

Chemical Modification of Metal Complexes. An Efficient Procedure for O-Acylation of an Anionic Metal Complex Having a Noncoordinated Hydroxyl Group

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Received July 20, 1993[®]

The noncoordinated hydroxyl group of $[\text{Co}(\text{dhpta})]^-$ (where dhpta = 1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetate ion) was O-acylated by reaction with a series of acid anhydrides (acetic anhydride, *n*-valeric anhydride, benzoic anhydride, phthalic anhydride, succinic anhydride, octanoic anhydride, and dodecanoic anhydride) in the presence of 4-(dimethylamino)pyridine, after the potassium salt of the complex was dissolved in acetonitrile by using cryptand 222. Fairly high yields under remarkably mild conditions were achieved without altering the coordination sphere. The esterified complexes were characterized by elemental analysis, electronic absorption and NMR spectroscopies, and X-ray crystallography. X-ray crystal structure determinations of (DMAP-H)[Co(Ben-dhpta)] (10) and (STC-H)[Co(Val-dhpta)]·6H₂O (11) are reported, where DMAP-H, Ben-dhpta, STC-H, and Val-dhpta represent 4-(dimethylamino)pyridinium cation, O-benzoylated dhpta, strychnine cation, and O-valerylated dhpta, respectively. Crystal data for 10: formula C₂₅H₂₉N₄O₁₀Co, space group *P*2₁2₁2₁ (orthorhombic); *a* = 12.5709 (9) Å, *b* = 25.338 (3) Å, *c* = 8.0707 (6) Å, *Z* = 4, *R* = 0.1034. Crystal data for 11: formula C₃₇H₅₇N₄O₁₈Co, space group *P*2₁ (monoclinic); *a* = 19.498 (10) Å, *b* = 11.625 (5) Å, *c* = 9.038 (2) Å, *β* = 95.33 (3)°, *Z* = 2, *R* = 0.072. In both complexes, the cobalt is octahedrally coordinated with a hexadentate dhpta unit. The oxygen atom of the noncoordinated hydroxyl group of dhpta binds to the carboxylic carbon atom of each acid residue to form an ester bond. Measurements of cobalt-59 NMR for the aqueous solutions of the cobalt(III) complexes having a long alkyl (octyl and dodecanoyl) chain ligand indicated the formation of ion-aggregates above cmc (critical micelle concentration), which was determined from the surface tension.

Introduction

Development of effective chemical modification procedures for metal complexes having potentially useful properties without altering the coordination sphere is highly desirable in various fields of chemistry and technology. However, chemical modifications of metal complexes with organic reagents frequently result in failure due to low solubility of metal complexes in aprotic solvents. In contrast, it was expected that the potassium salts of anionic metal complexes would be solubilized in organic solvents by macrocyclic polyethers, crown ethers, and cryptand.

H₄dhpta (1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid) is a typical analog of ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA). When dhpta functions as a six-coordinated ligand to transition metal ions, the hydroxyl group remains noncoordinated and may provide an effective reacting point for organic reagents. Therefore, the potassium salt of the cobalt(III) complex of dhpta is the most appropriate target for our purpose. In this study the esterification of $[\text{Co}(\text{dhpta})]^-$ was investigated, in order to examine the reactivity of a noncoordinated hydroxyl group in the complex to acid anhydrides, after the complex was dissolved in acetonitrile by using cryptand 222,² which is well-known as a powerful K⁺ ion capture.³ Furthermore, we applied this synthetic method to an introduction of long alkyl chains

into $[\text{Co}(\text{dhpta})]^-$, and the properties of the aqueous solutions containing newly prepared complexes were examined by ⁵⁹Co NMR.

Experimental Section

Measurements. Electronic absorption (AB) spectra were obtained on a Shimadzu UV-3100 double-beam spectrophotometer. Circular dichroism (CD) spectra were obtained on a JASCO J-20 spectropolarimeter. These measurements were made on aqueous solutions. ¹H and ¹³C NMR spectra in D₂O were obtained on JEOL GX-270 and GX-400 spectrometers. Internal references used were sodium 3-(tri-

- (2) Abbreviations: cryptand 222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; Ac-dhpta = 1,3-diamino-2-acetoxyp propane-*N,N,N',N'*-tetraacetate ion; Val-dhpta = 1,3-diamino-2-(pentanoyloxy)propane-*N,N,N',N'*-tetraacetate ion; Suc-dhpta = 1,3-diamino-2-((hydroxysuccinyl)oxy)propane-*N,N,N',N'*-tetraacetate ion; Ben-dhpta = 1,3-diamino-2-(benzoyloxy)propane-*N,N,N',N'*-tetraacetate ion; Pht-dhpta = 1,3-diamino-2-((hydroxyphthaloyl)oxy)propane-*N,N,N',N'*-tetraacetate ion; Oct-dhpta = 1,3-diamino-2-(octanoyloxy)propane-*N,N,N',N'*-tetraacetate ion; Dod-dhpta = 1,3-diamino-2-(dodecanoyloxy)propane-*N,N,N',N'*-tetraacetate ion.
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[®] Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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methylsilyl)propanesulfonate (DSS) for ^1H NMR and dioxane for ^{13}C NMR. ^{59}Co NMR spectra were measured on a JEOL GX-270 spectrometer at 27 °C, where the cobalt(III) complexes were dissolved in 5% deuterated water for deuterium lock. The surface tension was measured with a Kyowa CBVP-A3 Wilhelmy tensiometer (at 27 °C).

