CHEMISTRY LETTERS, pp. 565-568, 1979. Published by the Chemical Society of Japan

A KINETIC STUDY OF THE REACTION OF THE 5,5,7R(S),12,12,14R(S)-HEXAMETHYL-1S(R),4S(R),8S(R),11S(R)-TETRAAZACYCLOTETRADECANENICKEL(II) ION AND DIMETHYLSULFOXIDE INVOLVING A SINGLET-TRIPLET SPIN-STATE EQUILIBRIUM[1)]

Yukiyasu MASUDA, né ENDO, Tasuku ITO,[†] Noboru YOSHIDA,
and Masatoshi FUJIMOTO
Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060
† Institute for Molecular Science, Okazaki 444

A kinetic study on the spin-state equilibrium in dimethylsulfoxide-water media, $[\mathrm{NiL}]^{2+}$ (singlet, square planar) + 2 DMSO $\rightleftharpoons$ $[\mathrm{NiL(dmso)_2}]^{2+}$ (triplet, pseudo O_h), is carried out with a temperature-jump method, where L denotes the title ligand (hereafter abbreviated as α-rac-$\mathrm{Me_6[14]aneN_4}$). The results are consistent with a two-step mechanism involving a rate-determining step $[\mathrm{NiL(dmso)}]^{2+} \rightleftharpoons [\mathrm{NiL}]^{2+}$ + DMSO via formation of a 5-coordinated intermediate $[\mathrm{NiL(dmso)}]^{2+}$.

The perchlorate of the title complex ion (Fig. 1) dissolves in acidic H_2O to give a yellow solution which shows the single electronic absorption band at 454 nm that is characteristic of four-coordinate square planar nickel(II) complexes having a singlet ground state (Spectrum 1 in Fig. 2).[2)] On the other hand, the complex dissolves in organic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile (AN), to give a green, a blue, and a violet solution, respectively. The electronic absorption spectrum of the neat DMSO solution (Curve 2 in Fig. 2) shows the characteristic absorptions for square planar nickel(II) complex at 445 nm, and for tetragonally distorted pseudo-octahedral nickel(II) complex having a triplet ground state at 380 and 610 nm.[2)] In the present study, we have observed that the intensity of the singlet band increases while those of the triplet bands decreases as the mole fraction of DMSO, x_{DMSO}, in the DMSO-H_2O mixed solvent decreases. Figure 3 shows the temperature-dependence of the absorption spectra of the complex in a DMSO-H_2O mixed solvent, which shows the isosbestic points. All these observations indicate the presence of a temperature-dependent equilibrium between a singlet- and a triplet-species in the solutions. As the temperature rises, the equilibrium is shifted in favor of the planar, singlet nickel(II) species.

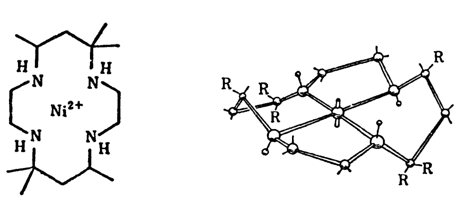


Fig. 1. $[\mathrm{Ni(\alpha\text{-}rac\text{-}Me_6[14]aneN_4)}]^{2+}$

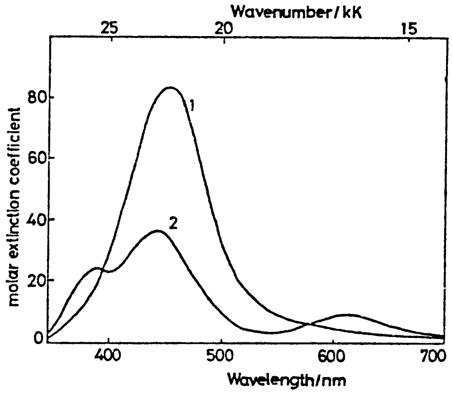


Fig. 2. Absorption spectra of $[Ni(\alpha\text{-rac-Me}_6[14]aneN_4)]^{2+}$ in acidic H_2O (10^{-2} mol dm^{-3} HBF_4) (1) and DMSO (2) at 25 °C and $I = 0.1$ mol dm^{-3} (Et_4NClO_4).

