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Coordination of Cyclodextrin: Synthesis and Characterization of Two Diastereomers of (α- and β-Cyclodextrinato)bis(ethylenediamine)cobalt(III)(1+) and Their Related Complexes

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The salts of two kinds of novel cyclodextrinato complexes, (α- or β-cyclodextrinato)bis(ethylenediamine)cobalt(III)(1+), $[Co(\alpha\text{- or }\beta\text{-}CDX^{2-})(en)_2]^+$, and (α- or β-cyclodextrinato)(1,4,7,10-tetraazacyclododecane)cobalt(III)(1+), $[Co(\alpha\text{- or }\beta\text{-}CDX^{2-})(cyclen)]^+$, are prepared, the former being separated into two diastereomers by fractional crystallization. The compounds are characterized by electronic absorption, circular dichroism (CD), and ^{13}C NMR spectra. In these complexes, it is confirmed that cyclodextrins coordinate directly to cobalt(III) ions through their two deprotonated secondary hydroxy groups $O^-(2)$ and $O^-(3)$ of the same glucose unit. A large CD contribution due to α- or β-cyclodextrin is also found, especially in the d–d absorption band region.

Introduction

Cyclodextrins are cyclic oligosaccharides consisting of six or more α-D-glucopyranose units. They form inclusion compounds with various molecules that fit into their 5–8-Å cavity.[1] Such inclusion compounds have been reported for the metal complexes of Co(III),[2] Fe(0),[3] Rh(I),[4] and Pt(II).[5] In these compounds, cyclodextrins can be considered to act as second-sphere ligands. The direct coordination of cyclodextrins to metal ions has been found only in Cu(II) complexes[6] because of the poor coordinating ability of their hydroxy groups.

In the course of column separations of cobalt(III) rotaxanes, which are composed of a dinuclear cobalt(III) complex $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]^{6+}$ (n = 8, 10, and 12) and α- or β-cyclodextrin, we noticed a slight amount of a purple product.[7] This band showed a very strong circular dichroism (CD) spectrum in the d–d absorption band region, even though the racemic cobalt(III) complex was used as a starting material. Since a drastic change of optical rotation from dextro to levo has been reported upon the formation of the Cu(II)–cyclodextrin complex,[6] the appearance of such a large CD spectrum was considered to indicate Co(III)–cyclodextrin complex formation. The inference was confirmed by a ^{13}C NMR measurement.

Here, we report the syntheses of two kinds of novel cyclodextrinato complexes, $[Co(\alpha\text{- or }\beta\text{-}CDX^{2-})(en)_2]^+$ and $[Co(\alpha\text{- or }\beta\text{-}CDX^{2-})(cyclen)]^+$ where en and cyclen denote ethylenediamine and 1,4,7,10-tetraazacyclododecane, respectively.[8] They were derived from *trans*-$[CoCl_2N_4]^+$ or $[CoCO_3N_4]^+$ (N_4 = en_2 or cyclen), α- or β-cyclodextrin, and 2 equiv of alkali in a hot aqueous solution in a moderate yield. The complex $[Co(\alpha\text{- or }\beta\text{-}CDX^{2-})(en)_2]^+$ was further separated into the Δ and Λ diastereomers by fractional crystallization. The coordinating mode of cyclodextrins in these complexes was determined based on their ^{13}C NMR spectra, molecular model consideration, and comparisons with the absorption and CD spectra of the referential methyl-α-D-glucoside complex. The properties and utilities of the present complexes are also discussed.

