rate data in Table I). Addition of an excess of bromide to the equilibrated solution produces the spectrum of the bromo complex. From these and the spectral properties of the aquo species, K_{eq} can be determined in the usual way. The results are also included in Table I. It is however important to note that the accuracy with which K_{eq} can be determined depends strongly on the spectral characteristics of the species involved. Furthermore, adequate time must be allowed for such solutions to reach equilibrium as seen from the rate constants in Table I. In the case of the pyridine complex equilibration is indeed very slow, and possible protonation of free pyridine (pK_a = 5.25) must also be taken into account. The values of K_{eq} (in Table I) were determined for complex concentrations between 2×10^{-4} and 2×10^{-3} M and are the average of between three and seven determinations depending on the accuracy of the spectral method. Furthermore, these values are independent of the complex concentration employed and show no trend when the free nucleophile concentration is changed by addition of small quantities of the nucleophile.

Although the values of K_{eq} are subjected to considerably larger error limits than those of K_{kin}, a good correlation between these data does exist. An important result is the observation that both K_{kin} and K_{eq} are fairly constant for the series of complexes for which k_{aq} and k_{an} vary by at least 6 orders of magnitude. In addition, the magnitude of the equilibrium constants is such that for instance approximately 80% of the Pd(MeEt$_4$dien)Br$^+$ species will exist in solution as the aquo complex when the total complex concentration is 8×10^{-5} M. It follows that although the values of K_{kin} and K_{eq} are relatively small (ca. 3×10^{-4} M), they are such that considerable solvolysis occurs especially at low complex concentrations. Furthermore, these values are very close to that found for the solvolysis of Pt(dien)Cl$^+$ in aqueous medium, viz. 3.3×10^{-4} M[1] (see Introduction). Even more surprising is the fact that equilibrium constants estimated for the spontaneous solvolysis of *cis*-Pt(PEt$_3$)$_2$(R)Br in methanol also vary from $(0.7-2) \times 10^{-4}$ M for R = C_6H_5, *p*-MeC_6H_4, *o*-MeC_6H_4, *o*-EtC_6H_4, and 2,4,6-Me$_3C_6H_2$.[6] Very similar results were reported for a series of complexes of the type *cis*-Pt(PEt$_3$)$_2$(C_6H_5)X (X = Cl, Br, I).[8] It follows that such completely different complexes do exhibit solvolysis equilibrium constants very similar to that found in this investigation.

Although it is obvious that one cannot generalize this tendency, the good agreement does stress the fundamental importance of spontaneous solvolysis reactions in processes involving such complexes, especially in the case of the antitumor or catalytic activity of Pt(II) and Pd(II) complexes in general.

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Registry No. Pd(dien)Cl$^+$, 17549-31-4; Pd(1,1,7,7-Me$_4$dien)Cl$^+$, 89397-61-5; Pd(1,1,4,7,4-Me$_5$dien)Cl$^+$, 21007-58-9; Pd(1,4,7-Et$_3$dien)Cl$^+$, 88056-33-1; Pd(1,1,4-Et$_3$dien)Cl$^+$, 88228-48-2; Pd(1,1,7,7-Et$_4$dien)Cl$^+$, 17787-28-9; Pd(1,1,7,7-Et$_4$dien)Br$^+$, 17685-73-3; Pd(4-Me-1,1,7,7-Et$_4$dien)Cl$^+$, 46848-25-3; Pd(4-Me-1,1,7,7-Et$_4$dien)Br$^+$, 58619-24-2; Pd(4-Me-1,1,7,7-Et$_4$dien)I$^+$, 58619-25-3; Pd(4-Me-1,1,7,7-Et$_4$dien)py^{2+}, 91606-31-4.

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Syntheses and Properties of Rotaxane Complexes. 2.[1] Rotaxanes Consisting of α- or β-Cyclodextrin Threaded by (μ-α,ω-Diaminoalkane)bis[chlorobis(ethylenediamine)cobalt(III)] Complexes

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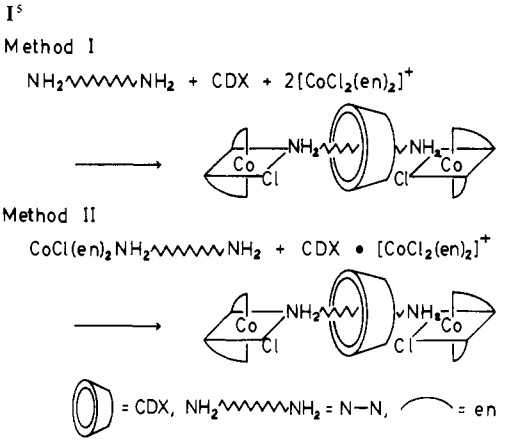
The reactions between *cis*-[CoCl$_2$(en)$_2$]Cl and 1,10-, 1,12-, and 1,14-diaminoalkanes (N–N) in the presence of α- or β-cyclodextrin (α- or β-CDX) gave the rotaxanes [2]-[[(en)$_2$ClCo(N–N)CoCl(en)$_2$]X$_4$]–[CDX]. These rotaxanes were characterized by the decomposition of CDX in the compounds, elemental analyses, SP-Sephadex C-25 column chromatography, molecular rotations, and electronic absorption, circular dichroism, and ^{13}C NMR spectroscopy. The best yields were obtained for N–N = 1,12-diaminododecane (19% for the rotaxane containing α-CDX and 7% for that containing β-CDX).

