Preparation of Cobalt(III) and Nickel(II) Complexes Having an Alkyl Long Chain and Their Surface Tension Reducing Abilities

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Synopsis. Cobalt(III) and nickel(II) complexes having an alkyl long chain were newly prepared. The critical micelle concentration and surface tension-reducing ability largely depend on the length of the alkyl-chain, the position of its substitution on the ligand, and counter ions. Solvatochromism was observed for a nickel(II)–tetraamine complex having a dodecyl chain.

Organized molecular aggregates of synthetic amphiphiles have attracted much attention as a mimic of biological systems.[1] Metal complexes introduced in the aggregates have been shown to exert useful catalytic functions.[2] Therefore, amphiphilic metal complexes are promising as components of synthetic assemblies which can exert highly organized functions.[3]

We have previously reported that amphiphilic cobalt(III) complexes having an alkyl long-chain can aggregate in aqueous solutions at very low concentrations, and can exert remarkable surface tension-reducing abilities.[4] Such amphiphilic compounds provide an interesting problem: How does the structure of the huge polar head affect the aggregation behavior? Understanding the interrelationships between the molecular structure of an amphiphile and its organization is of fundamental interest. In the present study, cobalt(III) and nickel(II) complexes of *N*-alkylethylenediamine, 6-alkyl-2,3,2-tetramine, or 2-alkyl-1,3-propanediaminetetraacetate were prepared, and their aggregation was examined by surface-tension measurements.

Experimental

Preparation. *N*-Butylethylenediamine (*N*-Butyl-en), *N*-octylethylenediamine (*N*-Octyl-en), and *N*-dodecylethylenediamine (*N*-Dodecyl-en) were prepared by the reported procedures.[5] Dihydrochloride salts of these diamines were recrystallized from aqueous methanol. Anal. ($C_6H_{18}N_2Cl_2$, $C_{10}H_{26}N_2Cl_2$, $C_{14}H_{34}N_2Cl_2$) C, H, N, Cl.

2-Dodecyl-1,3-propanediaminetetraacetic Acid (2-Dodecyl-1,3-pdtaH$_4$). 2-Dodecylmalonic acid diethyl ester[3b] (15 g) was dissolved in methanolic ammonia (250 ml) and let standing for one week. The resulting precipitates were collected by filtration and dried in vacuo. The solid was treated with $LiAlH_4$ in THF by a reported procedure for the reduction of amides.[6] 2-Dodecyl-1,3-propanediamine was obtained by vacuum distillation (bp 88 °C/0.1 mmHg, 1 mmHg=133.322 Pa, 40%).

A propanol solution (20 ml) of the resulting diamine (6 mmol) was added to an aqueous solution (10 ml) of monochloroacetic acid (30 mmol) and sodium hydroxide (30 mmol), and stirred for 6 h at 85 °C. The addition of 1 equiv HCl gave white precipitates, which were collected by filtration then dried in vacuo (45%). Found: C, 57.90; H, 9.17; N, 5.95%. Calcd for $C_{23}H_{38}N_2O_8$: C, 58.21; H, 8.92; N, 5.90%.

2-Decyl-1,3-propanediaminetetraacetic Acid (2-Decyl-1,3-pdtaH$_4$) was prepared in a similar manner to that described above.

[Co(*N*-R-en)(2,3,2-tet[7])](ClO_4)$_3$ (R=H (1), Butyl (2), Octyl (3), Dodecyl (4)). [$CoCl_2$(2,3,2-tet)]ClO_4[8] (6 mmol) and *N*-R-en (6 mmol) were dissolved in DMSO (50 ml) and stirred for 12 h. 100 ml of water was added to the solution and poured on a column of SP-Sephadex C-25 (Na^+ form). Elution with a 0.5 mol dm^{-3} $NaClO_4$ aqueous solution, and subsequently with a 1 mol dm^{-3} $NaClO_4$ methanol–water (1 : 1) solution, produced an orange band. The concentration of the eluate from the band resulted in orange precipitates, which were collected by filtration and dried in vacuo.

[Co(*N*-Dodecyl-en)(2,3,2-tet)]Cl_3 (5). The method was similar to that described above, with the exception that the eluent for the development of the column was a NaCl solution.

[Co(6-Dodecyl-2,3,2-tet[9])(en)] (ClO_4)$_3$ (6) was prepared from [$CoCl_2$(6-Dodecyl-2,3,2-tet)]ClO_4[3b] and ethylenediamine (en) by a procedure similar to that described above.

