Stereoselective Formation of Rotaxanes Composed of Polymethylene-bridged Dinuclear Cobalt(III) Complexes and α- or β-Cyclodextrin

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[2]-[[(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]Cl$_6$]-[α- or β-CDX]-rotaxanes were prepared with partial stereoselectivity and characterized from their absorption and ^{13}C NMR spectra, molar conductance, and elemental analysis (CDX=cyclodextrin; n=8, 10, and 12). The rotaxanes always showed apparently $\Delta\Delta$-rich CD spectra, the highest selectivity (16% $\Delta\Delta$-rich) being found in the case of n=10 and α-CDX. The results are related to the direct preparation of [2]-[$\Delta\Delta$-[(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxanes (n=8, 10, and 12) in relatively higher yields than the corresponding $\Lambda\Lambda$ rotaxanes: 3.5% for n=8, 21% for n=10, and 28% for n=12. Inclusion complexes of a new type [Co(en)$_2${NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$Br}]Cl$_3$·2(α-CDX) were also isolated (n=10 and 12).

Cyclodextrin (CDX)[1] forms a large number of inclusion complexes with such organic compounds as benzene derivatives, carboxylic acids, alcohols, and alkane derivatives.[2] The inclusion-complex-forming property of CDX was recently applied to the synthesis of novel rotaxanes consisting of a dinuclear cobalt(III) complex [(en)$_2$ClCo{NH$_2$(CH$_2$)$_{12}$NH$_2$}CoCl(en)$_2$]$^{4+}$ and α- or β-CDX.[3] We have recently prepared another kind of polymethylene-bridged dinuclear complexes [(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]$^{6+}$ from the reaction of [Co(aet)(en)$_2$]$^{2+}$ with α,ω-dibromoalkane Br(CH$_2$)$_n$Br,[4] the complexes also being expected to form rotaxanes (aet=2-aminoethanethiolato, NH$_2$CH$_2$CH$_2$S$^-$).

Here we report the preparation of a series of [2]-[[(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]Cl$_6$]-[α- or β-CDX]-rotaxanes[5] by two methods. The bridging tetradentate ligands are abbreviated to dtdd for n=8: 3,12-dithiatetradecane-1,14-diamine, dhdd for n=10: 3,14-dithiahexadecane-1,16-diamine, and dodd for n=12: 3,16-dithiaoctadecane-1,18-diamine. In these rotaxanes, four diastereomers are possible 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 cobalt(III) rotaxanes isolated were characterized from their elemental analyses, absorption, circular dichroism (CD) and ^{13}C NMR spectra, and molar conductance measurements. The optically active rotaxanes, [$\Delta\Delta$]-[α-CDX] and [$\Lambda\Lambda$]-[α-CDX], were also prepared starting from the resolved mononuclear complexes and characterized. A preliminary report has been presented.[6]

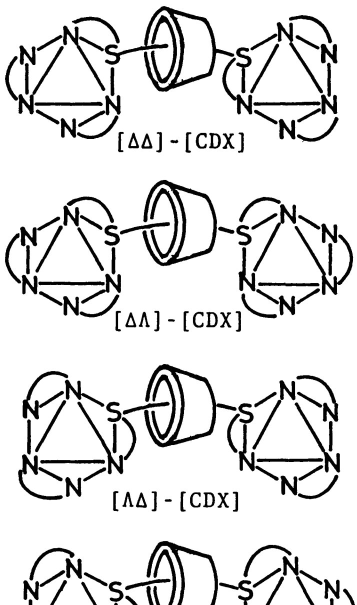

Fig. 1. Four possible diastereomers of [2]-[[(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]Cl$_6$]-[CDX]-rotaxane.

Experimental

Preparation and Separation. *[Co(aet)(en)$_2$](ClO$_4$)$_2$*: The complex was prepared according to the literature,[7] and used as a starting material. It was found that the racemic perchlorate salt crystallizes as a conglomerate, our racemate being incidentally Λ-rich (*ca.* 1.5%) even when a portion of *ca.* 60 g was recrystallized in a lot. Therefore, a sample of the pure racemate was prepared by addition of an appropriate amount of Δ-form ($\Delta\varepsilon_{522}=-1.32$ mol^{-1} dm^3 cm^{-1}), which was obtained from optical resolution of the racemic chloride salt.[8]

To confirm the spontaneous resolution, we determined the solubilities in binary and ternary systems containing *rac*- and/or Λ-[Co(aet)(en)$_2$](ClO$_4$)$_2$ in water. Solubility (g/100 g H$_2$O): 5.39 (5 °C), 6.88 (10 °C), 8.61 (15 °C), 11.1 (20 °C), 14.0 (25 °C), 18.1 (30 °C), 23.0 (35 °C), 30.7 (40 °C), and 39.0 (45 °C) for racemic perchlorate; 3.85 (5 °C), 4.71 (10 °C), 5.98 (15 °C), 7.28 (20 °C), 9.04 (25 °C), 13.7 (35 °C), 17.0 (40 °C), and 19.0 (45 °C) for Λ-complex perchlorate. Solubility (mol fraction $\chi\times10^3$) in the ternary system, H$_2$O–Λ-[Co(aet)(en)$_2$](ClO$_4$)$_2$–Δ-[Co(aet)(en)$_2$](ClO$_4$)$_2$ at 30 °C, (χ_Λ, χ_Δ): (4.34, 0), (4.07, 1.04), (4.00, 1.20), (3.99, 1.30), (3.94, 1.61), (3.69, 2.89), (3.64, 3.29), (3.67, 3.54), and (3.65, 3.65). The solubility ratio of racemate/Λ-complex is 1.40 at 5 °C, 1.55 at 25 °C, and 2.05 at 45 °C. Since the ratio is larger than $2^{1/3}=1.26$ the perchlorate salt is spontaneously resolvable.[9] The ternary solubility isotherm at 30 °C showed the only one invariant point. The results confirm that the two enantiomers form a racemic mixture in the solid state.

