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Supplementary Material Available: Figures showing the ^{1}H and ^{13}C NMR, IR, positive ion FABMS, and UV–vis spectra of β-CD–Ts and ^{13}C NMR, FABMS, and ^{1}H NMR COSY spectra of β-CD$\cup^1$aza (9 pages). Ordering information is given on any current masthead page.

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Variable-Temperature and -Pressure Multinuclear Magnetic Resonance Study of Solvent Exchange at the Tris(ethylenediamine)nickel(II) Ion in Ethylenediamine

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The solvent exchange between ethylenediamine molecules in the bulk solvent and ethylenediamine molecules coordinated to the nickel(II) ion in neat ethylenediamine and mixtures involving *N,N*-dimethylformamide as a diluent has been studied by the ^{1}H, ^{13}C, and ^{14}N NMR line-broadening technique. The exchange rate constant at 298 K and activation parameters are as follows: $k = 19.6$ s^{-1}, $\Delta H^{*} = 69 \pm 3$ kJ mol^{-1}, $\Delta S^{*} = 10 \pm 11$ J mol^{-1} K^{-1}, $\Delta V^{*} = 11.4 \pm 2.0$ cm^3 mol^{-1} (383 K). The exchange rate is independent of the concentration of ethylenediamine in solvent. It has been proposed that the exchange reaction proceeds via a dissociative mechanism and that it involves a hexacoordinated intermediate with two equivalent monodentate ethylenediamine molecules.

Introduction

Solvent-exchange processes at solvated metal ions are fundamental phenomena of metal ions in solution and are important for elucidating the reaction mechanisms of metal complex formation.[1,2] In most cases, the rate-determining step for metal complex formation with multidentate ligands is the substitution of the coordinated solvent molecule by one of the donor atoms of the entering ligand and the subsequent chelate-ring closure is not rate limiting.[1,2] The solvent-exchange reaction has not been studied in a solvent which acts as a multidentate ligand. Saito's group has published a series of papers dealing with the exchange of acetylacetonate on a variety of metal ions in neat acetylacetone and acetonitrile.[3] The exchange of acetylacetonate is not a simple exchange reaction, and it necessarily involves proton dissociation. In this work, ethylenediamine was selected as a solvent which acts as a bidentate ligand. The exchange of ethylenediamine does not involve proton dissociation, and it can be compared with other solvent-exchange reactions on a common basis.

Experimental Section

Reagents. Ethylenediamine (en) was purified by the following procedure. Under dry nitrogen gas, reagent grade en (200 cm^3) was shaken with activated 4A molecular sieves (18 g) for ca. 3 days; the supernatant liquid was decanted and then agitated for ca. 30 h in the presence of both calcium oxide (11 g) and potassium hydroxide (3 g). The supernatant liquid was distilled under vacuum in the presence of freshly activated 4A molecular sieves (20 g). The obtained en was again distilled under vacuum over sodium metal (3 g), and the purified en was stored over 4A molecular sieves (20 g). Just before use, it was transferred by distillation on a standard vacuum line.

Reagent grade *N,N*-dimethylformamide (DMF) agitated with barium oxide (20 g) for 3 days was distilled twice under vacuum. The purified DMF stored over 4A molecular sieves (10 g) was transferred by distillation for sample preparation. Tris(ethylenediamine)nickel(II) perchlorate was obtained by the addition of ca. 0.5 mol dm^{-3} sodium perchlorate solution (100 g) to a solution containing 40 g of ethylenediamine and 50 g of nickel(II) nitrate. The purple precipitate was recrystallized from water, and the crystals were dried at 373 K in vacuum. The composition was confirmed as [Ni(C$_2$H$_8$N$_2$)$_3$](ClO$_4$)$_2$ by C, H, N, and Ni elemental analyses. The electronic absorption spectrum of the solution of [Ni(en)$_3$](ClO$_4$)$_2$ was recorded on a Shimazu UV-265FW spectrophotometer (Figure S1 in the supplementary material).