Introduction

A rotaxane is a compound consisting of a ring threaded by chain-bearing end groups that are so bulky that the chain cannot be extruded from the ring. In a previous paper,[1] the syntheses of rotaxanes in relatively high yields were reported, where the ring was α- or β-cyclodextrin (α- or β-CDX) and the chain was the dimeric cobalt(III) complexes, (μ-α,ω-diaminoalkane)bis[chlorobis(ethylenediamine)cobalt(III)] ([(en)$_2$ClCo(N–N)CoCl(en)$_2$]$^{4+}$).[1,2] This was the first example of the rotaxanes containing chiral rings and also the first example of the rotaxanes containing metal complexes.

Syntheses of rotaxanes will provide a better understanding of nonbonded interactions and inclusion phenomena. This paper describes more extensive preparations of a number of [2]-[[(en)$_2$ClCo(N–N)CoCl(en)$_2$]X$_4$]–[α- or β-CDX] rotax-

Scheme I[5]



(1) Part 1: Ogino, H. *J. Am. Chem. Soc.* **1981**, *103*, 1303.
(2) Abbreviations: en, ethylenediamine; ocn, 1,8-diaminooctane; den, 1,10-diaminodecane; don, 1,12-diaminododecane; tden, 1,14-diaminotetradecane; pxyn, *p*-xylenediamine; N–N, α,ω-diaminoalkane; Me_2SO, dimethyl sulfoxide; tart, tetranegative ion of tartrate.

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Table I. Analytical Data

complex	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
$[CoCl(Me_2SO)(en)_2](ClO_4)_2 \cdot 0.5H_2O$	14.40	14.68	4.63	4.84	11.19	10.94
$[Co(Me_2SO)_2(en)_2](ClO_4)_3$	15.16	15.46	4.45	4.68	8.84	8.89
$[CoCl(en)_2(ocnH)]Cl_3 \cdot 1.5H_2O$	29.22	28.81	8.17	8.16	17.04	17.37
$[CoCl(en)_2(denH)]Cl_3 \cdot 2H_2O$	31.69	31.92	8.56	8.74	15.84	15.80
$[CoCl(en)_2(donH)]Cl_3 \cdot 0.5H_2O$	36.16	36.02	8.73	8.88	15.81	15.56
$[CoCl(en)_2(tdenH)]Cl_3 \cdot 0.5H_2O$	38.65	38.67	9.01	9.11	15.02	14.90
$[CoCl(en)_2(pxynH)]Cl_3 \cdot 1.5H_2O$	29.71	29.62	6.65	6.63	17.32	17.02
$[(en)_2ClCo(ocn)CoCl(en)_2]Cl_4 \cdot 2H_2O$	25.58	25.35	7.51	7.49	18.64	18.60
$[(en)_2ClCo(den)CoCl(en)_2]Cl_4 \cdot 3H_2O$	27.11	26.90	7.84	7.67	17.57	17.31
$[(en)_2ClCo(don)CoCl(en)_2]Cl_4 \cdot 3.5H_2O$	28.79	28.55	8.09	8.07	16.79	16.95
$[(en)_2ClCo(tden)CoCl(en)_2]Cl_4 \cdot 4H_2O$	30.32	30.33	8.33	7.91	16.07	15.97
$[(en)_2ClCo(pxyn)CoCl(en)_2]Cl_4 \cdot 1.5H_2O$	26.18	26.28	6.45	6.52	19.08	18.98
rotaxane [2]-$[[(en)_2ClCo(den)CoCl(en)_2]Br_4]$-[α-CDX]$\cdot 9H_2O$	31.55	31.26	6.57	6.28	6.81	6.71
rotaxane [2]-$[[(en)_2ClCo(don)CoCl(en)_2]Br_4]$-[α-CDX]$\cdot 7H_2O$	32.84	32.50	6.59	6.62	6.34	6.87
rotaxane [2]-$[[(en)_2ClCo(tden)CoCl(en)_2]Cl_4]$-[α-CDX]$\cdot 8H_2O$	36.35	36.52	7.36	7.15	7.31	7.05
rotaxane [2]-$[[(en)_2ClCo(den)CoCl(en)_2](ClO_4)_4]$-[β-CDX]$\cdot 4H_2O$	32.66	32.69	6.12	6.39	6.35	6.46
rotaxane [2]-$[[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4]$-[β-CDX]$\cdot 3H_2O$[a]	33.60	33.76	6.19	6.50	6.32	5.91
rotaxane [2]-$[[(en)_2ClCo(tden)CoCl(en)_2](ClO_4)_4]$-[β-CDX]$\cdot 6H_2O$	33.44	33.51	6.40	6.49	6.09	6.01

[a] Calcd: Co, 5.32; β-CDX, 51.2. Found: Co, 5.14; β-CDX, 50.5 ± 2.0.

anes[3] and some of their properties.