Preparations. All materials used were of reagent grade. One millimole of $\text{K}[\text{Co}(\text{dhpta})]^{4-}$ and 1 mmol of cryptand 222 were added to 15 mL of acetonitrile, and the suspended solution was stirred at room temperature and became transparent after about 1 day. To the solution was added 2 mmol of an acid anhydride (acetic anhydride, *n*-valeric anhydride, benzoic anhydride, phthalic anhydride, succinic anhydride, octanoic anhydride, or dodecanoic anhydride) and 1 mmol of 4-(dimethylamino)pyridine (DMAP). The stirring was continued for another 2 days. The solution was evaporated to near dryness. The residue was dissolved in water, and the solution was treated with a Dowex 50W-X8 (K^+ form) resin. After being desalted by gel permeation chromatography, the resulting violet solution was concentrated, followed by an addition of methanol to yield a violet crystalline solid, which was recrystallized from a minimum amount of warm water–methanol. The solution was cooled to give pure crystals. Anal. Calcd for $\text{K}[\text{Co}(\text{Ac-dhpta})]^{3-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_{11.5}\text{KCo}$), **1**: C, 32.17; H, 3.95; N, 5.77. Found: C, 32.17; H, 3.84, N, 5.90. Calcd for $\text{K}[\text{Co}(\text{Val-dhpta})]\cdot 2\text{H}_2\text{O}$ ($\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_{11}\text{KCo}$), **2**: C, 37.07; H, 4.67; N, 5.40. Found: C, 37.44; H, 4.64; N, 5.49. Calcd for $\text{K}[\text{Co}(\text{Suc-dhpta})]\cdot \text{H}_2\text{O}$ ($\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_{13}\text{KCo}$), **3**: C, 33.72; H, 3.77; N, 5.24. Found: C, 33.50; H, 3.62; N, 5.12. Calcd for $\text{K}[\text{Co}(\text{Ben-dhpta})]^{3-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_{11.5}\text{KCo}$), **4**: C, 39.50; H, 3.87; N, 5.12. Found: C, 39.59; H, 3.51; N, 5.21. Calcd for $\text{K}_2[\text{Co}(\text{Pht-dhpta})]^{2-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_{14}\text{K}_2\text{Co}$), **5**: C, 35.74; H, 3.31; N, 4.39. Found: C, 35.82; H, 3.18; N, 4.47. Anal. Calcd for $\text{K}[\text{Co}(\text{Oct-dhpta})]^{3-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{19}\text{H}_{31}\text{N}_2\text{O}_{11.5}\text{KCo}$), **6**: C, 40.07; H, 5.49; N, 4.92. Found: C, 40.06; H, 5.19, N, 4.93. Calcd for $\text{K}[\text{Co}(\text{Dod-dhpta})]^{1-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{23}\text{H}_{37}\text{N}_2\text{O}_{10.5}\text{KCo}$), **7**: C, 45.47; H, 6.14; N, 4.61. Found: C, 45.38; H, 6.09; N, 4.49. Calcd for $\text{NH}_4[\text{Co}(\text{Oct-dhpta})]^{3-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{19}\text{H}_{35}\text{N}_3\text{O}_{11.5}\text{Co}$), **8**:⁵ C, 41.61; H, 6.43; N, 7.66. Found: C, 41.92; H, 6.26; N, 7.25. Calcd for $\text{NH}_4[\text{Co}(\text{Dod-dhpta})]\cdot \text{H}_2\text{O}$ ($\text{C}_{23}\text{H}_{42}\text{N}_3\text{O}_{11}\text{Co}$), **9**:⁵ C, 46.39; H, 7.11; N, 7.06. Found: C, 45.97; H, 6.97; N, 6.74. The yields based on the starting $\text{K}[\text{Co}(\text{dhpta})]$ for complexes **1–9** were 87%, 45%, 95%, 88%, 38%, 87%, 94%, 62%, and 81%, respectively. During the benzooylation the crystalline complex having 4-(dimethylamino)pyridinium cation (DMAP-H) as a counteranion ($(\text{DMAP-H})[\text{Co}(\text{Ben-dhpta})]$) was obtained. Anal. Calcd for $(\text{DMAP-H})[\text{Co}(\text{Ben-dhpta})]$ ($\text{C}_{25}\text{H}_{29}\text{N}_4\text{O}_{10}\text{Co}$), **10**: C, 49.68; H, 4.84; N, 9.27. Found: C, 49.65; H, 4.82; N, 9.29.

Optical Resolution of $\Delta\Delta\Delta$ -(STC-H)[Co(Val-dhpta)] $\cdot 6\text{H}_2\text{O}$ (11**).** A 1.01 g (2 mmol) sample of $\text{K}[\text{Co}(\text{Val-dhpta})]\cdot \text{H}_2\text{O}$ was dissolved in 25 mL of water at 35 °C. To the solution was added 0.45 g (1.1 mmol) of strychnine nitrate as a resolving agent, and the solution was warmed at the same temperature until complete dissolution was achieved. After filtration, the solution was kept in a refrigerator for 4 days. The deep purple prismatic crystals formed were collected, washed with cold water, and air-dried. Yield: 0.42 g. The crystals formed after recrystallization in water at 35 °C and gave the same $\alpha(589\text{ nm})/\epsilon(\text{absorption coefficient})$ ratio as that of the crystals before recrystallization. Elemental analysis of this complex was performed after the X-ray crystal structure determination was made. The crystals were ground to a powder and kept in a dry environment. In this process, the crystals lost 4 mol of water. Anal. Calcd for $(\text{STC-H})[\text{Co}(\text{Val-dhpta})]^{2-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{37}\text{H}_{49}\text{N}_4\text{O}_{14}\text{Co}$) of $(\text{STC-H})[\text{Co}(\text{Val-dhpta})]\cdot 6\text{H}_2\text{O}$: C, 53.37; H, 5.93; N, 6.73. Found: C, 52.95; H, 6.02; N, 6.67. $(\text{STC-H})[\text{Co}(\text{Val-dhpta})]^{2-}\cdot 2\text{H}_2\text{O}$ was dissolved in water. The solution was treated with a Dowex 50W-X8 (K^+ form) resin. The resulting solution was concentrated, followed by an addition of methanol to yield a violet crystalline solid, which was recrystallized from a minimum amount of warm water–methanol. The solution was cooled to give pure crystals. Anal. Calcd for $\text{K}[\text{Co}(\text{Val-dhpta})]^{2-}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_{12}\text{KCo}$), **12**: C, 35.83; H, 4.89; N, 5.22. Found: C, 35.98; H, 5.09; N, 5.30.