Sample Preparation. Ten solutions for NMR measurements were prepared in a glovebox by dissolving weighed quantities of the perchlorate of Ni(en)$_3^{2+}$ in suitable amounts of freshly distilled en and DMF. The compositions of the solutions are given in Table SI (supplementary material). Samples for variable-temperature NMR measurements were introduced into 5 mm o.d. NMR glass tubes that were then flame-sealed after degassing. The variable-pressure sample was contained in a 7 mm o.d. thin glass tube capped with a flexible Teflon tube, as previously described.[4,5]

NMR Measurements. Variable-temperature ^{1}H, ^{13}C, and ^{14}N NMR measurements were performed on a JEOL JNM-GX270 FT-NMR spectrometer operating at 270, 67.89, and 19.52 MHz, respectively. Some ^{14}N NMR spectra were also measured with a JEOL JNM FX100 instrument. The ^{1}H NMR spectra were measured using a 5 mm o.d. NMR sample tube. A 5 mm o.d. NMR sample tube for ^{13}C and ^{14}N NMR measurements was placed into a 10 mm o.d. NMR tube containing a lock solvent (D$_2$O and/or deuterated ethylene glycol) and nitromethane as a chemical shift standard. The temperature was measured by a substitution technique with a thermistor (D111-1031 or D641, Takara Thermistor Co.). About 20 min was required for the temperature equilibration of the NMR sample solution, and the temperature stability was ±0.2 K.

The variable-pressure NMR experiment was carried out using a high-pressure NMR probe constructed for the wide-bore superconducting magnet (6.34 T) of a JEOL JNM-GX270 FT-NMR spectrometer.[5] A 7 mm o.d. glass tube with a flexible Teflon cap was used. The pressure generated by a pressure-generating pump (KBP56, Hikarikouatsu Co., Hiroshima) was measured with a Heise Bourdon gauge. Daifloil No. 1 (poly(chlorotrifluoroethylene), Daikin-Kogyo Co.) was used as a pressure-transmitting liquid. The temperature of the sample was measured by a substitution technique with a thermistor before applying high pressure and then monitored with a thermocouple in the pressure vessel during the high-pressure experiment. The temperature was kept to within ±0.2 K. *Caution!* Concentrated solutions of nickel(II) perchlorate in en or en/DMF at high temperature constitute a potential explosion hazard.

Results and Discussion

Variable-Temperature Study. Immediately before or after each NMR measurement of a sample solution at a given temperature,

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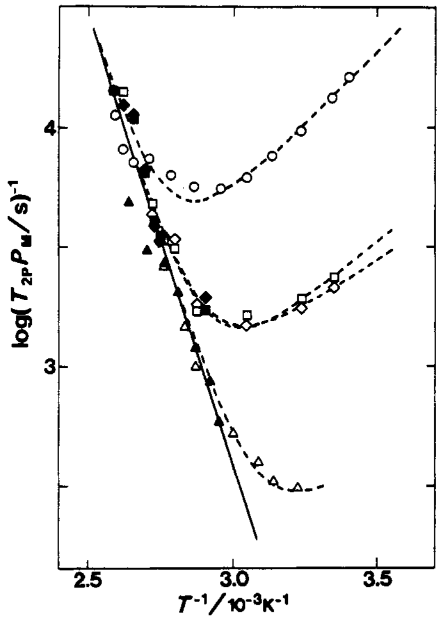

Figure 1. $(T_{2P}P_M)^{-1}$ data for ^1H, ^{13}C, and ^{14}N nuclei as a function of temperature. 19.52-MHz ^{14}N NMR: (○) $P_M = 1.37 \times 10^{-1}$. 270-MHz ^1H NMR: (□) amine proton, $P_M = 1.37 \times 10^{-1}$; (■) amine proton, $P_M = 2.72 \times 10^{-2}$; (◇) methylene proton, $P_M = 1.37 \times 10^{-1}$; (◆) methylene proton, $P_M = 2.72 \times 10^{-2}$. 67.89-MHz ^{13}C NMR: (△) $P_M = 1.37 \times 10^{-1}$; (▲) $P_M = 2.72 \times 10^{-2}$. The solid line was calculated using the obtained values of ΔH^* and ΔS^*.