In the previous paper,[1] the two methods shown in Scheme I were developed for the preparation of the rotaxanes. In method I, $[CoCl_2(en)_2]Cl$ was added to a Me_2SO solution containing N–N and CDX and the solution heated to give the rotaxane. In method II, a Me_2SO solution containing $[CoCl(en)_2(N\text{–}NH)]^{3+}$ and CDX was treated with an appropriate base to remove the proton from the coordinated N–NH, and $[CoCl_2(en)_2]Cl$ was then added and allowed to react with $[CoCl(en)_2(N\text{–}N)]^{2+}$. Though comparable yields of the rotaxanes are obtained from the both methods, method I is simpler and more convenient. In the present investigation, method I was employed for most preparations.

Experimental Section

Syntheses of Complexes. The analytical data for the complexes described below are summarized in Table I.

(1) Rotaxane [2]-$[[(en)_2ClCo(don)CoCl(en)_2]Br_4]$-[α-CDX]$\cdot 6H_2O$. Method I. α-CDX (5.0 g, 5.1 mmol) and don (0.40 g, 2 mmol) were dissolved at 80 °C in 10 mL of Me_2SO with stirring, and *cis*-$[CoCl_2(en)_2]Cl$ (1.1 g, 4 mmol) was added.[6] The solution was heated at 75 °C for 30 min and then cooled to room temperature. After dilution with 200 mL of water containing 2 mL of glacial acetic acid, the solution was poured on an SP-Sephadex C-25 column (2.6 × 40 cm). The adsorbed species were eluted with a KCl solution. The chromatogram thus obtained is shown in Figure 1. The fastest moving band, which was green, was followed by a violet band (both are designated as f1 in Figure 1). These species are *trans*- and *cis*-$[CoCl_2(en)_2]^+$, respectively. Eluate f2 was reloaded on an SP-Sephadex column, washed with 0.2 M HCl to remove K^+ ions, and then eluted with a 0.5 M $NaClO_4$ solution. The concentrated eluate deposited $NaClO_4$ crystals, which were removed by filtration. When the filtrate was cooled, reddish violet crystals, *cis*-$[CoCl(Me_2SO)(en)_2](ClO_4)_2 \cdot 0.5H_2O$, appeared.[7] The eluate of f3 was treated in a manner similar to that of f2 and afforded *cis*-$[Co(Me_2SO)_2(en)_2](ClO_4)_3$.[7,9]

The species f4 was reloaded on an SP-Sephadex column and was eluted with a 0.4 M NH_4Br solution. The eluate was concentrated with a rotary evaporator. The NH_4Br deposited was removed by filtration, and acetone was added to the filtrate, yielding an oily layer that solidified upon trituration. The solid was collected and washed with acetone. The crude product was dissolved into a small amount of water, filtered, and poured into 100 mL of acetone. A pink powder of rotaxane [2]-$[[(en)_2ClCo(don)CoCl(en)_2]Br_4]$-[α-CDX]$\cdot 6H_2O$ precipitated. The orange f5 species was not characterized.[9,10]

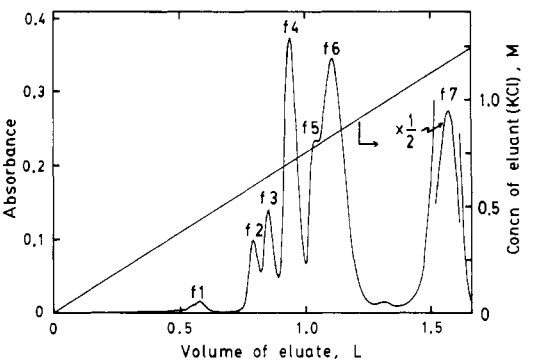

Figure 1. Chromatogram for the solution produced in the reaction between *cis*-$[CoCl_2(en)_2]^+$ and *cis*-$[CoCl(en)_2(don)]^{2+}$ in the presence of α-CDX.

Method II. α-CDX (5.0 g, 2 mmol) and $[CoCl(en)_2(donH)]Cl_3 \cdot 0.5H_2O$ (1.1 g, 2 mmol) were dissolved at 80 °C in 10 mL of Me_2SO with stirring and cooled to room temperature. Diethylamine (0.31 mL, 3 mmol) or piperidine (0.2 mL, 2 mmol) were added to the solution that was heated for 2 min at 80 °C and then cooled. *cis*-$[CoCl_2(en)_2]Cl$ (0.61 g, 2 mmol) was then added and the solution heated at 75 °C for 30 min. The resulting solution was diluted with water containing 2 mL of glacial acetic acid and then chromatographed as described in method I. The product distribution was found to be quite similar to that described in Method I.

