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Stereoselective Formation of Rotaxanes Composed of Polymethylene-bridged Dinuclear Cobalt(III) Complexes and α-Cyclodextrin. II[1]

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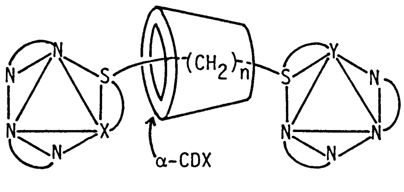
[2]-[[(en)$_2$Co{XCH$_2$S(CH$_2$)$_n$SCH$_2$Y}Co(en)$_2$]Cl$_m$]-[α-CDX]-rotaxanes (n=8, 10, and 12 for X=Y=CO$_2^-$ (m=4); n=10 for X=CO$_2^-$ and Y=CH$_2$NH$_2$(m=5); α-CDX=α-cyclodextrin) were prepared with partial stereoselectivity and characterized from their visible-UV absorption, circular dichroism(CD), and ^{13}C NMR spectra, and elemental analysis. The rotaxane formation could be identified by the down field shift of the chemical shift due to α-CDX in the ^{13}C NMR spectra and the increase of the CD intensity in the ligand-to-metal charge transfer band region in the CD spectra. The rotaxanes always showed apparently ΔΔ-rich CD spectra, the highest selectivity(10% ΔΔ-rich) being found in the case of n=10.

α-Cyclodextrin (CDX) has the hydrophobic cavity and is an excellent host molecule for a great variety of guest molecules.[2] Using this inclusion property of CDX, Ogino first prepared the novel cobalt(III) rotaxane complexes.[3] We recently prepared similar rotaxanes consisting of a dinuclear cobalt(III) complex [(en)$_2$Co{NH$_2$(CH$_2$)$_2$S(CH$_2$)$_n$S(CH$_2$)$_2$NH$_2$}Co(en)$_2$]$^{6+}$ (n=8, 10, and 12) and α- or β-CDX starting from a mononuclear thiolato complex [Co(aet)(en)$_2$]$^{2+}$ (Haet =2-aminoethanethiol, NH$_2$CH$_2$CH$_2$SH).[1] Interestingly, the rotaxanes showed the partial stereoselectivity, which led to the relatively higher yield of ΔΔ-rotaxanes as compared with that of ΛΛ-rotaxanes.

In this paper, another thiolato complex [Co(maa)(en)$_2$]$^+$ (H$_2$maa=mercaptoacetic acid, HSCH$_2$CO$_2$H) was used as a starting material for the synthesis of [2]-[[(en)$_2$Co{XCH$_2$S(CH$_2$)$_n$SCH$_2$Y}Co(en)$_2$]Cl$_m$]-[α-CDX].[4] As shown in Fig. 1, the preparation was carried out for the two kinds of rotaxanes: X=Y=CO$_2^-$ (m=4), and X=CO$_2^-$ and Y=CH$_2$NH$_2$(m=5). The bridging quadridentate ligands are abbreviated to dtda for n=8 (X=Y=CO$_2^-$): 3,12-dithiatetradecanedioic acid; dhda for n=10 (X=Y=CO$_2^-$): 3,14-dithiahexadecanedioic acid; doda for n=12 (X=Y=CO$_2^-$): 3,16-dithiaoctadecanedioic acid; and adha for n=10 (X=CO$_2^-$ and Y=CH$_2$NH$_2$): 16-amino-3,14-dithiahexadecanoic acid. The cobalt(III) rotaxanes and the bridged complexes (=dinuclear complexes without α-CDX) were characterized from the elemental analysis, absorption, circular dichroism(CD) and ^{13}C NMR spectra. The optically active ΔΔ- and ΛΛ-rotaxanes were also prepared starting from the resolved mononuclear complexes.



[2]-[[(en)$_2$Co{XCH$_2$S(CH$_2$)$_n$SCH$_2$Y}-
Co(en)$_2$]Cl$_m$]-[α-CDX]-rotaxane

abbr.	n	X	Y	m
dtda	8	CO$_2^-$	CO$_2^-$	4
dhda	10	CO$_2^-$	CO$_2^-$	4
doda	12	CO$_2^-$	CO$_2^-$	4
adha	10	CO$_2^-$	CH$_2$NH$_2$	5

Fig. 1. The rotaxanes prepared and abbreviations of the bridging quadridentate ligands.

Experimental

Preparation and Separation of Complexes. rac-, Δ'-, *and* Λ'*-[Co(aet)(en)$_2$](ClO$_4$)$_2$*:[5] This complex was prepared and optically resolved according to the published procedure.[6]

rac-, Δ- *and* Λ*-[Co(maa)(en)$_2$]ClO$_4$*: The racemate was prepared according to the literature[6] and used as a starting material. The perchlorate salt was converted into the chloride by the use of QAE-Sephadex A-25 (Cl$^-$ form).

Optical resolution of this complex was attempted using resolving agents such as K$_2$[Sb$_2$(d-tart)$_2$]·3H$_2$O, Ag(d-H$_3$tart), NH$_4$(d-BCS), K[Co(edta)]·2H$_2$O, and Na(d-HDBT) (abbrev: d-H$_3$tart$^-$=hydrogen (R,R)-tartrate(1−), d-BCS$^-$=(1R,3S,4S,7R)-3-bromocamphor-9-sulfonate, edta^{4-}=ethylenediaminetetraacetate (4−), and d-HDBT$^-$=hydrogen (R,R)-di-O-benzoyltartrate(1−)), only the last resolving agent leading to the successful result. The racemic complex [Co(maa)(en)$_2$]Cl (10.6 g, 35 mmol) was dissolved in 150 cm^3 of water. To this solution was added dropwise a solution of Na(d-HDBT) (19 mmol), which was previously prepared from 7.2 g of d-H$_2$DBT and 0.7 g of NaOH in 200 cm^3 of water at 50 °C. The mixture was allowed to stand at room temperature for overnight with stirring. The less soluble diastereomer $(-)_{543}^{\mathrm{CD}}$-[Co(maa)(en)$_2$](d-HDBT) was filtered off and washed with water and then ethanol. The filtrate was later used for gaining $(+)_{543}^{\mathrm{CD}}$-antipode. The excess of QAE-Sephadex A-25 (Cl$^-$ form) resin was added to a suspension of the diastereomer, and the mixture was stirred for 1 h. The resultant dark violet solution was collected by filtration and 6 g of NaClO$_4$ was added to it to yield the crystals of $(-)_{543}^{\mathrm{CD}}$-[Co(maa)(en)$_2$]ClO$_4$. This was recrystallized by dissolving in a minimum amount of water, adding NaClO$_4$, and filtering. The yield was 3 g. $\Delta\varepsilon_{543}^{\mathrm{CD}}=-2.32$. Found: C, 19.49; H, 4.93; N, 15.29%. Calcd for Δ-[Co(maa)(en)$_2$]ClO$_4$=C$_6$H$_{18}$N$_4$SO$_6$ClCo: C, 19.55; H, 4.92; N, 15.20%. The initial filtrate was condensed to *ca.* 130 cm^3 by rotaevaporation at 30 °C and 2 g of NaClO$_4$ was added to it. The first crystals deposited (2.5 g) were almost racemate and removed by filtration. Further addition of NaClO$_4$ (*ca.* 4 g) gave the desired $(+)_{543}^{\mathrm{CD}}$-[Co(maa)(en)$_2$]ClO$_4$. The yield was 3.5 g. $\Delta\varepsilon_{543}^{\mathrm{CD}}=+2.32$. Found: C, 19.55; H, 4.89; N, 15.19%. Calcd for Λ-[Co(maa)(en)$_2$]ClO$_4$=C$_6$H$_{18}$N$_4$SO$_6$ClCo: C, 19.55; H,4.92; N, 15.20%.