the NMR spectra of a reference solution not involving the nickel(II) complex were recorded under the same conditions. NMR line broadening, $(T_{2P}P_M)^{-1}$, due to a paramagnetic metal ion is expressed as

$$(T_{2P}P_M)^{-1} = \pi(\Delta\nu_{samp} - \Delta\nu_{solv})P_M^{-1} = (T_{2samp}^{-1} - T_{2solv}^{-1})P_M^{-1} \qquad (1)$$

where $\Delta\nu_{samp}$ and $\Delta\nu_{solv}$ are the half-height widths of the NMR spectra of ethylenediamine in the bulk in the presence and in the absence of the nickel(II) ion, respectively, P_M is the molar fraction of bound solvent molecules, and T_{2samp} and T_{2solv} are the corresponding transverse relaxation times of the observed nucleus of en. The spectrum in Figure S1 is characteristic of the octahedrally coordinated Ni^{2+} ion.[6] Therefore, we may safely state that the Ni^{2+} ion is octahedrally coordinated by three en molecules. ^1H, ^{13}C, and ^{14}N NMR line-broadening data for $[Ni(en)_3](ClO_4)_2$ at various temperatures are summarized in Tables SII–SV (supplementary material).

Figure 1 shows the $(T_{2P}P_M)^{-1}$ data for three different nuclei, ^1H, ^{13}C, and ^{14}N, as a function of reciprocal temperature. The relaxation rate has been confirmed to be proportional to the nickel(II) ion concentration. Thus the T_{2P}^{-1} value was normalized by dividing by P_M as in eq 1. These data were analyzed by means of the modified Swift–Connick equation[7,8]

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M}\,\frac{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + (\Delta\omega_M)^2}{(T_{2M}^{-1} + \tau_M^{-1})^2 + (\Delta\omega_M)^2} + \frac{1}{T_{2o}} \qquad (2)$$

in which the symbols have their usual meanings.[9] Over the present temperature range from 293 to 388 K where $T_{2M}^{-2} \gg (\Delta\omega_M)^2$, τ_M^{-2} is valid, eq 2 is reduced to

$$(T_{2P}P_M)^{-1} = \tau_M^{-1} + T_{2o}^{-1} \qquad (3)$$

The residence time τ_M is related to the pseudo-first-order rate constant k for solvent exchange, and its temperature dependence may be obtained from the transition-state theory: $k = \tau_M^{-1} = k_BTh^{-1}\exp(-\Delta H^*/RT + \Delta S^*/R)$, where ΔH^* and ΔS^* are the enthalpy and entropy of activation, respectively. The relaxation term due to the interaction in the outer sphere of the paramagnetic ion (T_{2o}) can be expressed as the exponential form:[8] $T_{2o}^{-1} = (C_o/T)\exp(E_o/RT)$.

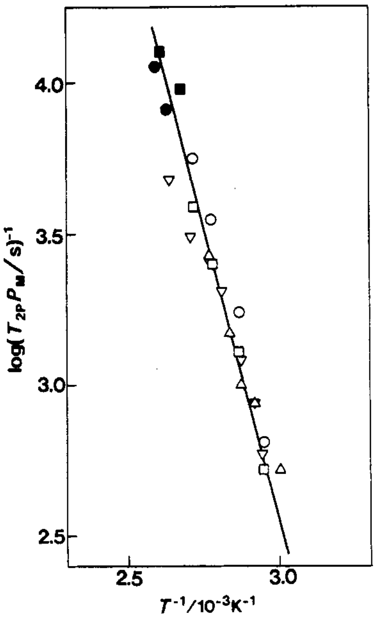

Figure 2. $(T_{2P}P_M)^{-1}$ data in the chemical-exchange region for three different concentrations (100, 70.1, and 38.0%) of en: (△) $P_M = 1.37 \times 10^{-1}$, 100% en; (▽) $P_M = 2.72 \times 10^{-2}$, 100% en; (○) $P_M = 2.17 \times 10^{-2}$, 70.1% en; (□) $P_M = 2.27 \times 10^{-2}$, 38.0% en. Some data points were added for different observed frequencies of the ^{14}N nucleus: (●) 19.52-MHz ^{14}N NMR; (■) 7.20-MHz ^{14}N NMR. The solid line is the same as in Figure 1.

