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Interactions of Some Cationic Cobalt(III) Complexes with Anions Studied by the ^{59}Co NMR Chemical Shifts

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Synopsis. The NMR peak of ^{59}Co(III) cationic complexes shifts upfield upon interacting with anions when the interaction is mainly electrostatic; it shifts downfield when the hydrophobic interaction acts additively with the electrostatic interaction. These trends are enhanced in micellar solution systems.

^{59}Co NMR spectroscopy has provided useful information concerning the interactions of cobalt(III) complexes in solutions with either counterions or solvents.[1,2] The use of this tool for ion association is limited to only a few kinds of the complexes, such as $[Co(en)_3]^{3+}$ (en = ethylenediamine)[3—5] and $[Co(CN)_6]^{3-}$ ones;[6] furthermore, although that for a micellar solution is little used, one of the present authors studied the interactions of $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ in amphiphilic liquid crystalline solutions.[7] There is a merit for studying ionic interactions in a system containing cobalt(III) complexes, since various kinds of cobalt(III) complex cations and anions are useful for observing how electrostatic interactions govern the binding, and to examine what interactions are effective in addition to the electrostatic ones.[8] The present study is part of our continuing studies concerning the specific interactions of cobalt(III) complexes with anions, including detergents.[7,8] We used such cobalt(III) complexes as $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)(NH_3)_5]^{2+}$, $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$ (bpy=2,2′-bipyridine), and $[Co(phen)_3]^{3+}$ (phen = 1,10-phenanthroline). All of them were studied in sulfate solutions; some of them were studied in amphiphilic solutions. The added electrolytes used were sodium sulfate, sodium 1-hexanesulfonate, sodium benzenesulfonate, and a few kinds of detergents. The difference between the 1-hexanesulfonate and the benzenesulfonate is that the former amphiphile forms micelles below 1.0 mol dm^{-3},[9,10] while the latter does not, even at 4.5 mol dm^{-3}.[11] Specific interactions between the cationic complexes and the anions are expected to appear by using various kinds of ligands.

Experimental

Materials. The cobalt(III) complexes ($[Co(NH_3)_6]Cl_3$,[12] $[Co(NO_2)(NH_3)_5]Cl_2$,[13] $[Co(en)_3]Cl_3\cdot 3H_2O$,[14] $[Co(bpy)_3]Cl_3\cdot 3H_2O$,[15] and $[Co(phen)_3]Cl_3\cdot 7H_2O$,[16]) were prepared according to standard literature procedures. The sodium sulfate was a guaranteed reagent of Wako Pure Chemical Industries, Ltd. The sodium benzenesulfonate and 1-hexanesulfonate (a practical grade from the same company) were recrystallized from a water–ethanol solution and dried in vacuo. Potassium dodecanoate (KDodec) was prepared from dodecanoic acid by neutralization with potassium hydroxide, followed by recrystallization from ethanol (95%) several times. Cesium *N*-dodecanoyl-L-alaninate[17] (CsDDA) was prepared by a standard method, and the purification (absence of the dodecanoate) was confirmed by using ^{13}C NMR spectrum. Tetradecyltrimethylammonium bromide (TDTMABr) was obtained from Sigma Co., and was recrystallized twice from their ethyl acetate–ethanol solutions.

NMR Measurements. The ^{59}Co NMR spectra were obtained on a JEOL GX-270 FT NMR spectrometer operating at 64.1 MHz. The temperature of the sample solution was controlled to 27±0.5°C.

The concentrations of all the cobalt(III) complexes were adjusted to 5×10^{-3} mol dm^{-3}.

Results and Discussion

1. ^{59}Co Chemical Shifts for the Complexes in Sulfate Solutions. The effects of the sulfate ion on the ^{59}Co chemical shifts of the cationic cobalt(III) complexes are shown in Fig. 1. The interactions with the sulfate ion caused the ^{59}Co chemical shift upfield for all of the complexes. The magnitude of the change was in the order $[Co(en)_3]^{3+} > [Co(NO_2)(NH_3)_5]^{2+} > [Co(NH_3)_6]^{3+} > [Co(bpy)_3]^{3+} > [Co(phen)_3]^{3+}$. This order