Experimental Section

Preparation and Separation of Complexes. (1) Δ- and Λ-$[Co(\alpha\text{-}CDX^{2-})(en)_2]Cl$. To a solution of *trans*-$[CoCl_2(en)_2]Cl$ (2 g) in 50 cm^3 of water were added a mixture of α-CDX (6.8 g) and sodium hydroxide (0.56 g) dissolved in 50 cm^3 of water and then activated charcoal (1 g). The mixed solution was heated at 80 °C for 3 h with stirring to give a reddish purple one, which was allowed to stand overnight. After the charcoal was filtered off, the filtrate was poured onto a column of SP-Sephadex C-25 (Na^+ form, 4 (o.d.) × 50 cm) and then eluted with 0.2 mol dm^{-3} NaCl. Several bands appeared. All purple bands showed very strong CD peaks in the d–d absorption band region. The second main band, whose mole ratio Co(III)/α-CDX is unity, was the desired complex and was composed of two overlapping components, a reddish purple one (α-**1**) and a purplish red one (α-**2**), in this order. The first minor purple band is not yet characterized but the third and fourth purple bands turned out to contain the complexes with a mole ratio Co(III)/α-CDX = 2, where α-cyclodextrin acts as tetraalcoholato(4−) ligand. The desired complexes α-**1** and α-**2** were collected together and the solvent was evaporated, and after repeated removal of the NaCl that deposited out, the filtrate was allowed to stand at room temperature for several days. The purplish red crystals of α-**2** precipitated. Complex α-**1** was obtained by addition of ethanol to the resulting filtrate and then cooling it. Each complex was recrystallized from a minimum amount of water by addition of ethanol. The total formation ratio was 58%. The shares were 47% for α-**1** and 53% for α-**2**. Anal. Found for α-**1**: C, 35.38; H, 6.82; N, 3.96. Calcd for Δ-$[Co(\alpha\text{-}CDX^{2-})(en)_2]Cl\cdot 0.5C_2H_5OH\cdot 10H_2O$ = $C_{41}H_{97}N_4O_{40.5}CoCl$: C, 35.46; H, 7.04; N, 4.03. Found for α-**2**: C, 34.57; H, 6.88; N, 4.01. Calcd for Λ-$[Co(\alpha\text{-}CDX^{2-})(en)_2]Cl\cdot 11H_2O$ = $C_{40}H_{96}N_4O_{41}CoCl$: C, 34.72; H, 6.99; N, 4.05. The nitrate of α-**1** and the bromide of α-**2** were obtained by using a column of QAE-Sephadex A-25. Anal. Found for the nitrate of α-**1**: C, 34.67; H, 6.75; N, 4.81. Calcd for Δ-$[Co(\alpha\text{-}CDX^{2-})(en)_2]NO_3\cdot 0.5C_2H_5OH\cdot 9.5H_2O$ = $C_{41}H_{96}N_5O_{43}Co$: C, 34.46; H, 6.77; N, 4.90. Found for the bromide of α-**2**: C, 33.96; H, 6.71; N, 3.88. Calcd for Λ-$[Co(\alpha\text{-}CDX^{2-})(en)_2]Br\cdot 10.5H_2O$ = $C_{40}H_{95}N_4O_{40.5}CoBr$: C, 33.86; H, 6.75; N, 3.95.

From the third and fourth purple bands, other kinds of α-cyclodextrin complexes, α-**3** and α-**4**, respectively, were obtained in the same way. Anal. Found for α-**3**: C, 32.06; H, 6.89; N, 6.67. Calcd for $[\{Co(en)_2\}_2(\alpha\text{-}CDX^{4-})]Cl_2\cdot 14H_2O$ = $C_{44}H_{116}N_8O_{44}Co_2Cl_2$: C, 32.03; H, 7.09; N, 6.79. Found for α-**4**: C, 32.08; H, 6.95; N, 6.37. Calcd for $[\{Co(en)_2\}_2(\alpha\text{-}CDX^{4-})]Cl_2\cdot 1.5C_2H_5OH\cdot 13H_2O\cdot NaCl$ = $C_{47}H_{123}N_8O_{44.5}Co_2NaCl_3$: C, 32.08; H, 6.87; N, 6.37. The present complexes could be also prepared by using $[CoCO_3(en)_2]Cl$ instead of *trans*-$[CoCl_2(en)_2]Cl$.

(2) Δ- and Λ-$[Co(\beta\text{-}CDX^{2-})(en)_2]Cl$. The complexes were prepared and chromatographed in the same way described above except for the use of β-CDX instead of α-CDX. The total yield was 40%. The shares were almost equal: 49% for β-**1** and 51% for β-**2**. Anal. Found for β-**1**: C, 34.52; H, 6.82; N, 3.44. Calcd for Δ-$[Co(\beta\text{-}CDX^{2-})(en)_2]Cl\cdot 12.5H_2O\cdot 0.5NaCl$ = $C_{46}H_{109}N_4O_{47.5}CoNa_{0.5}Cl_{1.5}$: C, 34.49; H, 6.86; N, 3.50. Found for β-**2**: C, 37.83; H, 6.68; N, 3.73. Calcd for Λ-$[Co(\beta\text{-}CDX^{2-})(en)_2]Cl\cdot 6.5H_2O$ = $C_{46}H_{97}N_4O_{41.5}CoCl$: C, 37.72; H, 6.67; N,

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[†] Deceased July 15, 1987.

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(8) α- and β-Cyclodextrins have 18 and 21 hydroxy groups, respectively and will be potentially 18- and 21-dentate ligands. The ligating CDX is expressed as CDX^{n-} according to the number of the deprotonated groups.

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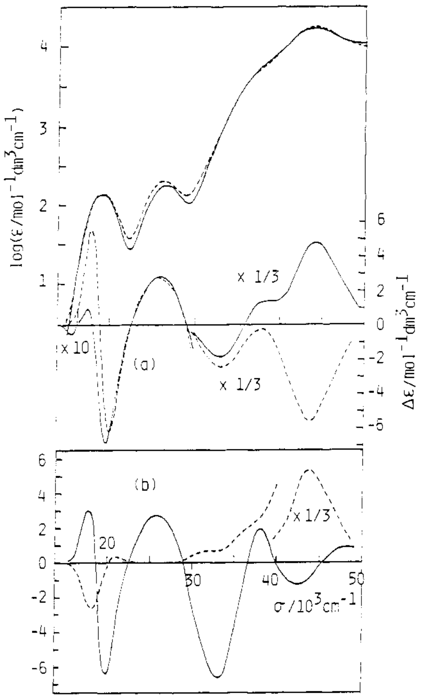

Figure 1. (a) Absorption and CD spectra of Δ-[Co(α-CDX^{2-})(en)$_2$]$^+$ (α-**1**, —) and Λ-[Co(α-CDX^{2-})(en)$_2$]$^+$ (α-**2**, - - -). (b) Calculated CD curves: $^1/_2\{\Delta\epsilon(\alpha\text{-}\mathbf{1}) + \Delta\epsilon(\alpha\text{-}\mathbf{2})\}$ (—) and $^1/_2\{\Delta\epsilon(\alpha\text{-}\mathbf{1}) - \Delta\epsilon(\alpha\text{-}\mathbf{2})\}$ (- - -).