Table 1. Crystal Data and Experimental Conditions for $\Delta\Delta\Delta$ -(DMAP-H)[Co(Ben-dhpta)] (**10**) and $\Delta\Delta\Delta$ -(STC-H)[Co(Val-dhpta)] $\cdot 6\text{H}_2\text{O}$ (**11**)

	10	11
formula	$\text{CoC}_{25}\text{H}_{29}\text{N}_4\text{O}_{10}$	$\text{CoC}_{37}\text{H}_{57}\text{N}_4\text{O}_{18}$
mol wt	604.46	904.81
cryst color	purple	purple
cryst size, mm	$0.4 \times 0.4 \times 0.2$	$0.5 \times 0.42 \times 0.25$
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
<i>a</i> , Å	12.5709(9)	19.498(10)
<i>b</i> , Å	25.338(3)	11.625(5)
<i>c</i> , Å	8.0707(6)	9.038(2)
β , deg		95.33(3)
<i>V</i> , Å ³	2570.7(4)	2039.7(14)
<i>d</i> (obsd), g cm ⁻³	1.562	1.473
<i>d</i> (calcd), g cm ⁻³	1.562	1.45
<i>Z</i>	4	2
λ , Å	0.710 73 (Mo K α)	0.710 73 (Mo K α)
abs coeff, mm ⁻¹	0.766	0.497
monochromator	graphite	graphite
scan method	ω ($2\theta < 15^\circ$) $\theta - 2\Theta$ ($15^\circ < 2\theta < 60^\circ$)	ω ($2\theta < 30^\circ$) $\omega - 2\theta$ ($55^\circ > 2\theta > 30^\circ$)
<i>T</i> , °C	23	12
scan speed, deg min ⁻¹	3	2
stds	3 every 50 reflections	3 every 50 reflections
2θ limit, deg	60	55
data collcd	$+h, +k, +l$	$\pm h, +k, +l$
no. of data	5436	4648
no. of obsd data	5371 ($F_o \geq 3\sigma(F_o)$)	4054 ($F_o \geq 3\sigma(F_o)$)
transm coeff	0.7558–0.8506	
<i>R</i>	0.103	0.072
<i>R</i> _w	0.092	0.104

X-ray Data Collection. Crystal data and experimental conditions for **10** and **11** are listed in Table 1. The intensity data were collected on Rigaku AFC-5 and AFC-6A automatic four-circle diffractometers. Since **11** is extremely unstable at room temperature, collection of data was carried out at 12 °C in a glass capillary. The intensities were corrected for Lorentz–polarization effects. An absorption correction for **10** ($\mu = 7.66\text{ cm}^{-1}$) was applied. No absorption correction was made for **11**, since its μ value (4.97 cm^{-1}) was low.

Structure Determination and Refinement. Compound 10. All calculations were done by the FACOM system in the Information Processing Center of Nara Women's University by using the UNICS III program.⁶ A weighting scheme, $1/w = \sigma c^2 + (0.015 |F_o|)^2$, was employed, where σc is a counting statistics error. Atomic scattering factors were taken from ref 7. The structure was solved by heavy atom methods and Fourier methods and refined by block-diagonal least-squares techniques. The effects of anomalous dispersion included in F_c values of both $\Delta f'$ and $\Delta f''$ for non-hydrogen atoms were taken from ref 8, since the crystals were spontaneously resolved. DMAP-H cation was located at two positions with populations of 0.6 and 0.4, respectively. Idealized positions of hydrogen atoms were calculated geometrically and were included in the subsequent cycles of least-squares refinement as isotropic contributions where the damping factor for hydrogen atoms was 0.1. Hydrogen atom scattering factors were taken from the compilation of Stewart et al.⁹ The final cycles of least-squares refinement gave $R = 0.103$ and $R_w = 0.092$. A final difference-Fourier map still showed peaks at heights up to $1.5\text{ e } \text{Å}^{-3}$ around the cobalt atom, although the electron density did not rise above $1.5\text{ e } \text{Å}^{-3}$ elsewhere. Final atomic parameters are listed in Table 2.

Compound 11. The initial position of the cobalt atom was determined by successive structure factor and electron density map calculations. The known absolute configurations of the asymmetric carbon atoms of strychnine were used as internal reference asymmetric centers to determine the absolute configuration of the whole complex

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(5) Each obtained complex (**6** and **7**) was dissolved in water, and the solution was passed through a Dowex 50W-X8 (NH_4^+ form) resin. The resulting solution was concentrated followed by an addition of methanol to yield a violet crystalline solid, which was recrystallized from a minimum amount of warm water–methanol, and the solution was cooled to give pure crystals (complex **8** and complex **9**).

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Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors for (DMAP-H)[Co(Ben-dhpta)]²⁺·2H₂O^a