[Co(en)$_2${NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$Br}](ClO$_4$)$_3$ (n=8, 10, and 12): These complexes were also used as a starting material. Only the perchlorate salts are highly soluble in dimethyl sulfoxide (DMSO), which turned out to be the most favorable

solvent for the preparation of rotaxanes.

The chloride salts were isolated previously as a by-product in the column chromatography of the bridged complexes, $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]^{6+}$ ($n=8$ and 10).[4] They were prepared more effectively in the following way. To a 20 cm^3 of DMSO solution containing $[Co(aet)(en)_2](ClO_4)_2$ (0.004 mol) was added 0.01 mol of relevant α,ω-dibromoalkane $Br(CH_2)_nBr$, and then the mixture was kept at 30 °C for 2 d. The unreactive dibromoalkane was extracted into diethyl ether for several times. The resulting dark red oil was diluted by *ca.* 20 cm^3 of water, and 10 cm^3 of a saturated aqueous solution of NaCl was added to it . An oily product appeared immediately and was kept standing for 2 h to give a powder precipitate of the chloride salt. The corresponding bromide (or iodide) salt could be obtained by the same procedure except for the use of NaBr (or KI) instead of NaCl. The halide salts were converted into the perchlorate salt by using QAE-Sephadex A-25 (ClO_4^- form). The eluate was concentrated on a rotary evaporator to dryness, the residue being used for the preparation of rotaxane without further purification.

[2]-[[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**1**). *Method [A]*: 2.2 mmol of *rac*-$[Co(aet)(en)_2](ClO_4)_2$ and 1.3 mmol of 1,12-dibromododecane (20% excess) were dissolved in 6 cm^3 of DMSO containing 2.5 g of α-CDX. The mixture was kept at 30 °C for 10 d, leading to deep red solution. During this period, white crystals appeared gradually at the bottom of a reaction vessel, which were identified as the inclusion compound of $Br(CH_2)_{12}Br$ and α-CDX. The unreactive dibromoalkane was extracted into diethyl ether. The resulting dark red oil was dissolved in water, adsorbed on a cation exchange column (SP-Sephadex C-25, Na$^+$ form), and eluted with a 0.8 mol dm^{-3} NaCl solution. Six colored bands, f1—f6, were eluted in this order. The species, f2 (dark brown), f3 (orange), f5 (orange), and f6 (orange), were identical to the products formed by the "blank reaction" without CDX and therefore corresponded to $[Co(aet)(en)_2]^{2+}$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}OH\}]^{3+}$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}]^{3+}$, and the bridged complex $[(en)_2Co(dodd)Co(en)_2]^{6+}$, respectively.[4] The species isolated from the f1 eluate agreed with the composition of $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}]Cl_3\cdot 2(\alpha\text{-CDX})\cdot 18H_2O$. The eluate from the orange band f4 was evaporated to a small volume and, after repeated removal of NaCl deposited out, the solution was treated with a large amount of ethanol (or acetone) to give an orange precipitate of the desired rotaxane. Analytical data are shown in Table 2. The yields based on the starting mononuclear complex *rac*-$[Co(aet)(en)_2](ClO_4)_2$ were 5±1% for f1, 4±1% for f3, 16±2% for f4, 6±1% for f5, and 34±3% for f6 (The mean for 4 preparations).

In the above preparation, pronounced stereoselectivity was observed. All eluates of each band were collected together and its optical purity was checked by CD measurements.[10] Each band showed the CD spectrum. The species f4 always showed apparently ΔΔ-rich CD spectra (*ca.* 8%) and f6 ΛΛ-rich (*ca.* 3%). The selectivities for f1, f3, and f5 species were not definitive because of their low CD values, which were also varied depending upon the preparative method ([A] or [B]) and conditions such as the molar ratio and concentrations of *rac*-$[Co(aet)(en)_2]^{2+}$ and CDX.

Method [B]: The complex $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}](ClO_4)_3$ was used as a starting material. This complex (0.6 mmol), $[Co(aet)(en)_2](ClO_4)_2$ (0.72 mmol, 20% excess), and α-CDX (1.5 g) were allowed to react in 5 cm^3 of DMSO and the reaction mixture was separated in a similar manner described above. The yields based on $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}](ClO_4)_3$ were 1.5±0.5% for f1, 5±1% for f3, 26±1% for f4, 4±1% for f5, and 46±2% for f6 (2 preparations). The apparent selectivity was *ca.* 8% ΔΔ-rich for f4 and *ca.* 4% ΛΛ-rich for f6.