3.82. The chloride of β-**2** was converted into the nitrate by using QAE-Sephadex A-25 (NO$_3^-$ form). Anal. Found for the nitrate of β-**2**: C, 36.18; H, 6.58; N, 4.57. Calcd for Λ-[Co(β-CDX^{2-})(en)$_2$]NO$_3$·8.5H$_2$O = $C_{46}H_{101}N_5O_{46.5}Co$: C, 36.18; H, 6.67; N, 4.59.

(3) [Co(α-CDX^{2-})(cyclen)](ClO$_4$). To a solution of β-CDX (2.62 g) and sodium hydroxide (0.24 g) in 30 cm^3 of water was added 1.38 g of [CoCO$_3$(cyclen)]Cl, which was prepared from Na$_3$[Co(CO$_3$)$_3$] and cyclen·4HCl.[9] The solution was heated at 50 °C for 5 h with stirring to give a violet solution, which was cooled to room temperature. After the precipitate was filtered off, the filtrate was adsorbed on a column of SP-Sephadex C-25 (Na$^+$ form, 4 (o.d.) × 30 cm). The column was washed with water, and at this stage three bands, light brown, red, and blue, were eluted in this order. The absorbed complexes were then eluted with 0.05 mol dm^{-3} Na(ClO$_4$). Three bands, violet, red, and violet, were eluted in this order. The first violet band, whose mole ratio Co(III)/α-CDX was unity, was evaporated to a small amount and after removal of Na(ClO$_4$), addition of ethanol and acetone gave a violet powder, which was recrystallized from a minimum amount of water by addition of ethanol and acetone. Anal. Found: C, 36.77; H, 6.61; N, 3.94. Calcd for [Co(α-CDX^{2-})(cyclen)](ClO$_4$)·8H$_2$O = $C_{44}H_{94}N_4O_{42}CoCl$: C, 36.56; H, 6.58; N, 3.88.

(4) [Co(β-CDX^{2-})(cyclen)](ClO$_4$). This complex was prepared and purified in the same way described above except for the use of β-CDX instead of α-CDX. Anal. Found: C, 34.43; H, 6.34; N, 3.04. Calcd for [Co(β-CDX^{2-})(cyclen)](ClO$_4$)·10H$_2$O·C$_2$H$_5$OH·NaClO$_4$ = $C_{52}H_{114}N_4O_{54}CoNaCl_2$: C, 34.46; H, 6.34; N, 3.09.

(5) Λ-[Co(mg)(en)$_2$](ClO$_4$). To a solution of methyl-α-D-glucoside (H$_2$mg) (1.36 g) and sodium hydroxide (0.56 g) in 30 cm^3 of water were added 2 g of *trans*-[CoCl$_2$(en)$_2$]Cl and 0.7 g of activated charcoal. The solution was boiled for 2 h with stirring and then cooled to room temperature. After the charcoal was filtered off, the filtrate was adsorbed on a column of SP-Sephadex C-25 (Na$^+$ form, 3.2 (o.d.) × 40 cm) and eluted with 0.05 mol dm^{-3} Na(ClO$_4$). The first red band contained the desired complex but was composed of two overlapping components. The crystalline complex was obtained from the front part of the band by addition of ethanol and acetone. This was recrystallized by dissolution in a minimum amount of water, addition of ethanol and ether to the point of turbidity, and slow cooling. Isolation of another complex from the back part of the first band was attempted but was unsuccessful. Anal. Found: C, 26.30; H, 6.33; N, 10.64. Calcd for [Co(mg)(en)$_2$](ClO$_4$)·2H$_2$O = $C_{11}H_{32}N_4O_{12}CoCl$: C, 26.07; H, 6.36; N, 11.06.

Measurements. The visible and ultraviolet absorption spectra were measured with a Hitachi 330 spectrophotometer and the CD spectra with a JASCO J-500C spectropolarimeter in aqueous solutions at room temperature. The ^{13}C NMR spectra were recorded with JEOL FX-90Q and JEOL GSX400 spectrometers in D$_2$O containing dioxane (67.40 ppm) as an internal standard.