Δ- *and* Λ*-[Co{O$_2$CCH$_2$S(CH$_2$)$_{10}$Br}(en)$_2$](ClO$_4$)Br.* To 12 cm^3 of DMSO (dimethyl sulfoxide) solution containing Δ- or Λ-[Co(maa)(en)$_2$]ClO$_4$(2 g) was added 3.25 g of 1,10-dibromodecane, and then the mixture was kept at 30 °C for 2 d. The unreactive 1,10-dibromodecane was removed by extraction with diethyl ether for several times. To the resultant dark red oil was added *ca.* 20 cm³ of water. The precipitate of the desired product appeared immediately and then was filtered off and washed with water, ethanol, and diethyl ether. This complex was sparingly soluble in water but very soluble in DMSO, and used as a starting material for the preparation of adha rotaxanes described later. Found for the Δ-complex: C, 28.99; H, 5.85; N, 8.05%. Found for Λ-complex: C, 28.80; H, 5.85; N, 8.05%. Calcd for $[Co\{O_2CCH_2S(CH_2)_{10}Br\}(en)_2](ClO_4)Br=C_{16}H_{38}N_4SO_6ClBrCo$: C, 28.74; H, 5.73; N, 8.38%.

*[2]-[[(en)$_2$Co(dtda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R1**) and [(en)$_2$Co(dtda)Co(en)$_2$]Cl$_4$ (**B1**).* The starting materials of *rac*-$[Co(maa)(en)_2]ClO_4$ (1.4 mmol) and 1,8-dibromooctane (0.84 mmol, 20% excess) were dissolved in 4 cm³ of DMSO containing 1.25 g of α-CDX. The mixture was kept at 30 °C for 7 d, leading to the red solution. The unreactive dibromooctane was extracted into diethyl ether. The resultant red oil was dissolved in water, adsorbed onto a cation exchange column (SP-Sephadex C-25, Na^+ form) and eluted with 0.3 mol dm^{-3} NaCl. Six colored bands, f1—f6, were eluted in this order. The species f2(dark violet), f4(red), f5(red), and f6(red) were assigned to $[Co(maa)(en)_2]^+$, $[Co\{O_2CCH_2S(CH_2)_8Br\}(en)_2]^{2+}$, [2]-$[(en)_2Co(dtda)Co(en)_2]^{4+}$-[α-CDX]–rotaxane, and $[(en)_2Co(dtda)Co(en)_2]^{4+}$, respectively. The other red bands f1 and f3 were remained unknown. The eluate from the red band f6 was evaporated to a small volume. After repeated removal of NaCl deposited out, a large amount of ethanol was added to it. The resultant solution was refrigerated for 2—3 d at −15 °C. The supernatant solution was discarded, and then the precipitate was washed with ethanol several times and filtered off. Found for **B1**; C, 29.41; H, 7.09; N, 12.39%. Calcd for $[(en)_2Co(dtda)Co(en)_2]Cl_4\cdot C_2H_5OH\cdot 3.5H_2O=C_{22}H_{65}N_8S_2O_{8.5}Cl_4Co_2$: C, 29.31; H, 7.27; N, 12.43%. The rotaxane **R1** was not isolated as a solid but the yield was 3.3±0.5% (the mean for 2 preparations). The band of the rotaxane showed apparently $\Delta\Delta$-rich CD spectra (*ca.* 2% rich).[6]

*[2]-[ΔΔ-[(en)$_2$Co(dtda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R2**) and ΔΔ-[(en)$_2$Co(dtda)Co(en)$_2$]Cl$_4$ (**B2**):* These complexes were prepared and chromatographed by the same procedure as **R1** and **B1** except for the use of Δ-$[Co(maa)(en)_2]ClO_4$ instead of the racemate. The yield was 2.5±0.5% for **R2** and 60±5% for **B2**. Found for **R2**; C, 34.07; H, 6.73; N, 5.76%. Calcd for [2]-[$\Delta\Delta$-$[(en)_2Co(dtda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot 11H_2O=C_{56}H_{134}N_8S_2O_{45}Cl_4Co_2$: C, 34.26; H, 6.88; N, 5.71%. Found for **B2**; C, 26.90; H, 7.01; N, 12.32%. Calcd for $\Delta\Delta$-$[(en)_2Co(dtda)Co(en)_2]Cl_4\cdot 0.2C_2H_5OH\cdot 6H_2O=C_{20.4}H_{65.2}N_8S_2O_{10.2}Cl_4Co_2$: C, 26.93; H, 7.22; N, 12.32%.

[2]-[[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (***R3***) *and [(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$ (**B3**):* These complexes were prepared and chromatographed in the same manner as **R1** and **B1** except for the use of 1,10-dibromodecane instead of 1,8-dibromooctane. In the separation seven bands f1′—f7′ were eluted in this order. The species f3′(dark violet), f5′(red), f6′(red), and f7′(red) were assigned to $[Co(maa)(en)_2]^+$, [2]-$[(en)_2Co(dhda)Co(en)_2]^{4+}$-[α-CDX]-rotaxane, $[Co\{O_2CCH_2S(CH_2)_{10}Br\}(en)_2]^{2+}$, and $[(en)_2Co(dhda)Co(en)_2]^{4+}$, respectively. Three species f1′(pink), f2′(red), and f4′(pink) were unassignable as yet. When the eluate f2′ was allowed to stand for several days at room temperature, white precipitate of α-CDX was deposited. Therefore, this species is inferred as an inclusion compound of $[Co\{O_2CCH_2S(CH_2)_{10}Br\}(en)_2]^{2+}$ and α-CDX from the analogy of $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_{10}Br\}]Cl_3\cdot 2$(α-CDX) reported previously.[1] The yield was 9.6±2% for **R3** and 47±4% for **B3** (3 preparations). In this system, pronounced selectivity was observed[7]: The band f5′ showed apparently $\Delta\Delta$-rich (*ca.* 10%) CD spectra and f7′ $\Lambda\Lambda$-rich (*ca.* 3%). Found for **R3**; C, 34.98; H, 6.80; N, 5.55%. Calcd for [2]-[$[(en)_2Co(dhda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot 0.2C_2H_5OH\cdot 11H_2O=C_{58.4}H_{139.2}N_8S_2O_{45.2}Cl_4Co_2$: C, 35.06; H, 7.01; N, 5.60%. Found for **B3**; C, 29.83; H, 7.07; N, 12.36%. Calcd for $[(en)_2Co(dhda)Co(en)_2]Cl_4\cdot 0.2C_2H_5OH\cdot 4H_2O=C_{22.4}H_{65.2}N_8S_2O_{8.2}Cl_4Co_2$: C, 29.83; H, 7.29; N, 12.43%.

