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Thermodynamics of Tetrahedral-Octahedral Configurational Interconversions in Co(II) Complexes.
The Ligand Substitution Reaction between Tetrahedral $[Co(hmpa)_4]^{2+}$ Ion and L (L = FA, NMF, DMF, DEF, or DMSO) in Nitromethane

Yuriko ABE,* Makiko MORIKAWA,† and Goro WADA†
Graduate Division of Human Culture, Nara Women's University, Nara 630
†Faculty of Science, Nara Women's University, Nara 630

Tetrahedral $[Co(hmpa)_4]^{2+}$ ion undergoes a single step reaction with L (L=FA, NMF, DMF, DEF, or DMSO) to form an octahedral $[Co(hmpa)_2L_4]^{2+}$ ion in nitromethane. The temperature dependences of the equilibrium constants of tetrahedral-octahedral configurational interconversions exhibit similar values of ΔH = -30 - -33 kJ mol^{-1} and ΔS = -115 - -149 J mol^{-1} K^{-1} respectively except for larger values for the DMSO complex.

In solvents such as water, ethanol, dimethyl sulfoxide(DMSO), and N,N-dimethylformamide(DMF), solvated complex ions of the first transition metals are mostly octahedral.$^{1)}$ On the other hand, we have reported that, in hexamethylphosphoric triamide(HMPA), solvated complex ions prefer the tetrahedral configurations to the octahedral ones since HMPA molecule is very bulky as compared with DMSO or DMF.$^{2,3)}$ Thus, the existence of equilibria of tetrahedral-octahedral configurational interconversions between solvated complex ions would be expected in the mixed media of HMPA and one of the other donor solvents. In the present study, we examined the reaction of tetrahedral $[Co(hmpa)_4]^{2+}$ ion with another donor substance as a ligand L using nitromethane as an inert solvent, where the concentration of L could be arbitrarily varied.

The experiments were performed spectrophotometrically. All complexes were prepared as perchlorate salts and the ionic strength was kept at I=0.06 M (mol dm^{-3}) with tetraethylammonium perchlorate. Figure 1 shows the dependence of the absorption spectra of Co(II) complexes upon the concentrations of N-methylformamide(NMF) in nitromethane at $[[Co(hmpa)_4]^{2+}]_0 = 1.0 \times 10^{-3}$ M and $[HMPA]_0 = 0.1$ M, where $[\ ]_0$ represents the initial concentration. Essentially similar data were also obtained for formamide(FA), N,N-dimethylformamide(DMF), N,N-diethylformamide(DEF), and dimethyl sulfoxide(DMSO) systems. For the case of the N,N-dimethylacetamide(DMA) system, the variation of the absorption spectra is shown in Fig. 2. A spectral change similar to the DMA system was seen also for N,N-diethylacetamide(DEA).

The absorption spectrum at $[L]_0 = 0$ M (Curve 1 in Figs. 1 and 2) is due to the tetrahedral $[Co(hmpa)_4]^{2+}$ ion.$^{2)}$ In Fig. 1, the absorbance decreases monotonously without any shift on peaks as adding NMF. In general,$^{1)}$ the absorption bands due to ν_3 ($^4T_1(P)\leftarrow{}^4A_2$) transitions in tetrahedral Co(II) complexes appear at wavelengths 550 - 700 nm. The molar absorptivities at the peaks are 100 - 2000 M^{-1} cm^{-1}. But, absorption bands of octahedral Co(II) complexes such as $[Co(H_2O)_6]^{2+}$, $[Co(dmso)_6]^{2+}$, $[Co(pyo)_6]^{2+}$ (pyo=pyridine oxide), and $[Co(NH_3)_6]^{2+}$ are observed in the visible region near 500 nm, having far smaller molar absorptivities (5 - 40 M^{-1} cm^{-1}). These bands allow a fairly clear-cut distinction between tetrahedral and octahedral configurations of Co(II) complexes. Thus, it is suggested that, in the case of the FA, NMF, DMF, DEF, and DMSO systems, the absorptions at 550 - 650 nm are due to the tetrahedral $[Co(hmpa)_4]^{2+}$ ion and that the monotonous decreases in the absorptivities are attributed to the formation of octahedral Co(II) complexes which may show no absorption in this region. Therefore, the equilibria of configurational interconversions between tetrahedral and octahedral Co(II) complexes occur in the ligand substitution reaction in the FA, NMF, DMF, DEF, and DMSO systems.