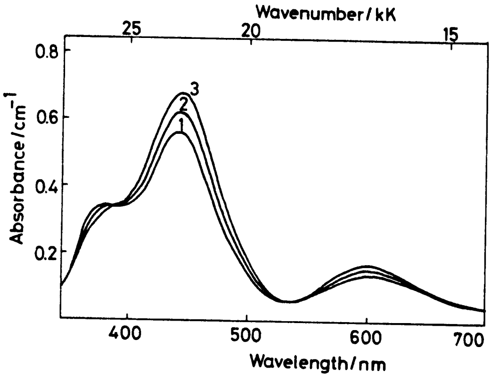
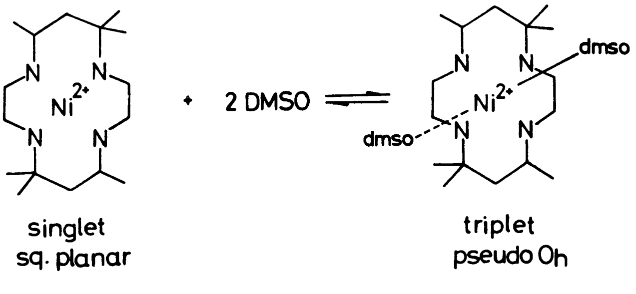


Fig. 3. Absorption spectra of 1.97×10^{-2} mol dm^{-3} solution of $[Ni(\alpha\text{-rac-Me}_6[14]aneN_4)]^{2+}$ in a DMSO-H_2O mixed solvent ($x_{DMSO} = 0.5$) at 15 (1), 25 (2), and 35 °C (3).

In the present communication we report the results of the kinetic measurements of the reaction of $[Ni(\alpha\text{-rac-Me}_6[14]aneN_4)]^{2+}$ with DMSO by the temperature-jump method. The kinetic measurements were carried out with a Union-Giken co-axial-cable temperature-jump apparatus Model RA-105. The absorption spectra were measured with a Hitachi recording spectrophotometer Model EPS-3T. The complex $[Ni(\alpha\text{-rac-Me}_6[14]aneN_4)](ClO_4)_2$ was prepared by the method described in the literature.[2] The equilibrium and kinetic measurements were carried out with the acidified (10^{-2} mol dm^{-3} HBF_4)[3] H_2O-DMSO mixed solutions in the range of x_{DMSO} = 0.3-0.6.[4]

The equilibrium constant for the spin-state equilibrium of the following type



(1)

is given by

$$K = [NiL(dmso)_2]/[NiL][DMSO]^2, \qquad (2)$$

where dmso is the axial ligand. The equilibrium constants for the reaction of $[Ni(\alpha\text{-rac-Me}_6[14]aneN_4)]^{2+}$ with DMSO molecule in DMSO-H_2O mixed solvent at 15, 25, and 35 °C were determined to be 7.7×10^{-3}, 5.7×10^{-3}, and 4.7×10^{-3} mol^{-2} dm^6, respectively. The thermodynamic parameters, ΔG, ΔH, and ΔS, for the reaction 1 were also determined from the temperature-dependence of K to be 12.8 kJ mol^{-1}, - 18.8 kJ mol^{-1}, and - 105 J K^{-1} mol^{-1} at 25 °C, respectively.

Table 1.

Dependence of τ^{-1} for the reaction of $[Ni(\alpha\text{-rac-}Me_6[14]aneN_4)](ClO_4)_2$ with DMSO on the concentration of the complex at $x_{DMSO} = 0.5$, $I = 0.1$ mol dm^{-3} (Et_4NClO_4), and 23.6 °C.

$[[Ni(\alpha\text{-rac-}Me_6[14]aneN_4)]^{2+}]/10^{-2}$ mol dm^{-3}	$\tau^{-1}/10^3$ s^{-1}
0.48	2.0
0.84	2.1
1.89	2.2
2.49	2.2
5.06	1.9

The kinetic data were obtained under pseudo-first-order conditions using an excess of DMSO. A single relaxation signal was observed in 10^{-3}-10^{-4} s region. The relaxation time, τ, was independent of the concentration of the complex (see Table 1). The kinetic data are interpreted in terms of a stepwise mechanism

$$[NiL(dmso)_2]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [NiL(dmso)]^{2+} + DMSO, \quad K_1 \qquad (3)$$

and

$$[NiL(dmso)]^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [NiL]^{2+} + DMSO, \quad K_2 \qquad (4)$$

with the assumption that the reaction 4 equilibrates slowly as compared with the reaction 3. The relaxation time, τ, can be expressed as

$$\tau^{-1}[DMSO]^{-1} = k_{-2} + (k_2K_1/[DMSO]^2). \qquad (5)$$

The plot of $\tau^{-1}[DMSO]^{-1}$ against $[DMSO]^{-2}$ gave a straight line with a slope k_2K_1 and an intercept k_{-2} (Fig. 4). The values of k_2K_1 and k_{-2} were determined to be 1.1×10^4 and 1.3×10^4 mol dm^{-3} s^{-1}, and 70 and 80 mol^{-1} dm^3 s^{-1} at 18.6 and 23.6 °C, respectively.[4] Equilibrium constants for reaction 1 were calculated using the kinetic data, k_{-2}/K_1k_2, i.e., the ratio of the intercept to the slope of the straight lines in Fig. 4, to be 6.4×10^{-3} and 6.2×10^{-3} mol^{-2} dm^6 at 18.6 and 23.6 °C, respectively. These values are in agreement with the equilibrium constants determined spectrally.