K[Co(2-Dodecyl-1,3-pdta)] (7). To an aqueous solution (10 ml) of $CoCl_2\cdot 6H_2O$ (0.48 g), potassium acetate (1.18 g), and 2-Dodecyl-1,3-pdtaH$_4$ (1.20 g), 3% H_2O_2 (2 ml) was added dropwise at 60 °C and stirred for 20 min. The resulting oily products were separated from the solvent by decantation. Violet precipitates were obtained by the addition of ethanol to the oil. They were collected by filtration and recrystallized from water–methanol.

K[Co(2-Decyl-1,3-pdta)]·1.5H_2O (8) was prepared in a manner similar to that described above.

[$NiCl_2$(6-Dodecyl-2,3,2-tet)] (9). A methanol solution of 6-Dedecyl-2,3,2-tet was added to a methanol solution of equimolar amounts of $NiCl_2\cdot 6H_2O$. The concentration of the solution gave violet precipitates, which were collected by filtration.

[Ni(2-Dodecyl-1,3-pdta)(H_2O)]·0.5H_2O (10). To an aqueous solution of potassium salt of Dodecyl-pdta, an aqueous solution of $NiCl_2\cdot 6H_2O$ was added dropwise. The pH of the solution was adjusted to 7 using KOH, then stirred at 70 °C. After the reaction mixture was cooled, the addition of ethanol gave light-blue precipitates.

The yields and analytical data are summarized in Table 1.

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Table 1. Yields, Elemental Analyses (Calculated Values in Parentheses), and Electronic Spectral Data

No.	Yield/%	C	H	N		λ_{max}/nm (ε)
1	91	18.59	4.66	14.43		474(114)
		(18.71	4.89	14.55	$C_9H_{28}N_6O_{12}Cl_3Co$)	344(104)
2	71	24.59	5.53	13.20		486(130)
		(24.29	5.80	13.07	$C_{13}H_{36}N_6O_{12}Cl_3Co\cdot0.5H_2O$)	350(121)
3	79	29.24	6.07	12.02		486(128)
		(29.21	6.49	12.03	$C_{17}H_{44}N_6O_{12}Cl_3Co\cdot0.5H_2O$)	350(117)
4	37	34.03	6.88	10.79		482(147)
		(33.81	7.03	11.27	$C_{21}H_{52}N_6O_{12}Cl_3Co$)	349(197)
5	86	44.28	9.18	14.77		485(113)
		(44.10	9.52	14.69	$C_{21}H_{52}N_6Cl_3Co\cdot H_2O$)	350(111)
6	58	33.08	6.78	10.98		473(132)
		(33.02	7.12	11.00	$C_{21}H_{52}N_6O_{12}Cl_3Co\cdot H_2O$)	343(129)
7	49	48.43	7.08	4.88		554(112)
		(48.59	6.74	4.93	$C_{23}H_{38}N_2O_8KCo$)	380(110)
8	15	44.23	6.12	5.11		554(134)
		(44.44	6.57	4.94	$C_{21}H_{34}N_2O_8KCo\cdot1.5H_2O$)	378(125)
9	30	49.58	9.36	12.26		444(13)
		(49.81	9.68	12.23	$C_{19}H_{44}N_4Cl_2Ni$)	346(9.3)
10	36	43.64	6.70	4.76		555(5.8)shoulder
		(43.54	6.51	4.42	$C_{23}H_{40}N_2O_9K_2Ni\cdot0.5H_2O$)	444(13.3)
						346(9.3)

Measurements. The surface tension was measured by the Wilhelmy method at 28 °C using a Kyowakagaku A3 surface tension meter with a glass plate. Much attention was paid during preparation of solutions and measurements in order to prevent any contamination due to impurities. Purification of the compounds was repeatedly performed until the γ values were sufficiently reproduced, since even a small amount of an impurity often causes a significant deviation from the true value of a pure compound.(10)

Electronic spectra were obtained on a Shimadzu UV-160 double-beam spectrometer. The measurements were made on aqueous solutions at concentrations near to 10^{-3} mol dm^{-3} at room temperature. The electronic spectrum of a methanol solution of each complex is almost identical with that of an aqueous solution. Consequently, it does not seem that micellization greatly influences the structure of the polar head.

Results and Discussion

Cobalt(III) and nickel(II) complexes having an alkyl chain could be prepared by similar procedures for their nonsubstituted homologues. Electronic spectroscopy indicates that the structures of the complex parts of **2**—**6**, **7**—**8**, **9**, and **10** are similar to those of [Co(en)(2,3,2-tet)]$^{3+}$, [Co(edta)]$^{-}$,(11) [NiCl$_2$(2,3,2-tet)],(12) and [Ni(edta)(H$_2$O)]$^{2-}$,(13) respectively. ^{13}C NMR spectroscopy of cobalt(III) complexes (**1**—**8**) indicated that a single stereoisomer is obtained for each compound.

