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Molecular Aggregates of Mixed Ligand Cobalt(III) Complexes Having One or Two Long Alkyl-Chains

Morio YASHIRO,* Katsuya MATSUMOTO, and Sadao YOSHIKAWA*
Department of Applied Chemistry, Faculty of Science and Technology,
Keio University, Hiyoshi, Kohoku-ku, Yokohama 223

Mixed ligand amphiphilic cobalt(III) complexes having one or two long alkyl-chains were prepared. Critical micelle concentration of the complex having one dodecyl group in aqueous solution is extremely low compared with that of the amphiphilic ligand, N-dodecylethylenediamine dihydrochloride.

Organized molecular aggregates of synthetic amphiphiles have attracted much attention as a mimic of biological systems.[1)] Introduction of metal complexes to the aggregates has been shown to exert useful catalitic functions.[2)] Thus, amphiphilic metal complexes are promising as components of synthetic assemblies which can exert highly organized functions. In order to design metal complex aggregates, it is an important subject to study the aggregation behavior of amphiphilic metal complexes.

A cobalt(III) complex is inert in ligand-substitution reactions, and its uniform structure is thus maintained even in solution. Therefore, amphiphilic cobalt(III) complexes are suitable for the study of the effects of the structure of metal complexes on their aggregation behavior. We now wish to report that amphiphilic cobalt(III) complexes having one or two alkyl-chains can be prepared selectively by using an appropriate ligand having no alkyl-chain along with a ligand having an alkyl-chain, N-dodecylethylenediamine (C12-en).

An amphiphilic cobalt(III) complex having one alkyl-chain, [Co(C12-en)(2,3,2-tet)]$(ClO_4)_3$ (1) (2,3,2-tet = 3,7-diaza-1,9-diaminononane), was prepared from N-dodecylethylenediamine[3)] (C12-en) and trans-[$CoCl_2$(2,3,2-tet)]ClO_4[4)] by refluxing in methanol with triethylamine and activated charcoal. The reaction mixture was filtered, and the filtrate was concentrated to driness. The residue was dissolved in water, and was poured on the column of SP-Sephadex C-25 (Na^+ form). Elution with the 1 mol dm^{-3} $NaClO_4$ aqueous solution, and subsequently with the 1 mol dm^{-3} $NaClO_4$ methanol-water (1:1) solution produced an orange band. Concentration of the eluate from the band resulted orange precipitates, which were collected by filtration and air dried (yield 37%). Found: C, 34.03; H, 6.88; N, 10.79%. Calcd for $C_{21}H_{52}N_6O_{12}Cl_3Co$: C, 33.81; H, 7.03; N, 11.27%. Absorption spectrum: $\nu/10^3$ cm^{-1} (ε) (H_2O) 20.7 (147), 28.7 (197), 44.0 (13862). The elemental analysis, electronic absorption and ^{13}C NMR spectral data indicate the formation of [Co(C12-en)(2,3,2-tet)]$(ClO_4)_3$, in which one dodecyl group has been introduced to the complex by a combination of one tetradentate ligand and one C12-en.[5)]

An amphiphilic cobalt(III) complex having two alkyl-chains, [Co(ox)(C12-en)$_2$]Cl (**2**) (ox = oxalato), was prepared from $K_3[Co(ox)_3]$[6)] and C12-en by refluxing in an aqueous methanol solution. The resulting red precipitate was treated with calcium chloride in hot methanol, then the white precipitate was filtered off. The filtrate was concentrated and the resulting precipitate was collected by filtration and dried in a reduced pressure (yield 59%). Found: C, 55.17; H, 9.77; N, 8.69%. Calcd for $C_{30}H_{66}N_4O_5ClCo$: C, 54.82; H, 10.12; N, 8.52%. Absorption spectrum: $\nu/10^3$ cm^{-1} (ε) (MeOH) 19.3 (170), 27.0 (175), 41.4 (23512). The elemental analysis and electronic absorption spectral data indicate the formation of [Co(ox)(C12-en)$_2$]Cl·H_2O (**2**), in which two dodecyl groups have been introduced to the complex by a combination of one bidentate ligand and two C12-en.

