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First Evidence of the Effect of Chirality around the Octahedral Metal Center on the Aggregation Behavior of an Amphiphilic Cobalt(III) Complex

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Mixed ligand amphiphilic cobalt(III) complexes containing N-dodecylethylenediamine and a chiral tetraamine provide a novel example that the chirality around the octahedral metal center affects the aggregation behavior of the complexes.

Some chiral amphiphiles construct characteristic aggregates which are very different from those of the racemic mixture.[1)] It is an interesting subject to elucidate the relation between the steric structure of an amphiphile and its aggregation behavior. We wish to report that amphiphilic mixed ligand cobalt(III) complexes can provide an important example from this standpoint.

A cobalt(III) complex is inert in ligand-substitution reactions, and its uniform structure is thus maintained even in an aqueous solution. Therefore, amphiphilic cobalt(III) complexes are suitable for the study concerning the effect of the steric structure of the complex in the hydrophilic part of the amphiphile on the aggregation behavior. In the present study, we have chosen a mixed ligand cobalt(III) complex containing N-dodecylethylenediamine and a chiral tetraamine.

N-Dodecylethylenediamine[2)] and trans-[$CoCl_2$(2S,10S-Me_2-2,3,2-tet[3)])]ClO_4[4)] were refluxed in methanol with triethylamine and activated charcoal. The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was dissolved in water, and was poured on the column of SP-Sephadex C-25 (Na^+ form). Elution with the 1 M $NaClO_4$ aqueous solution, and subsequently with 1 M $NaClO_4$ methanol-water (1:1) solution produced an orange band. Concentration of the eluate from the band resulted

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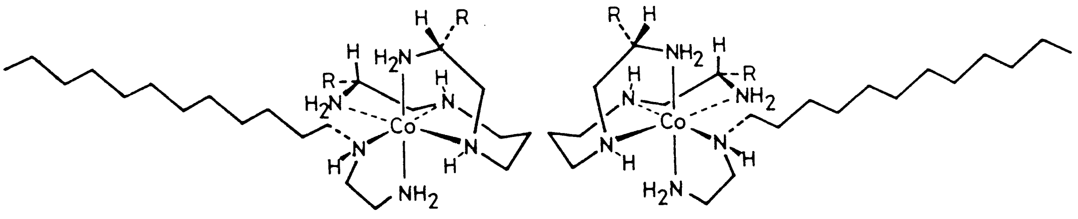

(a) (b)

Fig. 1. Proposed steric structures of the complex ions. (a) R=CH_3: Δ-β_2-[Co((S)-N-dodecylethylenediamine)(2R,10R-Me_2-2,3,2-tet)]$^{3+}$ (I-Δ), R=H: Δ-β_2-[Co((S)-N-dodecylethylenediamine)(2,3,2-tet)]$^{3+}$ (II-Δ), (b) R=CH_3: Λ-β_2-[Co((R)-N-dodecylethylenediamine)(2S,10S-Me_2-2,3,2-tet)]$^{3+}$ (I-Λ), R=H: Λ-β_2-[Co((R)-N-dodecylethylenediamine)(2,3,2-tet)]$^{3+}$ (II-Λ).

orange precipitates, which were collected by filtration and air dried (yield 34% (1)). They were recrystallized from aqueous methanol.$^{5)}$ When rac-2,10-Me_2-2,3,2-tet was used instead of 2S,10S-Me_2-2,3,2-tet, a similar product was obtained by the same procedure (yield 29% (2)).$^{6,7)}$

Elemental analysis and the electronic absorption spectrum of **1** indicate the formation of [Co(N-dodecylethylenediamine)(2S,10S-Me_2-2,3,2-tet)]-$(ClO_4)_3$. The ^{13}C NMR spectroscopy showed 21 signals due to 23 carbon atoms in the compound,$^{8)}$ which indicates one of the possible stereoisomers is obtained specifically. 2S,10S-Me_2-2,3,2-tet is known to take the Λ-β configuration stereospecifically in the cis type coordination.$^{4)}$ The circular dichroism spectrum of **1** strongly supports the Λ-β configuration. A molecular model study suggests that the most possible strereochemistry of the N-dodecyldiamine chelate is the $\beta_2$$^{9)}$ form and the absolute configulation of the secondary nitrogen is R. This structure is supported by the stereospecific coordination of the N-methyl derivative of glycinato in [Co(sarcosinato)(triethylenetetramine)]$^{2+}$.$^{10)}$ Accordingly, the plausible steric structure of **1** can be represented as Λ-β_2-[Co((R)-N-dodecylethylenediamine)(2S,10S-Me_2-2,3,2-tet)]$(ClO_4)_3$ (I-Λ in Fig. 1). The complex containing 2R,10R-Me_2-2,3,2-tet should be the mirror image of the complex containing 2S,10S-Me_2-2,3,2-tet. Therefore, **2** is the racemic mixture of Λ-β_2-[Co((R)-N-dodecylethylenediamine)(2S,10S-Me_2-2,3,2-tet)]$(ClO_4)_3$ (I-Λ) and Δ-β_2-[Co((S)-N-dodecylethylenediamine)(2R,10R-Me_2-2,3,2-tet)] $(ClO_4)_3$ (I-Δ).