A solution of **9** showed different colors, depending on the solvent, due to interconversion between octahedral ([NiCl$_2$(6-dodecyl-2,3,2-tet)], violet) and square planar ([Ni(6-dodecyl-2,3,2-tet)]$^{2+}$, orange) species. The color of a chloroform solution is violet, and that of an aqueous or a methanol solution is orange. Figure 1 shows the equilibrium between the two species in methanol–chloroform mixtures. A similar interconversion is known regarding the thermochromic behavior of an aqueous solution of [NiCl$_2$(2,3,2-tet)].(12)

The surface tensions of aqueous solutions of **1**—**10** were measured by the Wilhelmy method, and are plotted against concentration in Figs. 2 and 3. The slopes of the curves for complexes having a dodecyl chain change abruptly, indicating aggregation in solutions. The cmc and γ_{cmc} estimated from the curves are summarized in Table 2, along with the area per molecule estimated from Gibbs' equation.(14) The cmc values for complexes having a dodecyl chain span the range of 1.14×10^{-3}—3.3×10^{-5} mol dm^{-3}.

The effect of the length of the alkyl chain is demonstrated by **1**—**4**. As the chain length increases, the surface tension of the solution becomes more effectively reduced. A similar trend was observed for organic cationic surfactants: *N*-alkylethylenediamine dihydrochloride (**11**—**14**).

The arrangement of the dodecyl chain against the polar head dramatically affects the surface tension-reducing ability, which is clearly evidenced by a comparison of **4** with **6**. **4** has an *N*-substituted dodecyl chain on

Table 2. Critical Micelle Concentration (cmc) and Surface Tension at cmc (γ_{cmc})

No.	Compound	cmc/ 10^{-5} mol dm^{-3}	γ_{cmc}/ mN m^{-1}	A/ Å molec^{-1}
1	[Co(en)(2,3,2-tet)](ClO$_4$)$_3$	(20)$^{\text{a)}}$	(45.3)$^{\text{a)}}$	—
2	[Co(*N*-Butyl-en)(2,3,2-tet)](ClO$_4$)$_3$	(20)$^{\text{a)}}$	(40.9)$^{\text{a)}}$	—
3	[Co(*N*-Octyl-en)(2,3,2-tet)](ClO$_4$)$_3$	20	36.1	404
4	[Co(*N*-Dodecyl-en)(2,3,2-tet)](ClO$_4$)$_3$ [4)]	3.3	25.4	310
5	[Co(*N*-Dodecyl-en)(2,3,2-tet)]Cl$_3$	114	30.5	195
6	[Co(6-Dodecyl-2,3,2-tet)(en)](ClO$_4$)$_3$	60	39.2	369
7	K[Co(2-Dodecyl-1,3-pdta)]	32	31.0	97.4
8	K[Co(2-Decyl-1,3-pdta)]	140	31.4	90.9
9	[NiCl$_2$(6-Dodecyl-2,3,2-tet)]	19	31.9	201
10	K$_2$[Ni(2-Dodecyl-1,3-pdta)(H$_2$O)]	33	32.5	191
11	en•2HCl	—	(61)$^{\text{b)}}$	—
12	*N*-Butyl-en•2HCl	—	(46)$^{\text{b)}}$	—
13	*N*-Octyl-en•2HCl	11000	40.6	136
14	*N*-Dodecyl-en•2HCl	1100	32.8	138

a) The surface tension-concentration curve did not show a clear break point. An approximate value is shown. b) The surface tension-concentration curve did not show a break point. A surface tension value of a 1 mol dm^{-3} solution is given.

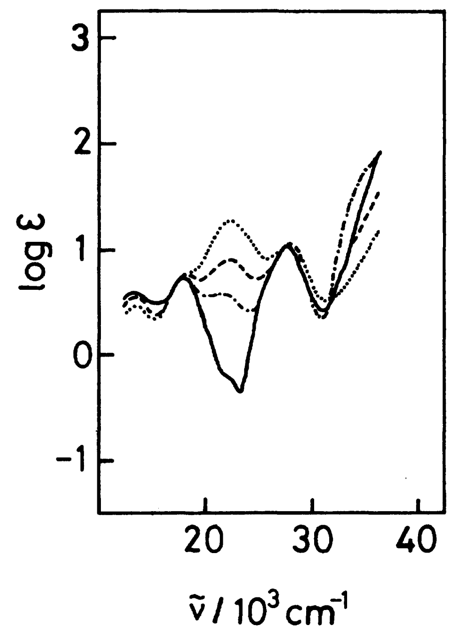

Fig. 1. Absorption spectra of **9**. ···· in MeOH, --- in MeOH–CHCl$_3$ (1 : 1), -·- in MeOH–CHCl$_3$ (2 : 1), and — in CHCl$_3$.