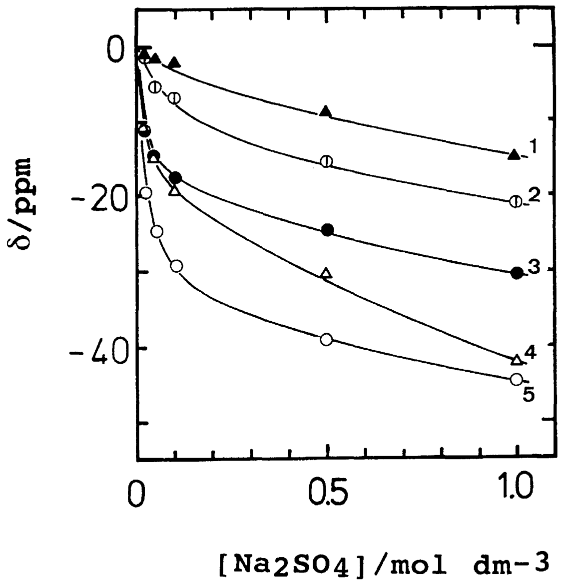

Fig. 1. Cobalt-59 chemical shifts for some cobalt(III) cationic complexes as a function of the sulfate concentrations. The numbering indicates the following complexes: 1: $[Co(phen)_3]^{3+}$, 2: $[Co(bpy)_3]^{3+}$, 3: $[Co(NH_3)_6]^{3+}$, 4: $[Co(NO_2)(NH_3)_5]^{2+}$, 5: $[Co(en)_3]^{3+}$.

is governed by the extent of the ion association and by the sensitivity of the chemical shift to the ion association. The extent of the ion association of the sulfate ion with these complexes, except for the pentaamminenitro complex, has been reported by one of the present authors.[8] The ion-association constant for the pentaamminenitrocobalt(III) complex has been reported by Masterton and Bierly.[18] The resulting order was $[Co(NH_3)_6]^{3+}$ ($\log K=3.02$, at ionic strength$=0.01$) $>$ $[Co(en)_3]^{3+}$ ($\log K=2.79$) $>$ $[Co(NO_2)(NH_3)_5]^{2+}$ (2.42) $>$ $[Co(bpy)_3]^{3+}$ (2.09) $>$ $[Co(phen)_3]^{3+}$ (1.98). When this order is compared with that for the chemical shift shown above, the larger chemical shifts were observed for the pentaamminenitro and tris(ethylenediamine) complexes. In these complexes, therefore, the ^{59}Co chemical shifts seem to have a higher sensitivity to the change in the ionic atmosphere than the chemical shifts in the other complexes.

2. ^{59}Co Chemical Shifts for the Complexes in the 1-Hexanesulfonate and Benzenesulfonate Solutions. The addition of 1-hexanesulfonate anions caused a downfield shift of the cobalt-59 spectra for those complexes having hydrophobic ligands, such as phen (Fig. 2). For a bpy complex whose hydrophobicity is less than that of the phen complex, the magnitude of the chemical shift change was less than that for the phen complex. As has been revealed by a ^{13}C NMR study for the interaction between the 1-hexanesulfonate ions and the $[M(phen)_3]^{2+}$ (M=Fe, Ni),[19] the hydrophobic ion interacts with the micelles through their hydrophobic regions. Furthermore, it has been revealed that the $[Fe(phen)_3]^{2+}$ complex is associated with the premicellar aggregations of the dodecanesulfonate stepwise in aqueous solutions.[20] Similarly, the hydrophobic association between the $[Co(phen)_3]^{3+}$ and 1-hexanesulfonate ion gradually proceeds in preference to the electrostatic association between the $[Co(phen)_3]^{3+}$ and 1-hexanesulfonate micelles. The ^{59}Co chemical shift is therefore more closely related to the formation of the $[Co(phen)_3]^{3+}$ $(\text{1-hexanesulfonate})_n$ aggregates, rather than the electrostatic interactions with the micelles of the 1-hexanesulfonate. For the less hydrophobic $[Co(bpy)_3]^{3+}$, the electrostatic interactions with the 1-hexanesulfonate micelles may be comparable to the hydrophobic ones; the curve in Fig. 2 for the bpy complex thus seems to be a result of the two kinds of the interactions (electrostatic and hydrophobic) with 1-hexanesulfonate. The characteristic effect was observed for the hydrophilic en complex ($[Co(NH_3)_6]^{3+}$ is precipitated in the 1-hexanesulfonate solutions). Figure 2 shows that the chemical shift starts to change from about 0.5 mol dm^{-3}, the cmc of the 1-hexanesulfonate.[9] Below this concentration, although the complex will interact with nearly free 1-hexanesulfonate ions through electrostatic interactions, this anion is only slightly effective concerning the ^{59}Co chemical shift. Above this concentration, the gradual upfield shift with an addition of the 1-hexanesulfonate shows that the electrostatic interactions between the hydrophilic $[Co(en)_3]^{3+}$ complex and the 1-hexanesulfonate become effective on the ^{59}Co chemical shift due to the formation of 1-hexanesulfonate micelles.

