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Surface-active Organo Manganese and Cobalt Complexes(1+) Having a Long-chain Alkyl Group

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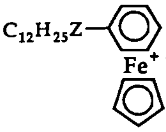
Surface-active tricarbonyl(dodecylamino- or dodecyloxo-benzene) manganese(1+) and (dodecylaminocarbonyl and dodecyloxycarbonyl) cobalticinium chlorides were prepared and their abnormally low cmc values and "redox-responsible" surface character were studied.

Ferrocenyl amphiphiles such as ω-ferrocenyl-alkyltrimethylammonium salts[1)] and alkylaminocarbonylferrocene have been of interest from the view point of micelle formation and thin-film preparation.[2-3)] The ferrocenyl moiety is charge neutral and easily oxidized to afford unstable ferrocenium cation in aqueous solution in air.[4)] Generally organotransition metal cationic complexes having long-chain alkyl group are unstable and could not be isolated, although such type of complexes were assumed to be reaction intermediate of, e. g., Oxo-type reactions.[5)] Recently, we reported the preparation and properties of (long-chain alkyl substituted benzene)(cyclopentadienyl)iron(1+) complexes (**1**) as a new model of surface-active organo transition metal complexes, which were chemically or electrochemically reduced irreversibly to surface-inactive products.[6-7)] In this letter, we provide new examples of surface-active organo-manganese (**2a-b**) and -cobalt cationic complexes (**3c-d**), the latter being a novel "redox-responsive" surfactant.



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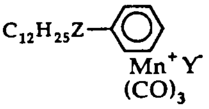

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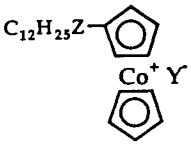

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a;Z=NH, b;Z=O, c;Z=NHCO, d;Z=OCO

The cationic complexes were prepared as follows: tricarbonyl(dodecylaminocbenzene)manganese(1+) hexafluorophosphate (**2a**; Y=PF_6) was obtained by the nucleophilic reaction of tricarbonyl(chlorobenzene)manganese(1+) hexafluorophosphate (0.2 g, 0.5 mmol) with dodecylamine (0.37 g, 2 mmol) in tetrahydrofuran (THF; 10 cm^3) for 4 h at room temperaure. The reaction mixture was passed through a diatom-earth column, followed by evaporation of THF. The residue was diluted with CH_2Cl_2 and dried ($MgSO_4$). Addition of diethyl ether precipitated **2a**. Yield 66%. Similarly, tricarbonyl(dodecyloxybenzene)manganese(1+) salt (**2b**) was prepared from sodium dodecanolate and the tricarbonyl(chlorobenzene)manganese(1+) complex. (Dodecylaminocarbonyl(**3c**), dodecyloxycarbonyl(**3d**),and docosanoxycarbonyl) cobalticinium hexafluorophosphates(**3d'**)$^{8)}$ were obtained by Shotten-Baumann's method.$^{6)}$ These hexafluorophosphates were insoluble in water but soluble in CH_2Cl_2, and used for cyclic voltammetry (sample $1X10^{-3}$ mol dm^{-3}, supporting electrite $Et_4N^+PF_6^-$ 0.1 mol dm^{-3}, scan rate 100 mV s^{-1}, in CH_3CN, Pt electrode, and vs. Ag/AgCl). The corresponding complex chlorides, prepared by passing through an anion-exchange column as methanol solution, were soluble in water and used for surface-(air/water) and interface-tension(water/$CHCl_3$) measurements at room temperature. The results are summarized in Table 1.

Table 1. Critical micelle concentration and cathodic potentials of the cationic organometallic complexes

Metal in complex	Compd. No.	Yield/% $^{a)}$	Mp/^oC $^{a)}$	Cmc/mmol dm^{-3} $^{b)}$	E_c/V $^{a)}$
Fe	**1a**	$94^{c)}$	77.0-8.7$^{c)}$	5.0	-1.35^e
Fe	**1b**	$73^{c)}$	53.0-5.2$^{c)}$	3.1	-1.21^e
Mn	**2a**	66	100.0-2.0	0.41	-1.03^e
Mn	**2b**	12	80.0-2.0	0.24	-0.96^e
Co	**3c**	85	140.5-2.5	0.15	-0.57^f
Co	**3d**	55	118.0-21.0	0.14	-0.47^f
$[C_{12}H_{25}N(CH_3)_3{}^+Br]$		-	-	$(16)^d$	$(< -2.5)^{d)}$

a) For PF_6^- salts. b) For Cl^- salts. c) Reference 5. d) Cited data.
e) Irreversible potentials. f) Reversivle potentials (redox-potentials).