Since, in the DMA system, the isosbestic points appear at 555 and 594 nm below $[DMA]_0$=0.08 M as shown in Fig. 2, it is supposed that the Co(II) complex equilibrates between tetrahedral $[Co(hmpa)_4]^{2+}$ and tetrahedral $[Co(hmpa)_3(dma)]^{2+}$ ions. Above $[DMA]_0$=0.08 M, the spectra exhibit no isosbestic point. There seems to take place an equilibrium between tetrahedral and octahedral configurations in Co(II) complexes as the second step of substitution.

In the case of the FA, NMF, DMF, DEF, and DMSO systems, it is considered that the first equilibrium holds only so long as $[L]_0$ is not much larger than $[HMPA]_0$. If tetrahedral $[Co(hmpa)_4]^{2+}$ reacts with x moles of L to form octahedral $[Co(hmpa)_{6-x}(L)_x]^{2+}$ ion where x should be larger than 2 and whose absorptivities are zero, the following equation should hold under the conditions of large excess of $[L]_0$ and $[HMPA]_0$ as compared with $[Co(II)]_0$,

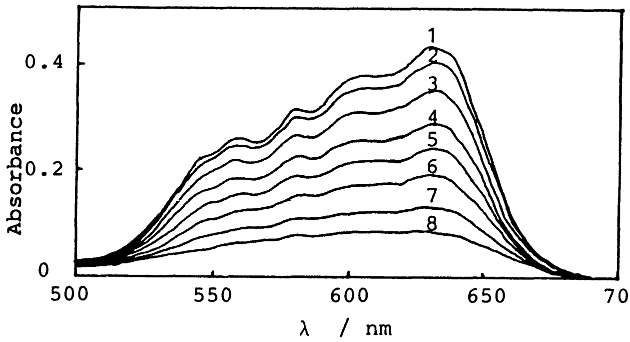

Fig. 1. Absorption spectra of Co(II) complex at various concentrations of NMF in nitromethane at $[[Co(hmpa)_4]^{2+}]_0$ =1×10^{-3} M, $[HMPA]_0$=0.1 M, I=0.06 M, and 25 °C. $[NMF]_0$: (1) 0 M (2) 0.20 M (3) 0.30 M (4) 0.35 M (5) 0.40 M (6) 0.45 M (7) 0.50 M (8) 0.60 M.

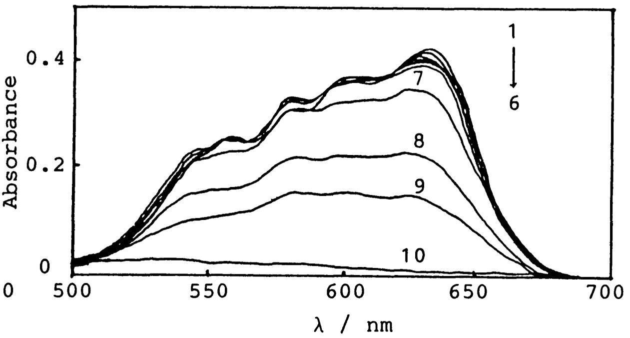

Fig. 2. Absorption spectra of Co(II) complex at various concentrations of DMA in nitromethane at $[[Co(hmpa)_4]^{2+}]_0$ =1×10^{-3} M, $[HMPA]_0$=0 M, I=0.06 M, and 25 °C. $[DMA]_0$: (1) 0 M (2) 0.01 M (3) 0.02 M (4) 0.04 M (5) 0.06 M (6) 0.08 M (7) 0.2 M (8) 0.5 M (9) 0.8 M (10) 9.56 M (pure DMA).