Table I. Absorption and CD Spectra of Complexes

complex	absorption[a] σ_{max} (log ϵ)	CD[a] σ_{ext} ($\Delta\epsilon$)
Δ-[Co(α-CDX^{2-})(en)$_2$]Cl (α-**1**)	18.96 (2.124)	15.6 (−0.06)
	26.53 (2.241)	17.5 (+0.94)
	37.7 (3.75)[b]	19.7 (−6.92)
	43.9 (4.22)	25.7 (+2.79)
		33.0 (−5.62)
		44.1 (+14.3)
Λ-[Co(α-CDX^{2-})(en)$_2$]Cl (α-**2**)	19.19 (2.134)	17.9 (+5.45)
	26.18 (2.302)	20.1 (−6.27)
	37.7 (3.72)[b]	25.6 (+2.76)
	44.1 (4.24)	33.2 (−5.57)
		43.7 (−16.9)
Δ-[Co(β-CDX^{2-})(en)$_2$]Cl (β-**1**)	18.98 (2.136)	16.0 (−0.09)
	26.53 (2.244)	17.4 (+0.44)
	37.7 (3.75)[b]	19.6 (−6.33)
	44.0 (4.22)	25.7 (+2.50)
		33.1 (−4.90)
		38.6 (+3.88)[b]
		44.4 (+16.0)
Λ-[Co(β-CDX^{2-})(en)$_2$]Cl (β-**2**)	19.19 (2.134)	17.9 (+5.29)
	26.25 (2.300)	20.1 (−6.36)
	37.7 (3.71)[b]	25.5 (+2.78)
	44.2 (4.24)	33.2 (−7.44)
		43.6 (−15.7)
[Co(α-CDX^{2-})(cyclen)](ClO$_4$)	17.9 (2.37)	17.9 (+1.45)
	26.0 (2.45)	20.1 (−6.04)
		26.2 (+5.88)
		33.9 (−5.18)
		38.4 (−8.14)
		45.0 (+12.1)
[Co(β-CDX^{2-})(cyclen)](ClO$_4$)	18.1 (2.31)	17.8 (+1.42)
	26.0 (2.37)	20.1 (−5.23)
		26.2 (+5.20)
		33.8 (−4.16)
		39.4 (−6.49)
		44.6 (+9.89)
Λ-[Co(mg)(en)$_2$](ClO$_4$)	19.1 (2.17)	17.8 (+1.46)
	26.1 (2.34)	20.0 (−2.15)
		25.4 (+0.94)
		33.3 (−2.21)
		44.6 (−2.85)

[a] Wavenumbers and ϵ values are given in units of 10^3 cm^{-1} and cm^{-1} mol^{-1} dm^3, respectively. [b] Shoulder.

Results and Discussion

Characterization of [Co(α- or β-CDX^{2-})(en)$_2$]$^+$ Complexes. The first and second d–d absorption bands appear at 528 (ϵ = 133) and 377 nm (ϵ = 174) for α-**1** and 521 (ϵ = 136) and 382 nm (ϵ = 200) for α-**2**, respectively (Figure 1a and Table I). These values are very similar to 523 (ϵ = 137) and 382 nm (ϵ = 195) of [Co(OCH$_2$CH$_2$O)(en)$_2$]$^+$.[10] It is common for both complexes that the second d–d absorption band has a significantly higher molar extinction coefficient than the first band. The protonated diol species shows a quite different d–d absorption spectrum compared to the diolato one:[10] that is, both d–d peaks blue shift by more than 20 nm and the molar extinction coefficient of the first d–d band becomes higher than that of the second one. The β-CDX complexes β-**1** and β-**2** showed very similar absorption spectra to those of the α-CDX complexes. These facts mean that α- or β-cyclodextrin functions as a bidentate-*O*,*O*(2−) ligand in these complexes, which was also identified by the elemental analyses.

Complexation of cyclodextrin was directly confirmed by ^{13}C NMR spectra (Figure 2). Owing to the presence of a C_6 symmetry axis on a CDX molecule in solution, only six sets of ^{13}C NMR signals are observed in the free molecule. Coordination to a cobalt(III) ion removes the C_6 symmetry of CDX and con-

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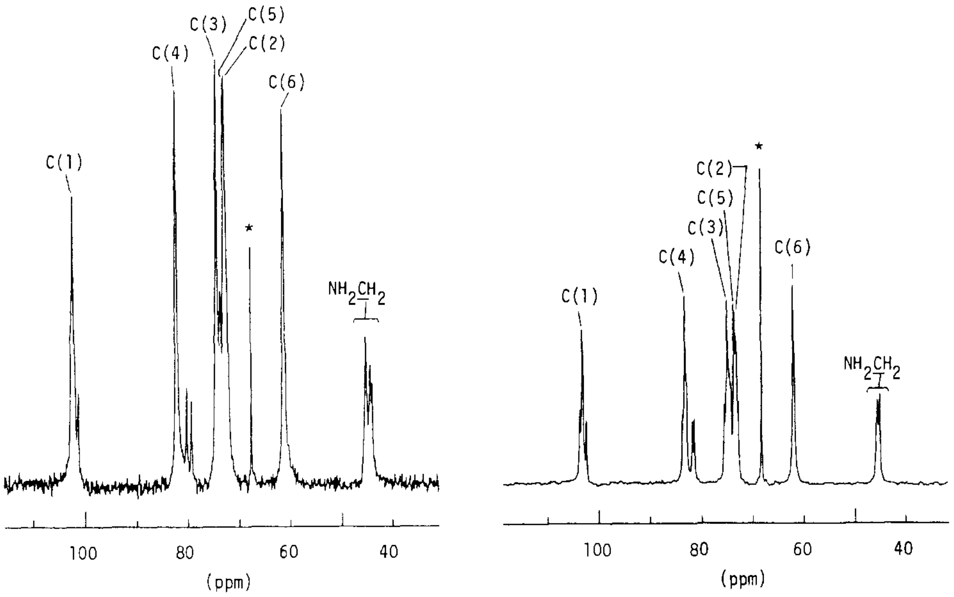