*[2]-[ΔΔ-[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R4**), ΔΔ-[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$ (**B4**), [2]-[ΛΛ-[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R5**), and ΛΛ-[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$ (**B5**):* These complexes were prepared and chromatographed in the same manner as **R3** and **B3** except for the use of Δ- or Λ-$[Co(maa)(en)_2]ClO_4$ instead of the racemate. The yield was 12% for **R4** and 52% for **B4** in the Δ-system (1 preparation), and 7% for **R5** and 49% for **B5** in the Λ-system (1 preparation). Found for **R4**; C, 36.14; H, 6.98; N, 5.38%. Calcd for [2]-[$\Delta\Delta$-$[(en)_2Co(dhda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot 2C_2H_5OH\cdot 9.5H_2O=C_{62}H_{147}N_8S_2O_{45.5}Cl_4Co_2$: C, 36.21; H, 7.20; N, 5.45%. Found for **R5**; C, 32.55 H, 6.35; N, 5.01%. Calcd for [2]-[$\Lambda\Lambda$-$[(en)_2Co(dhda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot 4NaCl\cdot 1.3C_2H_5OH\cdot 8H_2O=C_{60.6}H_{139.8}N_8S_2O_{43.3}Cl_8Na_4Co_2$: C, 32.62; H, 6.32; N, 5.02%. In the case of **B4** or **B5**, the addition of ethanol to the concentrated eluate yielded the gelatinous precipitate, which contained a large amount of NaCl. Therefore, no satisfactory analytical data were obtained for **B4** and **B5**. The concentrations of their CD spectra were calculated by reference to the molar absorption coefficient of the corresponding racemate **B3**.

*[2]-[ΔΛ-[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R6**) and ΔΛ-[(en)$_2$Co(dhda)Co(en)$_2$]Cl$_4$ (**B6**):* These complexes were prepared from Δ-$[Co\{O_2CCH_2S(CH_2)_{10}Br\}(en)_2](ClO_4)Br$ (1.3 mmol), Λ-$[Co(maa)(en)_2]ClO_4$ (1.4 mmol), and α-CDX (2.5 g) in DMSO (8 cm³). The reaction and separation conditions were the same as those for **R3** and **B3**. The yield was 8.8% for **R6** and 46% for **B6** (1 preparation). Found for **R6**; C, 35.13; H, 6.93; N, 5.43%. Calcd for [2]-[$\Delta\Lambda$-$[(en)_2Co(dhda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot C_2H_5OH\cdot 12H_2O=C_{60}H_{146}N_8S_2O_{47}Cl_4Co_2$: C, 35.06; H, 7.16; N, 5.45%. Found for **B6**; C, 29.45; H, 6.92; N, 12.07%. Calcd for $\Delta\Lambda$-$[(en)_2Co(dhda)Co(en)_2]Cl_4\cdot 0.1C_2H_5OH\cdot 5H_2O=C_{22.2}H_{66.6}N_8S_2O_{9.1}Cl_4Co_2$: C, 29.13; H, 7.34; N, 12.24%.

*[2]-[[(en)$_2$Co(doda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R7**) and [(en)$_2$Co(doda)Co(en)$_2$]Cl$_4$ (**B7**):* The complexes were prepared and chromatographed in the same manner as **R3** and **B3** except for the use of 1,12-dibromododecane instead of 1,10-dibromodecane. The yield was 21±2% for **R7** and 44±3% for **B7** (2 preparations). The apparent selectivity was *ca.* 8% for **R7** and *ca.* 3% for **B7**.[7] Found for **R7**; C, 36.57; H, 7.09: N, 5.36%. Calcd for [2]-[$[(en)_2Co(doda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot 1.8C_2H_5OH\cdot 10H_2O=C_{63.6}H_{150.8}N_8S_2O_{45.8}Cl_4Co_2$: C, 36.65; H, 7.29; N, 5.38%. Found for **B7**; C, 32.52; H, 7.33; N, 12.19%. Calcd for $[(en)_2Co(doda)Co(en)_2]Cl_4\cdot 0.4C_2H_5OH\cdot 2.5H_2O=C_{24.8}H_{67.4}N_8S_2O_{6.9}Cl_4Co_2$: C, 32.66; H, 7.45; N, 12.29%.

*[2]-[ΔΔ-[(en)$_2$Co(doda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R8**), ΔΔ-[(en)$_2$Co(doda)Co(en)$_2$]Cl$_4$ (**B8**), [2]-[ΛΛ-[(en)$_2$Co(doda)Co(en)$_2$]Cl$_4$]-[α-CDX]-rotaxane (**R9**), and ΛΛ-[(en)$_2$Co(doda)Co(en)$_2$]Cl$_4$ (**B9**):* The complexes were prepared and chromatographed in the same manner as **R7** and **B7** except for the use of Δ- or Λ-$[Co(maa)(en)_2]ClO_4$ instead of the racemate. The yield was 24±1% for **R8** and 39±2% for **B8** in the Δ-system (2 preparations), and 17±1% for **R9** and 43±2% for **B9** in the Λ-system (2 preparations). Found for **R8**; C, 36.89; H, 7.17; N, 5.29%. Calcd for [2]-[$\Delta\Delta$-$[(en)_2Co(doda)Co(en)_2]Cl_4$]-[α-CDX]-rotaxane$\cdot 2.5C_2H_5OH\cdot 10H_2O=C_{65}H_{155}N_8S_2O_{46.5}Cl_4Co_2$: C, 36.88; H, 7.38; N, 5.29%. Found for **B8**; C, 33.01; H, 7.29; N, 11.63%. Calcd for $\Delta\Delta$-$[(en)_2Co(doda)Co(en)_2]Cl_4\cdot 1.2C_2H_5OH\cdot 0.6NaCl\cdot H_2O=C_{26.4}H_{69.2}N_8S_2O_{6.2}Cl_{4.6}Na_{0.6}Co_2$: C, 33.14; H, 7.29; N, 11.71%. Found for **R9**: C, 35.83; H, 6.75; N, 5.47%. Calcd for [2]-[$\Lambda\Lambda$-$[(en)_2Co(doda)Co(en)_2]Cl_4$]–[α-CDX]–rotaxane$\cdot 0.5C_2H_5OH\cdot NaCl\cdot 8H_2O=C_{61}H_{139}N_8S_2O_{42.5}Cl_5NaCo_2$: C, 35.79; H, 6.84; N, 5.47%. Found for **B9**; C, 30.79; H, 7.33; N, 11.74%. Calcd for $\Lambda\Lambda$-$[(en)_2Co(doda)Co(en)_2]Cl_4\cdot 0.2C_2H_5OH\cdot$

$5H_2O=C_{24.4}H_{71.2}N_8S_2O_{9.2}Cl_4Co_2$: C, 30.92; H, 7.57; N, 11.82%.

