negative, and we believe that the same mechanism is responsible for the negative $^{n}\Delta$ values found for **3** and **5**.[7]

Comparing the $^{1}\Delta$ values of the cycloalkanes with the $^{1}J(^{13}C,^{1}H)$ data, we observe an inverse relation similar to the one derived from ^{31}P NMR data[11] (Figure 3). A closely related curve is obtained by plotting $^{1}\Delta$ against δ (^{13}C) of the cycloalkanes,[12] and this finding parallels observations made for $^{13}C/^{12}C$ isotope effects on ^{19}F chemical shifts and $^{13}C,^{19}F$ coupling constants.[1a] The earlier empirical relations were restricted to systems with similar hybridization, and linearity was found. In our case sp^2- (cyclopropane) and sp^3-hybridized C–H bonds (cyclohexane, etc.) are included. Indeed, the nonlinearity in Figure 2 is primarily due to the entries for cyclopropane and, in part, cyclobutane. Since it is known that the s character in the C–H bond hybrids increases with decreasing ring size, both ^{1}J and $\delta(^{13}C)$ follow the s character, whereas $^{1}\Delta$ is proportional to the p character and thus should increase with C–H bond length.

From the $^{13}C,^{2}H$ coupling constants the corresponding $^{13}C,^{1}H$ coupling constants can be calculated by using eq 1.[13] These

$$^{n}J(^{13}C,^{1}H) = 6.5144\,^{n}J(^{13}C,^{2}H) \qquad (1)$$

results are given in Table II. From the ^{1}J values precise data are available only for **1** and **4** (160.45 and 124.56 Hz, respectively[14,15]), and no primary isotope effect can be recognized.[16] The ^{2}J and ^{3}J values have not been measured so far. The latter show an interesting linear dependence on ring size if the value for **2** is divided by 2, due to the fact that two equivalent coupling pathways exist. The fact that the data measured are average values for different conformations precludes, however, a detailed discussion of their structural dependence. The same is true for the stereochemical aspects concerned with $^{n}\Delta$ in **2**–**5**.

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Note Added in Proof: Most recently, downfield ^{13}C NMR $^{2}H/^{1}H$ isotope shifts have been found over two bonds in carbocations (K. L. Servis and F.-F. Shue, *J. Am. Chem. Soc.*, **102**, 7233 (1980)) and over three bonds in cyclobutene (P. E. Hansen and J. J. Led, private communication).

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[7] The present finding also supports the possibility of a negative (downfield) vicinal isotope effect in tropylium ion,[8] where we had found $|^{4}\Delta| > |^{3}\Delta|$ from measurements on $C_4H_6D^+BF_4^-$ and $C_7HD_6^+BF_4^-$; $^{3}\Delta < 0$ was rejected at that time on the basis of the experimental evidence available.[9] Furthermore, at least part of the downfield vicinal isotope effect reported by Saunders et al.[10] for cyclopentenyl cation might be due to an intrinsic contribution rather than to "isotopic perturbation of resonance".

[8] H. Günther, H. Seel, and M.-E. Günther, *Org. Magn. Reson.*, **11**, 97 (1978).

[9] In an earlier paper [H. Günther and G. Jikeli, *Chem. Ber.*, **106**, 1863 (1973)] due to a misprint we reported a vicinal isotope effect of –0.01 ± 0.01 ppm. The correct value is +0.01 ± 0.01 ppm; furthermore, the data for the systems **20** and **23** in Table 7, p 1878, have to be interchanged.

[10] M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, **99**, 8071 (1977).

[11] A. A. Borisenko, N. M. Sergeyev, and Y. A. Ustynyuk, *Mol.* Phys., **22**, 715 (1971).

[12] J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **86**, 1870 (1964).

[13] P. Diehl and T. Leipert, *Helv. Chim. Acta*, **47**, 545 (1964).

[14] V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, **46**, 4165 (1967).

[15] V. A. Chertkov and N. M. Sergeyev, *J. Am. Chem. Soc.*, **99**, 6750 (1977).

[16] There are theoretical indications of a negative isotope effect on $^{1}J(^{13}C,^{1}H)$[17] of less than 1%; a clearcut experimental proof is still lacking, however, since the observed changes were always within experimental error [see, for example, a recent investigation by M. Alei, Jr., and W. E. Wageman, *J. Chem. Phys.*, **68**, 783 (1978)].

[17] N. M. Sergeyev and V. N. Solkan, *J. Chem. Soc., Chem. Commun.*, 12 1975.

