Proton Chemical Shift Study of the Hydrophobic Interaction between Tris(1,10-phenanthroline)ruthenium(II) Ions in Aqueous Solutions

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The proton NMR chemical shifts were measured in the D_2O solutions of $[Ru(phen)_3]SO_4$. The proton resonances of the phenanthroline ligand showed up-field shifts with increasing concentration of $[Ru(phen)_3]SO_4$, but they were not significantly affected by the addition of Na_2SO_4. The profile of the up-field shifts for the *Λ*-$[Ru(phen)_3]SO_4$ solution was different from that for the *rac*-$[Ru(phen)_3]SO_4$ solution. These results prove that the up-field shifts were caused by the interaction between $[Ru(phen)_3]^{2+}$ ions. Assuming the formation of the triple and quadrupole aggregates containing two $[Ru(phen)_3]^{2+}$ ions, the association constants of these aggregates and the up-field shifts of the proton signals in the aggregates were determined. A probable structure of the aggregates was deduced from the measured chemical shifts by attributing the up-field shift in the aggregates to the ring-current effect of the phenanthroline ligand. The importance of the hydrophobic interaction between $[Ru(phen)_3]^{2+}$ ions in aqueous solution was thus indicated.

Tris(1,10-phenanthroline) complex ions of bivalent metals, $[M(phen)_3]^{2+}$, are known to be hydrophobic with respect to their hydration[1,2] and also with respect to their interaction with hydrophobic anions in aqueous solutions.[3,4] The ion-pair between the complex cation and the alkanesulfonate anion shows an anomalously large ion-association constant[3] and has a structure which demonstrates the importance of the hydrophobic interaction between these ions.[4] Moreover, the $[Fe(phen)_3]^{2+}$ ions interact with alkyltrimethylammonium ions of a large alkyl group to form cation-cation pairs in aqueous solutions.[5] These findings suggest that the hydrophobic nature of the phenanthroline ligands might cause some mutual interaction between the ions of the $[M(phen)_3]^{2+}$type.

The object of the present study is to investigate how the $[M(phen)_3]^{2+}$ ions interact with each other. We observed the proton NMR of the 1,10-phenanthroline ligand of $[Ru(phen)_3]^{2+}$in aqueous solutions; evidence was obtained for a noticeable cation-cation interaction and information was gained about the structure of the aggregate containing two $[Ru(phen)_3]^{2+}$ ions.

Experimental

Materials. The preparation of tris(phenanthroline)-ruthenium(II)[6] and -cobalt(III)[7] chlorides and optical resolution for obtaining *Λ*-$[Ru(phen)_3]^{2+}$[8] were performed by the literature methods. The sulfate of each metal complex was obtained by double decomposition of Ag_2SO_4 and the chloride of the complex.

NMR Measurements. The ^1H NMR spectra were obtained on a JEOL FX-100 Fourier-transform spectrometer operating at 100 MHz with the D_2O and CD_3OD solutions of $[M(phen)_3](SO_4)_n$ (M=Ru(II) and Co(III)) at 28.0±0.5 °C. The chemical shifts, δ, were measured in ppm down-field from the central peak of the triplet resonance of the tetramethylammonium ion, which was added in the form of the nitrate as the internal reference. The concentration of the tetramethylammonium ion was 1/20 of that of the metal complex ion. The sample solutions for measuring NMR were prepared as follows. The sulfate of the metal complex was dissolved in D_2O and dried up by a rotary evaporator at room temperature. This procedure was repeated. The resulting complex salt was dissolved in D_2O. The methanol solutions were prepared in a similar manner, with CD_3OD in place of D_2O.