atom	x	y	z	B _{eq} ^d Å ²
Co	0.75469(8)	0.24621(4)	0.1545(1)	2.17(3)
O(1)	0.6701(4)	0.1971(2)	0.2674(7)	2.4(2)
O(2)	0.5045(5)	0.1756(2)	0.3400(8)	3.2(2)
O(3)	0.7311(5)	0.2047(2)	-0.0405(7)	2.8(2)
O(4)	0.6398(6)	0.2051(3)	-0.2753(8)	4.1(2)
O(5)	0.8758(4)	0.2058(2)	0.2148(8)	3.3(2)
O(6)	0.9602(5)	0.1777(3)	0.4445(8)	3.7(2)
O(7)	0.9349(5)	0.3677(3)	0.0583(8)	3.7(2)
O(8)	0.8331(4)	0.2963(2)	0.0343(6)	2.0(2)
O(9)	0.7017(4)	0.4032(2)	0.3084(8)	2.6(2)
O(10)	0.5527(5)	0.4502(3)	0.276(1)	4.5(2)
N(1)	0.6217(4)	0.2827(2)	0.0949(6)	0.7(2)
N(2)	0.7891(5)	0.2877(2)	0.3570(7)	1.8(2)
N(3) ^b	0.676(2)	0.1063(8)	0.608(3)	10.1(8)
N(4) ^b	0.750(2)	-0.0523(7)	0.545(3)	8.1(8)
N(3) ^c	0.782(2)	-0.103(1)	0.567(5)	10(2)
N(4) ^c	0.701(2)	0.062(1)	0.549(4)	8(3)
C(1)	0.6205(6)	0.3399(3)	0.139(1)	2.1(2)
C(2)	0.6386(6)	0.3552(3)	0.3161(9)	1.8(2)
C(3)	0.6965(6)	0.3152(3)	0.426(1)	2.3(2)
C(4)	0.5674(7)	0.2047(4)	0.273(1)	2.7(2)
C(5)	0.5308(5)	0.2544(4)	0.176(1)	3.0(2)
C(6)	0.6158(7)	0.2761(3)	-0.086(1)	2.4(2)
C(7)	0.6633(7)	0.2244(3)	-0.144(1)	2.6(2)
C(8)	0.8309(6)	0.2479(4)	0.469(1)	2.8(2)
C(9)	0.8954(6)	0.2065(3)	0.372(1)	2.3(2)
C(10)	0.8767(6)	0.3249(3)	0.3110(8)	2.1(2)
C(11)	0.8850(6)	0.3316(3)	0.116(1)	2.4(2)
C(12)	0.6484(7)	0.4480(4)	0.283(1)	2.9(2)
C(13)	0.7198(7)	0.4939(3)	0.2704(9)	2.4(2)
C(14)	0.6781(8)	0.5449(3)	0.288(1)	3.2(3)
C(15)	0.744(1)	0.5896(3)	0.275(1)	4.0(3)
C(16)	0.8520(9)	0.5823(4)	0.238(1)	3.9(4)
C(17)	0.8916(8)	0.5328(4)	0.215(1)	4.0(3)
C(18)	0.8267(7)	0.4879(4)	0.227(1)	2.9(2)
C(19) ^b	0.785(2)	0.0917(8)	0.634(4)	8.2(3)
C(20) ^b	0.804(2)	0.0391(9)	0.599(3)	6(1)
C(21)	0.7251(8)	0.0034(4)	0.558(1)	3.4(7)
C(22) ^b	0.619(2)	0.0216(9)	0.532(3)	7.0(5)
C(23) ^b	0.599(2)	0.0764(9)	0.562(4)	8.3(7)
C(24) ^b	0.852(1)	-0.0700(7)	0.575(2)	5(1)
C(25) ^b	0.657(2)	-0.0893(8)	0.504(3)	6(1)
C(19) ^c	0.864(3)	-0.069(1)	0.522(4)	6(3)
C(20) ^c	0.835(2)	-0.016(1)	0.572(5)	6(3)
C(22) ^c	0.647(3)	-0.031(1)	0.607(4)	7(3)
C(23) ^c	0.681(2)	-0.086(1)	0.638(3)	5(3)
C(24) ^c	0.769(3)	0.097(1)	0.506(5)	7(2)
C(25) ^c	0.589(4)	0.080(2)	0.507(5)	10(3)

^a Standard deviations are presented in parentheses. ^b Multiplicity of these atoms is 0.6. ^c Multiplicity of these atoms is 0.4. ^d Equivalent isotropic temperature factors ($B_{eq} = \frac{1}{3} \{ \sum \sum B_{ij} a_i a_j \}$).

ion. The effects of anomalous dispersion⁸ were introduced in F_c . Least-squares refinement, allowing all the atoms except for hydrogen atoms to vibrate anisotropically, converged to R and R' values of 0.072 and $R_w = 0.1101$ for the final structure factor. Final atomic parameters are listed in Table 3. A final difference-Fourier map showed no unusual feature. All calculations were performed by the FACOM M380 system in the Information Center of Okayama University of Science by using the SHELEX-86 program. The perspective views were drawn by using the program ORTEP 2.

Results and Discussion

Esterification of K[Co(dhpta)]. The esterification of the noncoordinated hydroxyl group of the complex with acetic anhydride was first examined. However, this experiment failed, because the complex was insoluble in the appropriate solvents for the reaction. It was expected that the potassium salts of anionic metal complexes would be solubilized in organic solvents by macrocyclic polyether, crown ethers, and cryptand. The noncoordinated hydroxyl group of [Co(dhpta)]⁻ was

Table 3. Atomic Coordinates and Equivalent Isotropic Temperature Factors for (STC-H)[Co(Val-dhpta)]·6H₂O^a