(2) Rotaxanes [2]-$[[(en)_2ClCo(den)CoCl(en)_2]Br_4]$-[α-CDX]$\cdot 9H_2O$ and [2]-$[[(en)_2ClCo(tden)CoCl(en)_2]Cl_4]$-[α-CDX]$\cdot 8H_2O$. The title rotaxanes were prepared from 5.0 g of α-CDX, 2 mmol of N–N (0.34 g for den and 0.46 g for tden), 10 mL of Me_2SO, and 1.1 g of *cis*-$[CoCl_2(en)_2]Cl$ by a method similar to method I in (1). The chromatograms were quite similar to that shown in Figure 1, although the yields of the rotaxanes were different. From the eluates, $[CoCl(en)_2(N\text{–}NH)]Cl_3 \cdot nH_2O$, $[(en)_2ClCo(N\text{–}N)CoCl(en)_2]Cl_3 \cdot nH_2O$, and rotaxane [2]-$[[(en)_2ClCo(tden)CoCl(en)_2]Cl_4$-[α-CDX]$\cdot 8H_2O$ were isolated by the concentration. The chloride salt of [2]-$[[(en)_2ClCo(den)CoCl(en)_2]^{4+}]$-[α-CDX] rotaxane could not be obtained as a solid. The eluate was diluted and passed through an SP-Sephadex column. The adsorbed rotaxane was eluted with a 0.4 M NH_4Br solution. The eluate was concentrated, and the deposited

(3) After Schill's nomenclature.[4]
(4) Schill, G. "Catenanes, Rotaxanes, and Knots"; Academic Press: New York, 1971.
(5) The absolute configuration of cobalt(III) moieties and the direction of the threaded CDX are not specified. Some ionic charges are omitted.
(6) Most preparations used *cis*-$[CoCl_2(en)_2]Cl$, although results similar to these were also obtained from the trans isomer.
(7) The cis configuration was proven by the measurement of the ^{13}C NMR spectrum. The complex is a known compound.[8]
(8) Lantzke, I. R.; Watts, D. W. *Aust. J. Chem.* **1967**, *20*, 35.
(9) The formulations of f3 and f5 species given in the previous paper[1] were found to be incorrect.
(10) The species is not $[Co(en)_3]^{3+}$ and seems not to contain don, because heating the species in HCl medium gives *trans*-$[CoCl_2(en)_2]Cl \cdot HCl \cdot 2H_2O$ crystals. Concentration of the eluates of species f6 and f7 gave $[CoCl(en)_2(donH)]Cl_3 \cdot 0.5H_2O$ and $[(en)_2ClCo(don)CoCl(en)_2]Cl_4 \cdot 3.5H_2O$, respectively.

NH_4Br was removed. From the filtrate, rotaxanes [2]-[$[(en)_2ClCo(den)CoCl(en)_2]Br_4$]-[α-CDX]·$9H_2O$ was isolated as powder upon addition of acetone.

(3) Rotaxanes [2]-[$[(en)_2ClCo(den)CoCl(en)_2](ClO_4)_4$]-[β-CDX]-$4H_2O$, [2]-[$[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$]-[β-CDX]-$3H_2O$, and [2]-[$[(en)_2ClCo(tden)CoCl(en)_2](ClO_4)_4$]-[β-CDX]-$6H_2O$. The title rotaxanes were prepared by a method similar to method I in (1), though 5.0 g of β-CDX (4.4 mmol) was used instead of α-CDX. The products adsorbed on SP-Sephadex columns were eluted with KCl solutions. Eluates of rotaxanes were reloaded on SP-Sephadex columns. The columns were washed with 0.1 M HCl to remove K^+ ions and the species eluted with $LiClO_4$. Each eluate was evaporated to a small volume and poured into 200 mL of acetone. The rotaxane was obtained as a pink powder.

(4) Attempts To Prepare [2]-[$[(en)_2ClCo(N-N)CoCl(en)_2]X_4$]-[α- or β-CDX] Rotaxanes (N-N = ocn, pxyn). In order to obtain the title rotaxanes, the reactions of ocn and pxyn with *cis*-$[CoCl_2(en)_2]Cl$ in the presence of CDX (α- and β-CDX for ocn and β-CDX for pxyn) were carried out by a method similar to method I in (1). The complexes $[CoCl(en)_2(N-NH)]Cl_3·1.5H_2O$ and $[(en)_2ClCo(N-N)CoCl(en)_2]Cl_4·nH_2O$ containing ocn or pxyn were obtained, but the rotaxanes were not formed. Since the chloride salt of $[CoCl(en)_2(ocnH)]^{3+}$ is very soluble in water and difficult to separate from KCl crystals, the eluate containing this salt was diluted and reloaded on an SP-Sephadex column. The adsorbed species was eluted with 0.4 M HCl. When the eluate was concentrated, a red oily layer separated. The oil was dissolved into a small amount of methanol, from which the powder of $[CoCl(en)_2(ocnH)]Cl_3·1.5H_2O$ precipitated upon addition of acetone.

(5) Resolution of *cis*-$[CoCl(en)_2(donH)]^{3+}$. To resolve the enantiomeric forms of this complex, $[CoCl(en)_2(donH)]Cl_3·0.5H_2O$ (75 mg) was loaded on an SP-Sephadex column (2.6 × 90 cm). Recycling chromatography (three cycles) using 0.15 M $Na_2[Sb_2(d\text{-tart})_2]$ as an eluant caused the adsorbed species to separate into two components that were labeled A1 and A2 in the order of elution.