*[2]-[[(en)$_2$Co(dhdd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**2**)*: The complex was prepared and chromatographed by the same manner as **1** except for the use of 1,10-dibromodecane instead of 1,12-dibromododecane. In this separation, the orange band f1 was small in amount, becoming very broad during the chromatography, finally obscuring. This species is inferred as an inclusion compound of $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{10}Br\}]Cl_3$ and α-CDX from the analogy with $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}Br\}]Cl_3\cdot 2(\alpha\text{-CDX})$ described above. The yields were 5±1% for f3, 6±1% for f4, 6±1% for f5, and 54±4% for f6 (3 preparations) in method [A] and 5±1% for f3, 9±1% for f4, 3.5±1% for f5, and 63±4% for f6 (2 preparations) in method [B]. The apparent selectivity was higher in method [A] than [B]: the band f4 was *ca.* 16% ΔΔ-rich and f6 *ca.* 2.5% ΛΛ-rich in method [A], but f4 was *ca.* 8% ΔΔ-rich and f6 *ca.* 0.7% ΛΛ-rich in method [B].

*[2]-[[(en)$_2$Co(dtdd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**3**)*: The complex was not detectable in method [A] but prepared in a 4±1% yield (3 preparations) in method [B]. In the separation, the inclusion compound between $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_8Br\}]^{3+}$ and α-CDX, which corresponds to the f1 band in the case of **1**, was almost undetectable and five bands corresponding to f2—f6 appeared. The rotaxane was eluted as the fourth band (*ca.* 5% ΔΔ-rich) just before the fifth band of the bridged 6+ complex. The isolation of the rotaxane, however, was incomplete: the analytical C/N ratio (51.2/10) was low as compared with the ideal value 5.80. Satisfactory analytical data were obtained for the corresponding optically active rotaxane described below.

*[2]-[ΔΔ-[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**4**) and [2]-[ΛΛ-[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**5**)*: The rotaxane [ΔΔ]-[α-CDX] or [ΛΛ]-[α-CDX] was prepared and chromatographed in the same manner as for **1** by the use of Δ- or Λ-$[Co(aet)(en)_2](ClO_4)_2$ as a starting material, respectively. Six bands were characterized, being corresponded to the species in the separation of **1** in both cases. The yields were 2±1% for f1, 6±1% for f3, 28±1% for f4, 4±1% for f5, and 44±2% for f6 (2 preparations) in the Δ-system, and 0.8% for f1, 6% for f3, 14% for f5, and 49% for f6 (1 preparation) in the Λ-system.

*[2]-[ΔΔ-[(en)$_2$Co(dhdd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**6**)*: The complex was prepared by the method [A] as for **2** except for the use of Δ-$[Co(aet)(en)_2](ClO_4)_2$ instead of the racemate. The yields were 10±1% for f3, 22±1% for f4, 0% for f5, and 49±2% for f6 (2 preparations). It is noteworthy that the yield of rotaxane **6** (f4 band) is considerably higher than that of **2**. An attempt to prepare the corresponding [ΛΛ]-[α–CDX] isomer was made in the same way by using Λ-$[Co(aet)(en)_2](ClO_4)_2$. The yield of [ΛΛ]-[α-CDX], which is not isolated in solid as yet, was below 7%.

*[2]-[ΔΔ-[(en)$_2$Co(dtdd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**7**)*: The complex was prepared and chromatographed in the same manner as for **3** by the use of Δ-$[Co(aet)(en)_2](ClO_4)_2$ as a starting material. Five bands appeared and the fourth band was the desired rotaxane with a 3.5±0.5% yield, which showed the satisfactory analytical data as seen in Table 2.

*[2]-[[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[β-CDX]-rotaxane (**8**)*: The complex was prepared by the method [A] except for the use of β-CDX instead of α-CDX. In the separation five bands f1′—f5′ were eluted in this order, though f2′ and f3′ were partly overlapped each other. The species, f1′(dark brown), f2′(orange), f3′(orange), f4′(orange), and f5′(orange), were characterized as $[Co(aet)(en)_2]^{2+}$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{12}OH\}]^{3+}$, the desired rotaxane, $[Co(en)_2\{NH_2(CH_2)_2$-

S(CH$_2$)$_{12}$Br}]$^{3+}$, and [(en)$_2$Co(dodd)Co(en)$_2$]$^{6+}$, respectively. Each band also showed a CD spectrum but the apparent selectivity was much lower than that in the corresponding system containing α-CDX: *ca.* 2% ΔΔ-ric for f3′ and *ca.* 0.3% ΛΛ-rich for f5′. The yield of f3′ rotaxane was 5±1% (3 preparations).

[*2*]-[[*(en)*$_2$*Co(dhdd)Co(en)*$_2$]*Cl*$_6$]-[*β-CDX*]*-rotaxane* (***9***): The complex was obtained in a 2±0.5% yield (3 preparations) by the same procedure as for **8**. The f3′ rotaxane indicated *ca.* 1% ΔΔ-rich CD. No β-CDX rotaxane was detectable for the corresponding dtdd case.