Figure 2. ^{13}C NMR spectra (90 MHz) of Δ-[Co(α-CDX^{2-})(en)$_2$]$^+$ (α-**1**, left) and Λ-[Co(α-CDX^{2-})(en)$_2$]$^+$ (α-**2**, right). The peak for 1,4-dioxane is denoted with an asterisk; δ = 67.40 ppm.

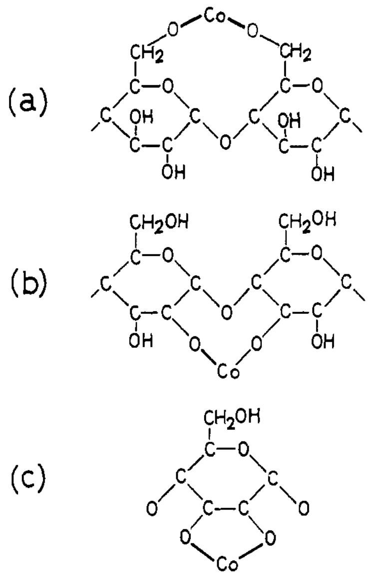

Figure 3. Three possible coordination modes of cyclodextrinate(2–).

sequently peak splitting is expected. In fact, the ^{13}C NMR spectra of α-**1** and α-**2** (90 MHz) showed the splitting tendency with some additional peaks at ca. 72–103 ppm.

Cyclodextrin has two kinds of hydroxy groups.[1] The narrow opening contains the primary hydroxy groups O(6)H, whereas the wide opening is occupied by secondary hydroxy groups O(2)H and O(3)H. Molecular model consideration indicates three possibilities for the bidentate coordination mode of cyclodextrin as shown in Figure 3. The first mode is due to the two O$^-$(6) groups on the contiguous glucose units, which form an 11-membered chelate ring. The second one is due to the O$^-$(2) and O$^-$(3) groups of the contiguous glucose units. The third mode is due to the O$^-$(2) and O$^-$(3) groups of the same glucose unit, and in this case a five-membered chelate ring is formed. The first mode is eliminated because the INEPT method[11] showed all the extra splitting peaks observed in 90-MHz ^{13}C NMR spectra of α-**1** and α-**2** to be assignable to the methine carbons and not to the methylene carbon. The secondary hydroxy group has been known to have an unexpectedly low pK_a value (~12.1)[12] and is expected to coordinate to the Co(III) ion. The ^{13}C NMR spectrum of 400 MHz verified completely the C_1 symmetric character of α-**2** as shown in Figure 4. In the regions of the C(1) and C(4) carbons centered at 102 and 82 ppm, respectively, six (102.65, 102.25, 102.14, 102.12, 101.90, and 101.31 ppm) and five signals (82.54, 82.34, 82.16 (strong), 82.03, and 81.90 ppm), which correspond to six carbons, were observed. In the C(6) carbon region, five signals (61.21 (strong), 61.13, 61.06, 61.05, and 60.88 ppm), which correspond to six carbons, appeared. In the C(3), C(5), and C(2) regions at 72–75 ppm, 14 signals (74.61, 74.36, 74.10, 74.02 (strong), 73.76, 73.55, 73.36, 72.88, 72.77, 72.69, 72.44 (strong), 72.28, 72.15, and 71.84 ppm), which correspond to 16 carbons, were observed. Therefore, two signals at 80.89 and 80.47 ppm can be assigned to the C(2) and C(3) carbons attached to the coordinated alcoholate. Coordination causes such a large downfield shift. However, the second mode, which contains a very hindered eight-membered chelate ring, seems unlikely.[13] Therefore, it is reasonable to consider that coordination of α-cyclodextrin in α-**1** and α-**2** occurs through the O$^-$(2) and O$^-$(3) of one glucose unit. To confirm this assignment, the reference