The manganese complex chloride (**2a** or **2b**) and cobalt complex (**3c** or **3d**) showed abnormally low critical micelle concentrations (cmc; less than 0.1 mmol cm^{-3}), comparing to that of dodecyl(trimethyl) ammonium bromide (16 mmol dm^{-3}). Recently, Yosikawa et al. reported the low cmc value (0.04 mmol dm^{-3}) of N-dodecylethylenediamine)(triethylenetetraamine)cobalt(III) chloride by measuring the surface tension and turbidity at various concentrations of the complex, suggesting that introduction of a cationic metal complex into the hydrophilic part of amphiphile remarkably enchances the aggregation in aqueous solution.[9] The similar phenomena were observed in the cases of **2a**, **2b**, **3c**, and **3d**, while cmc values of the iron surfactants (**1a** and **1b**) were not low. The extreme molecular area of 1-docosanoxycarbonylcobalticinium (1+) hexafluorophosphate (**3d'**) was determined to be approximately 70-80 A^2 by Langmuir-Blodgett's method,[10-11] which is only as four times as that of carboxylic acid in solid-state film. Therefore, the reason why organotransition metal surfactants have abnormaly low cmc values in aqueous solution is not clear yet. The fact that surface tention of the manganese carbonyl surfactant (**2a** or **2b**) at cmc was unusually low (20-30 mN cm^{-1}) is noteworthy (Fig. 1).[12] In addition, as shown in Table 1, there may be a relation between the cathodic potentials and the hydrophilicities (or cmc values) of organotransition metal amphiphiles.

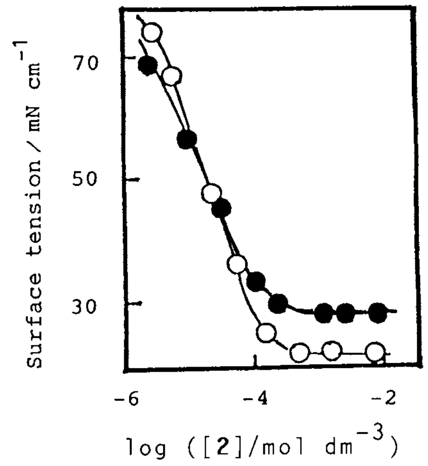
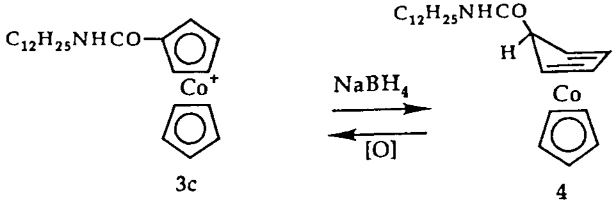


Fig. 1. Surface tension-[**2**] curves for the manganese complexes, **2a** (●) and **2b** (○).



The attractive nature of the cobalt surfactant (**3c**) is the novel example of "redox-responsible or -reversible" surfactant; **3c** was surface-active in air/water interface but inactive on treatment with aqueous $NaBH_4$. The reduced cobalt(II) complex (**4**) was isolated and found to be suface-inactive in $CHCl_3$/pure water interface. The complex **4** returned to be surface-active in $CHCl_3$/aq.H_2O_2-HCl interface, where **4** was oxidized to **3c**.[10] Detail studies are now in progress.

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References

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4) The unsubstituted ferrocenium salt is stable for several weeks in aq. soln. at room temperature, while the long-chain alkyl derivatives of ferrocene are unstable and decomposed in one hour under the same reaction conditions.

5) R.P.Houghton,"Metal complexes in Organic Chemistry," Cambridge Univ. Press, London(1979), p.283

6) S. Sakai, H. Kozawa, Y. Yoshinaga, K. Kosugi, S. Fukuzawa, and T. Fujinami, J. Chem. Soc., Chem. Commum., 1988, 663.

7) The iron complex(III) (**1**; Y=Cl) is stable for several days in aq. soln. in dark at room temperature. However, the reduced form was unstable and decomposed.

8) **2a** (Y=PF_6): ν_{CO} 2000, 1960, and 1920 cm^{-1}. ^1H NMR $[(CD_3)_2CO]$ δ 7.15-6.50 (m, 5H, C_6H_5), 6.35 (m, 2H, NCH_2), 1.23 (br s, 20H, CH_2), and 0.89 ppm (br t , 7 Hz, CH_3). Found: C, 46.53; H, 5.66%. Anal. Calcd for $C_{21}H_{31}NO_3F_6PMn$: C, 46.25; H, 5.73%. **2b** (Y=PF_6): ν_{CO} 2050, 1980, and 1940 cm^{-1}. ^1H NMR δ 5.82-6.18 (m, 5H, Arom.), 3.37 (t, 7 Hz, 2H, OCH_2), 1.25 (br s, 20H, CH_2), and 0.82 ppm (t, 7 Hz, 3H, CH_3). Anal. Found: C, 46.41%; H, 5.37%. Calcd for $C_{21}H_{30}O_4F_6PMn$: C, 46.16%; H, 5.53%. **3c**, **3d**, and **3d'**(Y=PF_6) were also identified by IR, NMR, and elemental analyses.

9) M. Yashiro, K. Matsumoto, and S. Yoshikawa, Chem. Lett., 1989, 985.

10) S. Sakai, H. Kozawa, K. Kosugi, S. Fukuzawa, T. Fujinami, and H. Saeki, The 19th World Congress of The Internat. Soc. for Fat Research, Sept. 1988, Tokyo.

11) Because the solid film of **3** (Y=PF_6) could not be obtained by LB method, the molecular area of **3d'** was used intsed of that of **3**.

12) Surface tention was measured by Wilhelmy's method for aqueous solution of about 15 °C and by using a glass plate, on which the complexes (**2a** and **2b**) were decomposed. Therefore, Pt-plate was used in these cases.

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