atom	x	y	z	B _{eq} ^b Å ²
Co	0.00741(5)	0.0(1)	0.8351(1)	2.06(2)
O(1)	0.0667(3)	0.1066(5)	0.7526(6)	3.0(1)
O(2)	0.0775(3)	0.2897(6)	0.6966(8)	4.3(2)
O(3)	0.0480(3)	0.0306(5)	1.0288(6)	3.1(1)
O(4)	0.0220(3)	0.1012(6)	1.2451(6)	3.8(2)
O(5)	0.0720(3)	-0.1187(5)	0.8126(6)	2.8(1)
O(6)	0.1186(3)	-0.2178(7)	0.6364(7)	4.1(2)
O(7)	-0.0549(3)	-0.1040(5)	0.9116(6)	2.9(1)
O(8)	-0.1428(4)	-0.2164(7)	0.8506(9)	5.2(2)
O(9)	-0.1900(3)	0.0551(5)	0.5626(6)	2.9(1)
O(10)	-0.2473(4)	0.2154(8)	0.597(1)	7.0(3)
O(11)	0.5308(4)	1.3893(8)	0.557(1)	5.4(2)
O(12)	0.4471(4)	1.0993(7)	0.8455(7)	4.3(2)
O(13)	-0.1394(3)	-0.5399(7)	0.6942(8)	4.6(2)
O(14)	-0.8151(4)	-0.5873(8)	0.857(1)	6.3(3)
O(15)	-0.2172(5)	-0.845(1)	0.175(1)	8.2(4)
O(16)	-0.7954(7)	-0.882(1)	0.987(2)	11.8(6)
O(17)	-0.8121(6)	-0.119(1)	0.041(1)	9.1(4)
O(18)	-0.2981(8)	-0.761(2)	0.947(2)	15.2(8)
N(1)	-0.0538(3)	0.1277(6)	0.8683(6)	2.5(2)
N(2)	-0.0332(3)	-0.0442(6)	0.6374(6)	2.4(1)
N(3)	0.4436(3)	1.2658(7)	0.4848(8)	3.1(2)
N(4)	0.2535(3)	1.0294(6)	0.4697(8)	3.2(2)
C(1)	-0.1248(4)	0.1152(8)	0.7903(9)	3.1(2)
C(2)	-0.1253(4)	0.1122(7)	0.6198(8)	2.7(2)
C(3)	-0.0668(5)	0.0541(8)	0.5520(8)	3.1(2)
C(4)	-0.0187(5)	0.2370(8)	0.8256(9)	3.3(2)
C(5)	0.0465(5)	0.2119(8)	0.7521(9)	3.2(2)
C(6)	-0.0606(5)	0.1253(8)	1.0325(9)	3.4(2)
C(7)	0.0076(4)	0.0853(8)	1.1104(8)	2.6(2)
C(8)	0.0281(4)	-0.0867(9)	0.5627(9)	3.1(2)
C(9)	0.0770(4)	-0.1490(7)	0.675(1)	3.1(2)
C(10)	-0.0818(4)	-0.1431(8)	0.6568(9)	3.0(2)
C(11)	-0.0950(4)	-0.1579(8)	0.818(1)	3.0(2)
C(12)	-0.2484(4)	0.1188(9)	0.552(1)	3.4(2)
C(13)	-0.3070(6)	0.055(1)	0.482(2)	5.8(4)
C(14)	-0.3621(8)	0.142(2)	0.406(3)	13.0(1)
C(15)	-0.4073(9)	0.090(2)	0.276(3)	9.9(7)
C(16)	-0.447(1)	0.162(2)	0.185(2)	10.9(8)
C(17)	0.3495(4)	1.2767(8)	0.310(1)	3.1(2)
C(18)	0.3091(5)	1.321(1)	0.191(1)	4.1(3)
C(19)	0.3376(7)	1.412(1)	0.116(1)	5.8(4)
C(20)	0.3999(6)	1.455(1)	0.156(1)	5.0(3)
C(21)	0.4427(5)	1.4113(9)	0.280(1)	4.3(3)
C(22)	0.4144(4)	1.3236(8)	0.355(1)	3.4(2)
C(23)	0.3931(4)	1.1814(7)	0.5353(9)	2.9(2)
C(24)	0.3370(4)	1.1718(7)	0.4066(9)	2.7(2)
C(25)	0.2623(4)	1.1599(8)	0.451(1)	2.8(2)
C(26)	0.2490(4)	1.2226(9)	0.594(1)	3.6(2)
C(27)	0.3024(5)	1.1829(8)	0.719(1)	3.5(2)
C(28)	0.3717(4)	1.2284(8)	0.6845(9)	3.1(2)
C(29)	0.4318(5)	1.2152(9)	0.801(1)	3.9(2)
C(30)	0.5010(5)	1.256(1)	0.735(1)	5.3(3)
C(31)	0.4923(4)	1.3119(9)	0.587(1)	3.9(2)
C(32)	0.3975(6)	1.046(1)	0.924(1)	5.6(3)
C(33)	0.3413(5)	0.991(1)	0.825(1)	4.5(3)
C(34)	0.2994(5)	1.0504(9)	0.731(1)	3.7(2)
C(35)	0.2450(5)	0.991(1)	0.627(1)	3.9(2)
C(36)	0.3135(5)	0.9677(8)	0.410(1)	3.7(2)
C(37)	0.3440(4)	1.0605(8)	0.316(1)	3.1(2)

^a Standard deviations are presented in parentheses. ^b Equivalent isotropic temperature factors ($B_{eq} = \frac{1}{3} \{ \sum \sum B_{ij} a_i a_j \}$).

O-acylated by reaction with a series of acid anhydrides in the presence of 4-(dimethylamino)pyridine, after the potassium salt of the complex was dissolved in acetonitrile by using cryptand 222, in fairly high yields and remarkably mild conditions. Only when cryptand 222 was employed was the esterification achieved. Figure 1 depicts the general schematic representation of the preparation for the O-acylated complexes.

The selected spectral data of ¹³C NMR spectra of the complexes in D₂O are summarized in Table 4. In each

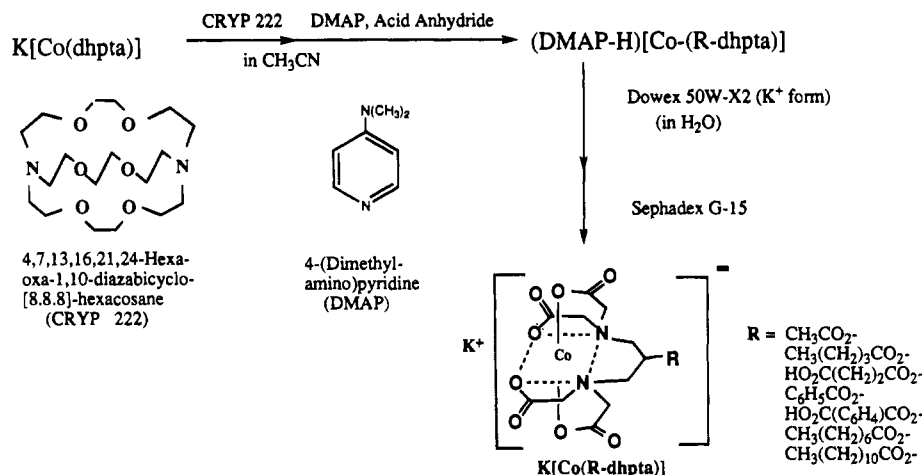


Figure 1. Reaction scheme.

Table 4. Selected ¹³C NMR Spectral Data Observed in D₂O (ppm)^a

complex	-CO ₂ ⁻ (carboxyl)	-CO ₂ ⁻ (ester)	-CH ₃ (methyl)
K[Co(dhpta)]	185.4, 184.8, 183.3, 183.2		
K[Co(Ac-dhpta)] ^{3/2} H ₂ O	182.2, 181.8, 180.5	171.3	20.2
K[Co(Val-dhpta)]·H ₂ O	184.9, 184.4, 183.0, 182.9	177.3	15.6
K[Co(Suc-dhpta)]·H ₂ O	184.8, 184.4, 183.0, 182.9, 180.1	175.6	
K[Co(Ben-dhpta)] ^{3/2} H ₂ O	184.6, 184.4, 182.9	170.3	
K ₂ [Co(Pht-dhpta)]·2H ₂ O	184.8, 184.5, 183.0	177.4	
K[Co(Oct-dhpta)] ^{3/2} H ₂ O	180.7, 180.6, 179.2	172.8	13.0
K[Co(Dod-dhpta)] ^{1/2} H ₂ O	180.6, 180.5, 179.2, 179.1	172.8	13.0