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Results and Discussion

Effect of the Ion-Ion Interaction on the Proton Chemical Shifts of the Ligands in $[Ru(phen)_3]^{2+}$. Figure 1 shows the representative examples of the proton NMR spectrum for the phenanthroline ligand of $[Ru(phen)_3]SO_4$ in D_2O. Different profiles of the spectra are found for different concentrations of the complex salt. The concentration dependence of the chemical shift was greatest for protons in the 5 and 6 positions. The dependences of the proton shifts on the concentration of $[Ru(phen)_3]SO_4$ in D_2O and CD_3OD are quantitatively shown in Fig. 2, where $\Delta\delta$ indicates the down-field shift with reference to each δ value at infinite dilution, $\delta(0)$. Each proton signal of the phenanthroline ligand of $[Ru(phen)_3]^{2+}$ in D_2O showed monotonous up-field shifts with increasing concentration of $[Ru(phen)_3]SO_4$. The magnitude of the up-field shifts increased in the order of the 2,9<3,8<4,7<5,6 positions of the protons.

If these up-field shifts were caused by the interaction with the sulfate ion, a similar change of the proton shifts of the phenanthroline ligands should be observed when Na_2SO_4 are added to the solution of $[Ru(phen)_3]SO_4$. However, only slight changes were observed in the proton shifts on the addition of Na_2SO_4 (up to about 0.25 mol dm^{-3}) to 0.0025 mol dm^{-3} $[Ru(phen)_3]SO_4$ solution in D_2O (Fig. 2, ◑). This indicates that the up-field shifts with the increase in the concentration of $[Ru(phen)]_3]SO_4$ (Fig. 2, ●) are not due to the interaction with the sulfate ion.

Then the change in the proton shifts may have arisen from interaction of $[Ru(phen)_3]^{2+}$ ions with each other.

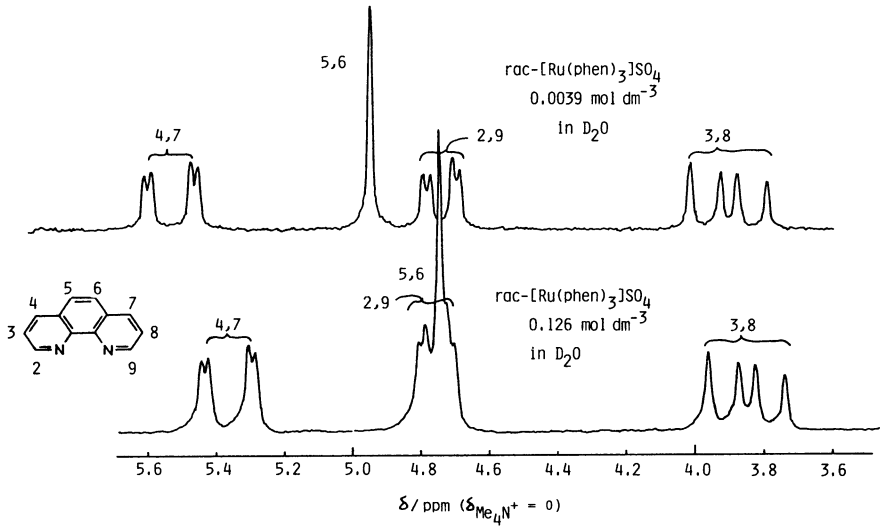

Fig. 1. ^1H NMR spectra of *rac*-$[Ru(phen)_3]SO_4$ in D_2O. (A) 0.0039 mol dm^{-3}. (B) 0.126 mol dm^{-3}. The chemical shift, δ, represents the down-field shift from the proton resonance of Me_4N^+.