Measurements. The visible and ultraviolet absorption spectra were measured on a Hitachi 330 spectrophotometer and CD spectra with a JASCO MOE-1 spectropolarimeter in aqueous solutions. The ^{13}C NMR spectra were recorded with a JEOL FX-90Q NMR spectrometer in D$_2$O containing dioxane as an internal standard. The conductance measurements were made in water on a TOA CM-30ET conductivity apparatus. The values at room temperature were converted automatically to those at 25 °C based on the assumption that the conductance changes by 2% per one degree. The solubility in water was determined in the same way as previously reported.[9]

Table 1. Percentage yield of rotaxanes

Bridging ligand	Co(III) component	α-CDX		β-CDX
		Method [A]	Method [B]	Method [A]
dtdd	*rac*	0	4(Δ-5)[a]	0
(*n*=8)	Δ	3.5		
dhdd	*rac*	6(Δ-16)[a]	9(Δ-8)[a]	2(Δ-1)[a]
(*n*=10)	Δ	21		
	Λ	<7		
dodd	*rac*	16(Δ-5)[a]	26(Δ-8)[a]	5(Δ-2)[a]
(*n*=12)	Δ	28		
	Λ	14		

a) Apparent optical purity[10] is indicated in parentheses with the configuration of the rich species.

Results and Discussion

Preparation and Characterization. The yields of rotaxanes are collected in Table 1. The two kinds of method were used for the preparation of rotaxane. The yield was usually higher in the method [B] because the formation of inclusion compounds Br(CH$_2$)$_n$Br·m(CDX) in DMSO lowered the yield in the method [A]. The yield of the rotaxane was higher for α-CDX than for β-CDX. This means that the annular structure of α-CDX is more suitable in size for the formation of rotaxane of the present complexes than that of β-CDX. The number of bridging methylene groups, *n*, also affected the yield in the decreasing order 12>10>8.

Table 2 shows the analytical data of the complexes containing CDX. The ratio C/N was most indicative of rotaxane formation, but somewhat higher than the ideal value (for example C/N=60/10=6.00 for the dodd rotaxane without organic solvent) because a large amount of ethanol or acetone was used for the isolation of rotaxane having high solubility. The experimental value of C/N ratio well agreed with the composition with a few molecules of the organic solvent (Table 2). In the preparation using 1,12-dibromododecane and α-CDX, the species f1 isolated from chromatography showed the C/N ratio about 18, which corresponded to [Co(en)$_2${NH$_2$(CH$_2$)$_2$S(CH$_2$)$_{12}$Br}]Cl$_3$·2(α-CDX). A similar inclusion complex could be prepared directly from an aqueous solution of [Co(en)$_2${NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$Br}]Cl$_3$ (*n*=10 or 12) and α-CDX (molar ratio 1 : 1). These inclusion complexes as well as the other compounds formed between Br(CH$_2$)$_n$Br and α-CDX in the method [A] are considered as precursors of the rotaxanes. The direct isolation of such precursors gives strong support for the formation of rotaxanes in the reaction mixtures.

The first spin-allowed d-d absorption bands of the cobalt(III) rotaxanes locate at 20440 cm^{-1} (Fig. 2), which are characteristic of the [Co(N)$_5$(S)] chromophore containing a thioether donor atom.[4] The absorption

Table 2. Analytical data of the rotaxane and other complexes

(a) [2]-[[(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]Cl$_6$]-[CDX]-rotaxane·X

n	CDX	Starting material	C/N ratio		X	Found (Calcd) (%)		
			Found	Calcd		C	H	N
8 (dtdd)	α	Δ	6.06	6.06	2.3C$_2$H$_5$OH·8H$_2$O	35.31 (35.36)	7.20 (7.34)	6.79 (6.80)
10 (dhdd)	α	*rac*	5.99	6.00	C$_2$H$_5$OH·9.5H$_2$O	35.02 (35.09)	7.08 (7.31)	6.82 (6.82)
	α	*rac*	6.11	6.10	(CH$_3$)$_2$CO·10H$_2$O	35.25 (35.32)	7.07 (7.29)	6.73 (6.75)
	α	Δ	6.16	6.16	1.8C$_2$H$_5$OH·7H$_2$O	36.21 (36.17)	7.29 (7.33)	6.86 (6.85)
	β	*rac*	6.84	6.80	2C$_2$H$_5$OH·10H$_2$O	36.06 (35.97)	7.09 (7.37)	6.15 (6.17)
12 (dodd)	α	*rac*	6.34	6.30	1.5C$_2$H$_5$OH·9.5H$_2$O	36.08 (35.95)	7.26 (7.47)	6.64 (6.66)
	α	*rac*	6.02	6.00	10.5H$_2$O	34.87 (35.09)	7.03 (7.31)	6.75 (6.82)
	α	Δ	6.49	6.50	2.5C$_2$H$_5$OH·8H$_2$O	36.74 (36.76)	7.48 (7.55)	6.60 (6.60)
	α	Λ	6.59	6.60	3C$_2$H$_5$OH·7H$_2$O	37.14 (37.24)	7.45 (7.58)	6.57 (6.58)
	β	*rac*	7.11	7.10	2.5C$_2$H$_5$OH·10H$_2$O	36.72 (36.73)	7.17 (7.51)	6.02 (6.03)
(b) [Co(en)$_2${NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$Br}]Cl$_3$·2(α-CDX)·X								
10	α	*rac*	17.80[a]	17.60	15H$_2$O	37.71 (37.78)	6.98 (6.92)	2.47 (2.50
12	α	*rac*	18.02	18.00	18H$_2$O	37.55 (37.54)	6.75 (7.07)	2.43 (2.43)
	α	*rac*	17.66[a]	18.00	15H$_2$O	38.29 (38.25)	6.82 (6.99)	2.53 (2.48)

a) These complexes were prepared directly from an aqueous solution of [Co(en)$_2${NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$Br}]Cl$_3$ (*n*=10 or 12) and α-CDX (molar ratio 1:1).