^a Methylene and phenyl carbon signals are omitted.Table 5. Electronic Absorption Spectral Data of Complexes in H₂O

no.	complex	$\nu/10^3, \text{cm}^{-1} (\log \epsilon)$
1	K[Co(Ac-dhpta)] ^{3/2} H ₂ O	18.13 (2.11) 26.35 (2.04)
2	K[Co(Val-dhpta)]·H ₂ O	18.10 (2.10) 26.40 (2.02)
3	K[Co(Suc-dhpta)]·H ₂ O	18.30 (2.15) 26.40 (2.10)
4	K[Co(Ben-dhpta)] ^{3/2} H ₂ O	18.15 (2.22) 26.39 (2.18)
5	K ₂ [Co(Pht-dhpta)]·2H ₂ O	18.30 (2.10) 26.30 (2.04)
6	K[Co(Oct-dhpta)] ^{3/2} H ₂ O	18.26 (2.06) 26.40 (2.00)
7	K[Co(Dod-dhpta)] ^{1/2} H ₂ O	18.45 (2.39) 26.40 (2.45)
8	NH ₄ [Co(Oct-dhpta)] ^{3/2} H ₂ O	18.18 (2.19) 26.32 (2.12)
9	NH ₄ [Co(Dod-dhpta)]·H ₂ O	18.12 (2.22) 26.32 (2.15)
10	(DMAP-H)[Co(Ben-dhpta)]	18.10 (2.11) 26.40 (2.05)

spectrum, the signal that could be assigned to the ester carbon was observed in the region of 169.1–177.3 ppm.

The spectral data of electronic absorption spectra of the complexes are summarized in Table 5, along with those of the starting [Co(dhpta)]⁻. These spectra of the complexes closely resemble each other in the d–d transition region and are characteristic of the *cis*-(N,N)-[CoN₂O₄] type.¹⁰ These observations suggested that the esterification proceeded without altering the coordination sphere.

We confirmed the existence of the ester bond formation by X-ray crystal structure studies of the complexes **10** and **11**, although the crystals were barely suitable for X-ray crystallography.

Description of the Structures. The perspective view of the complex ion for (DMAP-H)[Co(Ben-dhpta)] **10** is shown in

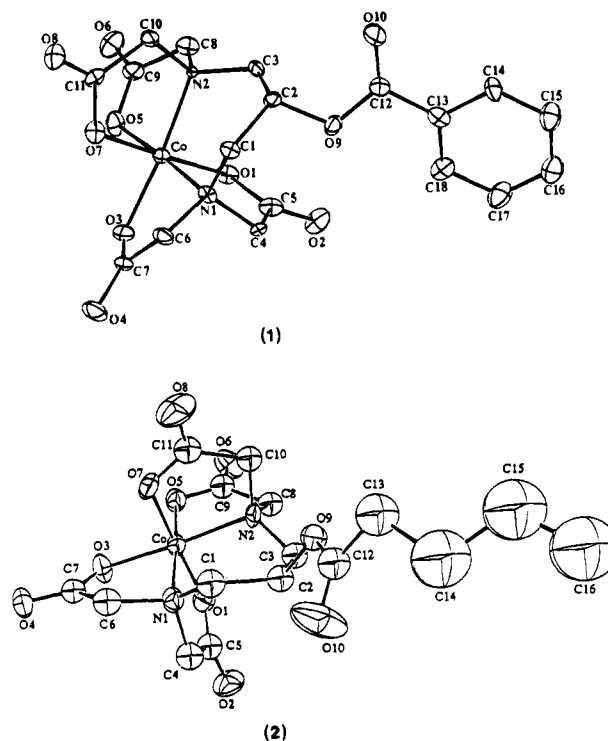
Figure 2. ORTEP drawings and atomic numbering schemes: (1) [Co(Ben-dhpta)]⁻ ion; (2) [Co(Val-dhpta)]⁻ ion.

Figure 2 along with that for (STC-H)[Co(Val-dhpta)]·6H₂O **11**. The dhpta unit binds to the slightly distorted octahedral cobalt center in the $\Delta\Delta\Delta$ ¹¹ (net Δ)¹² configuration. The steric features of the dhpta unit are quite similar to those in $\Delta\Delta\Delta$ -(+)₅₈₉-(STC-H)[Co(dhpta)]·1.5H₂O⁴ previously established crystallographically. The central six-membered chelate ring adopts a skew

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Table 6. Selected Interatomic Distances (Å)^a and Angles (deg)^b in (DMAP-H)[Co(Ben-dhpta)]·²/₂H₂O^a

Bond Distances			
Co—O(1)	1.876(6)	Co—O(3)	1.914(7)
Co—O(5)	1.896(8)	Co—O(7)	1.874(6)
Co—N(1)	1.969(6)	Co—N(2)	1.987(6)
O(9)—C(12)	1.332(12)		
Bond Angles			
O(1)—Co—O(7)	177.1(3)	O(1)—Co—N(1)	87.1(3)
O(3)—Co—N(1)	85.8(3)	O(3)—Co—N(2)	176.2(3)
O(5)—Co—N(1)	175.1(3)	O(5)—Co—N(2)	84.3(3)
O(7)—Co—N(2)	87.4(3)	N(1)—Co—N(2)	97.9(3)
O(9)—C(12)—C(13)	112.1(8)	O(10)—C(12)—C(13)	124.5(9)

^a Standard deviations are presented in parentheses.**Table 7.** Selected Interatomic Distances (Å) and Angles (deg) in (STC-H)[Co(Val-dhpta)]·6H₂O^a

Bond Distances			
Co—O(1)	1.895(6)	Co—O(3)	1.886(5)
Co—O(5)	1.891(6)	Co—O(7)	1.890(6)
Co—N(1)	1.946(7)	Co—N(2)	1.955(6)
O(9)—C(12)	1.353(11)		
Bond Angles			
O(1)—Co—O(7)	177.5(2)	O(1)—Co—N(1)	88.1(3)
O(3)—Co—N(1)	85.6(3)	O(3)—Co—N(2)	175.6(3)
O(5)—Co—N(1)	175.7(3)	O(5)—Co—N(2)	85.8(3)
O(7)—Co—N(2)	87.0(3)	N(1)—Co—N(2)	98.0(3)
O(9)—C(12)—C(13)	111.9(9)	O(10)—C(12)—C(13)	127.9(9)