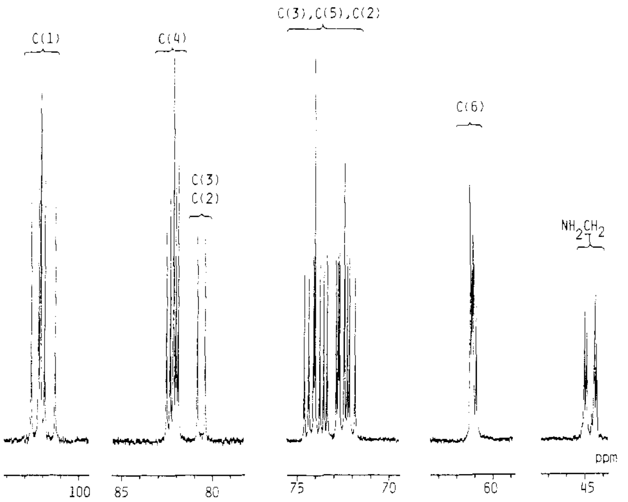

Figure 4. ^{13}C NMR spectrum (400 MHz) of Λ-[Co(α-CDX^{2-})(en)$_2$]$^+$ (α-**2**).

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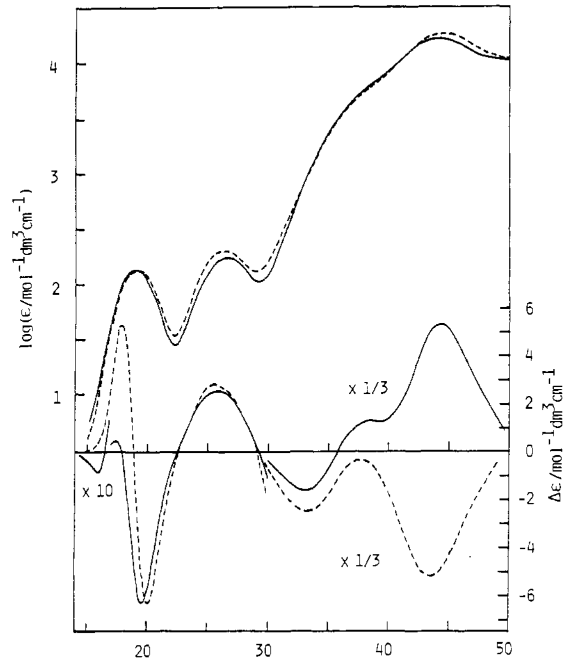

Figure 5. Absorption and CD spectra of Δ-[Co(β-CDX^{2-})(en)$_2$]$^+$ (β-**1**, —) and Λ-[Co(β-CDX^{2-})(en)$_2$]$^+$ (β-**2**, ---).

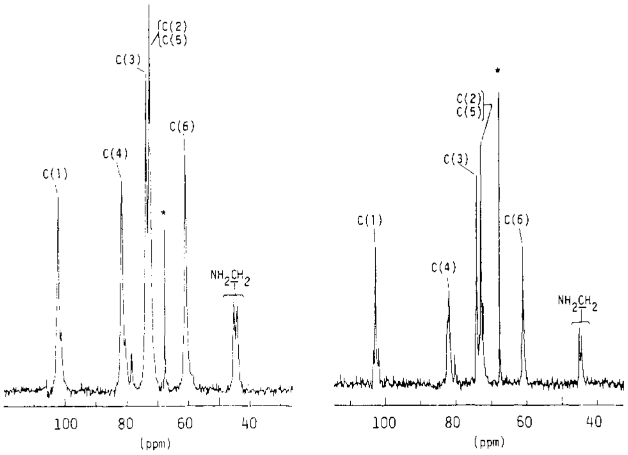

Figure 6. ^{13}C NMR spectra (90 MHz) of Δ-[Co(β-CDX^{2-})(en)$_2$]$^+$ (β-**1**, left) and Λ-[Co(β-CDX^{2-})(en)$_2$]$^+$ (β-**2**, right). The peak for 1,4-dioxane is denoted with an asterisk; δ = 67.40 ppm.

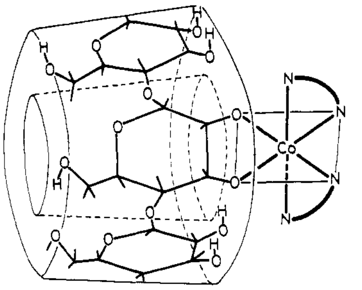

Figure 7. Proposed structure for [Co(α- or β-CDX^{2-})(en)$_2$]$^+$.

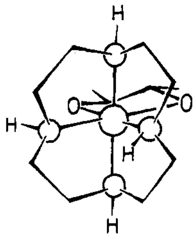

Figure 8. Most probable configuration of cyclen in [Co(α- or β-CDX^{2-})(cyclen)]$^+$.

complex containing methyl-α-D-glucoside was prepared and one diastereomer out of two possible ones was isolated. Its absorption curve and CD spectral pattern are very similar to those of α-**2** (Table I). Since methyl-α-D-glucoside contains only one glucose unit, such spectral similarity supports the third coordination mode.