TABLE 3. ABSORPTION AND CD DATA OF ROTAXANES

Bridging ligand	Co(III) component	CDX	Absorption[a]	$\sigma_{\max}$ (log ϵ)	CD[a] σ_{ext} ($\Delta\epsilon$)
dtdd	*ΔΔ*	α	20.45 (2.608) 35.35 (4.336)	28.5 (2.75)[b] 45.20 (4.552)	19.90 (−4.78), 23.53 (+0.045), 26.32 (−0,234) 29.4 (−0.94),[b] 34.90 (−27.8), 46.30 (+45.8)
dhdd	*rac*	α	20.44 (2.603) 35.25 (4.337)	28.5 (2.74)[b] 45.17 (4.556)	
	ΔΔ	α	20.43 (2.610) 35.28 (4.332)	28.5 (2.76)[b] 45.19 (4.555)	19.91 (−5.07), 26.18 (−0.195), 29.4 (−0.72)[b] 34.97 (−24.9), 45.87 (+46.2)
	rac	β	20.44 (2.599) 35.29 (4.328)	28.5 (2.74)[b] 45.15 (4.552)	
dodd	*rac*	α	20.45 (2.594) 35.32 (4.322)	28.5 (2.74)[b] 45.17 (4.547)	
	ΔΔ	α	20.45 (2.615) 35.27 (4.339)	28.5 (2.76)[b] 45.17 (4.564)	19.92 (−5.42), 26.32 (−0.180), 29.4 (−0.9)[b] 34.84 (−24.3), 45.66 (+47.9)
	ΛΛ	α	20.45 (2.608) 35.25 (4.330)	28.5 (2.75)[b] 45.27 (4.555)	19.96 (+5.23), 26.08 (+0.149), 29.4 (+0.7)[b] 34.97 (+20.2), 45.66 (−49.6)
	rac	β	20.44 (2.604) 35.33 (4.329)	28.5 (2.75)[b] 45.17 (4.554)	

a) Wave numbers are given in $10^3\,\mathrm{cm}^{-1}$ unit and log ϵ or $\Delta\epsilon$ values (in parentheses) in $\mathrm{mol}^{-1}\mathrm{dm}^3\mathrm{cm}^{-1}$.
b) Shoulder.

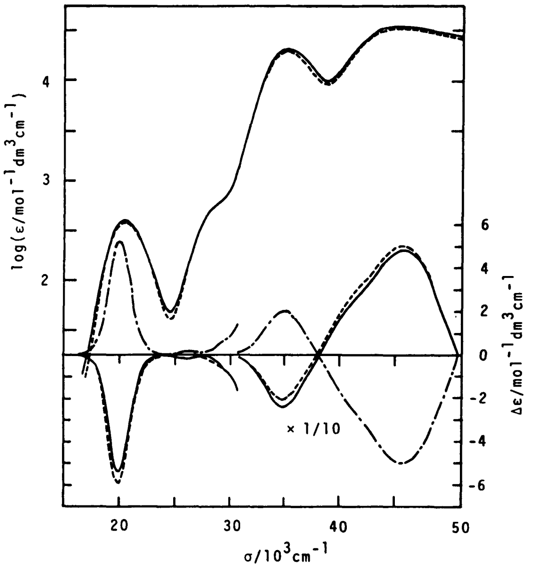

Fig. 2. Absorption and CD spectra of [2]-[ΔΔ-[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane(——), [2]-[ΛΛ-[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (-----), and ΔΔ-[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$ (------).

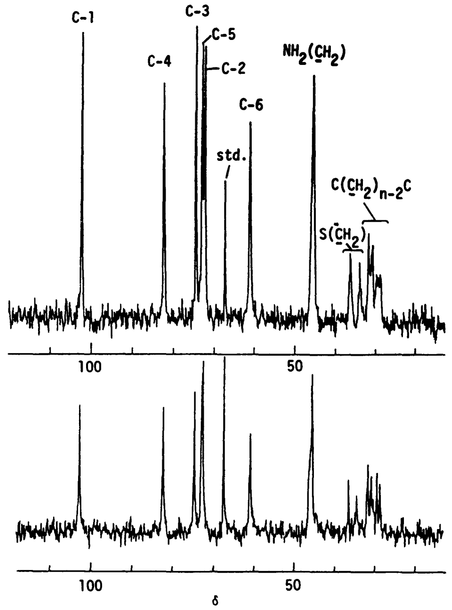

Fig. 3. ^{13}C NMR spectra of [2]-[[(en)$_2$Co(dhdd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**2**) (upper) and [2]-[[(en)$_2$Co(dodd)Co(en)$_2$]Cl$_6$]-[α-CDX]-rotaxane (**1**) (lower). 1,4-Dioxane (δ 67.4 *vs.* Me$_4$Si) was used as the internal reference. The signals of α-CDX (C1—C6) were assigned after Ref. 12.