*[2]-[ΔΔ′-[(en)$_2$Co(adha)Co(en)$_2$]Cl$_5$]-[α-CDX]-rotaxane (**R10**), ΔΔ′-[(en)$_2$Co(adha)Co(en)$_2$]Cl$_5$ (**B10**), [2]-[ΛΛ′-[(en)$_2$Co(adha)-Co(en)$_2$]Cl$_5$]-[α-CDX]-rotaxane (**R11**), and ΛΛ′-[(en)$_2$Co(adha)-(en)$_2$]Cl$_5$ (**B11**):*[5]. To 8 cm^3 of DMSO solution containing α-CDX (2.5 g) was added the complexes of *Δ*(or *Λ*)-[Co{O_2CCH_2S-$(CH_2)_{10}$Br}(en)$_2$](ClO_4)Br and *Δ*′(or *Λ*′)-[Co(aet)(en)$_2$](ClO_4)$_2$, and the mixture was kept at 30 °C for 10 d. The resulting reaction mixture was diluted with 20 cm^3 of water, poured onto a column of SP-Sephadex C-25 (Na^+ form), and eluted with 0.65 mol dm^{-3} NaCl. Seven bands, f1″(pink), f2″(pink), f3″(brown), f4″(pink), f5″(orange red), f6″(red), and f7″(orange red), were eluted in this order. The two orange red bands f5″ and f7″ were the desired bands and isolated as the chloride salt in the same manner as above. The other four bands except for [Co(aet)(en)$_2$]$^{2+}$ (f3″) were low in yield and unassignable as yet. The yield was 12% for **R10** and 54% for **B10** in the *ΔΔ*′-system (1 preparation), and 6.4% for **R11** and 58% for **B11** in the *ΔΔ*′-system (1 preparation). Found for **R10**; C, 36.38; H, 7.20; N, 6.15%. Calcd for [2]-[*ΔΔ*′-[(en)$_2$Co(adha)-Co(en)$_2$]Cl$_5$]-[α-CDX]-rotaxane·2C_2H_5OH·8H_2O=$C_{62}H_{148}N_9S_2O_{42}Cl_5Co_2$: C, 36.31; H, 7.27; N, 6.15%. Found for **B10**; C, 29.84; H, 7.66; N, 12.83%. Calcd for *ΔΔ*′-[(en)$_2$Co(adha)Co-(en)$_2$]Cl$_5$·C_2H_5OH·4.5H_2O=$C_{24}H_{75}N_9S_2O_{7.5}Cl_5Co_2$: C, 29.74; H, 7.80; N, 13.01%. Found for **R11**; C, 34.85; H, 7.06; N, 6.05%. Calcd for [2]-[*ΛΛ*′-[(en)$_2$Co(adha)Co(en)$_2$]Cl$_5$]-[α-CDX]-rotaxane·C_2H_5OH·0.5NaCl·10H_2O=$C_{60}H_{146}N_9S_2O_{43}Cl_{5.5}Na_{0.5}Co_2$: C, 34.81; H, 7.11; N, 6.09%. Found for **B11**; C, 30.03; H, 7.68; N, 12.97%. Calcd for *ΛΛ*′-[(en)$_2$Co(adha)Co(en)$_2$]Cl$_5$·1.1C_2H_5OH·4H_2O=$C_{24.2}H_{74.6}N_9S_2O_{7.1}Cl_5Co_2$: C, 30.12; H, 7.79; N, 13.06%.

Measurement. 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_2O containing dioxane as an internal standard.

Results and Discussion

Absorption and CD Spectra. The analytical data show explicitly the formation of the rotaxanes and the

TABLE 1. ABSORPTION AND CD DATA OF THE ROTAXANE AND BRIDGED COMPLEXES

Complex	Bridging ligand	Co(III) components	Absorption$^{a)}$	$\sigma_{\max}(\log\varepsilon)$	CD$^{a)}$ $\sigma_{\mathrm{ext}}(\Delta\varepsilon)$		
R2	dtda	*ΔΔ*	20.15(2.511)	27.8(2.81)$^{b)}$	18.90(−1.62)	21.25(−2.30)	27.47(+0.824)
			35.8(4.14)$^{b)}$	43.40(4.492)	38.76(−11.8)	43.1(+26.4)	
B1	dtda	*rac*	19.95(2.513)	27.8(2.71)$^{b)}$			
			35.50(4.186)	43.30(4.486)			
B2	dtda	*ΔΔ*	20.00(2.513)	27.8(2.71)$^{b)}$	18.90(−2.42)	21.16(−3.07)	27.47(+1.06)
			35.40(4.184)	43.40(4.495)	37.17(−9.29)	42.9(+35.5)	
R3	dhda	*rac*	20.04(2.514)	27.8(2.74)$^{b)}$			
			35.60(4.173)	43.50(4.483)			
R4	dhda	*ΔΔ*	20.02(2.505)	27.8(2.75)$^{b)}$	18.90(−2.32)	21.25(−2.91)	27.46(+1.02)
			35.60(4.170)	43.48(4.480)	37.33(−10.2)	42.9(+27.9)	
R5	dhda	*ΛΛ*	19.97(2.500)	27.8(2.76)$^{b)}$	18.98(+2.08)	21.28(+2.59)	27.46(−0.902)
			35.50(4.144)	43.45(4.459)	37.33(+8.42)	42.9(−29.9)	
R6	dhda	*ΔΛ*	19.97(2.518)	27.8(2.75)$^{b)}$			
			35.58(4.183)	43.26(4.496)			
B3	dhda	*rac*	19.95(2.511)	27.8(2.70)$^{b)}$			
			35.30(4.189)	43.40(4.478)			
B4	dhda	*ΔΔ*			18.92(−2.79)	21.14(−3.41)	27.46(+1.19)
					37.17(−10.7)	42.9(+40.2)	
B6	dhda	*ΔΛ*	19.98(2.497)	27.8(2.70)$^{b)}$			
			35.38(4.152)	43.30(4.458)			
R7	doda	*rac*	19.98(2.540)	27.8(2.75)$^{b)}$			
			35.50(4.175)	43.24(4.475)			
R8	doda	*ΔΔ*	19.95(2.530)	27.8(2.75)$^{b)}$	18.90(−1.53)	21.28(−1.89)	27.47(+0.632)
			35.55(4.161)	43.30(4.460)	37.31(−8.06)	43.1(+22.0)	
R9	doda	*ΛΛ*	19.90(2.534)	27.8(2.75)$^{b)}$	18.96(+1.44)	21.23(+1.71)	27.43(−0.641)
			35.60(4.162)	43.40(4.474)	37.04(+5.81)	43.1(−20.2)	
B7	doda	*rac*	19.98(2.538)	27.8(2.73)$^{b)}$			
			35.35(4.172)	43.24(4.453)			
B9	doda	*ΛΛ*	19.97(2.549)	27.8(2.75)$^{b)}$	18.98(+1.45)	21.19(+1.82)	27.47(−0.636)
			35.40(4.209)	43.40(4.500)	37.31(+6.03)	42.9(−21.2)	
R10$^{c)}$	adha	*ΔΔ*′	20.25(2.536)	28.2(2.77)$^{b)}$	20.04(−3.13)	27.40(+0.353)	
			35.28(4.221)	44.72(4.481)	35.34(−11.6)	44.4(+30.3)	
R11$^{c)}$	adha	*ΛΛ*′	20.28(2.556)	28.2(2.77)$^{b)}$	20.04(+3.27)	27.46(−0.342)	
			35.34(4.232)	44.62(4.490)	35.46(+9.87)	44.4(−31.3)	
B10$^{c)}$	adha	*ΔΔ*′	20.26(2.560)	28.1(2.73)$^{b)}$	20.12(−4.03)	27.46(+0.560)	
			35.20(4.250)	44.52(2.514)	35.34(−11.5)	44.3(+39.2)	
[Co(maa)(en)$_2$]ClO$_4$		*Δ*	16.2(1.50)$^{b)}$	19.33(2.180)	18.40(−2.32)	26.32(+0.714)	
			27.0(2.49)$^{b)}$	35.45(4.073)	34.84(+4.81)	44.6(+19.4)	
			45.20(4.180)				
[Co(aet)(en)$_2$]-(ClO$_4$)$_2$$^{c)}$		*Λ*′	16.7(1.66)$^{b)}$	20.72(2.158)	16.8(+0.844)$^{b)}$	19.12(+1.34)	21.88(−0.278)
			27.3(2.49)$^{b)}$	35.45(4.118)	26.32(+0.677)	35.09(−4.68)	45.7(−11.3)
			49.90(4.221)				

a) Wave numbers are given in 10^3 cm^{-1} unit and log *ε* or *Δε* values (in parentheses) in mol^{-1} dm^3 cm^{-1}. b) Shoulder. c) Ref. 7.

corresponding bridged complexes. The ratios C/N in these complexes are somewhat higher than the ideal values because a large amount of ethanol was used for the isolation of them. It seems that the high ability of adduct formation with organic solvent is common in the present complexes with the hydrophobic polymethylene bridging atoms.