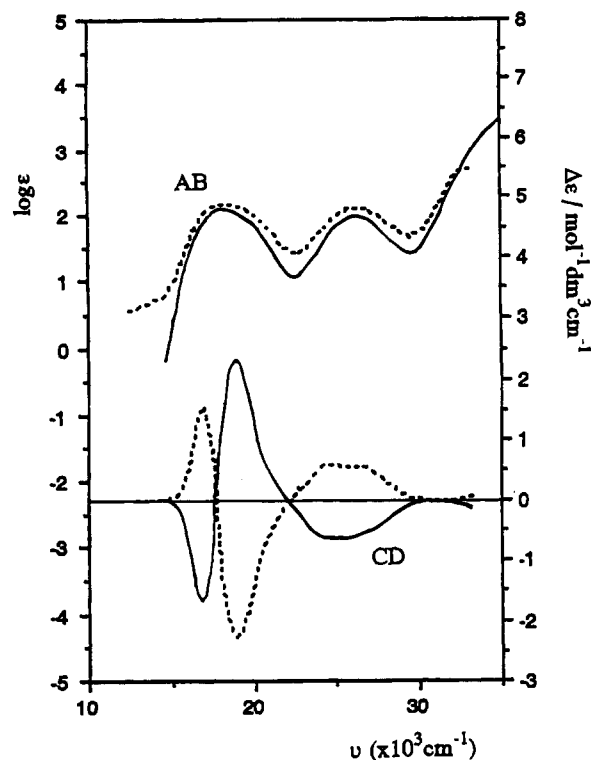
^a Standard deviations are presented in parentheses.

boat conformation, and the five-membered glycinato chelate rings have envelope conformations. Selected bond distances and angles are listed in Table 6. The bond distances and angles are typical values for an ester bond. Thus, the oxygen atom of the central diamine part of dhpta binds to the carboxylic carbon atom of the benzoic acid residue to form an ester bond.

The steric features of the compound **11** are quite similar to those of compound **10**. The dhpta unit attaches to the slightly distorted octahedral cobalt center in the $\Lambda\Delta\Lambda$ configuration. The central six-membered diamine chelate ring takes the skew boat conformation. A selection of intramolecular bond distances and bond angles are given in Tables 7. The oxygen atom of the noncoordinated hydroxyl group of dhpta binds to the carboxylic carbon atom of the valeric acid residue to form an ester bond.

Absolute Configuration and Circular Dichroism. The electronic absorption (AB) and circular dichroism (CD) spectra of $\Lambda\Delta\Lambda$ -K[Co(Val-dhpta)]·2H₂O **12** in H₂O are shown in Figure 3. Numerical data are summarized in Table 8, along with those of the $\Delta\Delta\Delta$ -K[Co(dhpta)].⁴ The AB spectra of both complexes are quite similar to each other, and their CD curves are nearly mirror images. X-ray structure analyses and circular dichroism studies of the series of EDTA type complexes, whose CD spectra usually show two Cotton effects of opposite sign in the first absorption region, suggest the following empirical rule; the sign of the CD band in the region can be related to the configuration around the cobalt centers. When they give a positive and negative Cotton effect, respectively, from the lower energy band of the first absorption region, they should be assigned to the $\Lambda\Delta\Lambda$ configuration around the asymmetric cobalt center. In the CD spectrum of $\Lambda\Delta\Lambda$ -K[Co(Val-dhpta)]·2H₂O, a positive and negative Cotton effect has been observed, from the lower energy band in the region. The absolute configuration of the present complex has been determined as $\Lambda\Delta\Lambda$ from the X-ray study. Consequently, the empirical rule appears to be applicable to the series of the dhpta type complexes.

Cobalt(III) Complexes Having a Long Alkyl Chain. The aqueous solutions of the cobalt(III) complexes having a long

**Figure 3.** Electronic absorption (AB) and circular dichroism (CD) spectra in H₂O: $\Delta\Delta\Delta$ -K[Co(dhpta)] (—); $\Lambda\Delta\Lambda$ -K[Co(Val-dhpta)]·2H₂O (---).**Table 8.** Electronic Absorption (AB) and Circular Dichroism (CD) Data for Λ -[Co(Val-dhpta)]·2H₂O, with Data for Δ -K[Co(dhpta)] in Parentheses^a

AB		CD	
peak position × 10 ³ cm ⁻¹	log ε	peak position × 10 ³ cm ⁻¹	Δε
18.18 (18.25)	2.15 (2.15)	16.95 (16.72)	+1.57 (-2.12)
26.32 (26.46)	2.10 (2.08)	18.87 (18.73)	-2.28 (+3.01)
		24.39 (24.39)	+0.60 (-0.80)

^a Reference 4.

alkyl chain obtained are expected to be surface-active. The concentration-dependency curves are shown in Figure 4 (triangles). The steep decrease in the surface tension shows the surface-active properties of the aqueous solutions and break points at around 0.07–0.10 mol dm⁻³ for the octyl and at 2.0 × 10⁻³ mol dm⁻³ for the dodecanoyl complexes are regarded as cmc. These values are appreciably smaller than the cmc obtained for the corresponding conventional amphiphiles such as potassium alkanecarboxylates (0.4–0.6 mol dm⁻³ for the octyl and 0.02–0.03 mol dm⁻³ for the dodecanoyl).¹³ As the effect of the simple counterions on the cmc is slight,¹³ the introduction of the present metal complex to the polar group of the amphiphile will facilitate the formation of ion-aggregates as suggested in a previous study.¹⁴

The cobalt-59 NMR signal for the octyl complex of 5 × 10⁻³ mol dm⁻³ was observed at +2203 ppm relative to the [Co(NH₃)₆]³⁺ of the same concentration and the value coincides with that for the dodecanoyl complex within an error of 2 ppm. Although the dependence of the chemical shift on the concentration was slight for both of the complexes, a small but sudden change (5–6 ppm upfield shift) was observed for the octyl complex in the range of 0.06–0.07 mol dm⁻³ which nearly coincides with the cmc determined from the surface tension.