spectra of rotaxanes are very similar to one another irrespective of the kind of CDX (Table 3). Molar absorption coefficients of the rotaxanes are slightly higher in the thioether charge transfer (CT) band region around *ca.* 35000 cm^{-1} than those of the corresponding bridged complexes. A similar increase of CD intensity is observed in the CT band region (Fig. 2). 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). Interestingly, the ratio in the [ΔΔ]-[α-CDX] series increased regularly with the decrease of the methylene chain length: 4.48, 4.91, and 5.82 for the dodd-, dhdd-, and dtdd-rotaxanes, respectively. On the other hand, all the corresponding bridged complexes of ΔΔ-form showed the identical ratio *ca.* 3.5. This fact clearly shows that the steric repulsion between the cobalt(III) moiety and α-CDX becomes larger with the shortening of the methylene chain. The CD spectra of both ΔΔ and ΛΛ dodd-rotaxanes are not completely enantiomeric to each other. The deviation 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 frotaxane formation (Fig. 3). The rotaxanes **1** and **2** gave strong six signals in a lower magnetic field (60—110 ppm), which were assigned to *α*-CDX moiety.[11,12] Similarly, the rotaxanes of *β*-CDX **8** and **9** showed five signals in this region. The spectral patterns and chemical shifts of *α*- and *β*-CDX moieties are similar to those of free *α*- and *β*-CDX, respectively. The other signals in a higher field (0—60 ppm) were assigned to methylene carbons of $NH_2(CH_2)$–, –$S(CH_2)$–, and –$C(CH_2)_{n-2}C$– regions from the lower magnetic field side. These spectral patterns, however, were complicated since the present rotaxanes are a mixture consisted of four diastereomers. Figures 4 and 5 show the ^{13}C NMR spectra of the optically active rotaxanes **4**, **5**, **6**, and **7**, which are composed of a single diastereomer without symmetry element. In the –$C(CH_2)_{n-2}C$– region, the rotaxanes **4** (or **5**), **6**, and **7** showed seven (three strong and four weak), seven (one strong and six weak), and five (one strong and four weak) methylene resonances, respectively. Since it can be assumed that each of the strong signals corresponds to two methylene carbons, the total number of the methylene resonances becomes ten for **4** (or **5**), eight for **6**, and six for **7**. The results gave the direct evidence of the rotaxane formation with C_1 symmetry. Both the dodd rotaxanes, [$\Delta\Delta$]-[*α*-CDX] and [$\Lambda\Lambda$]-[*α*-CDX], showed seven signals in the –$C(CH_2)_{10}C$– region but the spectral patterns are obviously different from each other as expected from the fact that they are diastereomeric.

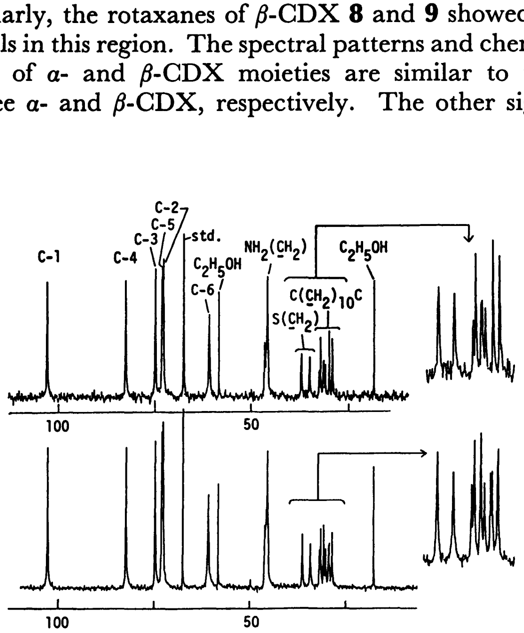

Fig. 4. ^{13}C NMR spectra of [2]-[$\Lambda\Lambda$-[$(en)_2Co(dodd)Co(en)_2]Cl_6$]-[*α*-CDX]-rotaxane (**5**) (upper) and [2]-[$\Delta\Delta$-[$(en)_2Co(dodd)Co(en)_2]Cl_6$]-[*α*-CDX]-rotaxane (**4**) (lower).

The chemical shifts due to CDX in the rotaxanes were summarized in Table 4. The signals of *β*-CDX were assigned in the same manner by Usui *et al.*[11] and Colson *et al.*[12] but the assignment of *α*-CDX became reverse at C2 and C5 resonances, our assignment being after

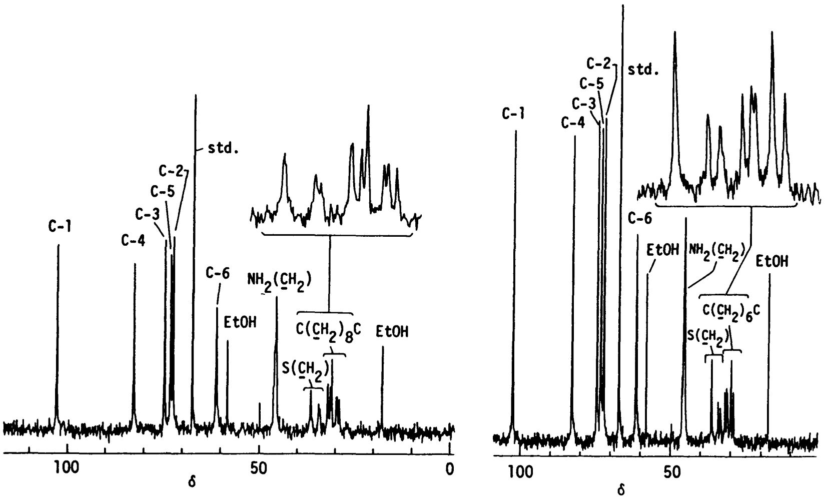

Fig. 5. ^{13}C NMR spectra of [2]-[$\Delta\Delta$-[$(en)_2Co(dhdd)Co(en)_2]Cl_6$]-[*α*-CDX]-rotaxane (**6**) (left) and [2]-[$\Delta\Delta$-[$(en)_2Co(dtdd)Co(en)_2]Cl_6$]-[*α*-CDX]-rotaxane (**7**) (right).