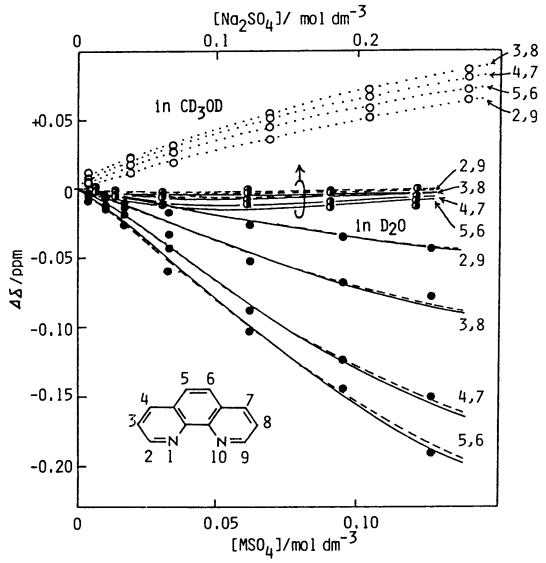

Fig. 2. Plots of the $\Delta\delta$ values *vs.* the concentration of *rac*-$[Ru(phen)_3]SO_4$ in D_2O (●) and in CD_3OD (○), and *vs.* the concentration of Na_2SO_4 added to 0.0025 mol dm^{-3} *rac*-$[Ru(phen)_3]SO_4$ in D_2O (◑). Broken and solid lines indicate the $\Delta\delta$ values calculated with the $\Delta\delta_{t,q}$ values for ion-size parameters, $a=10$ and 12 Å, respectively (Table 1).

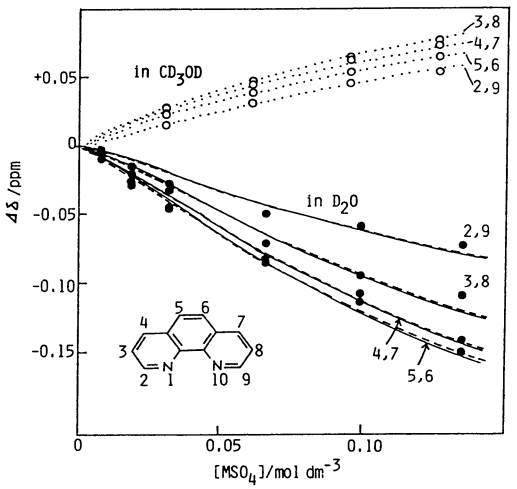

Fig. 3. Plots of the $\Delta\delta$ values *vs.* the concentration of Λ-$[Ru(phen)_3]SO_4$ in D_2O (●) and in CD_3OD (○). Broken and solid lines indicate the $\Delta\delta$ values calculated with the $\Delta\delta_{t,q}$ values for ion-size parameters, $a=10$ and 12 Å, respectively (Table 1).

Hydrophobic interaction between the ions may outweigh the coulombic repulsion between them. In order to confirm this, the proton shifts of the phenanthroline ligand were measured with optically active Λ-$[Ru(phen)_3]SO_4$ at various concentrations in D_2O (Fig. 3, ●). While the trend of the changes in the proton shifts of Λ-$[Ru(phen)_3]SO_4$ is similar to that for *rac*-$[Ru(phen)_3]SO_4$, the magnitudes of the changes are distinctly different. This difference between the racemate and the optical isomer indicates that these up-field shifts are caused by the interaction between two $[Ru(phen)_3]^{2+}$ ions. Either the manner of their interaction or the equilibrium constant for the aggregate formation may differ between the aggregate of a Λ and a Λ-$[Ru(phen)_3]^{2+}$ ion and that of two Λ ions. A further discussion of this problem will be given below.

In the CD_3OD solution of $[Ru(phen)_3]SO_4$, on the other hand, the proton resonances of the phenanthroline ligands (Fig. 2, ○) showed small down-field shifts with increasing concentration of the complex salt, and no meaningful differences were detected between the Λ isomer and the racemate. The D_2O solutions of $[Co(phen)_3](SO_4)_{3/2}$ showed only slight down-field shifts (within 0.02 ppm) when the concentration of the complex salt increased up to 0.1 mol dm^{-3} and when Na_2SO_4 was added up to 0.25 mol dm^{-3}. These results indicate that no significant short-range interaction exists

between the metal complex ions in these solutions. The stronger electrostatic repulsion between the complex cations in methanol solutions and that between the tripositive cations of the cobalt complex most probably prevented the complex ions from approaching each other.