Table 1 collects the absorption and CD data of the present complexes. The representative absorption and CD spectra of the rotaxanes and the bridged complexes are shown in Figs. 2 and 3, respectively, together with those of dhdd complexes (n=10, X=Y=CH$_2$NH$_2$) for comparison. The starting thiolato complex [Co(maa)(en)$_2$]ClO$_4$ exhibits a characteristic absorption at *ca.* 610 nm (16000—17000 cm^{-1}). It is well known that this band disappears by alkylation of the thiolato groups.[6,8] Since all present complexes lack this ab-

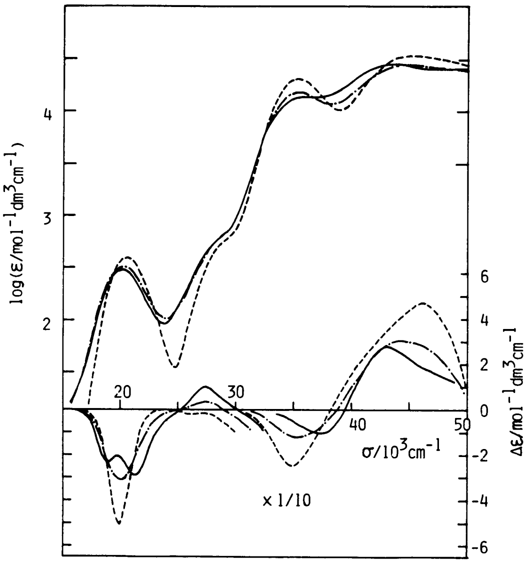


Fig. 2. Absorption and CD spectra of the rotaxanes with the bridging methylene chain length n=10: **R4** (dhda, X=Y=CO$_2^-$) ——; **R10** (adha, X=CO$_2^-$ and Y=CH$_2$NH$_2$) —·—·; dhdd rotaxane (X=Y=CH$_2$NH$_2$)[1] ------.

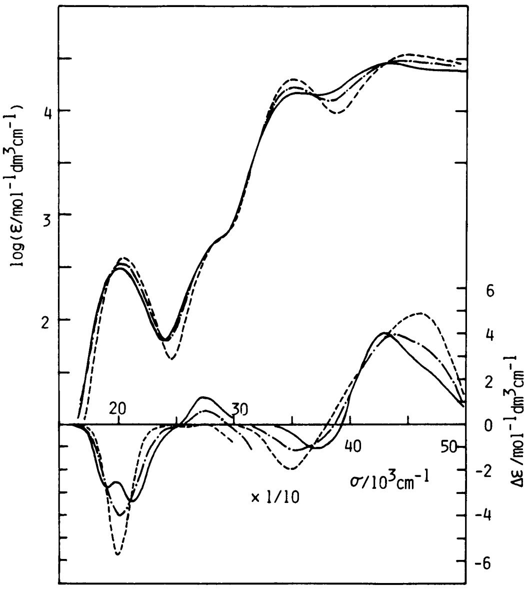


Fig. 3. Absorption and CD spectra of the bridged complexes with n=10: **B4** (dhda, X=Y=CO$_2^-$) ——; **B10** (adha, X=CO$_2^-$ and Y=CH$_2$NH$_2$) —·—·; dhdd complex (X=Y=CH$_2$NH$_2$)[1] ------.

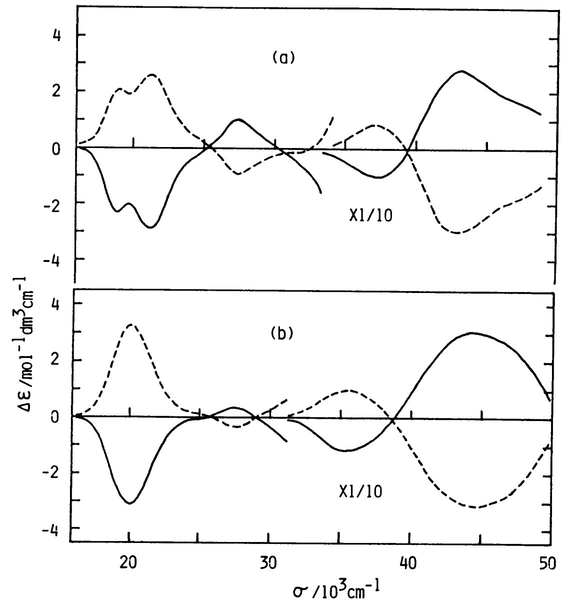


Fig. 4. CD spectra of the dhda and adha rotaxanes: (a) **R4** (ΔΔ) —— and **R5** (ΛΛ) ------; (b) **R10** (ΔΔ) —— and **R11** (ΛΛ) ------.

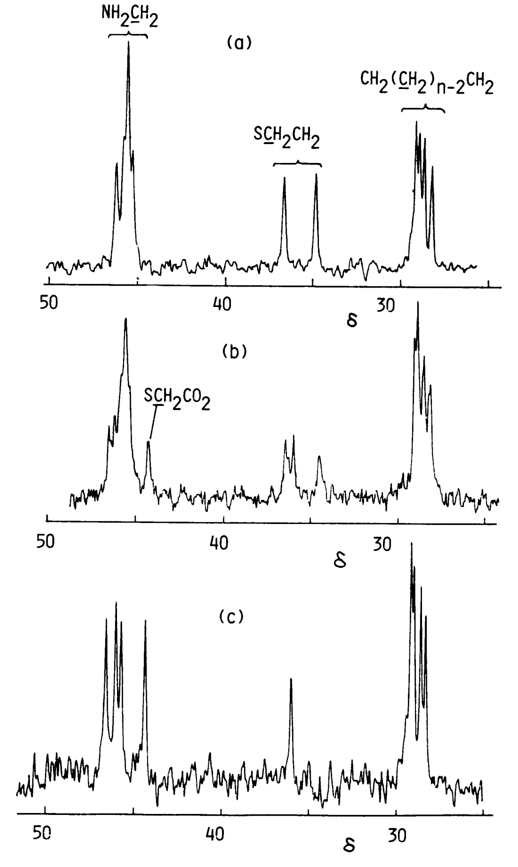


Fig. 5. ^{13}C NMR spectra of the bridged complexes: (a) dhdd complex (X=Y=CH$_2$NH$_2$),[1] (b) **B10** (X=CO$_2^-$ and Y=CH$_2$NH$_2$), and (c) **B4** (X=Y=CO$_2^-$). 1,4-Dioxane (δ=67.40 *vs.* Me$_4$Si) was used as the internal reference. The spectral region due to the carboxyl group was omitted in (b) and (c).