The CD patterns establish A1 and A2 to be enantiomers; the pattern for A1, which is shown in Figure 2 (supplementary material), is quite similar to that of Λ-$[CoCl(NH_3)(en)_2]^{2+}$.[11-13] This observation indicates that the absolute configuration of A1 is Λ.

(6) Separation of ΔΔ-, ΛΛ-, and ΔΛ-[$(en)_2ClCo(don)CoCl(en)_2]^{4+}$. To separate $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ into optical and geometric isomers, the following procedures were employed: $[(en)_2ClCo(don)CoCl(en)_2]Cl_4·3.5H_2O$ (70 mg) was loaded on an SP-Sephadex column (2.6 × 87 cm), and recycling chromatography (three cycles) was carried out with 0.20 M $Na_2[Sb_2(tart)_2]$ as an eluant. The adsorbed band separated into three components (approximate mole ratios of the components were 1:2:1), but the separation was incomplete. From the measurements of CD spectra, the species of the first, second, and third bands were assigned to ΔΛ, meso, and ΔΔ isomers, respectively, though the isolation of each isomer was not possible owing to the mutual overlapping of the bands.

Apparatus. Electronic spectra were recorded with a Union SM-401 spectrophotometer. CD spectra and optical rotations were measured with a Jasco J-40A spectropolarimeter and a Union PM-101 digital polarimeter, respectively. ^{13}C NMR spectra were measured in D_2O solutions with a Varian XL-200 spectrometer. 1,4-Dioxane (δ 67.4 vs. Me_4Si) was used as the internal standard.

Results and Discussion

Syntheses. Reactions of $[CoCl_2(en)_2]Cl$ with various amines in water or ethanol are known to give *cis*-$[CoCl(en)_2(amine)]Cl_2$.[14,15] It was shown previously that the use of Me_2SO facilitates the coordination of amino groups to a cobalt(III) center:[16-19] The reaction of $[CoCl_2(en)_2]Cl$ with N-N in Me_2SO afforded $[CoCl(en)_2(N-NH)]^{3+}$ and $[(en)_2ClCo(N-N)CoCl(en)_2]^{4+}$. At higher dilution even large chelate-ring compounds of the types $[Co(en)_2(N-N)]^{3+}$ and $[(en)_2Co(N-N)_2Co(en)_2]^{6+}$ were formed.[17]

Chromatography of the products of the reactions of $[CoCl_2(en)_2]Cl$ with den, don, and tden in the presence of CDX yielded chromatograms such as that shown in Figure 1. When the reaction was carried out in the absence of CDX, only the band corresponding to f4 disappeared. Each f4 species gives analytical results that are in satisfactory agreement with the formulation $[(en)_2ClCo(N-N)CoCl(en)_2]X_4$- [α- or β-CDX]·$nH_2O$ (Table I). The f4 species is, however, not the simple equimolar mixture of $[(en)_2ClCo(N-N)CoCl(en)_2]X_4$ and CDX, because such a mixture readily chromatographed into its separate compondnts. These results suggest that the f4 species is the rotaxane. The solubility of β-CDX is rather low(1.9 g/100 mL of H_2O),[20] whereas the rotaxanes containing β-CDX are quite soluble in water. Addition of $[(en)_2ClCo(don)CoCl(en)_2]Cl_4$ to the suspension of β-CDX in water does not lead to the dissolution of the suspended β-CDX. The solubility of $[(en)_2ClCo(don)CoCl(en)_2]Br_4·3H_2O$ is also low, but the addition of HBr to the f4 species does not cause $[(en)_2ClCo(don)CoCl(en)_2]Br_4·3H_2O$ to precipitate. These observations provide additional indirect evidence of the formulation of the rotaxanes. The observations that will be given below also lead to the conclusion that the f4 species is the rotaxane.

It is quite interesting that the rotaxane, which has a charge of 4+, is eluted more easily than $[CoCl(en)_2(N-NH)]^{3+}$. The presence of bulky CDX in the species may hinder intimate interaction of the complex cations with the sulfopropyl groups in the resin, and/or this behavior of the rotaxanes may reflect the gel filtration effect due to Sephadex resin. The R_f values of the rotaxanes are almost identical, irrespective of the kinds of N-N. Those of $[CoCl(en)_2(N-NH)]^{3+}$ and $[(en)_2ClCo(N-N)CoCl(en)_2]^{4+}$, however, increase with the decrease of the methylenic chain length.

Removal of CDX from a Rotaxane. If the CDX contained in a rotaxane is decomposed and the dimeric cobalt(III) component remains intact, $[(en)_2ClCo(N-N)CoCl(en)_2]X_4$ can be isolated. An unsuccessful attempt to decompose the β-CDX in rotaxane [2]-[$[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$]-[β-CDX]·$3H_2O$ was made with a digestive enzyme (takadiastase supplied by Sankyo Co.). However, the following procedure gave satisfactory results: Rotaxane [2]-[$[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$]-[β-CDX]·$3H_2O$ (35 mg) was dissolved into 1 mL of 4.3 M HBr solution and heated at 75 °C for 2 h. The solution was diluted with 20 mL of water whereupon $[(en)_2ClCo(don)CoCl(en)_2]Br_4·3H_2O$ deposited; yield 90%, as verified by elemental analysis, the absorption spectrum, and the chromatographic pattern.