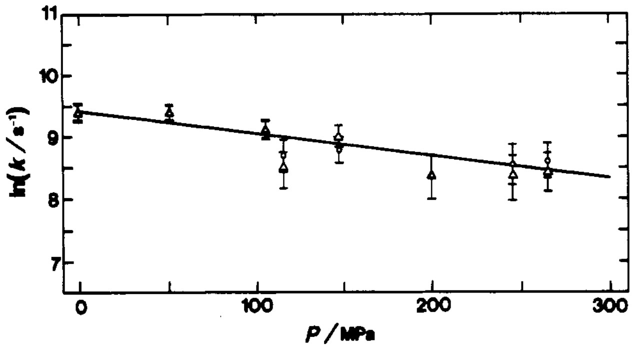

Figure 3. Pressure dependence of k at 383 K. ($P_M = 2.74 \times 10^{-2}$): methylene proton (○); amine proton (△). A vertical bar shows the error range of each point. The solid line was calculated using the activation volume of 11.4 $cm^3\ mol^{-1}$.

The nonlinear least-squares analyses according to eq 3 were applied to the data for each nucleus while the common values of ΔH^* and ΔS^* for solvent exchange were maintained. In Figure 2 are given several data in the chemical-exchange region for different concentrations (100, 70.1, and 38.0%) of en and for different observed frequencies (19.52 and 7.20 MHz) of ^{14}N. As is apparent from Figure 2, the values of $(T_{2P}P_M)^{-1}$ in the chemical-exchange region do not vary with observed NMR frequencies and the exchange rate is independent of the concentration of ethylenediamine in solvent. The values of ΔH^* and ΔS^* for solvent exchange at the nickel(II) ion have been determined to be 69 ± 3 kJ mol^{-1} and 10 ± 11 J $mol^{-1}\ K^{-1}$, respectively. Moreover, no line broadening of the ^1H and ^{14}N NMR spectra of DMF in the presence of $Ni(en)_3^{2+}$ has been observed. This implies no interaction of DMF with $Ni(en)_3^{2+}$ in the first coordination sphere.

Variable-Pressure Study. As is apparent from Figure 1, the term τ_M^{-1} is predominant at 383 K where $(T_{2P}P_M)^{-1}$ is equal to k. The ^1H NMR line-broadening data at various pressures are

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Table I. Activation Parameters for Solvent Exchange at the Nickel(II) Ion in Various Solvents

solvent	k(298 K)/s^{-1}	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/J mol^{-1} K^{-1}	ΔV^{*}/cm^3 mol^{-1} (T/K)	ref
en	1.96×10	69 ± 3	10 ± 11	+11.4 ± 2.0 (383)	this work
H_2O	3.8×10^4	49.2 ± 2.5	8 ± 8	+7.2 ± 0.2 (311)	4, 12
CH_3OH	1.0×10^3	66.1	33.5	+11.4 (307)	13
DMF	3.8×10^3	62.8	33.5	+9.1 (297)	13
NH_3(aq)[a]	7.0×10^5	57.3	40	+5.9 (283–303)	14
acetonitrile	6.24×10^3	41.4 ± 0.5	−30 ± 2	+12.0 ± 0.4 (332)	5
propionitrile	1.33×10^4	42.0 ± 0.4	−25 ± 2	+13.7 ± 0.5 (330)	5
butyronitrile	1.04×10^4	43.3 ± 0.7	−23 ± 2	+13.1 ± 0.5 (329)	5
isobutyronitrile	1.59×10^4	43.3 ± 0.5	−19 ± 2	+12.4 ± 0.6 (328)	5
valeronitrile	9.99×10^3	47.1 ± 1.2	−10 ± 4	+14.4 ± 0.4 (329)	5
benzonitrile	9.38×10^3	51.6 ± 1.9	+4 ± 6	+13.1 ± 0.6 (332)	5

[a] Aqueous ammonia containing 1 M NH_4NO_3 and 15 M NH_3.