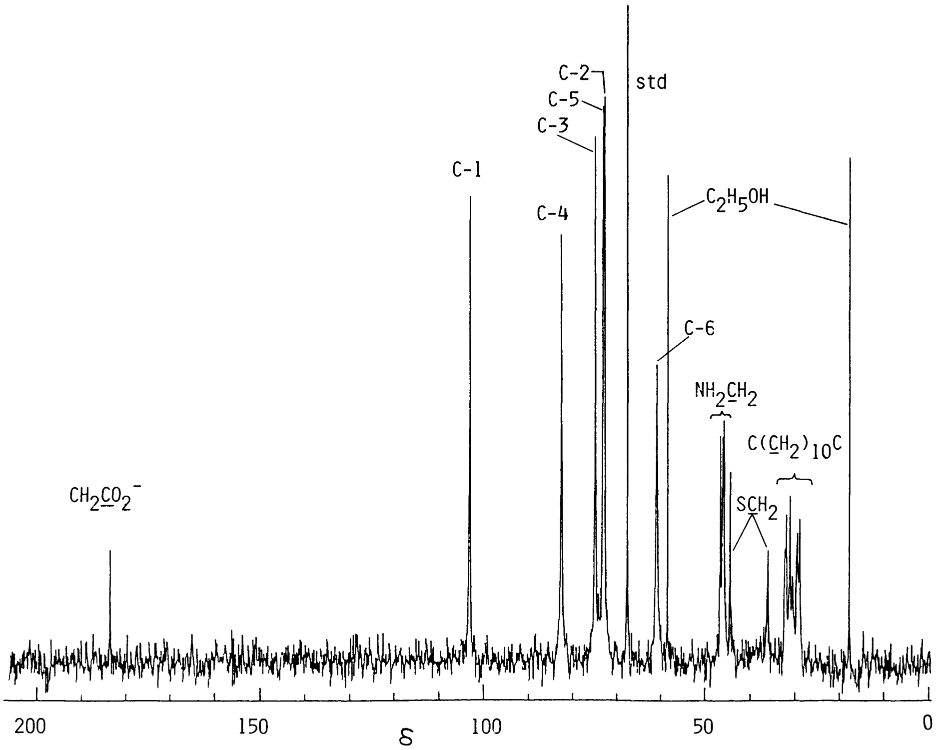


Fig. 6. ^{13}C NMR spectra of the rotaxane **R8**.

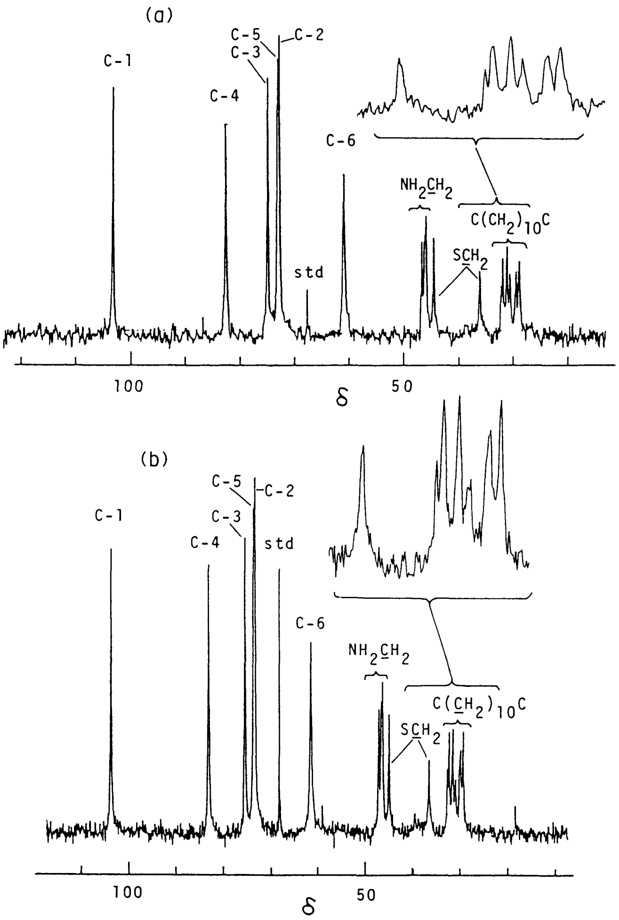


Fig. 7. ^{13}C NMR spectra of the rotaxanes **R9** (a) and **R7** (b). The spectral region due to the carboxyl group was omitted in both.

sorption, they contain only thioether donor atoms as sulfur atom. The first spin-allowed d-d absorption bands of the rotaxanes with the bridging methylene chain length $n=10$ gradually red-shift with the increase of oxygen atom, locating at 20440 cm^{-1} for the dhdd rotaxane with $2[Co(N)_5(S)]$ chromophore, at 20250 cm^{-1} for the adha one with $[Co(N)_5(S)]$ and $[Co(N)_4(S)(O)]$, and 20020 cm^{-1} for the dhda one with $2[Co(N)_4(S)(O)]$ (Fig. 2). The intense bands at *ca.* 35000 cm^{-1}, which can be assigned to the $Co(\sigma^*) \leftarrow S(\sigma)$ ligand-to-metal charge transfer (LMCT) band,[9] show apparently no such shift. The LMCT band intensity of the adha rotaxane is intermediate between those of the dhdd and dhda rotaxanes. Such a mean behavior of the adha rotaxane is also realized in the CD spectra. The absolute configurations of the present complexes can be assigned on the basis of the net CD sign in the first spin-allowed d-d absorption band region, that is, *Δ*-configuration for negative and *Λ*-one for positive.[1,6] The bridged complexes (Fig. 3) show the analogous absorption and CD spectral changes as the corresponding rotaxanes.

The rotaxanes prepared from *rac*-$[Co(maa)(en)_2]^+$ are each the mixture of four diastereomers, *ΔΔ*-, *ΛΛ*-, and two *ΔΛ*-forms (pseudo-*meso*) with respect to the bridged cobalt(III) moieties(neglecting the *R* and *S* chiralities of the donor sulfur atoms).[1] The optically active *ΔΔ* (or *ΛΛ*) rotaxane could be obtained in a pure form from the resolved starting material *Δ*(or *Λ*)-$[Co(maa)(en)_2]ClO_4$. The CD spectra of the dhda and adha rotaxanes are shown in Figs. 4(a) and 4(b), respectively. The CD spectra of the *ΔΔ*- and *ΛΛ*-rotaxanes are not completely enantiomeric to each other in each pair of diastereomers. The deviation is eminent by comparing the diastereomers in the CD intensity ratio,

$\Delta\varepsilon_{\mathrm{LMCT}}/\Delta\varepsilon_{\mathrm{I}}$, where $\Delta\varepsilon_{\mathrm{I}}$ and $\Delta\varepsilon_{\mathrm{LMCT}}$ denote the CD peak intensities in the first d-d absorption and LMCT band (*ca.* 35000 cm^{-1}) regions, respectively: The ratio is 3.25 for $\Lambda\Lambda$-dhda (**R5**) and 3.49 for $\Delta\Delta$-dhda (**R4**) rotaxanes, and 3.02 for $\Lambda\Lambda$-adha (**R11**) and 3.70 for $\Delta\Delta$-adha (**R10**) rotaxanes. It is noteworthy that all the ratios in the rotaxanes are higher than those of the corresponding bridged complexes, namely, 3.14 for dhda bridged complex (**B4**) and 2.85 for adha bridged one (**B10**). This is correlated with the sterically crowded structure of the rotaxane containing α-CDX as compared with the corresponding bridged complexes. The ratio becomes a measure to distinguish between the rotaxane and the bridged complex by the CD spectra.

