Variable-Temperature and -Pressure Nitrogen-14 Magnetic Resonance Studies on Solvent Exchange of Nickel(II), Iron(II), and Manganese(II) Ions in Neat 1,3-Propanediamine and *n*-Propylamine

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The solvent exchanges of nickel(II), iron(II), and manganese(II) ions in 1,3-propanediamine (tn) and *n*-propylamine (pa) have been studied by the ^{14}N NMR line-broadening method. The rate constants of the amine exchanges for the first-row transition metal ions are in the order of ethylenediamine (en) < tn < pa, which is largely affected by the difference in the activation enthalpies. The differences in the rate constants and the activation enthalpies among the three amine solvents become greater along the series from manganese(II) ion to nickel(II) ion. These kinetic results have clarified that the differences in the kinetic chelate strain effect in the transition state and the chelate strain effect in the ground state can be attributed to the difference in the chelate ring sizes and the ion radii.

The solvent exchange studies on metal ions have been focused upon the bidentate ethylenediamine (en) exchange on the first-row transition metal(II) ions,[1,2] and we have so far investigated the origin of the kinetic chelate strain effect in the transition state and the chelate strain in the ground state.[2] The kinetic chelate strain effect is attributed to the angular distortion around the leaving amine nitrogen in the chelate ring opening process of en, which causes large $\Delta H^\ddagger$ and small k_{ex} values for the en exchange. On the other hand, the five-membered en chelate is too small to form the regular octahedral geometry for the relatively large metal(II) ions, high-spin cobalt(II), iron(II), and manganese(II) ions.[2] Such a chelate strain effect destabilizes the ground state and consequently cancels out the kinetic chelate strain effect. For further investigation of the bidentate solvent exchange, we have performed solvent exchange of the cobalt(II) ion both in the bidentate amine with a larger chelate ring size, 1,3-propanediamine (tn), and in the monodentate alkylamine, *n*-propylamine (pa), previously.[3] The results clearly indicate that the kinetic chelate strain effect for the five-membered en chelate is significantly large where the difference in $\Delta H^\ddagger$ between the en and pa exchanges is more than 20 kJ mol^{-1}, while the six-membered tn chelate can flexibly elongate the metal–nitrogen (M–N) bond to form an enthalpically less activated transition state where the difference in $\Delta H^\ddagger$ relative to the pa exchange is ca. 13 kJ mol^{-1}.

Considering the difference in the ion radii and the electronic configurations among the first-row transition metal(II) ions, one must clarify the difference in the kinetic chelate strain effect and the chelate strain effect in the ground state between five- and six-membered chelates for a series of the first-row transition metal(II) ions. Accordingly, we have investigated the solvent exchanges of Ni(II), Fe(II), and Mn(II) in tn as well as Co(II) in order to complete the series of the solvent exchanges in bidentate solvents. Furthermore, in order to more precisely clarify the features of the bidentate amine exchange reactions, we have also studied the monodentate pa exchange of the corresponding metal(II) ions as a reference reaction, because there are so far no available data for the solvent exchange in the monodentate alkylamine.

Experimental

Reagents. 1,3-Propanediamine (tn) and *n*-propylamine (pa) were purified by the procedures described previously.[3] Each hexaaquametal(II) trifluoromethanesulfonate (triflate) of Ni(II),[4] Fe(II),[2] and Mn(II)[2] was prepared from $NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$ (Wako, Pr. Gr.), iron sponge (Wako, 99.99 %), and $MnCO_3$ (Wako, Special Gr.), respectively. Each hydrate salt of Ni(II), Fe(II), and Mn(II) was dried at 170 °C, 70 °C under vacuum and 300 °C, respectively, for a few hours to obtain the anhydrous salt. Completion of the dehydration was confirmed by the EDTA titration. UV/vis (in tn), $\lambda_{\max}$/nm (ε/mol^{-1} kg cm^{-1}) 907 (4.5), 556 (5.5), 351 (8.3) for Ni(II); 1010sh (1.8), 866 (2.1) for Fe(II); 633 (0.12), 478 (0.33), 420 (0.46), 377 (0.61), 353 (0.74) for Mn(II).