The visible and ultraviolet absorption and CD spectra of β-**1** and β-**2** ([Co(β-CDX^{2-})(en)$_2$]$^+$) are shown in Figure 5. They quite resemble those of the corresponding α-CDX complexes. In the ^{13}C NMR spectra in Figure 6, both β-CDX complexes showed some splitting peaks of β-cyclodextrin in the regions of ca. 80–101 ppm, which indicates lowering of the symmetry of β-CDX by coordination. These facts mean that the same discussion described above is valid for the β-CDX complexes. Thus, the structure in Figure 7 is proposed for [Co(α- or β-CDX^{2-})(en)$_2$]$^+$.

Absolute Configurations of [Co(α- or β-CDX^{2-})(en)$_2$]$^+$. The CD spectra of α-**1** and α-**2** shown in Figure 1a resemble each other, especially between 19 000 and 35 000 cm^{-1}, which means the large CD contribution due to α-cyclodextrin in this region. In order to estimate each CD contribution due to the asymmetric carbon atoms of α-cyclodextrin and the skew pairs of chelate rings, an additivity rule was applied to the CD spectra of α-**1** and α-**2**. The configurational contribution can be obtained by subtracting the observed CD of one isomer from that of the counterpart, while the asymmetric carbon chirality is obtained by summing up the two CD curves. The calculated CD curves are shown in Figure 1b. As expected, the CD contribution due to α-cyclodextrin is very large in the d–d band region. Such large vicinal CD contribution seems to be characteristic of the alcoholato ligand because a similar result has been reported for the diastereomers of Δ- and Λ-[Co{S-NH$_2$CH(CH$_3$)CH$_2$O}(en)$_2$]$^{2+}$.[14]

The configurational chirality has a normal value for the tris-chelate complex. The diastereomers α-**1** and α-**2** are assigned to the Δ and Λ absolute configurations, respectively, based on the signs of the calculated configurational curve in the first d–d and ultraviolet band region.[14,15] By the same token, the complexes β-**1** and β-**2** are assignable to the Δ and Λ configurations, respectively.

Characterization of [Co(α- or β-CDX^{2-})(cyclen)]$^+$ Complexes. There are a few possible configurations for cis-octahedral complexes of cyclen. All cobalt(III) cyclen complexes whose structures have been determined by X-ray crystallography[16] have exclusively the one configuration shown in Figure 8. Therefore, we assumed that the present complexes take the same configuration of cyclen. When an unsymmetrical bidentate ligand occupys the remaining two coordination sites, two isomers are possible as found in [Co{S-NH$_2$CH$_2$CH(CH$_3$)S}(cyclen)]$^{2+}$.[17] However, these isomers are known to be stable only in acidic water and isomerize in neutral and alkaline solution. In fact, our experiments on column chromatography showed no evidence for the presence of such isomers.

The preparation of the complex was confirmed by the elemental analysis and column chromatographic behavior where the desired band with a +1 complex charge exhibited a strong CD spectrum. The absorption and CD spectra are shown in Figure 9. The cyclen complexes showed the strikingly red-shifted spectra compared to those of the corresponding bis(ethylenediamine) complexes. Besides, a splitting tendency of the first d–d absorption band, though difficult to explain, was observed for both complexes. The CD patterns of the cyclen complexes are similar to that of the calculated vicinal curve of Figure 1b. Since the cyclen complexes have the only CD contribution due to the chiral carbons of cy-

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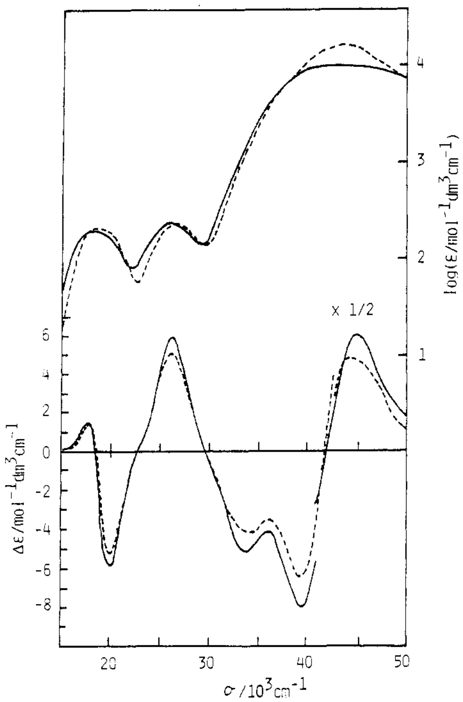

Figure 9. Absorption and CD spectra of $[\mathrm{Co}(\alpha\text{-CDX}^{2-})(\mathrm{cyclen})]^+$ (---) and $[\mathrm{Co}(\beta\text{-CDX}^{2-})(\mathrm{cyclen})]^+$ (—).

clodextrin, the spectral similarity indicates that cyclodextrins coordinate to cobalt(III) ion through the $\mathrm{O}^-(2)$ and $\mathrm{O}^-(3)$ groups of one glucose unit in the same way as they do in $[\mathrm{Co}(\alpha$- or $\beta\text{-CDX}^{2-})(\mathrm{en})_2]\mathrm{Cl}$.