Quantitative Treatment of the Proton Chemical Shifts. For the quantitative treatment of the proton shifts of $[Ru(phen)_3]SO_4$ in D_2O, the equilibria between chemical species existing in the solution are considered. The $[Ru(phen)_3]^{2+}$ ion forms the 1:1 ion-pair with the sulfate ion:

$$M + X \rightleftharpoons MX, \tag{1a}$$

where M, X, and MX indicate the $[Ru(phen)_3]^{2+}$ ion, the sulfate ion, and their ion-pair, respectively. The ion association constant at infinite dilution, K, is expressed by:

$$K = \frac{[MX]}{y_M y_X [M][X]}, \tag{1b}$$

where y_M and y_X represent the activity coefficient of each species. Among the species containing two $[Ru(phen)_3]^{2+}$ ions, the aggregate only of two $[Ru(phen)_3]^{2+}$ ions, M_2, is less probable than the triple ions, M_2X, and the quadrupole ions, M_2X_2, because of the large coulombic repulsion between the ions. Thus, the formation of the M_2 ion-pair is disregarded here. Equilibria and equilibrium constants for M_2X and M_2X_2 are:

$$MX + M \rightleftharpoons M_2X, \tag{2a}$$

$$K_t = \frac{y_{M_2X}[M_2X]}{y_M[MX][M]}, \tag{2b}$$

$$M_2X + X \rightleftharpoons M_2X_2, \tag{3a}$$

$$K' = \frac{[M_2X_2]}{y_X y_{M_2X}[M_2X][X]}, \tag{3b}$$

$$2MX \rightleftharpoons M_2X_2, \tag{4a}$$

$$K_q = \frac{[M_2X_2]}{[MX]^2}. \tag{4b}$$

The following relation exists between the four association constants:

$$\frac{K_q}{K_t} = \frac{K'}{K}. \tag{5}$$

For the sake of simplicity, we assume that the value of K' is equal to K. This assumption is justified as an approximation if the ion association in Eqs. la and 3a is caused by electrostatic interaction. Since both K and K' are association constants between dipositive and dinegative ions, it can be expected that their values are nearly equal. Substituting $K'=K$ in Eq. 5, we obtain $K_t=K_q$. This result is also reasonable even if hydrophobic interaction between two $[Ru(phen)_3]^{2+}$ ions is involved in the aggregation shown by Eqs. 2a and 4a. Similar results were obtained by Yokoyama and Yamatera by measuring the vapor pressure of aqueous $[Ru(phen)_3]SO_4$ solutions.[9]

Next, we consider the $\Delta\delta$ value for each aggregate. As shown in Fig. 2, the addition of sodium sulfate had only trivial effects on the proton shifts of $[Ru(phen)_3]^{2+}$. Therefore, we assume that the change in each proton chemical shift of the $[Ru(phen)_3]_2^{+}$ ion in D_2O is solely caused by the interaction between the $[Ru(phen)_3]^{2+}$ ions. We further assume for simplicity's sake that the $\Delta\delta$ values are the same for M_2X and M_2X_2 and denote them by $\Delta\delta_{t,q}$. This assumption is justified if the formation of these aggregates is essentially caused by the hydrophobic interaction between the $[Ru(phen)_3]^{2+}$ ions. Then, the observed $\Delta\delta$ value is represented by:

$$\Delta\delta = (x_t + x_q)\Delta\delta_{t,q}. \tag{6}$$

Here x_t and x_q denotes the mole fractions of $[Ru(phen)_3]^{2+}$ existing in the forms of the M_2X and M_2X_2 aggregates, respectively, defined by:

$$x_t = 2[M_2X]/c_M \text{ and } x_q = 2[M_2X_2]/c_M,$$

where c_M is the total concentration of $[Ru(phen)_3]^{2+}$.