[18] H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew. Chem.*, **85**, 826 (1973); *Angew. Chem. Int. Ed. Engl.*, **12**, 762 (1973).

Relatively High-Yield Syntheses of Rotaxanes. Syntheses and Properties of Compounds Consisting of Cyclodextrins Threaded by α,ω-Diaminoalkanes Coordinated to Cobalt(III) Complexes

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Rotaxane is a compound consisting of a ring threaded by a chain having such large end groups that the chain cannot be extruded from the ring. This paper describes the syntheses of rotaxanes in relatively high yield, where the ring is α- or β-cyclodextrin (α- or β-CDX)[1] and the chain is the dimeric cobalt(III) complex, μ-(α,ω-diaminoalkane)bis[chlorobis(ethylenediamine)cobalt(III)] ($[(en)_2ClCo(N{-}N)CoCl(en)_2]^{4+}$).[2]

The reaction between $[CoCl_2(en)_2]Cl$ and N-N gives *cis*-$[CoCl(en)_2(N{-}N)]^{2+}$ and *cis*-$[(en)_2ClCo(N{-}N)CoCl(en)_2]^{4+}$.[3] Dimethyl sulfoxide (Me_2SO) has been found to be an excellent solvent for this purpose.[3d,4] Moreover, CDX has the notable property of forming inclusion compounds with various substrates.[5] Therefore, the reaction between $[CoCl_2(en)_2]Cl$ and N-N in the presence of CDX is expected to give rotaxane in the sequence shown in Scheme I.[6] As the internal diameter of the cavity of CDX is 4.5 Å for α-CDX and 7.0 Å for β-CDX,[5] $[CoCl(en)_2]^{2+}$ moiety is bulky enough to prevent dethreading.[7] This expectation was indeed realized.

Synthesis of [2]-[[$(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$]-[β-CDX]-rotaxane·$3H_2O$.[2,8] Method I: 2 mmol of don was dissolved in 10 mL of Me_2SO saturated with β-CDX and 2 mmol of *cis*-$[CoCl_2(en)_2]Cl$ was added. The solution was kept at 75 °C for 30 min and then acidified with 2 mL of glacial acetic acid. Chromatographic separation by an SP-Sephadex C-25 (SPC) column afforded the rotaxane with a yield of 5 ± 2% (2 preparations). Method II: β-CDX and *cis*-$[CoCl(en)_2(donH)]Cl_3\cdot 0.5H_2O$[10] were dissolved in Me_2SO. After the addition of diethylamine, *cis*-$[CoCl_2(en)_2]Cl$ was added. The solution was then treated as described in method I; yield was 7 ± 1% (6 preparations). Figure 1 shows an example of the chromatograms. The species f1, f5, f6, and f7 were characterized as $[CoCl_2(en)_2]^+$, $[Co(Me_2SO)_2(en)_2]^{3+}$, $[CoCl(en)_2(donH)]^{3+}$, and $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$, respectively. The species f2 and f3 are considered to be geometric isomers of $[CoCl(Me_2SO)(en)_2]^{2+}$. When the reaction was carried out in the absence of β-CDX, the chromatogram lacked only the band corresponding to f4. The solution containing the f4 species ($LiClO_4$ medium) was evaporated. The addition of acetone yielded a pink powder. Anal. Calcd for $[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4\cdot\beta\text{-CDX}\cdot 3H_2O$: C, 33.60; H, 6.19; N, 6.32; Co, 5.32; β-CDX, 51.2. Found: C, 33.76, H, 6.50; N, 5.91; Co, 5.14; β-CDX, 50.5 ± 2.0.[11]

All observations which will be given below lead to the conclusion

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[1] α-CDX = cyclohexaglucopyranose. β-CDX = cycloheptaglucopyranose.

[2] Abbreviations used here: en, ethylenediamine; den, 1,10-diaminodecane; don, 1,12-diaminododecane; N-N, α,ω-diaminoalkane.

[3] (a) Alexander, M. D.; Spillert, C. A. *Inorg. Chem.* **1970**, *9*, 2344. (b) Chan, S. C.; Chan, S. F. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1247. (c) Alexander, M. D.; Kilcrease, H. G. *Ibid.* **1973**, *35*, 1583. (d) Ogino, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1836.

[4] (a) Ogino, H. *Bull. Chem. Soc. Jpn* **1977**, *50*, 2459 and references cited therein. (b) Ogino, H.; Orihara, Y.; Tanaka, N. *Inorg. Chem.* **1980**, *19*, 3178.