^{13}C NMR Spectra. Figure 5 shows the ^{13}C NMR spectra of the bridged complexes with $n=10$. The dhdd and dhda complexes with C_2 symmetry clearly shows four resonances in the $-C(CH_2)_8C-$ region. The adha complex with C_1 symmetry exhibited the intermediate pattern. The ^{13}C NMR spectra of rotaxanes are quite different from the bridged complexes, giving the direct evidence of the rotaxane formation with α-CDX (Figs. 6—10). The rotaxane **R8** exhibited strong six signals in a low magnetic field (δ=60—105), which were assigned to α-CDX moiety[1] (Fig. 6). The other signals were assigned to $CH_2\underline{C}O_2^-$ (δ=*ca.* 182.7) and methylene carbons (δ=25—50) of $NH_2\underline{C}H_2-$, $-S\underline{C}H_2-$, and $-C(\underline{C}H_2)_{n-2}C-$ from the lower megnetic field side. The rotaxanes **R8** (Fig. 6) and **R9** (Fig. 7(a)) are composed of a single diastereomer, which has a C_1 symmetry because of the inequality of both openings of α-CDX. In the $-C(CH_2)_{10}C-$ region, they showed four strong (δ=31.75, 30.94, 29.32, and 28.72 for **R9**) and two weak (δ=32.13 and 30.45 for **R9**) resonances. Since it is reasonable to consider that each of the strong signals corresponds to two methylene carbons, the total number of the methylene resonances becomes ten in both the rotaxanes as expected. The results are consistent

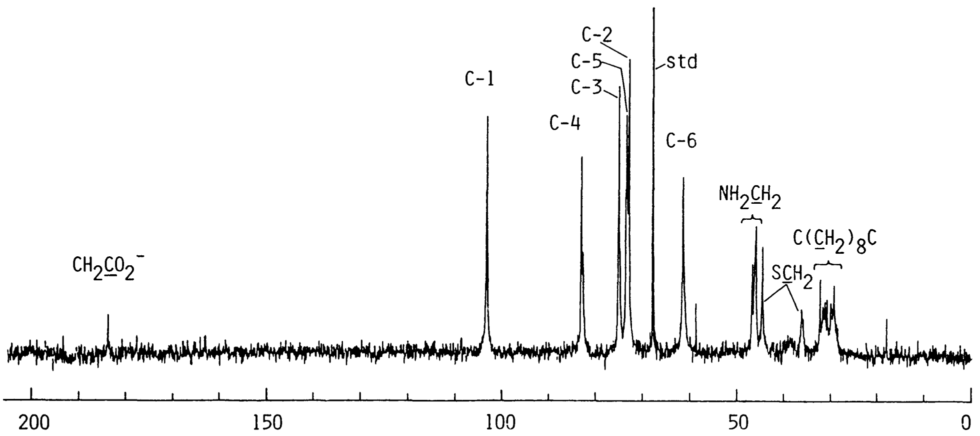


Fig. 8. ^{13}C NMR spectra of the rotaxane **R4**.

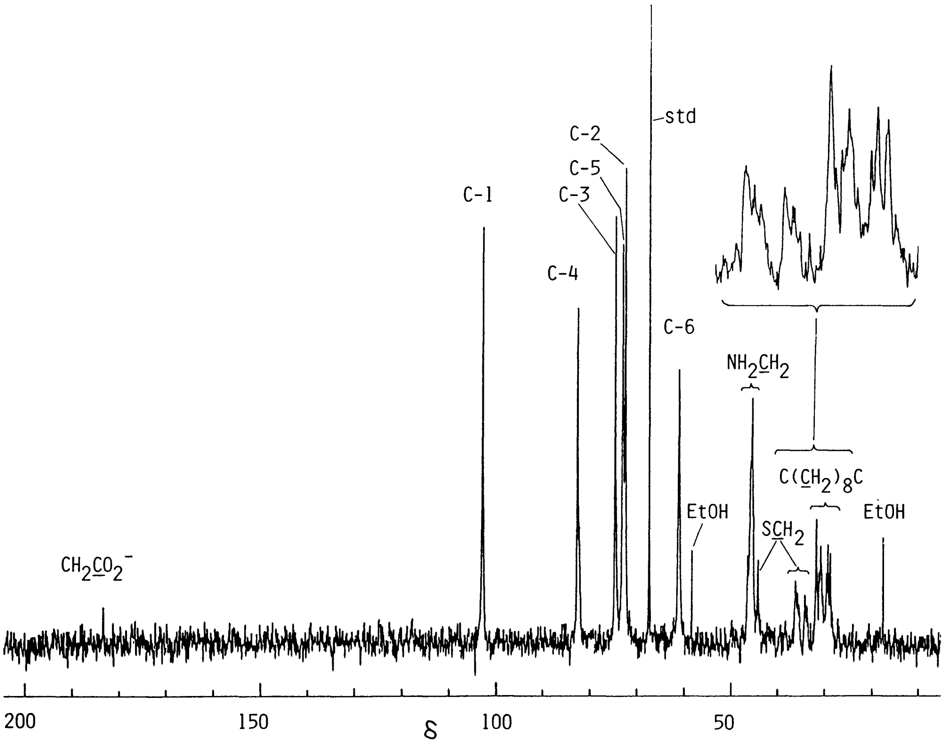


Fig. 9. ^{13}C NMR spectra of the rotaxane **R10**.

with the formation of the rotaxane with C_1 symmetry.

The characteristic features of ^{13}C NMR spectra are the same in the rotaxanes with n=10 (**R4** in Fig. 8 and **R10** in Fig. 9) and n=8 (**R2** in Fig. 10). However, a significant spectral change was observed in **R2**; two signals for each of C4, C5, and C6 in α-CDX appeared during the first several hours (Fig. 10(a)) and the higher field component in each pair became dominant with time (Fig. 10(b)). None of the final resonances corresponded to the chemical shifts of the free α-CDX. The absorption and CD spectra of the same sample after the ^{13}C NMR measurement were checked to elucidate the origin of such a change. The absorption spectrum was the same as the initial one except for the *ca.* 11% intensity decrease in the LMCT region. The pattern of the CD spectrum was the same but the CD intensity reduced to one-half its initial value. The results indicate that the decomposition reaction releasing free α-CDX does not occur and that the species with the uncoordinated thioether atoms, which will be formed by the Co–S cleavage, is also very low in concentration, if any, as judged by the absorption intensity in LMCT region. The most plausible explanation may be that the species with the uncoordinated carboxyl group in -SCH_2CO_2 moiety is partly produced owing to the steric crowding imposed by α-CDX. In fact, the ^{13}C-NMR change with time is most eminent only in **R2** with rather short chain length n=8. Such a splitting is observed only for C4 carbon in **R4** and **R10** with n=10 and the rotaxanes with n=12 had no splitting tendency.