If the K value (Eq. lb) is known,[9] we have here two unknown parameters, $\Delta\delta_{t,q}$ and K_t $(=K_q)$. (The activity coefficient, y, was calculated with the Debye-Hückel equation). The unknown parameters for the racemic solution, $K_t(rac)$ $(=K_q(rac))$ and $\Delta\delta_{t,q}(rac)$ and those for the Λ-isomer solution, $K_t(\Lambda)$ $(=K_q(\Lambda))$ and $\Delta\delta_{t,q}(\Lambda)$ were determined so as to give the best fit to the measured proton shifts for the racemic and the Λ-isomer solutions, respectively. The association constant obtained for the racemic solution, $K_t(rac)$ $(=K_q(rac))$, was practically identical with that for the Λ-isomer solution, $K_t(\Lambda)$ $(=K_q(\Lambda))$. The *rac*-$[Ru(phen)_3]SO_4$ solution contains two chemically different species of paired $[Ru(phen)_3]^{2+}$ ions, Δ-Δ and Λ-Λ (or Δ-Δ). The approximate equality of $K_t(rac)$ and $K_t(\Lambda)$ indicates that no significant difference exists between the values of the association constants for the Δ-Λ pair $(K_t(\Delta\text{-}\Lambda))$ and for the Λ-Λ pair $(K_t(\Lambda\text{-}\Lambda))$. This gives the relation:

$$\Delta\delta_{t,q}(rac) = (1/2)[\Delta\delta_{t,q}(\Delta\text{-}\Lambda) + \Delta\delta_{t,q}(\Lambda\text{-}\Lambda)]. \tag{7}$$

With Eq. 7, we obtained the $\Delta\delta_{t,q}(\Delta\text{-}\Lambda)$ value from the experimental values of $\Delta\delta_{t,q}(rac)$ and $\Delta\delta_{t,q}(\Lambda)(=\Delta\delta_{t,q}(\Lambda\text{-}\Lambda))$. Table 1 summarizes the association constants and the chemical-shift changes for M_2X and M_2X_2 in each case, where the ion-size parameter (a) in Debye-Hückel equation is assumed to be 10 or 12 Å[10] (1 Å= 10^{-10} m). The values in Table 1 were used to calculate the gross $\Delta\delta$ values for each solution (broken and solid lines in Figs. 2 and 3).

In the case of the Δ-Λ aggregate, the proton up-field shifts strongly depend on the position of the proton in the phenanthroline ligand; the magnitude of the up-field shifts increases in the order of 2,9<3,8<4,7<5,6. For the Λ-Λ aggregate, the up-field shifts were less strongly dependent on the position of the proton, although the order was the same as the Δ-Λ case. These results can be taken as the evidence for the operation of short-range interaction between the cations.

The Structure of the Aggregate Containing Two [Ru(phen)$_3$]$^{2+}$ Ions. The up-field shifts in the M_2X and M_2X_2 aggregates probably result from the ring-current effect[11] of the phenanthroline ligand. Such up-field shifts were previously observed for the ^{13}C chemical shifts of the hexanesulfonate ion in the ion-pair with the $[Fe(phen)_3]^{2+}$ ion,[4] and on the methyl proton shift of the amino acid with a large alkyl group in a mixed-ligand Zn(II) complex containing phenanthroline.[12] If

Table 1. The up-field shifts of the protons in the M_2X and M_2X_2 aggregates and the association constants for these aggregates (28 °C)

	$K(=K')$/mol^{-1} dm^3	$K_t(=K_q)$/mol^{-1} dm^3			$-\Delta\delta_{t,q}$/ppm			
a/Å[a]	Lit[b]	This work	Lit[b]	M^{2+}-M^{2+}	2.9	3.8	4.7	5.6
10	25	5	5	Δ-Δ	0.18	0.49	0.96	1.11
				Λ-Λ	0.21	0.30	0.38	0.40
12	40	4	3	Δ-Δ	0.13	0.40	0.83	1.06
				Λ-Λ	0.17	0.25	0.32	0.34

a) Ion size parameter. b) Ref. 10.