Molecular Rotations and CD Spectra of Rotaxanes. The molecular rotation is always somewhat smaller than that of the corresponding CDX (Table II),[13] indicating a specific interaction between CDX and $[(en)_2ClCo(N-N)CoCl(en)_2]^{4+}$. This is also reflected in the CD spectra. The CD patterns of [2]-[$[(en)_2ClCo(N-N)CoCl(en)_2]^{4+}$]-[β-CDX] rotaxanes are quite different from those of optically active $[CoCl(en)_2(donH)]^{3+}$ and $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ (Figure 2).[13] The former disappeared when the CDX in the rotaxane was removed by HBr. Therefore, the CD patterns of the rotaxanes are induced by the presence of chiral CDX and not by stereoselective formation of the rotaxanes. Numerical data on CD bands are summarized in Table III. The following general trends are seen. The intensities of the bands at around 18 500 cm^{-1} increase with the decrease of the methylenic chain length

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Table III. CD Spectral Data

complex	λ_{max}/ 10^3 cm^{-1}	$\Delta\epsilon$
Λ-[CoCl(en)$_2$(donH)]$^{3+}$	18.0	+0.31
	20.8	+0.26
	25.3	+0.08
	27.8	−0.07
[2]-[[(en)$_2$ClCo(den)CoCl(en)$_2$]$^{4+}$]-[α-CDX] rotaxane	18.9	+0.061
	22.2	−0.009
[2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$]-[α-CDX] rotaxane	18.2	+0.057
[2]-[[(en)$_2$ClCo(tden)CoCl(en)$_2$]$^{4+}$]-[α-CDX] rotaxane	18.9	+0.010
	20.7	+0.013
[2]-[[(en)$_2$ClCo(den)CoCl(en)$_2$]$^{4+}$]-[β-CDX] rotaxane	18.3	+0.12
	21.8	−0.011
	25.2	+0.008
[2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$]-[β-CDX] rotaxane	18.4	+0.040
	21.7	−0.003
[2]-[[(en)$_2$ClCo(tden)CoCl(en)$_2$]$^{4+}$]-[β-CDX] rotaxane	18.0	+0.051
	22.0	+0.013

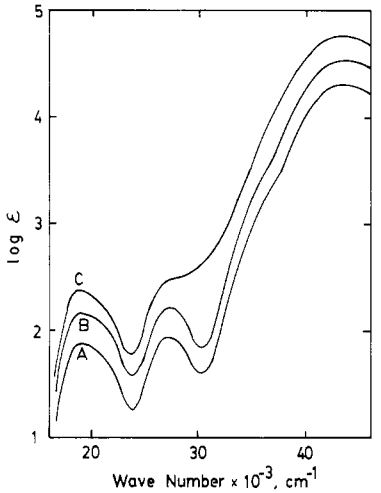

Figure 3. Electronic spectra of *cis*-[CoCl(en)$_2$(donH)]$^{3+}$ (A), [2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$]-[β-CDX] rotaxane (B), and [(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$ (C). Curve C is shifted upward by 0.2 log ϵ unit.

of N–N, and the CD bands of the rotaxanes containing β-CDX are stronger than those containing α-CDX. Quite recently, stereoselective formation 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-CDX] rotaxane was reported by use of the method that we have developed.[21]

Electronic Spectra of [CoCl(en)$_2$(N–NH)]$^{3+}$, [(en)$_2$ClCo(N–N)CoCl(en)$_2$]$^{4+}$, and [2]-[[(en)$_2$ClCo(N–N)CoCl(en)$_2$]$^{4+}$]-[α- or β-CDX] Rotaxanes. Figure 3 shows the electronic spectra of the title compounds containing don as N–N. The spectral patterns are quite similar to one another and are characteristic of the [CoClN$_5$] chromophore. The intensities of the rotaxane and dimer are roughly twice that of [CoCl(en)$_2$(donH)]$^{3+}$. The complexes containing N–N other than don also give spectra almost identical with those of the corresponding complexes containing don. As is seen in Figure 3, the spectrum of the rotaxane, although quite similar to that of the dimer, is subtly different. This also indicates that the rotaxane is not a simple mixture of the dimeric cobalt(III) complex and β-CDX.