The chemical shifts due to α-CDX in the rotaxanes are summarized in Table 2. The assignment is after Colson *et al.*10) and our results.1) The chemical shifts of free α-CDX were significantly altered by the rotaxane formation, especially those of C1, C3, and C5 shifting to the down field. One of the substituent groups on each of the carbons undergoing such a large shift is directed toward the center part of the cavity of α-CDX and sterically interacted with the included polymethylene chain. This situation is responsible for the above shift. The values of the rotaxanes **R3**, **R4**, **R5**, and **R6** are very similar to one another irrespective of the absolute configurations of the cobalt(III) moieties, which is in good agreement with the earlier results.1) The change of the bridging methylene length, however, affects the chemical shift. The resonances of C4, C5, and C6 were shifted regularly to the down field with the decrease of the methylene chain length from n=*ca.* 17 to n=7,11) whereas the chemical shifts of C1, C2, and C3 were hardly affected. The latter is relevant to the rigid hydrogen bonding network at the side of secondary hydroxyl groups on C2 and C3,12) which makes the chemical shifts of C1, C2, and C3 insensitive to the

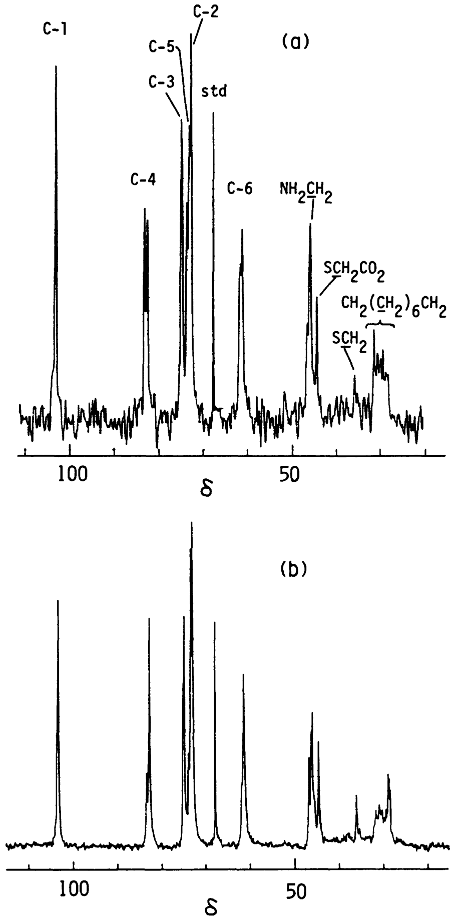


Fig. 10. ^{13}C NMR spectra of the rotaxane **R2**: (a) accumulated for *ca.* 6 h after dissolution in D_2O; (b) accumulated for *ca.* 20 h after dissolution in D_2O.

TABLE 2. ^{13}C NMR RESONANCES DUE TO α-CDX IN THE ROTAXANE (δ from Me_4Si)

Rotaxane	Chain length		Chemical shift					Ref.
		C1	C4	C3	C5	C2	C6	
U1(ΔΔ)	7	102.50	82.95	74.55	73.47	72.36	61.63	11
R2(ΔΔ, dtda)	8	102.61	82.89	74.71	73.41	72.55	61.44	
7(ΔΔ, dtdd)	8	102.64	83.06	74.71	73.47	72.44	61.66	1
R3(*rac*, dhda)	10	102.72	82.46	74.61	72.98	72.49	61.01	
R4(ΔΔ, dhda)	10	102.72	82.51	74.66	73.03	72.49	61.06	
R5(ΛΛ, dhda)	10	102.78	82.46	74.66	72.98	72.49	61.01	
R6(ΔΛ, dhda)	10	102.75	82.49	74.66	73.01	72.47	61.03	
R10(ΔΔ′, adha)	10	102.72	82.54	74.66	73.06	72.47	61.09	
2(*rac*, dhdd)	10	102.78	82.68	74.72	73.15	72.50	61.23	1
R7(*rac*, doda)	12	102.83	82.27	74.63	72.84	72.57	60.79	
R8(ΔΔ, doda)	12	102.83	82.30	74.66	72.87	72.55	60.79	
R9(ΛΛ, doda)	12	102.78	82.24	74.61	72.82	72.49	60.74	
1(*rac*, dodd)	12	102.78	82.24	74.60	72.81	72.54	60.79	1
U2(*rac*)	*ca.* 17	102.78	81.92	74.71	72.71	72.49	60.52	11
free α-CDX		102.18	82.03	74.06	72.82	72.44	61.17	

TABLE 3. PERCENTAGE YIELD OF [2]-[[$(en)_2Co\{XCH_2S(CH_2)_nSCH_2Y\}Co(en)_2]Cl_m$]-[α-CDX]-rotaxane

n	Co(III) components	$X=CO_2^-$ $Y=CO_2^-$	$X=CO_2^-$ $Y=CH_2NH_2$	$X=CH_2NH_2$ $Y=CH_2NH_2$
$n=8$	*rac*	$2.5(\Delta-2)$[b)]		~0
	ΔΔ	2.5		3.5
$n=10$	*rac*	$10(\Delta-10)$[b)]		$6(\Delta-16)$[b)]
	ΔΔ	12	12[c)]	21
	ΛΛ	7	6.4[c)]	<7
	ΔΛ	8.8[c)]		
$n=12$	*rac*	$21(\Delta-8)$[b)]		$16(\Delta-5)$[b)]
	ΔΔ	24		28
	ΛΛ	17		14

a) The data from Ref. 1. b) Apparent optical purity[7)] is indicated in parentheses with the configuration of the rich species. c) The preparative procedures are different from those of other rotaxanes. See Experimental section.

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, the rotaxan formation is explicitly identified by the ^{13}C NMR spectra.

Synthesis and Stereoselectivity. The yields of rotaxanes are summarized in Table 3, together with the earlier results for comparison. The yield is the highest in the doda rotaxanes with $n=12$ and decreases with the decrease of the chain length, namely, in the order 12>10>8. The *ΔΔ*-rotaxane was prepared in the highest yield among the rotaxanes with the identical chain length. This is attributable to the stereoselective inclusion by α-CDX.[13)] The results are very similar to those for the earlier system ($X=Y=CH_2NH_2$) except for that the yields starting from the racemate are somewhat higher in the present system ($X=Y=CO_2^-$).

The highest selectivity was *ca.* 10% in the dhda rotaxane **R3**. The partial selectivity was also observed in the other rotaxanes **R1** and **R7**. It should be noted that the selectivity decreases in the order 10>12>8. This means that there is the optimum methylene length for the chiral discrimination. The rotaxanes of the present system ($X=Y=CO_2^-$, and $X=CO_2^-$ and $Y=CH_2NH_2$) are relatively unstable compared with those in the earlier system ($X=Y=CH_2NH_2$), because it was observed that the former underwent the partial racemization in the prolonged column chromatography. In conclusion, the yield and the selectivity of rotaxane are mainly dependent on the length of the bridging methylene chain and the absolute configuration of the starting cobalt(III) complex. The difference between the bidentate thiolate ligands aet and maa has a small influence on the yield and the selectivity of rotaxane.

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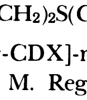
11) K. Yamanari and Y. Shimura, to be published. The rotaxanes **U1** and **U2** denote [2]-[*ΔΔ*-[$(en)_2Co\{NH_2(CH_2)_2S(CH_2)_7S(CH_2)_2NH_2\}Co(en)_2]Cl_6$]-[α-CDX]-rotaxane and [2]-[[$(en)_2Co\{NH_2(CH_2)_2S(CH_2)_6O$–  –$O(CH_2)_6S(CH_2)_2NH_2\}$-$Co(en)_2]Cl_6$]-[α-CDX]-rotaxane, respectively.

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