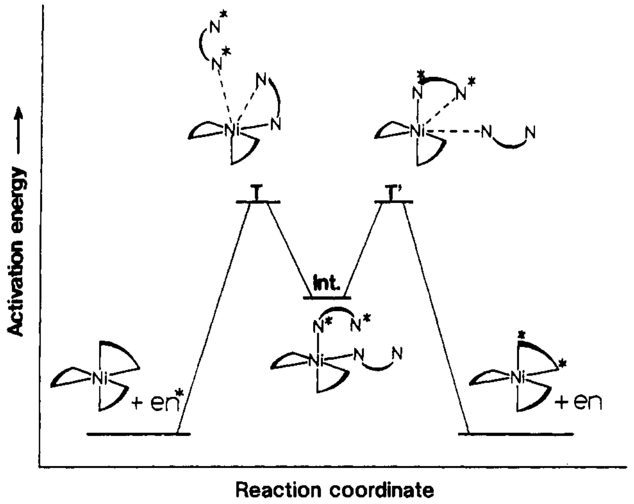

Figure 4. Proposed mechanism for ethylenediamine exchange at the nickel(II) ion.

summarized in Tables SVI and SVII (supplementary material). The pressure dependence of k at 383 K for the methylene and amine protons is shown in Figure 3.[10] The pressure dependence of the rate constant is derived from the transition-state theory: $(\partial \ln k/\partial P)_T = -\Delta V^{*}/RT$. Since plots of the logarithmic values of k for the solvent exchange vs P are linear within experimental errors, the activation volume can be estimated to be 11.4 ± 2.0 cm^3 mol^{-1} (Table I) from the slope in Figure 3.

Proposed Solvent-Exchange Mechanism. The relaxation rate (T_{2P}^{-1}) is proportional to the nickel(II) ion concentration over the observed temperature range. The solvent-exchange rate is independent of the concentration of en in solvent and also independent of observed nuclei such as ^1H, ^{13}C, and ^{14}N. These findings strongly indicate that the solvent-exchange process proceeds through a whole molecule of ethylenediamine and via a dissociative mode of activation.

The activation parameters including the activation volume for solvent exchange at the nickel(II) ion in various solvents so far studied are summarized in Table I.[11] The slowest rate of exchange is observed for ethylenediamine, and this is a characteristic feature of en. The chelate effect of en as a bidentate ligand should lead to the slowest exchange rate. The activation volume for the en exchange is comparable to those in the other solvents where the dissociative mechanism has been claimed to be operative.[5,12-14] The en-exchange rate was not affected by the presence of a large amount of DMF, which has a considerably high coordination ability. This fact strongly indicates the limiting dissociative mechanism. A proposed mechanism has been depicted in Figure 4. One of the two bonds of a coordinated en molecule should be elongated dissociatively to form a transition state (T), followed by entering of an en molecule in the bulk to form an intermediate (Int) with two equivalent monodentate en molecules. Both activated complexes (T and T′) in the transition state for the solvent-exchange reaction should be structurally equivalent.

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Registry No. en, 107-15-3; Ni(en)$_3^{2+}$, 15390-99-5.

Supplementary Material Available: Absorption spectrum of [Ni(en)$_3$](ClO$_4$)$_2$ in en (Figure S1), compositions of sample solutions (Table SI), and observed NMR line-broadening data at various temperatures and pressures (Tables SII–SVII) (7 pages). Ordering information is given on any current masthead page.

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(10) Using the high-pressure NMR probe, the half-height width ($\Delta\nu_{solv}$) of 270-MHz ^1H NMR signals of ethylenediamine as a solvent is 60 Hz at 383 K and 0.1 MPa (see Table SVI). This broadening reflects the inhomogeneities due mainly to no spinning of a high-pressure NMR sample tube. Under the present high-pressure experimental conditions, the signal/noise ratios for ^1H NMR signals for the solvent and the sample are ca. 13 and 5–3, respectively. Values of the half-height width for the sample ($\Delta\nu_{samp}$) have ca. 8% errors.

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