TABLE 4. ^{13}C NMR RESONANCES DUE TO CDX IN THE ROTAXANES (ppm from Me_4Si)

Rotaxane	Chemical shift					
	C-1	C-4	C-3	C-5	C-2	C-6
7 ($\Delta\Delta$,dtdd, *α*)	102.64	83.06	74.71	73.47	72.44	61.66
2 (*rac*, dhdd, *α*)	102.78	82.68	74.72	73.15	72.50	61.23
6 ($\Delta\Delta$, dhdd, *α*)	102.73	82.62	74.69	73.11	72.46	61.20
1 (*rac*, dodd, *α*)	102.78	82.24	74.60	72.81	72.54	60.79
4 ($\Delta\Delta$, dodd, *α*)	102.75	82.25	74.60	72.85	72.52	60.76
5 ($\Lambda\Lambda$, dodd, *α*)	102.78	82.27	74.60	72.85	72.55	60.85
9 (*rac*, dhdd, *β*)	102.67	82.08	74.17	72.87	72.87	61.22
8 (*rac*, dodd, *β*)	102.72	81.92	74.17	72.87	72.87	61.00

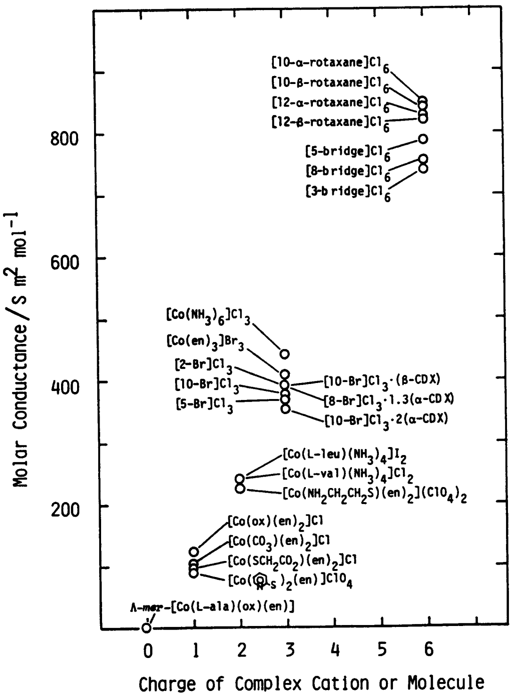

Fig. 6. Molar conductivity of the rotaxanes and other cobalt(III) complexes in water at 25 °C. Abbreviation, complex: [n-α-rotaxane]Cl_6=[2]-[[$(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2$] Cl_6]-[α-CDX]-rotaxane, [n-bridge] Cl_6 = [$(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2$]$Cl_6$, and [$n$-Br]$Cl_3$=[$Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}$]$Cl_3$; ligand: L-ala=L-alaninato, L-leu=L-leucinato, L-val=L-valinato, and ox=oxalato.

Colson *et al.*[12] The values of the dodd rotaxanes containing α-CDX are very similar to one another irrespective of the absolute configurations of the cobalt(III) moieties. The change of the bridging length affects the chemical shift. Three resonances of C4, C5, and C6 were shifted regularly to the down field with the decrease of the methylene chain length, whereas the chemical shifts of C1, C2, and C3 were hardly affected. It is well known that the intra hydrogen bonding between adjacent glucose units in α- or β-CDX is found as a stabilization factor of the cyclic structure in DMSO solution[13] as well as in solid.[14] Since the hydroxyl groups at C2 and C3 are relevant to this hydrogen bonding network, the chemical shifts of C1, C2, and C3 are almost insensitive to the change of the bridging length. On the other hand, the hydroxyl group at C6 can rotate freely and is sensitive to the steric change. Such a steric change at C6 also influences the chemical shifts of C4 and C5. Thus, our results support the assignment of the C2 and C5 resonances for α-CDX by Colson *et al.*[12] but not Usui *et al.*[11]

Chromatography and Molar Conductance. The rotaxane complex cations should have a 6+ charge, but eluted before the 3+ cations $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$ (n=10 and 12). The species f1 containing α-CDX (3+) also eluted before $[Co(aet)(en)_2]^{2+}$. Such anomalous chromatographic behaviors as well as a similar observation reported in a similar system[3] can be ascribed to the property of SP-Sephadex ion exchangers, which have a kind of non-ionic effect in addition to the dominant ionic one. The former effect, as seen in gel filtration by Sephadex G-type, is based on the molecular size. The bulky complexes such as the rotaxanes are expected to be more rapidly eluted than the corresponding bridged complexes. The rotaxanes **3** and **7**, however, showed a normal elution order as expected from the complex charge. This fact means that the rotaxanes **3** and **7** with n=8 are relatively small in size than the other **1**, **2**, **4**, **5**, **6**, **8**, and **9** with n=10 and 12.