^{13}C NMR Spectra of the Rotaxanes and the Related Compounds. ^{13}C NMR spectra of [2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$]-[α-CDX] rotaxane and [(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$ are shown in Figure 4. [(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$ contains 20 carbon atoms but shows only 10 signals, which indicates that each [CoCl(en)$_2$(N–)]$^{2+}$ moiety has a cis configuration and that the chemical shifts of racemic isomer are the same as those of meso isomer. The latter assumption would be justified because two [CoCl(en)$_2$(N–)]$^{2+}$ moieties are connected by a long methylenic chain. The spectral pattern of α-CDX moiety in the rotaxane is almost the same as that of free α-CDX. This indicates that there is no chemical bond between the CDX and the cobalt(III) moiety. The chemical shifts of free CDX and the CDX moieties in the rotaxanes containing don are compared in Table IV.[13] These values are similar to each other, but not the same. Although the spectral pattern of the dimeric cobalt(III) moiety of the rotaxane in Figure 4 is similar to that of [(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$, the former spectrum is more complicated and broadened. This phenomenon can be rationalized only by assuming a rotaxane structure. Since the α-CDX is chiral and has the shape of a truncated cone, the rotaxane is a mixture of equimolar amounts of four diastereoisomers. The meso form in the dimeric cobalt(III) ions is no longer meso in the rotaxane. Therefore, the rotaxane should show 20 × 4 peaks. This explains the signal broadening observed for the rotaxane.

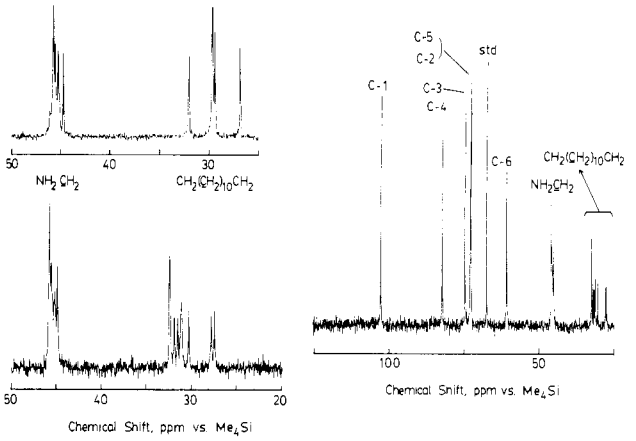

Figure 4. ^{13}C NMR spectra of [(en)$_2$ClCo(don)CoCl(en)$_2$](ClO$_4$)$_4$ (left upper) and [2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$](ClO$_4$)$_4$]-[α-CDX] rotaxane (left lower and right). Dioxane (δ 67.4 vs. Me$_4$Si) was used as the internal standard. Chemical shifts were referenced to Me$_4$Si, downfield shifts having positive values. The signals of α-CDX (C-1 ~ C-6) were assigned after: Colson, P.; Jennings, H. J.; Smith, Ian C. P. *J. Am. Chem. Soc.* **1974**, *96*, 8081.

Table V. Yield of Rotaxanes[a]

rotaxane	yield/%
[2]-[[(en)$_2$ClCo(den)CoCl(en)$_2$]$^{4+}$]-[α-CDX]	5.7
[2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$]-[α-CDX]	19
[2]-[[(en)$_2$ClCo(tden)CoCl(en)$_2$]$^{4+}$]-[α-CDX]	12
[2]-[[(en)$_2$ClCo(ocn)CoCl(en)$_2$]$^{4+}$]-[β-CDX]	0
[2]-[[(en)$_2$ClCo(pxyn)CoCl(en)$_2$]$^{4+}$]-[β-CDX]	0
[2]-[[(en)$_2$ClCo(den)CoCl(en)$_2$]$^{4+}$]-[β-CDX]	2.4
[2]-[[(en)$_2$ClCo(don)CoCl(en)$_2$]$^{4+}$]-[β-CDX]	6.7
[2]-[[(en)$_2$ClCo(tden)CoCl(en)$_2$]$^{4+}$]-[β-CDX]	1.9

[a] Yield = mol of rotaxane formed/mol of don or [CoCl(en)$_2$(donH)]Cl$_3$·0.5H$_2$O.

Yields of Rotaxanes. Agam et al. prepared rotaxanes by statistical threading of poly(ethylene glycols) in crown polyethers.[22,23] They also derived an empirical equation to show the effect of various factors such as the lenght of chain, the radius of ring, volume of the system, etc., on the amount of threading. According to their results, when a ring having such a long cavity as CDX is threaded by α,ω-diaminoalkane, the probability of threading should be extremely low. However, the yields of the rotaxanes prepared in this work are sur-

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(22) Agam, G.; Graiver, D.; Zilkha, A. *J. Am. Chem. Soc.* **1976**, *98*, 5206.
(23) Agam, G.; Zilkha, A. *J. Am. Chem. Soc.* **1976**, *98*, 5214.

prisingly high. The formation of the rotaxanes is good evidence that the CDX includes the α,ω-diaminoalkane and aminoalkyl group in $[CoCl(en)_2(N\text{-}N)]^{2+}$. Table V shows that the yield of rotaxanes containing α-CDX is higher than that containing β-CDX. α-CDX, which has a narrower cavity than β-CDX, appears to be more effective for threading N-N. The yield of the rotaxanes also depends on the methylenic chain length of N-N. The formation of rotaxanes was not observed for N-N = ocn and pxyn. The yield increases with the increase of methylenic chain length of N-N up to don. In N-N = tden, with 14 methylenic chains, however, the yield decreased. A possible explanation for this phenomenon would be as follows: As more than one CDX molecule is threaded by tden, attack of $[CoCl_2(en)_2]^+$ on the free amino group is hindered and/or as the methylenic chain of tden is folded by internal hydrophobic interaction no effective threading can occur.