the ring-current effect is responsible for the up-field shifts, the proton of a $[Ru(phen)_3]^{2+}$ ion placed just above the aromatic rings of a phenanthroline ligand of another $[Ru(phen)_3]^{2+}$ ion will show the largest up-field shift, and increasing distance from this position will decrease the magnitude of the shift. Thus, the difference in the up-field shifts between the Δ-Δ and the Λ-Λ aggregate reflects the difference in the configuration between them. This result is similar to Yamagishi's recent report that the arrangement of the Λ-$[Fe(phen)_3]^{2+}$ ions adsorbed on soil from a solution of the Λ isomer is largely different from the alternate arrangement of the Δ and Λ ions adsorbed from a solution of the racemate.[13]

We first consider the aggregate containing the Λ and Δ complex ions. In the M_2X or M_2X_2 aggregate, the 5 and 6 protons with the largest up-field shifts are considered to be placed closest to the position just above the aromatic rings of a phenanthroline ligand of the other $[Ru(phen)_3]^{2+}$ ion and the other protons are farther from that position in the order of 5,6<4,7<3,8 <2.9. Figure 4 shows a probable configuration of two $[Ru(phen)_3]^{2+}$ ions in the aggregate, where the edge of a phenanthroline ligand (**A**) of one $[Ru(phen)_3]^{2+}$ ion is placed in an opening between two phenanthroline ligands of the other $[Ru(phen)_3]^{2+}$ ion. Then the 5 and 6 protons of the **A** phenanthroline ligand are considerably influenced by the ring-current of those two phenanthroline ligands. Either the 4 or the 7 proton of the **A** phenanthroline ligands is placed above one of those phenanthroline ligand and none of the 2, 3, 8, and 9 protons are placed above them. The same applies to the protons of the **B** phenanthroline ligand.

For estimating the up-field shifts of the 5 and 6 protons, we assumed that the ring-current effect of phenanthroline is approximated by that of phenanthrene. Then, Hazato's theory[14] predicts an up-field shift of 4.1—4.3 ppm for the 5 and 6 protons of the **A** and **B** ligands.[15] Since only a single signal was observed for the 5 and 6 protons (Fig. 1), the observed chemical shift corresponds to the average over six equivalent protons of $[Ru(phen)_3]^{2+}$. Then, assuming that the proton chemical shifts of the ligands other than the **A** or **B** ligand are not affected by the aggregate formation, the average up-field shift of the 5 and 6 protons was estimated to be about 1.4 ppm. The experimental value of about 1.1 ppm (Table 1) shows a reasonable agreement with this value; the small difference may be explained if the aggregate does not always take the optimum configuration. Such flexibility of the configuration will also explain the small but appreciable up-field shifts for the 2, 3, 8, and 9 protons in the aggregate.

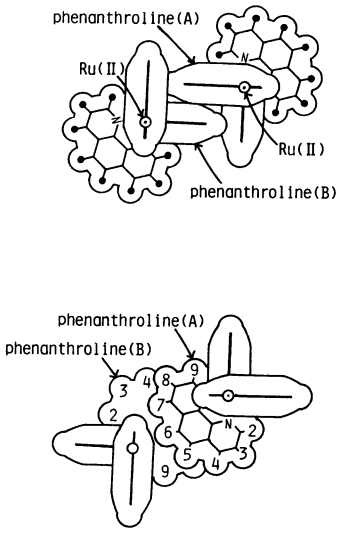

Fig. 4. Probable configuration of a pair of Λ- and Δ-$[Ru(phen)_3]^{2+}$ ions in the M_2X and M_2X_2 aggregates: the elevation (top) and the plan (bottom).

The up-field shifts of the protons of the Λ-Λ aggregate span an obviously narrower range than spanned by those of the Δ-Δ aggregate. This may indicate that the configuration of the Λ-Λ aggregate is more labile and/or more manifold than that of the Δ-Δ one. Actually, examinations with the CPK model demonstrated that a well-fitted structure like that shown in Fig. 4 is not possible for the Λ-Λ aggregate because of the steric hindrance between the phenanthroline ligands.

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