$$\log\left(\frac{\varepsilon_1}{\varepsilon}-1\right)-2\log[\mathrm{L}]_0=\log K+(x-2)\log\frac{[\mathrm{L}]_0}{[\mathrm{HMPA}]_0} \qquad (1)$$

where ε_1 is the molar absorptivity of tetrahedral $[\mathrm{Co(hmpa)_4}]^{2+}$ ion, ε the apparent one of all Co(II) complexes, and K the equilibrium constant between tetrahedral $[\mathrm{Co(hmpa)_4}]^{2+}$ and octahedral $[\mathrm{Co(hmpa)_{6-x}(L)_x}]^{2+}$ ions. Figure 3 shows the plots according to Eq. 1 at 633 nm for various systems. The values of (x - 2) and log K can be obtained from the slopes and the intercepts of the straight lines, respectively. As shown in Fig. 3, (x - 2) is equal to 2, namely x = 4 in all cases. Thus, the following equilibrium is revealed to exist in the ligand substitution reaction, the values of log K at 25 °C being summarized in Table 1.

$$\underset{\text{tetrahedral}}{[\mathrm{Co(hmpa)_4}]^{2+}} + 4\,\mathrm{L} \overset{K}{\rightleftharpoons} \underset{\text{octahedral}}{[\mathrm{Co(hmpa)_2L_4}]^{2+}} + 2\,\mathrm{hmpa} \qquad (2)$$

L = FA, NMF, DMF, DEF, or DMSO

Figure 4 shows the temperature dependence of the absorption spectra for the DMF system. Fairly large temperature dependence of the absorption spectra in Fig. 4 allows us to estimate the thermodynamic parameters of the interconversions between tetrahedral and octahedral configurations.4,5) The values of ΔH and ΔS for respective equilibria are summarized in Table 1.

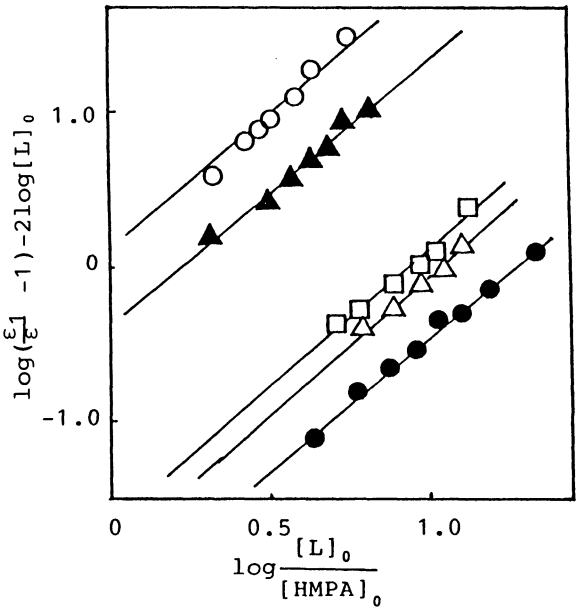

Fig. 3. Plots of $\{\log(\frac{\varepsilon_1}{\varepsilon}-1)-2\log[\mathrm{L}]_0\}$ vs. $\log\frac{[\mathrm{L}]_0}{[\mathrm{HMPA}]_0}$. ○ : DMSO ▲ : NMF □ : DEF △ : FA ● : DMF.