Syntheses and Properties of Cyclodextrinato Complexes. The preparations of CDX complexes were successfully carried out by the reaction of *trans*-$[\mathrm{CoCl_2N_4}]^+$ or $[\mathrm{CoCO_3N_4}]^+$ and CDX neutralized with 2 equiv of alkali. However, the properties of the present CDX complexes in a neutral aqueous solution largely depend upon the remaining amine ligands. For example, the violet band of $[\mathrm{Co}(\mathrm{CDX}^{2-})(\mathrm{NH_3})_4]\mathrm{Cl}$ was temporarily formed by the reaction of $[\mathrm{CoCl(H_2O)(NH_3)_4}]\mathrm{Cl}$ and CDX neutralized with 2 equiv of NaOH in an ammoniacal solution at room temperature but soon decomposed to give brown species. Even in the cyclen complexes, partial decomposition into an aqua or diaqua complex was observed. The complexes of Δ- and Λ-$[\mathrm{Co}(\mathrm{CDX}^{2-})(\mathrm{en})_2]^+$ were, however, stable and showed no indication of isomerization or decomposition. Thus, the complex stability decreases in the order $(\mathrm{en})_2 > \mathrm{cyclen} > (\mathrm{NH_3})_4$.

Preparations of anionic CDX complexes were also attempted. Both complexes $[\mathrm{Co}(\alpha\text{-CDX}^{2-})(\mathrm{acac})_2]^-$ and $[\mathrm{Co}(\alpha\text{-CDX}^{2-})(\mathrm{edda})]^-$ where acac and edda denote acetylacetonate(1−) and ethylenediamine-*N*,*N'*-diacetate(2−) were successfully prepared and separated by using a column of QAE-Sephadex A-25. But they easily lost their optical activities and decomposed to neutral species in an aqueous solution.

The CDX complexes have generally high solubilities, and sometimes an organic solvent was used for the isolation of the complex. The CDX complexes tend to contain such organic solvent and a small amount of inorganic salts used for the column elution because they preserve the intrinsic properties arising from cyclodextrin, that is, the cavities to include various kinds of substrates. This trend was observed in other cobalt(III)–cyclodextrin complexes.[7]

Since the present complexes carry a positive charge, they can be adsorbed on ion-exchange resins. This means the facile preparation of a column containing a cyclodextrinato complex. The column will be applicable to optical resolution of neutral and anionic metal complexes. Experiments are now in progress.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution. Cf. ref 18.

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Organometallic Precursors to AlN: Synthesis and Crystal Structures of $[(\mathrm{CH_3})_2\mathrm{AlNH_2}]_3$ and the Planar Species $[(t\text{-}\mathrm{C_4H_9})_2\mathrm{AlNH_2}]_3$

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The reaction of the trialkylaluminum compounds $(\mathrm{CH_3})_3\mathrm{Al}$ and $(t\text{-}\mathrm{C_4H_9})_3\mathrm{Al}$ with ammonia gas in hydrocarbon solvents followed by heating affords the trimeric species $[(\mathrm{CH_3})_2\mathrm{AlNH_2}]_3$ (**1**) and $[(t\text{-}\mathrm{C_4H_9})_2\mathrm{AlNH_2}]_3$ (**2**) in moderate yield. The crystal and molecular structures of these compounds have been determined by X-ray diffraction methods in connection with their investigation as precursors to aluminum nitride. Both aluminum and nitrogen atoms in these two ring compounds exhibit distorted tetrahedral geometries with the greatest deviation occurring at N. This deviation from tetrahedral geometry about N is reflected largely in the endocyclic Al–N–Al angle, which averages 122° for **1** and 134° for **2**. The $(\mathrm{AlN})_3$ ring in **1** is in a skew-boat conformation with no unusual intermolecular contacts. Unlike the case of **1**, the *tert*-butyl derivative **2** features an unprecedented planar $(\mathrm{AlN})_3$ ring. All six atoms of alternating Al and N are coplanar, as required by crystallographic 3-fold symmetry axes. The effects of the Al and N substituents on the $(\mathrm{AlN})_x$ ring size and conformation, as well as on the endocyclic Al–N–Al bond angles, are discussed in the context of the structural results obtained for these and other $(\mathrm{AlN})_x$ heterocycles. Crystallographic data with Mo Kα radiation ($\lambda = 0.71069$ Å): $\mathrm{C_6H_{24}N_3Al_3}$ (**1**), $a = 12.105$ (4) Å, $b = 8.853$ (2) Å, $c = 14.343$ (4) Å, $\beta = 108.26$ (2)°, $Z = 4$, monoclinic, space group $P2_1/c$, $R = 0.066$; $\mathrm{C_{24}H_{60}N_3Al_3}$ (**2**), $a = 10.401$ (3) Å, $c = 50.783$ (39) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $Z = 6$, rhombohedral, space group $R\bar{3}c$, $R = 0.038$.

Introduction

Although the structures and properties of the alkylaluminum amides $\mathrm{R_2AlNR'R''}$ have been the subject of considerable attention for many years,[1–6] there has been renewed interest recently due to the application of certain of these compounds as precursors to aluminum nitride and to AlN-containing ceramics.[7–9] A key issue

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