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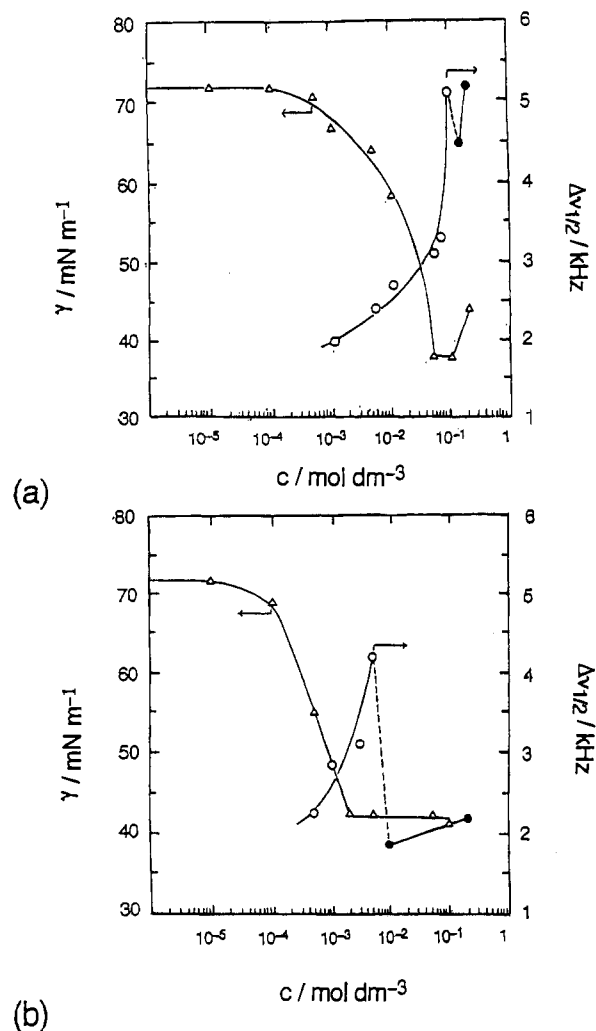


Figure 4. The surface tension (Δ) and width at half-height of ^{59}Co NMR spectra (\circ , \bullet) depending on the concentration for the $[\text{Co}(\text{Oct-dhpta})]^-$ (a) and the $[\text{Co}(\text{Dod-dhpta})]^-$ (b) complexes. The open circles are the values for the Lorentzian spectra and the closed ones are for the non-Lorentzian.

The width at half-height which is inversely proportional to the transverse relaxation time (T_2) showed a large concentration dependency for both the octyl and dodecanoyl complexes as depicted (circles) in Figure 4. The results showed that at around the cmc the width increased steeply. This steep increase suggested that the motions of the molecules were appreciably restricted by the formation of the assemblies of the cobalt(III) molecules. A sudden drop of the magnitude of the width at half-height was then observed at a slightly higher concentration. Below this concentration, the Fourier-transformed signals were typical Lorentzian as shown in Figure 5a, while above it they were not Lorentzian as shown in Figure 5b. The criterion whether the signal is a Lorentzian line or not is determined by taking the $\Delta\nu_{1/8}/\Delta\nu_{1/2}7^{1/2}$ ratio,¹⁵ and this value was significantly larger than 1 for the signals represented by the closed circles in Figure 4. The simulation for the non-Lorentzian NMR signal was performed by using the program "Gonta" which has been developed by the laboratory of Professor Isao Ando in Tokyo Institute of Technology. The latter signal represents a superimposition of the two Lorentzian components of the type given as broken lines in Figure 5b. This change in shape of the spectrum indicates that the aggregation of the cobalt(III)

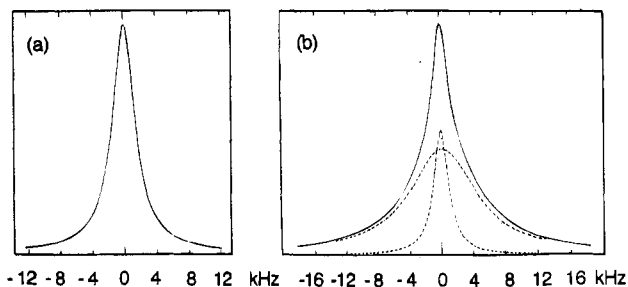


Figure 5. Fourier-transformed signals of ^{59}Co of the $[\text{Co}(\text{Oct-dhpta})]^-$ in the aqueous solutions: (a) 0.04 mol dm^{-3} ; (b) 0.10 mol dm^{-3} . The dotted lines are the two Lorentzian components of a calculated signal.

complexes further proceeds with an increase in the concentration and that the aggregates then separate into the following two types: one is the assembly of the faster motional molecules where the extent of the aggregation is smaller, and the other is those of the slower motional ones where the extent of the aggregation is larger. The faster motional molecules will appreciably contribute to the width at half-height above this critical concentration, and thus the apparent width at half-height is reduced by the separation into the two types of aggregations.

Conclusion

We presented here an efficient new organic chemical modification method for anionic complex having a functional group that can give high yields and be applied under remarkably mild conditions. This procedure is based on the dissolution of anionic complexes associated with alkaline or alkali earth metal cations in organic solvents using cryptand 222. This procedure should be widely applicable for chemical modification of general anionic complexes having various types of functional group(s). We found the usefulness of the application of ^{59}Co NMR to the micellar solutions of cobalt(III) complexes having a long alkyl chain. The ^{59}Co NMR should be widely applicable for the studies of the aggregations of the surfactants having cobalt(III) complexes as a polar group.

We have started to examine several methods for chemical modification of the Co-dhpta complex, minus the use of cryptand 222. We recently prepared the tris(*n*-butyl)ammonium salt of Co-dhpta and tetrakis(*n*-butyl)ammonium salt of Co-dhpta. We observed that these salts were soluble in DMF. A preliminary study showed that acetylation of hydroxyl group in the tris(*n*-butyl)ammonium salt of the Co-dhpta complex was achieved also with this procedure, although the yield of the acetylated product was not quite sufficient. These results will be published in the following paper.¹⁶

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Nos. 63612002, 01850190, 03241106, 02854074, 03650687, and 03555184) and from the CIBA-GEIGY Foundation (Japan) for the Promotion of Science, Iwatani Naoji Foundation's research grants, and grants from Nippon Sheet Glass and Mitsubishi Yuka Foundations and Nagase Science and Technology Foundation. We are grateful to Professor Isao Ando in Tokyo Institute of Technology for his kind supply of the program "GONTA".

Supplementary Material Available: Tables giving the anisotropic thermal parameters and complete of bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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