Complex **1** is soluble in water and in methanol. ^{13}C NMR spectroscopy of **1** suggests one of the possible stereoisomers is obtained selectively. Therefore, arrangement of the N-dodecyl group of the ethylenediamine chelate is effectively regulated as well as stereospecific coordination of 2,3,2-tet.[7)] From the analogy to stereospecific coordination of the N-methyl derivative of glycinato in [Co(sarcosinato)(triethylenetetramine)]$^{2+}$,[8)] the stereochemistry of **1** can be proposed as is drawn in Fig. 1.

Surface tension of the aqueous solution of **1** was measured using the Wilhelmy tensiometer (at 28 °C), and was plotted against concentration of **1** in Fig. 2. Slope of the curve changes abruptly. This phenomenum is commonly observed for usual surfactants, and indicates the formation of aggregates. The critical micelle concentration (cmc) estimated from the curve is 3.3×10^{-5} mol dm^{-3}, and the surface tension at cmc (γ_{cmc}) is 25.4 mN m^{-1}. cmc of **1** is extremely low compared with that of the amphiphilic ligand, N-dodecylethylenediamine dihydrochloride (cmc = 1.1×10^{-2} mol dm^{-3}, γ_{cmc} = 32.8 mN m^{-1}). This suggests introduction of a trivalent metal complex to the hydrophilic part of the amphiphile remarkably enhances the ability of aggregation. It is important to note that such cobalt(III) complex is inert for ligand substitution reactions, thus the polyamine chelates do not dissociate under these experimental conditions, in contrast to the labile complex systems. Therefore, the observed value unambiguously expresses the effect of introduction of a metal complex to the hydrophilic part of the amphiphile.

When the aqueous solution of **1** was sonicated in the presence of chloroform, the solution became turbid. The turbidity can be estimated by transmittance at the absorption maxima of the complex. Relative transmittance (T'/T), where T' is transmittance of the aqueous solution after sonication in the presence of chloroform and T is transmittance of the aqueous solution, is plotted against concentration of **1** in Fig. 2.[9)] The relative transmittance decreases abruptly at the concentration 1 - 3 X 10^{-5} mol dm^{-3}. This value agrees well with the cmc obtained from the surface tension-concentration curve. This suggests the turbidity is due to solubiliza-

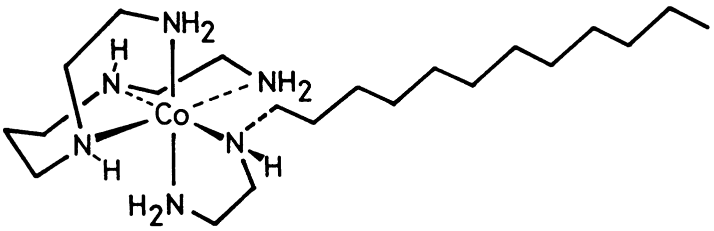

Fig. 1. A proposed structure of **1**.

tion of chloroform in the aggregates of amphiphilic complexes. Thus, cmc of the complex is expected to be determined by this method.

Complex **2** is insoluble in water but soluble in methanol and in chloroform.