Sample Preparation. The NMR sample preparations for the tn and pa solutions were carried out in a glovebox and a vacuum line as described previously.[3] The compositions of the sample solutions are given in Table S1 as supporting data.

Sample solutions of ca. 0.3 mol dm^{-3} for EXAFS measurements were prepared by dissolving known amounts of anhydrous metal(II) triflate in freshly distilled tn and pa in a glovebox,[5] and the sample glass tubes containing the sample solutions were flame-sealed after degassing in a vacuum line. Just before the EXAFS measurements, a glass filter disk (25-mm diameter and 2-mm thickness) was immersed in each sample solution and doubly sealed in PET (poly(ethylene terephthalate), Toray Co.) film bags in a glovebox.[5]

Measurements. The ^{14}N NMR measurements at various tem-

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peratures were performed on JEOL JNM-GX270 FT and BRUKER AMX-400 NMR spectrometers operating at 19.52 and 29.91 MHz, respectively. The sample tubes for various-temperature NMR measurements were coaxially mounted in 10 mm o.d. NMR tubes containing deuterated water, acetone or dimethyl sulfoxide as a lock solvent. The temperatures were measured by a substitution technique using a thermistor (D641, Takara Thermistor Co.) or a copper–constantan thermocouple. About 15 min was required for the temperature equilibration of the sample solution and the temperature stability was ±0.1 K. The NMR measurements at various pressures were 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, as described in detail previously.[4,6]

Electronic absorption spectra were recorded on Shimadzu UV-3100PC and UV-265FW spectrophotometers. EXAFS spectra were measured around the K edge of each metal using the BL6B station at the Photon Factory of the National Laboratory for High Energy Physics.[7] Details of the EXAFS measurements and analyses have been described previously.[3,8,9] The values of the threshold energy of a K-shell electron, E_0, and the mean free path of a photoelectron, λ, were evaluated using the EXAFS data for the aqueous solution of each metal(II) triflate by fixing the scatterer number n at 6, because the six-coordinate octahedral structure of each metal(II) ion has been confirmed.[10,11] The obtained values for E_0 and λ were maintained constant for the structural analyses for the tn and pa solutions.

Table 1. Structure Parameters for Solvated Mn(II), Fe(II), Co(II), and Ni(II) Ions in Water, tn, and pa[a]

	Solvent	Mn(II)	Fe(II)	Co(II)[b]	Ni(II)
R/pm[c]	Water	217(1)	211(1)	208(1)	205(1)
	tn	228(1)	222(1)	217(1)	214(1)
	pa	227(1)	222(1)	217(1) 201(1)	—[j]
σ/pm[d]	Water	7.2(0.2)	7.1(0.2)	6.9(0.2)	6.2(0.2)
	tn	7.8(0.2)	7.8(0.2)	7.3(0.2)	7.1(0.2)
	pa	8.2(0.2)	7.3(0.2)	7.3[f,g] 5.0(2)[h]	—[j]
n[e]	Water	6[f]	6[f]	6[f]	6[f]
	tn	6.1(0.2)	5.7(0.2)	6.1(0.2)	5.9(0.1)
	pa	5.9(0.2)	6.2(0.2)	4.3(0.2)[g,i] 1.3(0.2)[h,i]	—[j]

a) The standard deviations are given in parentheses. E_0/keV and λ/pm are 6.5522 and 543 for Mn(II) in tn, 6.5521 and 537 for Mn(II) in pa, 7.1272 and 502 for Fe(II), 7.7234 and 528 for Co(II) and 8.3488 and 545 for Ni(II). b) Ref. 3 c) The interatomic distance between metal(II) ion and coordinated atoms. d) The Debye–Waller factor. e) The number of scatterers. f) Fixed value. g) For the octahedral complex. h) For the tetrahedral complex. i) The n value corresponds to the product of the coordination number and the mole ratio of each species. j) See Ref. 5.