the diamine chelate, and **6** has a *C*-substituted one on the tetraamine chelate. γ_{cmc} of **6** is 13.8 mN m^{-1} higher than that of **4**. We recently reported that the chirality around the octahedral metal center of a cobalt(III) complex considerably affects the surface tension-reducing ability.[4b)] This may be attributed to a difference in steric packing of complexes which causes a different arrangement of the alkyl chain in the surface. The present result suggests that the mode of alkyl substitution on the ligand can contribute to this factor very effectively.

The effect of counter anions is also significant. **5** is a chloride salt of the same complex cation as **4** (a perchlorate salt). The cmc of **5** is 35-times higher than that of **4**, and γ_{cmc} of **5** is 5.1 mN m^{-1} higher than that of **4**.

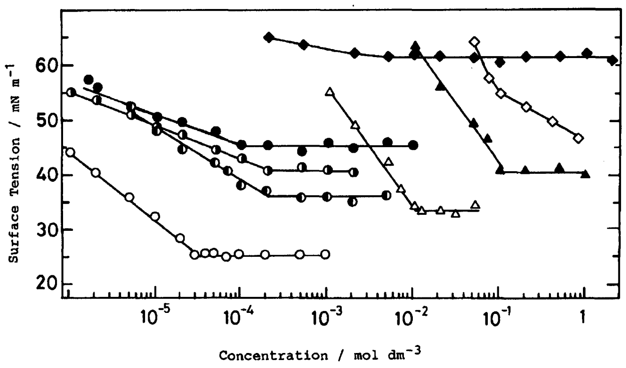

Fig. 2. Surface tension–concentration curves. ●: **1**, ◑: **2**, ◐: **3**, ○: **4**, ◆: **11**, ◇: **12**, ▲: **13**, and △: **14**.

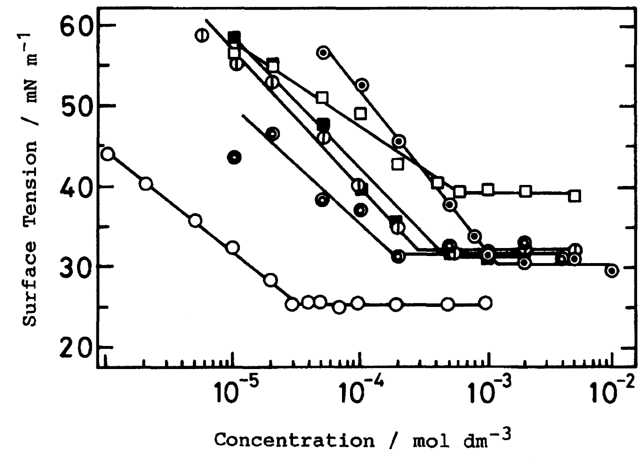

Fig. 3. Surface tension–concentration curves. ○: **4**, ◉: **5**, □: **6**, ■: **7**, ◎: **9**, and ⦶: **10**.

Anionic cobalt(III) complexes of the edta-type chelate (**7**) and nickel(II) complexes of the tetraamine (**9**) or the edta-type chelate (**10**) gives cmc and γ_{cmc} values in the range of those of the above-mentioned complexes (**4**—**6**). The surface tension–concentration plot for **9** deviates from linearity at low concentration (1×10^{-5} mol dm^{-3}), possibly due to a dissociation of the coordination bonds. It is important to note that plots for cobalt(III) complexes do not show such deviations. Therefore, the values of cmc and γ_{cmc} for cobalt(III) complexes clearly reflect the effect of the geometry of the complex part.

In conclusion, cobalt(III) and nickel(II) complexes having a dodecyl-chain showed clear break points in the surface tension–concentration curves, indicating their aggregation in aqueous solutions. A previous study concerning amphiphilic cobalt(III)- or nickel(II)-tetraamine complexes suggested that the geometry around the metal ion does not influence the cmc's very much.[3b] However, the present results indicate that the structure of the complex part can influence the cmc and γ_{cmc} considerably. Therefore, amphiphilic metal complexes are expected to be used to construct a variety of aggregation morphologies.

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