[5] Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag: Berlin, 1978 and references cited therein.

[6] The absolute configuration of cobalt(III) moieties and the direction of the threaded CDX are not specified. Some ionic charges are omitted.

[7] Matsumoto, K.; Ooi, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3801.

[8] After Schill's nomenclature.[9]

[9] Schill, G., "Catenanes, Rotaxanes, and Knots"; Academic Press: New York, 1971.

[10] $donH^+$ denotes monoprotonated don.

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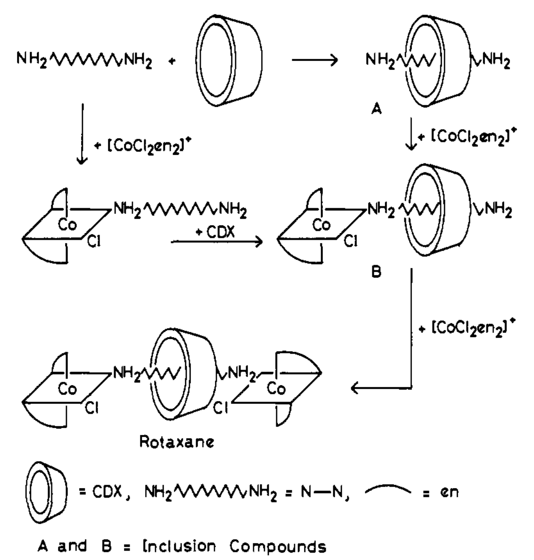
Scheme I[6]



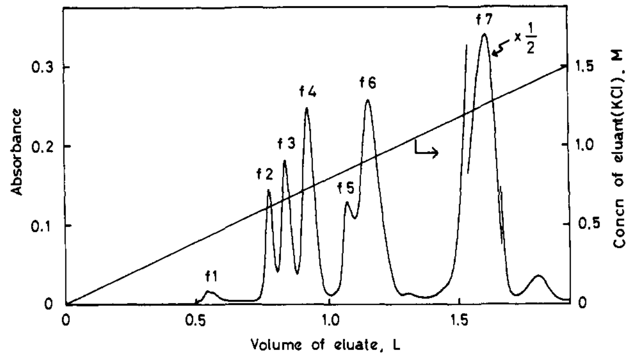


Figure 1. Chromatogram for the solution produced in the reaction between *cis*-$[CoCl_2(en)_2]^+$ and *cis*-$[CoCl(en)_2(don)]^{2+}$ in the presence of β-CDX. Absorbance was measured at 530 nm with a flow cell of 0.5-cm optical cell length. Column (SPC) size: 2.6 × 45 cm.

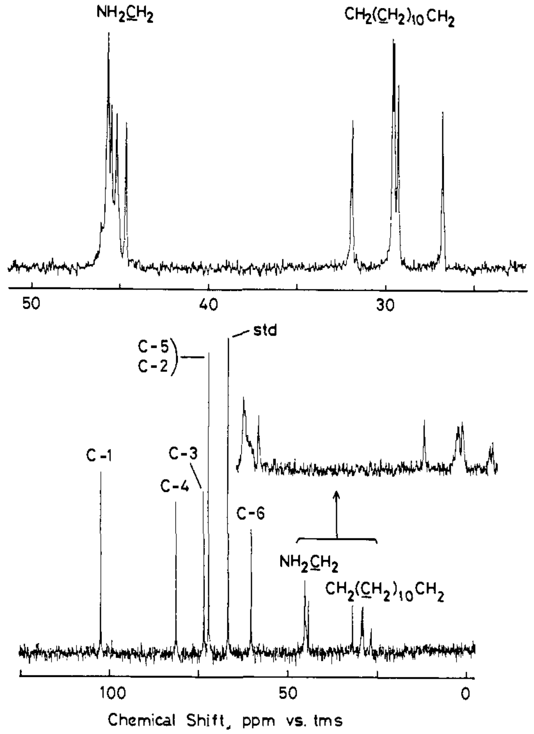


Figure 2. ^{13}C NMR spectra of $[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$ (upper) and [2]-$[[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4]$-[β-CDX]-rotaxane·$3H_2O$ (lower). Dioxane (δ 67.4 vs. Me_4Si) was used as the internal standard. Chemical shifts were referenced to Me_4Si, downfield shifts having positive values. The signals of β-CDX (C-1 ~ C-6) were assigned after ref 13.