Results and Discussion

The observed EXAFS oscillations, the Fourier transforms, and the Fourier filtered EXAFS oscillations for water, tn, and pa solutions are given in Figs. S1-S3 as supporting data, respectively. The structure parameters for Ni(II), Co(II), Fe(II), and Mn(II) ions in tn and pa obtained by the EXAFS method are listed in Table 1 together with those for the corresponding metal(II) ions in water. The n values indicate that the solvated Ni(II), Fe(II), and Mn(II) ions are six-coordinate in tn and pa solutions.[5,12] The R value of 214±1 pm for the Ni(II) ion in tn solution is in reasonable agreement with the Ni–N bond distances reported for octahedral $[\mathrm{Ni(en)_3}]^{2+}$ in the solid state, ca. 213 pm.[13—15] The R values for the tn and pa solutions of Fe(II) and Mn(II) ions are comparable with the metal–nitrogen (M–N) bond distances estimated from the crystal ion radii for the octahedral high-spin $[\mathrm{M(en)_3}]^{2+}$ (221 pm for M = Fe(II) and 226 pm for M = Mn(II)).[2] These results allow us to perform the NMR study for octahedral paramagnetic metal(II) ions which is also supported by the visible absorption spectrum for each metal(II) ion in tn.[16]

The NMR line-broadening of solvent molecules in the bulk due to the paramagnetic ion is expressed as $T_{2\mathrm{P}}^{-1} = \pi(\Delta\nu_{\mathrm{obsd}} - \Delta\nu_{\mathrm{solv}})$, where $T_{2\mathrm{P}}^{-1}$ is the transverse relaxation rate and $\Delta\nu_{\mathrm{obsd}}$ and $\Delta\nu_{\mathrm{solv}}$ are the half-height widths of the NMR spectra of the solvent molecules in the bulk in the presence and absence, respectively, of the paramagnetic ion. The $T_{2\mathrm{P}}^{-1}$ value is normalized by dividing by the molar fraction of the bound solvent molecules, P_M. The NMR line broadening data were analyzed by means of the modified Swift–Connick equation:[17,18]

$$\frac{1}{T_{2\mathrm{P}}P_\mathrm{M}} = \frac{1}{\tau_\mathrm{M}}\frac{T_{2\mathrm{M}}^{-2}+(\tau_\mathrm{M}T_{2\mathrm{M}})^{-1}+(\Delta\omega_\mathrm{M})^2}{(\tau_\mathrm{M}^{-1}+T_{2\mathrm{M}}^{-1})^2+(\Delta\omega_\mathrm{M})^2}+\frac{1}{T_{2\mathrm{o}}}, \qquad (1)$$

in which the symbols have their usual meaning.[19] The solvent exchange rate constant k_ex is equal to $\tau_\mathrm{M}^{-1}=(k_\mathrm{B}T/h)\exp(-\Delta H^\ddagger/RT+\Delta S^\ddagger/R)$. The temperature dependences of $\Delta\omega_\mathrm{M}$, $T_{2\mathrm{M}}^{-1}$, and $T_{2\mathrm{o}}$ are expressed as $\Delta\omega_\mathrm{M}=-C_\omega/T$, $T_{2\mathrm{M}}^{-1}=(C_\mathrm{M}/T)\exp(E_\mathrm{M}/RT)$, and $T_{2\mathrm{o}}^{-1}=(C_\mathrm{o}/T)\exp(E_\mathrm{o}/RT)$, respectively. When the $T_{2\mathrm{M}}^{-1}$ term is small enough compared with the other relaxation terms, Eq. 1 is reduced to

$$(T_{2\mathrm{P}}P_\mathrm{M})^{-1} = (\tau_\mathrm{M}^{-1}(\Delta\omega_\mathrm{M})^{-2}+\tau_\mathrm{M})^{-1}+T_{2\mathrm{o}}^{-1}. \qquad (2)$$

When the $T_{2\mathrm{o}}^{-1}$ term is negligible, Eq. 2 becomes

$$(T_{2\mathrm{P}}P_\mathrm{M})^{-1} = (\tau_\mathrm{M}^{-1}(\Delta\omega_\mathrm{M})^{-2}+\tau_\mathrm{M})^{-1}. \qquad (3)$$