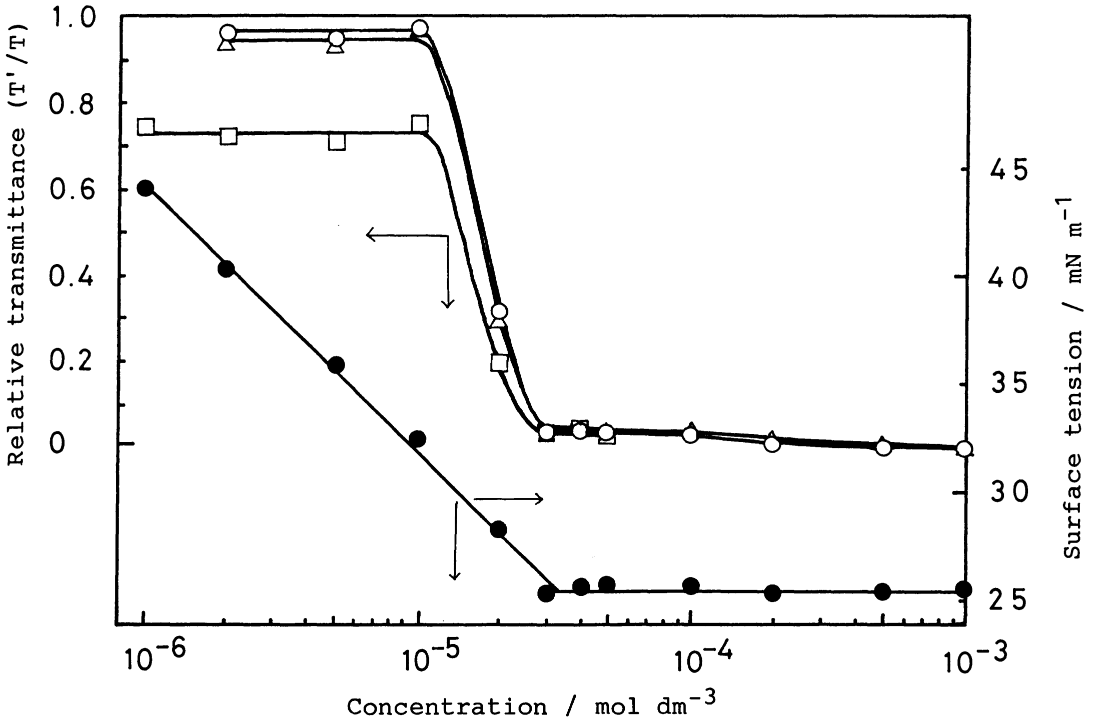

Fig. 2. The surface tension-concentration curve (●) and relative transmittance (T'/T) at the absorption maxima of **1**. T'; Transmittance of the aqueous solution after sonication in the presence of chloroform, T; transmittance of the aqueous solution. ○; 485 nm, △; 346 nm, □; 227 nm.

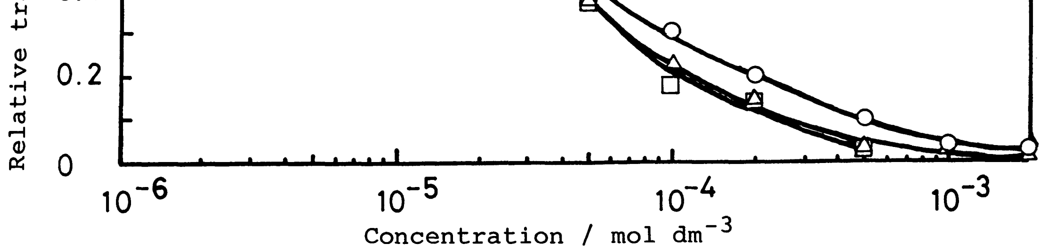

Fig. 3. Relative transmittance (T'/T) at the absorption maxima of **2**. T'; transmittance of the chloroform solution after sonication in the presence of water, T; transmittance of the chloroform solution. ○; 520 nm, △; 370 nm, □; 242 nm.

When the chloroform solution of **2** was sonicated in the presence of water, the solution became turbid. Relative transmittance (T'/T), where T' is transmittance of the chloroform solution after sonication in the presence of water and T is transmittance of the chloroform solution, is plotted against concentration of **2** in Fig. 3.$^{9)}$ The slopes of the curves change abruptly similarly to the case of **1**. This observation suggests the aggregation of **2** at these experimental conditions, and cmc estimated from the curves is 4×10^{-5} mol dm^{-3}.

NMR spectra of **2** are very characteristic. ^{13}C NMR spectrum obtained in chloroform shows carbon signals due to alkyl-chains, and does not show those of the chelate rings both of ethylenediamine and oxalato. ^{1}H NMR spectrum obtained in chloroform-d_1 shows very broad methylene signals of the chelate rings. The methylene signals became sharp by the addition of methanol-d_4 to the solution. These observations strongly suggest the aggregation of **2** in chloroform. The remarkable broadening of the ^{13}C and ^{1}H NMR signals in the chloroform solution indicates that the motion of the metal complex part, which is placed in the center of the aggregates, is extremely reduced.$^{10)}$

In conclusion, amphiphilic cobalt(III) complexes having one or two alkyl-chains can aggregate in solutions. A variety of amphiphilic metal complexes can be designed in the mixed ligand systems of cobalt(III) complexes by combinations of an appropriate ligand having no alkyl-chain and a ligand having an alkyl-chain. They could be useful in elucidating the unique effects of the metal complex on the aggregation behavior. The informations should be important in designing supramolecular assemblies of metal complexes having useful functions.

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