An alternative mechanism, in which reaction 3 proceeds slowly compared with reaction 4, does not account for the results. The relationship $\tau^{-1} = k_1 + (k_{-1}/K_2) \times [DMSO]^2$ for this mechanism does not hold as shown in the plot of τ^{-1} against $[DMSO]^2$ (Fig. 5). The slope in Fig. 5 leads to the negative value of k_{-1}/K_2.

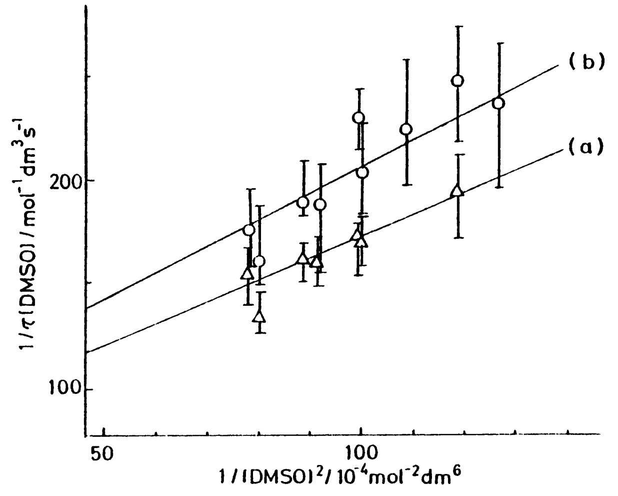


Fig. 4. Plots of $\tau^{-1} \times [\mathrm{DMSO}]^{-1}$ against $[\mathrm{DMSO}]^{-2}$ for the reaction of $[\mathrm{Ni}(\alpha\text{-rac-Me}_6[14]\mathrm{aneN}_4)]^{2+}$ and DMSO in DMSO-H_2O mixed solvent at 18.6 (a) and 23.6 °C (b), and $I = 0.1$ mol dm^{-3} ($\mathrm{Et_4NClO_4}$).

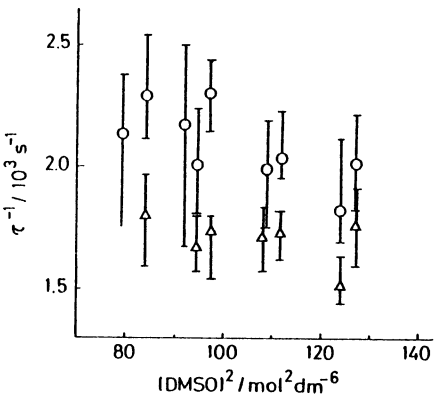


Fig. 5. Plots of τ^{-1} against $[\mathrm{DMSO}]^2$ for the reaction of $[\mathrm{Ni}(\alpha\text{-rac-Me}_6[14]\mathrm{aneN}_4)]^{2+}$ and DMSO in DMSO-H_2O at 18.6 (Δ) and 23.6 °C (o), and $I = 0.1$ mol dm^{-3} ($\mathrm{Et_4NClO_4}$).

REFERENCES

1) Presented in part at the 1978 Winter Meeting in Hokkaido of the Chemical Society of Japan and Japan Society for Analytical Chemistry, Sapporo, February 2, 1978, Abstract p. 13 and at the 28th Annual Meeting on Coordination Chemistry, Matsuyama, October 13, 1978, Abstract p. 341.

2) L. G. Warner and D. H. Busch, J. Am. Chem. Soc., 91, 4092 (1969).

3) The complex ion isomerizes to the 1S(R),4R(S),8S(R),11R(S)-isomer (β-isomer), unless the solution is kept acidic.[2)]

4) At higher x_{DMSO}, the plots for the determination of the equilibrium constant (K) and the plot, $\tau^{-1}[\mathrm{DMSO}]$ vs. $[\mathrm{DMSO}]^{-2}$ (eq. 5), deviated from the linear relation. The reason is uncertain. The equilibrium constants were derived from the data in the range of $x_{\mathrm{DMSO}} = 0.3\text{-}0.5$, where the solvent-structure of the system DMSO-H_2O is regarded to be uniform.[5)]

5) "Dimethyl Sulfoxide" ed by S. W. Jacob, E. E. Rosenbaum, and D. C. Wood, Marcel Dekker, Inc., New York, (1971), Vol. 1, Chap. 1.

(Received March 12, 1979)