that the f4 species is the desired rotaxane. The molecular rotation ($[M]_D$) of the f4 species is 1600°, which is similar to the value for β-CDX ($[M]_D$ = 1840°)[12] but is not the same. The electronic spectrum is characteristic of the $[CoN_5Cl]$ chromophore. The spectrum of the $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ solution is not affected by the addition of β-CDX but is somewhat different from that of the f4 species. CDX has no affinity to SPC resin, but the β-CDX and the cobalt(III) complex in the f4 species move together on an SPC column; hence the f4 species is not a mixture of $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ and β-CDX. The f4 species gives a weak positive circular dichroism band which is considered to be induced in the complex entity by the presence of chiral β-CDX (λ_{max} = 545 nm, $\Delta\epsilon$ = +0.04). Solutions of β-CDX as well as the mixture of β-CDX and $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ do not give any circular dichroism band. In contrast to the previous observations,[3d] the f4 species, although it must have a charge of 4+, is eluted more easily than $[CoCl(en)_2(donH)]^{3+}$. The presence of bulky β-CDX in the species may hinder intimate interaction of the complex ions with the sulfopropyl groups in SPC resin. ^{13}C NMR spectra of the f4 species and $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ are shown in Figure 2. The spectral pattern and chemical shifts of β-CDX moiety in the f4 species are almost the same as those of free β-CDX.[13] This provides evidence that there is no chemical bond between the β-CDX and cobalt(III) moieties. The spectrum of $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ shows 10 signals and is compatible with the cis configuration.[14] Although the spectral pattern of the dimeric cobalt(III) moiety of the f4 species is similar to that of $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$, the signals of the former species are more complicated. This can be understood if β-CDX is threaded by the dimeric cobalt(III) ion. As β-CDX is chiral and has the shape of a truncated cone, the magnetic environments of the two cobalt(III) centers in the rotaxane are no longer identical. Therefore, the dimeric cobalt(III) moiety should show 20 × 4 peaks theoretically, because the $[(en)_2ClCo(don)CoCl(en)_2]^{4+}$ ions are a mixture of equimolar amounts of racemic ions (ΔΔ and ΛΛ) and meso ions (ΔΛ and ΛΔ).

When den[2] was used instead of don, [2]-$[[(en)_2ClCo(den)CoCl(en)_2](ClO_4)_4]$-[β-CDX]-rotaxane·$4H_2O$ was obtained with a yield of 2.4%. α-CDX which has a narrower cavity than β-CDX appears to be more effective for threading don. When don was used as the chain and α-CDX as the ring, [2]-$[[(en)_2ClCo(don)CoCl(en)_2]Br_4]$-[α-CDX]-rotaxane·$7H_2O$ was obtained with a yield of 19%.

So far, only a few examples of rotaxanes are known, and in general, the yields of these are very low.[9,15] The present work may open a new possibility—high-yield syntheses of rotaxanes by utilizing the inclusion phenomenon.[16] The compounds prepared here are the first example of the rotaxanes containing chiral rings and also the first example of the rotaxanes containing metal complexes.

Acknowledgment. Support from the Kurata Foundation and the Ministry of Education (No. 434029) is gratefully acknowledged.

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(11) The analysis of β-CDX: The complex in an aqueous solution containing HCl was reduced by zinc amalgam. Then the solution was poured into an SPC column. The passed solution and the washings were combined and subjected to the measurement of optical rotation.

(12) French, D.; Levine, M. L.; Pazur, J. H.; Norberg, E. *J. Am. Chem. Soc.* **1949**, *71*, 353.

(13) (a) Usui, T.; Yamaoka, N.; Matsuda, K.; Tuzimura, K.; Sugiyama, H.; Seto, S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2425. (b) Colson, P.; Jennings, H. J.; Smith, Ian C. P. *J. Am. Chem. Soc* **1974**, *96*, 8081.

(14) The complex ions are the mixture of racemic and meso isomers, whose chemical shifts are the same.

(15) (a) Agam, G.; Graiver, D.; Zilkha, A. *J. Am. Chem. Soc.* **1976**, *98*, 5206 and references cited therein. (b) Agam, G.; Zilkha, A. *Ibid.* **1976**, *98*, 5214.

(16) In connection with this it should be noted that there was an unsuccessful attempt to prepare a catenane containing β-CDX.[17]

(17) Lüttringhaus, A.; Cramer, F.; Prinzbach, H.; Henglein, F. M. *Liebigs Ann. Chem.* **1958**, *613*, 185.