The rotaxanes prepared in this work are regarded as intermediates to catenanes. That is, for example, the substitution of two Cl^- ions in a rotaxane by an N-N molecule should lead to a catenane. In connection with this, an unsuccessful attempt to prepare a catenane[24] yielded an inclusion compound consisting of α-CDX and 1,10-dodecanedithiol. The attempt failed in the conversion of the dithiol in the compound to a macrocyclic disulfide.

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Registry No. α-CDX, 10016-20-3; β-CDX, 7585-39-9; $[CoCl(Me_2SO)(en)_2](ClO_4)_2$, 15618-10-7; $[Co(Me_2SO)_2(en)_2](ClO_4)_3$, 14781-36-3; $[CoCl(en)_2(ocnH)]Cl_3$, 91686-73-6; $[CoCl(en)_2(denH)]Cl_3$, 91686-74-7; $[CoCl(en)_2(donH)]Cl_3$, 76793-16-3; $[CoCl(en)_2(tdenH)]Cl_3$, 91686-75-8; $[CoCl(en)_2(pxynH)]Cl_3$, 91686-76-9; $[(en)_2ClCo(ocn)CoCl(en)_2]Cl_4$, 91686-77-0; $[(en)_2ClCo(den)CoCl(en)_2]Cl_4$, 91740-99-7; $[(en)_2ClCo(don)CoCl(en)_2]Cl_4$, 91741-00-3; $[(en)_2ClCo(tden)CoCl(en)_2]Cl_4$, 91686-78-1; $[(en)_2ClCo(pxyn)CoCl(en)_2]Cl_4$, 91686-79-2; $[(en)_2ClCo(den)CoCl(en)_2]Br_4$, 91796-34-8; $[(en)_2ClCo(don)CoCl(en)_2]Br_4$, 77069-99-9; $[(en)_2ClCo(den)CoCl(en)_2](ClO_4)_4$, 76748-10-2; $[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$, 76748-07-7; $[(en)_2ClCo(tden)CoCl(en)_2](ClO_4)_4$, 91741-02-5; Λ-$[CoCl(en)_2(donH)]^{3+}$, 91741-03-6; $[CoCl_2(en)_2]Cl$, 14040-32-5.

Supplementary Material Available: Table II (molecular rotation data), Table IV (^{13}C NMR spectral data), and Figure 2 (circular dichroism curves) (3 pages). Ordering information is given on any current masthead page.

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A Menschutkin Type Amine Alkylation Involving Methyl Transfer to Benzylamine from Palladium(II) Chelate Complexes of *o*-(Diphenylphosphino)thioanisole

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The reactions between the complexes $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ and benzylamine yield the respective thiolato compounds $[PdCl(\mu\text{-}SC_6H_4PPh_2\text{-}o)]_2$ and $Pd(o\text{-}Ph_2PC_6H_4S)_2$. The other product is *N*-methylbenzylamine. Conductivity measurements on acetonitrile solutions of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ show partial substitution of chloride by benzylamine to give $[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]Cl$. Time-dependent intensity measurements on the decrease in the ^1H NMR resonance of the methyl group of the palladium(II) complexes give a rate law: rate = k_2[Pd complex][$PhCH_2NH_2$]. Respective rate constants for $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ are in the 10^{-5} and 10^{-3} mol^{-1} s^{-1} range. The complex $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ has cis stereochemistry ($^4J(PH)$ = 4 Hz), and the partially demethylated intermediate $[Pd(o\text{-}Ph_2PC_6H_4SMe)(o\text{-}Ph_2PC_6H_4S)]BF_4$ also has cis stereochemistry ($^4J(PH)$ = 3.6 Hz). The final complex $Pd(o\text{-}Ph_2PC_6H_4S)_2$ has trans stereochemistry, which is confirmed by X-ray crystallography. The complex $PdS_2P_2C_{36}H_{28}$ has a = 9.735 (3) Å, b = 12.865 (3) Å, and c = 12.732 (4) Å and crystallizes in the monoclinic $P2_1/c$ space group with Z = 2. The activation parameters for the methylation of benzylamine in acetonitrile solvent are ΔH^* = 12 (2) kcal mol^{-1} and ΔS^* = -41 (10) cal K^{-1} mol^{-1}. A mechanism is proposed for these reactions whereby the amine undergoes nucleophilic attack by an S_N2 Menschutkin type reaction at the methyl group of the coordinated thioether. The complex $PtCl_2(o\text{-}Ph_2PC_6H_4SMe)$ has been prepared, and the complex $NiCl_2(o\text{-}Ph_2PC_6H_4SMe)$ also was found to methylate benzylamine.

Introduction

Methyl transfer is a topic of considerable significance in biological chemistry. Two of the most important compounds that have been implicated in such reactions are methylcobalamin and *S*-adenosylmethionine. This latter compound is of interest to use because of its widespread involvement as an in vivo carbonium ion type methylating agent.[2]

In 1966 it was suggested that the dealkylation reaction of dichloro(*o*-(diphenylphosphino)thioanisole)palladium(II) under

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