CDX]-rotaxane(————), [2]-[ΛΛ-$[(en)_2Co(ddod)Co(en)_2]Cl_6$]-[α-CDX]-rotaxane (-—-—-—), and ΔΔ-$[(en)_2Co(ddod)Co(en)_2]Cl_6$(--------).

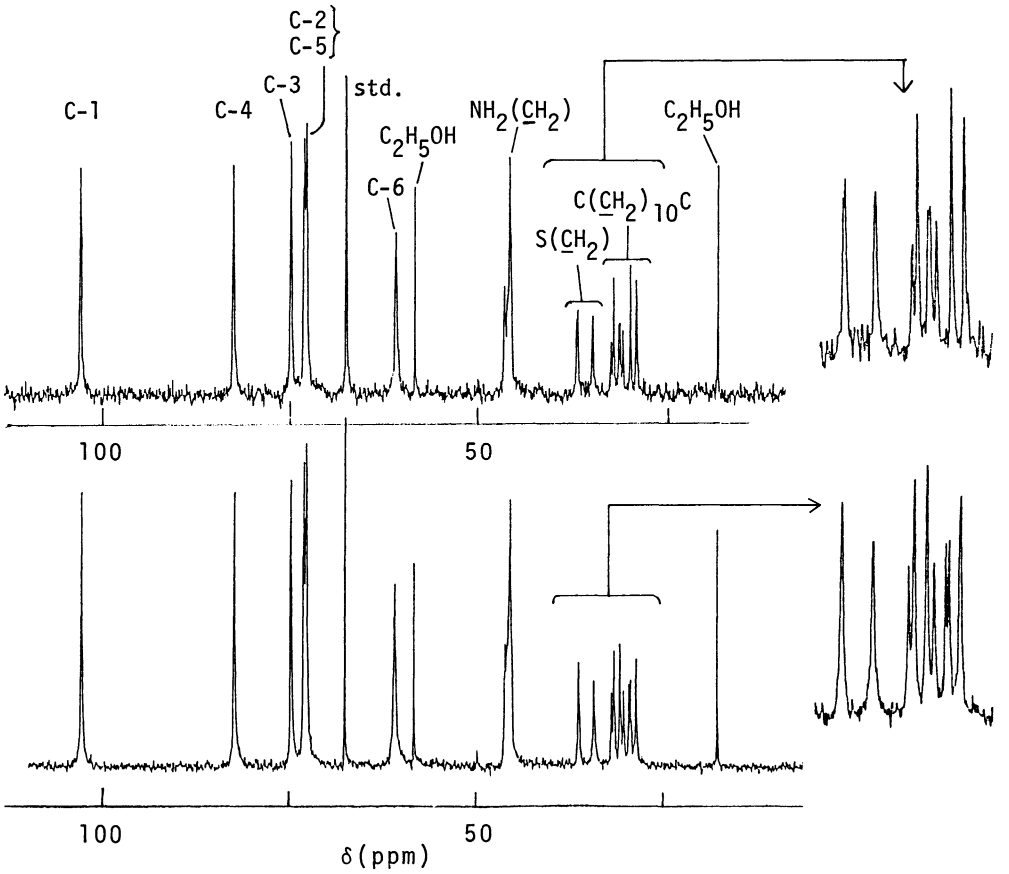

Fig 3. ^{13}C NMR spectra of [2]-[ΛΛ-[(en)$_2$Co(ddod)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane(upper) and [2]-[ΔΔ-[(en)$_2$Co(ddod)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane(lower). 1,4-dioxane(δ 67.4 vs Me$_4$Si) was used as the internal reference. The signals of α-CDX(C-1∼C-6) were assigned after ref. 5.

thioether donor atom. Molar extinction coefficients of the rotaxanes are slightly higher in the regions of the first d-d absorption and thioether charge transfer(CT) bands than those of the corresponding bridged complex. A similar increase of CD intensity is observed in the CT band region. The ratio of $\Delta\varepsilon_{287}/\Delta\varepsilon_{502}$ is rather higher in the rotaxanes(4.48 and 3.86 for [ΔΔ]-[α-CDX] and [ΛΛ]-[α-CDX], respectively) than the bridged ΔΔ-complex(3.43). The CD spectra of both rotaxanes are not enantiomeric to each other. The difference is eminent in the CT band region. The CD intensity ratio of $\Delta\varepsilon_{219}/\Delta\varepsilon_{287}$ is 1.97 for [ΔΔ]-[α-CDX] and 2.46 for [ΛΛ]-[α-CDX].

^{13}C NMR spectra offered the direct evidence of the rotaxane formation(Fig. 3). The spectral patterns and chemical shifts of α-CDX moiety in both the isomers are almost the same as those of free α-CDX. The implication is that there is no intimate interaction between the α-CDX and cobalt(III) moieties.[2)] All isomers of the rotaxane have C_1 symmetry because of α-CDX. Indeed, both the isomers showed seven signals in the -C(CH$_2$)$_{10}$C- region, of which each of the strong three signals corresponds to two CH_2 and each of weak four to one CH_2. The spectra of both rotaxanes are obviously different from each other, especially in the $-S(CH_2)-$ and $-C(CH_2)_{10}C-$ regions. Thus, the [ΔΔ]-[α-CDX] and [ΛΛ]-[α-CDX] rotaxanes have C_1 symmetry and are diastereomeric with each other.

The rotaxane with a charge of 6+ was eluted before $[Co(en)_2\{NH_2(CH_2)_2S-(CH_2)_{12}Br\}]^{3+}$. The rotaxanes have slightly higher values of the molar conductance at 25°C than the corresponding bridged complexes with a charge of 6+. Therefore, the behavior of column chromatography is ascribed to the presence of bulky CDX, which weakens the interaction between the complex ion and sulfopropyl groups in SP-Sephadex resin. Similar chromatographic behavior has been observed in the system of $[CoCl_2(en)_2]^+$, α,ω-diaminoalkanes, and CDX.$^{2)}$

Interestingly, the yield of [ΔΔ]-[α-CDX] rotaxane is about twice higher than that of [ΛΛ]-[α-CDX]. This is compatible with the fact that the preparation starting from *rac*-$[Co(NH_2CH_2CH_2S)(en)_2](ClO_4)_2$ leads to the stereoselective formation of the Δ-rich rotaxane and Λ-rich bridged complex.$^{6)}$ The stereoselectivity found for the present system is relevant to the chiral α-CDX, which was successfully applied to the optical resolution of cobalt(III) complexes.$^{7)}$

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(Received October 4, 1982)