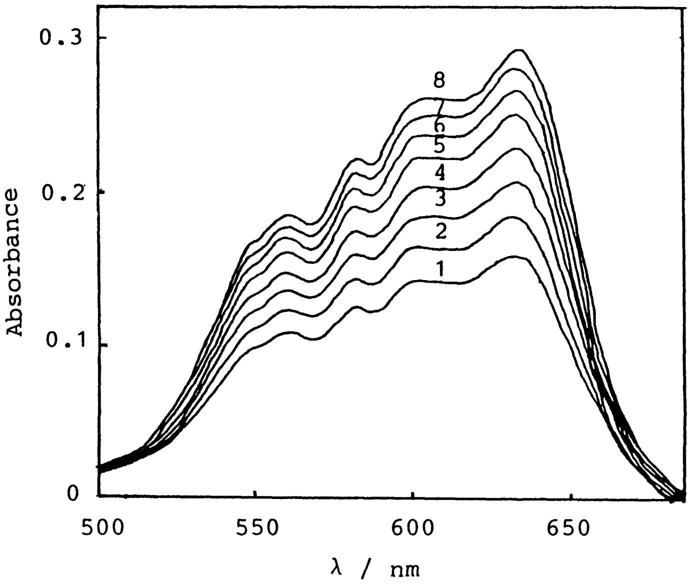

Fig. 4. Temperature dependence of absorption spectra in nitromethane at $[[\mathrm{Co(hmpa)_4}]^{2+}]_0=1\times10^{-3}$ M, $[\mathrm{HMPA}]_0=$ 0.1 M, $[\mathrm{DMF}]_0=1.25$ M, and I=0.06 M. (1) 15 °C (2) 20 °C (3) 25 °C (4) 30 °C (5) 35 °C (6) 40 °C (7) 45 °C (8) 50 °C .

In spite of the large negative values of ΔH, the K values are fairly small. This fact is due to the large negative values of ΔS, since two more moles of ligand molecules are bound to Co(II) ion in the course of Eq. 2 as the configurational change from tetrahedron to octahedron. As seen in Table 1, for formamide derivatives, the replacement of hydrogen atoms on amino radicals by methyl or ethyl radicals exhibits a little influence on the values of ΔH and ΔS. The main factors by which the solvent molecules(L) affect the equilibrium of Eq. 2 might be their basic and steric natures. The steric hindrance between the bulky HMPA and the L molecules could increase in the following order: FA<NMF<DMF<DEF, similarly to the order of the increase in the donor number FA<DMF<DEF.[6] Thus, the basic and the steric effects are canceled by each other, resulting in the similar values of ΔH and ΔS among the formamide derivatives. Next, since DMA and DEA correspond to the compounds to DMF and DEF whose hydrogen atom bonding to the carbon atom is replaced by a methyl radical respectively, a more steric interaction between the bulky HMPA and DMA or DEA molecules may lead to the retardation of coordination of DMA or DEA to Co(II) ion. Consequently, for the systems of acetamide derivatives, reaction 2 can not occur, but the tetrahedral configuration is maintained during the first step in the ligand substutition. In the case of the DMSO system, however, the reaction of Eq. 2 can hold because the DMSO molecule is smaller than that of DMA or DEA. The fact that the values of ΔH and ΔS for DMSO are larger than those for the formamide derivatives seems to be attributed to a decrease in the strength of bonding of the oxygen atom to Co(II) and accordingly to an increase in the degree of freedom of motion related to the DMSO molecules in their coordination sphere.

Table 1. The values of K (25 °C), ΔH, and ΔS

Solvent(L) (Donor Number)	K M^{-2}(25 °C)	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}
FA(~24)	1.2×10^{-2}	-33	-149
NMF(-)	3.2×10^{-1}	-32	-115
DMF(26.6)	4.9×10^{-3}	-30	-147
DEF(30.9)	2.2×10^{-2}	-31	-139
DMA(27.8)[a]	-	-	-
DEA(30.2)[a]	-	-	-
DMSO(29.8)	1.1	-18	-59

a) In the DMA and DEA systems, the equilibrium of Eq. 2 does not occur.

References

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