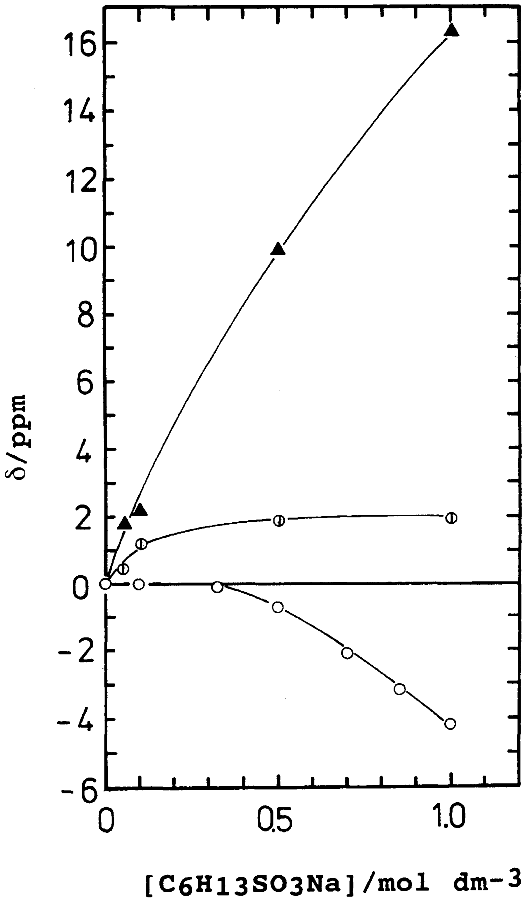

Fig. 2. Dependences of the cobalt-59 chemical shifts on the 1-hexanesulfonate concentrations (▲: $[Co(phen)_3]^{3+}$, ⦶: $[Co(bpy)_3]^{3+}$, ○: $[Co(en)_3]^{3+}$.

The results for the sulfate and the 1-hexanesulfonate systems thus suggest that the hydrophobic interaction of the cobalt(III) complexes with the anions makes the ^{59}Co NMR signal shift downfield, while the electrostatic one causes it to shift upfield.

Since conductivity measurements detected specific interactions between the hydrophobic cobalt(III) complex cations and the benzenesulfonate ion,[8] this system was also studied. Figure 3 shows the effect of benzenesulfonate on the ^{59}Co NMR chemical shifts of the cobalt(III) complexes. The results for both the $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ complexes are similar to those in the 1-hexanesulfonate systems. In these cases it is thus reasonable to consider that hydrophobic interactions are effective. However, even hydrophilic $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ complexes have also been shown to shift downfield. To explain the result, we must consider the difference between the 1-hexanesulfonate solution and the benzenesulfonate one; in the former system, the formation of micelles was detected at around 0.5

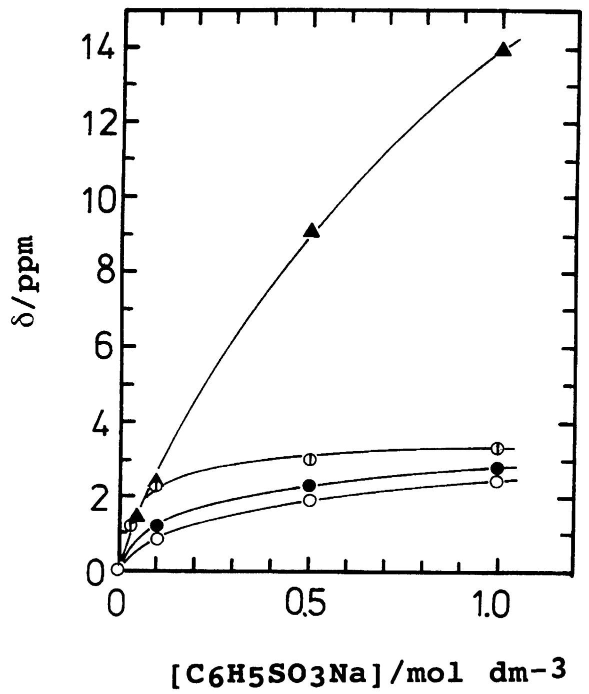

Fig. 3. Dependences of the cobalt-59 chemical shifts on the benzenesulfonate concentrations (▲: [Co(phen)$_3$]$^{3+}$, ⦶: [Co(bpy)$_3$]$^{3+}$, ○: [Co(en)$_3$]$^{3+}$, ●: [Co(NH$_3$)$_6$]$^{3+}$.

mol dm^{-3},[9,10] while no aggregations were detected in the latter system.[11] This difference is due to the less hydrophobicity of the phenyl group. The interactions of the cobalt(III) complexes with 1-hexanesulfonates are therefore sometimes affected by the formation of micelles, while those with the benzenesulfonates are not. Since the benzenesulfonate ion is also bulky, its electrostatic effect on the chemical shift should be much less than that of the sulfate and of the 1-hexanesulfonate-micelle. For such a weakly interacting system (when the chemical shift change is around 2—3 ppm), the rule proposed above for the direction of the chemical shift is not simply applicable.