Molar conductances of the rotaxanes and the related complexes at 25 °C are plotted in Fig. 6. The plots for the complexes of each the same charge are distributed in a narrow range, and well separated on the other hand from those of other complexes with the different charges. The rotaxanes have slightly higher values than the corresponding bridged 6+ complexes. Mononuclear inclusion complexes with the charge 3+ showed almost the same values as the corresponding complexes $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$. Thus, molar conductance was not affected by the presence of CDX. The anomalous column behavior is relevant to the interaction between the SP-Sephadex resin and bulky CDX.

Stereoselectivity. The rotaxanes prepared from *rac*-$[Co(aet)(en)_2]^{2+}$ are each the mixture of four diastereomers, $\Delta\Delta$-, $\Lambda\Lambda$-, and two $\Delta\Lambda$-forms (pseudo-*meso*) with respect to the bridged cobalt(III) moieties. Though the two pseudo-*meso* rotaxanes have no CD contribution due to the skew pairs of chelate rings around the central cobalt(III) ion, they will show the induced CD spectra owing to the chiral α- or β-CDX. This contribution is, however, considered to be relatively low and therefore the chiralities of the former two diastereomers contribute mainly to the CD spectra of the product, if an unequal distribution of them takes place. In fact, a very weak positive CD band ($\Delta\varepsilon_{545}$=+0.04) was reported as such induced CD of [2]-[$[(en)_2ClCo\ \{NH_2(CH_2)_{12}NH_2\}\ CoCl(en)_2]\ (ClO_4)_4$]-[$\beta$-CDX]-rotaxane.[3] In the present dodd system, the CD contribution due to α-CDX, which could be evaluated from the mean of the CD spectra of [$\Delta\Delta$]-[α-CDX] and [$\Lambda\Lambda$]-[α-CDX] in Fig. 2, was proved to be small. Therefore, it is reasonable that the two pseudo-*meso* type rotaxanes have a small CD contribution. The rotaxane **2** prepared by the method [A] showed a negative CD spectrum ($\Delta\varepsilon_{502}$=−0.80) in the first d-d absorption band region, which corresponded to a *ca.* 16% optical purity of $\Delta\Delta$-form (the highest selectivity observed). Thus the unequal distribution of [$\Delta\Delta$]-[α-CDX] and [$\Lambda\Lambda$]-[α-CDX] diastereomers is confirmed. This is also supported by the fact that the bridged complex formed concomitantly indicated the CD band of opposite sign ($\Delta\varepsilon_{502}$=+0.13). In general, the rotaxanes of β-CDX were less stereoselective, though they showed a positive CD band in the first d-d absorption band region. Because of the narrow cavity, α-CDX behaves more effectively to the stereoselectivity as well as to the formation of rotaxane than β-CDX. The bridging methylene chain length also influences the effectiveness of the selectivity: the order is 10>12>8 for the rotaxanes containing α-CDX.

The optically active [$\Delta\Delta$]-[α-CDX] rotaxane, **4** or **6**, was prepared by the method [A] in a considerably higher yield than the corresponding mixture **1** or **2**, respectively. The dtdd rotaxane with $n=8$ was not detectable in the method [A] starting from *rac*-[Co(aet)-(en)$_2$]$^{2+}$ but could be prepared in a 3.5% yield even by the same method using Δ-[Co(aet)(en)$_2$]$^{2+}$. The stereoselectivity will be more clear by comparison between the pure Δ- and Λ-systems. In the dodd system, the yield of [$\Delta\Delta$]-[α-CDX] isomer is 28%, whereas that of [$\Lambda\Lambda$]-[α-CDX] one only *ca.* 14%. Similarly in the dhdd system, the yield of [$\Delta\Delta$]-[α-CDX] is 21% but that of [$\Lambda\Lambda$]-[α-CDX] below 7%. These results are consistent with the stereoselective formation of rotaxanes, that is, $\Delta\Delta$-complex being included preferentially into α-CDX.

The formation reaction of rotaxane is stepwise one as shown schematically by Ogino.[3] In the course of bridge formation process, there is the step forming an intermediate inclusion complex of [Co(en)$_2${NH$_2$(CH$_2$)$_2$-S(CH$_2$)$_n$Br}]$^{3+}$ and CDX. This stage is expected to be the most important for the present stereoselectivity. The expectation is confirmed by the partial optical resolution of [Co(en)$_2$(NH$_2$CH$_2$CH$_2$SR)]$^{3+}$ with a long alkyl or bromoalkyl chain (R=(CH$_2$)$_n$Br and (CH$_2$)$_n$-CH$_3$).[15] Interestingly, the best resolution was achieved in the case of R=(CH$_2$)$_{10}$Br and α-CDX, corresponding to 61% optical purity of Δ-complex. The results are in fair agreement with the present selectivities.[16]

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1) α- and β-CDX denote cyclohexaglucopyranose and cycloheptaglucopyranose, respectively.

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10) The apparent optical purity of the rotaxane was calculated from the extremum values of the first d-d absorption band region, $\Delta\varepsilon=+2.50$ and $\varepsilon=200$ per one cobalt(III) ion, which were little affected by the kinds of complexes f3, f5, and f6 and the bridging methylene chain lengths.[4]

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16) β-CDX preferentially included Λ-complexes in the optical resolution contrary to the present system. The difference may result from the properties of used solvents: water for the former and DMSO for the latter.