Surface tension of the aqueous solution of the complex was measured using the Wilhelmy tensiometer (at 28 °C) and was plotted against the concentration of the complex in Fig. 2 along with the data of the similar complex containing 2,3,2-tet$^{11)}$ (3).$^{12)}$ **3** is the racemic mixture of II-Λ and II-Δ. The slopes of the curves change abruptly, which indicates the forma-

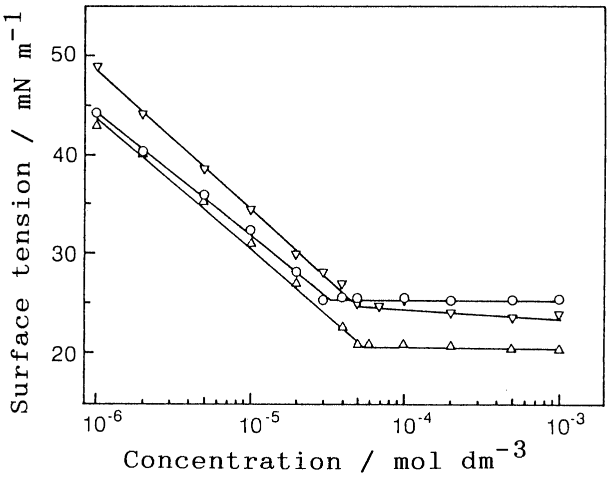

Fig. 2. Surface tension-concentration curves of the complexes. △ : **1** (I-Λ), ▽ : **2** (I-Λ + I-Δ), ○ : **3** (II-Λ + II-Δ).

Table 1. Critical micelle concentration (cmc), surface tension at cmc (γ_{cmc}), and area per molecule (A) of the complexes

Compound	cmc/10^{-5} mol dm^{-3}	γ_{cmc}/mN m^{-1}	A/Å^2
1 (I-Λ)	5.6	20.8	289
2 (I-Λ + I-Δ)	5.0	24.3	275
3 (II-Λ + II-Δ)	3.3	25.3	307

tion of aggregates. Critical micelle concentration (cmc) and surface tension at cmc (γ_{cmc}) estimated from the curves are summarized in Table 1. γ_{cmc} of the I-Λ enantiomer (**1**) is considerably lower than that of the racemic mixture of I-Λ and I-Δ (**2**) or II-Λ and II-Δ (**3**). The results indicate that the major factor which affects γ_{cmc} is not the methyl substitution on the tetraamine chelate, but chirality of the complex. The area per molecule in the surface of the solution can be calculated from Gibbs' equation.[13)] The results are shown in Table 1. The molecular areas of the complexes are considerably larger than those of usual surfactants.[13)] It is striking that the complexes remarkably reduce the surface tension of the aqueous solution, although they are less close-packed in the water surface. The difference in γ_{cmc} between **1** and **2** may be ascribable to the different contribution of the stereospecific arrangement in the surface,[14)] and the huge chiral structure of the metal complex can contribute effectively.

In conclusion, the chirality around the octahedral metal center can affect surface adsorption of the amphiphile. This is a novel example that the chirality in the hydrophilic part of the amphiphile can affect its surface activity. It should be important to elucidate the unique effects of the metal complex on the aggregation behavior of an amphiphile, both theoretically and practically. From this standpoint, mixed ligand amphiphilic cobalt(III) complexes are very useful.

References

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2) A. J. Bruno, S. Chaberek, and A. E. Martell, J. Am. Chem. Soc., **78**, 2723 (1956).
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5) Purification of the compounds were repeatedly performed until γ values were reproduced sufficiently, because small amount of an impurity often causes significant deviation from the true value of the pure compound.
6) Anal for **1** Found: C, 35.54; H, 6.89; N, 10.64%. Calcd for $C_{23}H_{56}N_6O_{12}Cl_3Co$: C, 35.69; H, 7.29; N, 10.86%. For **2** Found: C, 35.23; H, 6.86; N, 10.31%. Calcd for $C_{23}H_{56}N_6O_{12}Cl_3Co\cdot0.5H_2O$: C, 35.28; H, 7.34; N, 10.73%.
7) Absorption spectrum: $\nu/10^3$ cm^{-1} (ε) (in MeOH) 20.6 (154), 28.6 (172), 43.4 (20382). Circular dichroism spectrum: $\nu/10^3$ cm^{-1} ($\Delta\varepsilon$) (in MeOH) 19.3 (+1.67), 21.7 (-2.13), 28.2 (+0.59).
8) ^{13}C NMR spectroscopic data for **1** (D_2O, dioxane = 67.4 ppm); 62.11, 57.06, 53.77, 53.38, 53.10, 52.49, 49.79, 44.96, 44.43 (CH_2- or CH-N); 32.90, 30.61 (3C), 30.54, 30.31, 30.17, 28.98, 27.56, 23.57, 22.55 (CH_2); 17.65, 16.87, and 14.35 (CH_3).
9) We tentatively use β_1 and β_2 in order to express the two configurational isomers obtained using unsymmetrical diamine ligands in the remaining octahedral sites, from the analogy to the mixed ligand complex containing an aminoacidato and a tetraamine (D. A. Buckingham and L. G. Marzilli, Inorg. Chem., **6**, 1042 (1967)). β_2 refers to the configurational isomer with the secondary nitrogen of N-dodecylethylenediamine in a trans position to a secondary nitrogen atom of the tetraamine.
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