In summary, the ^{59}Co chemical shift was changed from upfield to downfield in the order [Co(en)$_3$]$^{3+}$ > [Co(bpy)$_3$]$^{3+}$ > [Co(phen)$_3$]$^{3+}$ in both 1-hexanesulfonate and benzenesulfonate solutions; in the former case, the differences between the complexes were enlarged because of the formation of micelles.

3. ^{59}Co Chemical Shifts in Detergent Solutions. The ^{59}Co NMR spectra of the cobalt(III) complexes were also studied regarding measurements in detergent systems. The ammine complexes formed precipitates with detergents in dilute solutions; the spectrum of the bpy complex was too broad to be detected in the detergent solutions, since the linewidth of the bpy complex is as much as 4 kHz, even in dilute solutions. We thus used [Co(en)$_3$]$^{3+}$ and [Co(phen)$_3$]$^{3+}$ complexes as a hydrophilic ion and a hydrophobic one, respectively. Figure 4 shows the change in the chemical shift of the complexes in the anionic and cationic detergent systems. Steep upfield or downfield shifts were observed in the KDodec system at around the critical micelle concentration of 2.4×10^{-2} mol dm^{-3}.[21] These changes in the chemical shift also follow the trend described in the above-mentioned simpler electrolyte solutions, i.e., interactions of the hydrophilic complexes with amphiphilic anions caused an upfield shift of the ^{59}Co NMR spectra, while those of complexes having hydrophobic ligands caused a downfield shift. The result shown in Fig. 4 thus suggests that [Co(phen)$_3$]$^{3+}$ strongly interacts with anionic micellar solutions, probably through a hydrophobic interaction with the hydrocarbon shells of the micelles, rather than being adsorbed on their hydration sheaths. In these detergent systems, the downfield shifts are also sensitive to the micelle formation. This means that the cooperative effects of the electrostatic and hydrophobic interactions are more effective in the aqueous solutions of amphiphiles having a longer alkyl chain. A larger change in the chemical shift of the carboxylate system (KDodec) than in the alaninate one (CsDDA) suggests that the carboxylate head

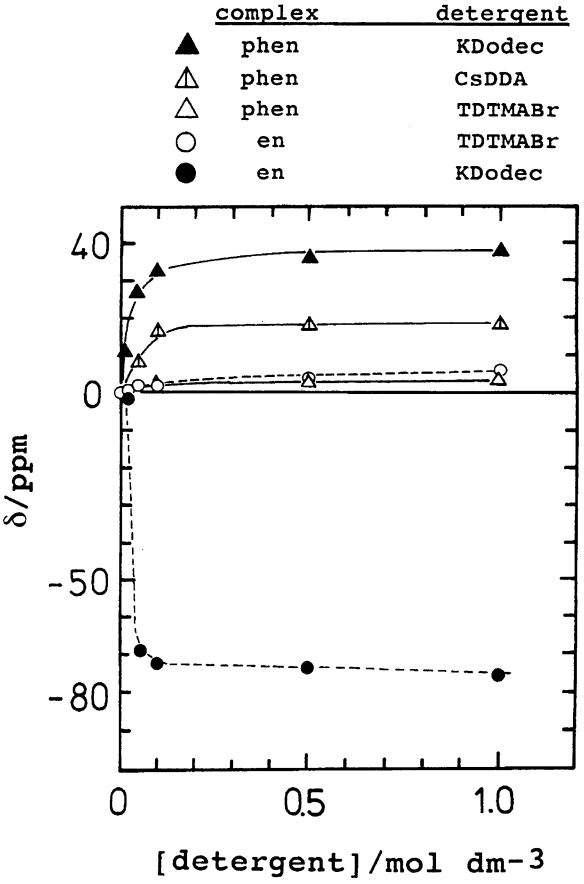

Fig. 4. Dependences of the cobalt-59 chemical shifts on the detergent concentrations for the [Co(en)$_3$]$^{3+}$ (abbreviated as en) and [Co(phen)$_3$]$^{3+}$ (as phen) complexes.

group facilitates an interaction with cobalt(III) cationic complexes more than the alaninate one does. Such a difference between the two head groups was also observed for the ^{59}Co quadrupole splittings and chemical shifts in the $[Co(en)_3]^{3+}$ complex, based on a comparison between nematic lyomesophase comprising KDodec and that comprising CsDDA.[22)] Small changes in the TDTMABr system for both the cobalt(III) complexes must be due to weak interactions of the complexes with the bromide ions, as has been observed for simple aqueous solution of $[Co(en)_3]Cl_3$.[4)]

In conclusion, the ^{59}Co NMR chemical shift is a good probe to monitor interactions of cationic cobalt(III) complexes with various anions in systems where the electrostatic and hydrophobic interactions cooperate extensively.

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