In the case of $T_{2\mathrm{M}}^{-2} \gg (\Delta\omega_\mathrm{M})^2$, $T_{2\mathrm{o}}^{-1}$, Eq. 1 is reduced to

$$(T_{2\mathrm{P}}P_\mathrm{M})^{-1} = 1/(T_{2\mathrm{M}}+\tau_\mathrm{M}). \qquad (4)$$

If $T_{2\mathrm{M}}^{-2} \gg (\Delta\omega_\mathrm{M})^2$, τ_M^{-2} is valid, Eq. 1 becomes

$$(T_{2\mathrm{P}}P_\mathrm{M})^{-1} = \tau_\mathrm{M}^{-1}+T_{2\mathrm{o}}^{-1}. \qquad (5)$$

Figure 1 shows the temperature dependences of $(T_{2\mathrm{P}}P_\mathrm{M})^{-1}$ for 19.52-MHz ^{14}N NMR of tn and pa for Ni(II), Fe(II), and Mn(II) ions, and all the line-broadening data are deposited in Table S2 as supporting data. For the tn and pa exchange of Fe(II) ion, nonlinear least-squares analysis according to Eq. 2 because of contribution of both $\Delta\omega_\mathrm{M}$ and $T_{2\mathrm{o}}^{-1}$ terms was applied to the line-broadening data. The line-broadening data for the tn and pa exchange of Mn(II) ion were analyzed by means of Eq. 4 because of the contribution of $T_{2\mathrm{M}}^{-1}$ without

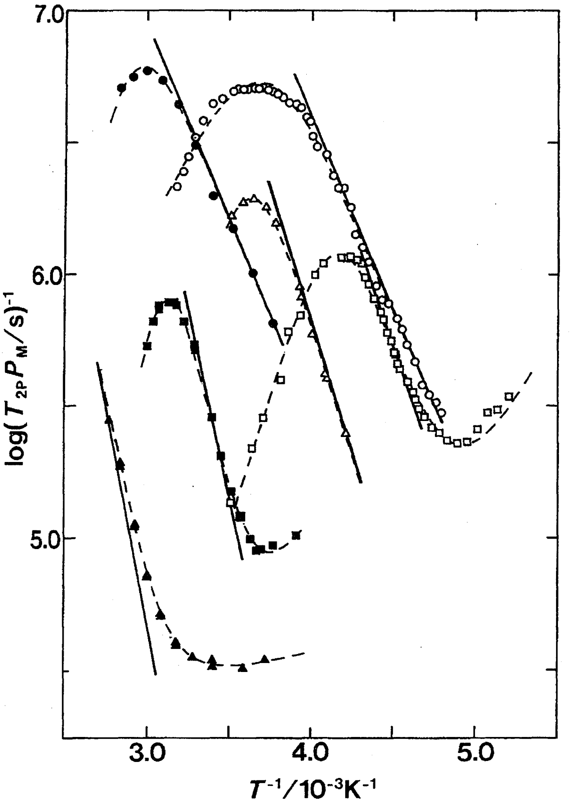

Fig. 1. Temperature dependence of $\log(T_{2P}P_M)^{-1}$ for 19.52-MHz ^{14}N NMR in tn and pa. Ni(II) (▲): $P_M = 9.97\times10^{-3}$ and 2.09×10^{-2}, Fe(II) (■): $P_M=2.17\times10^{-2}$ and 4.52×10^{-2}, and Mn(II) (●): $P_M=1.19\times10^{-3}$ for the tn exchange and Ni(II) (△): $P_M=5.83\times10^{-4}$ and 7.02×10^{-4}, Fe(II) (□): $P_M=3.79\times10^{-3}$, and Mn(II) (○): $P_M=4.70\times10^{-3}$, 3.12×10^{-3}, 1.34×10^{-3}, and 5.44×10^{-4} for the pa exchange. Each solid line indicates the contribution of $\tau_M{}^{-1}$. The dotted lines were obtained by the least-squares fitting of each line-broadening data to the respective equations.

$T_{2o}{}^{-1}$. The data for the tn and pa exchange of Ni(II) ion were analyzed by means of Eqs. 3 and 5, respectively. All the parameters obtained by least-squares fitting are summarized in Table S3 as supporting data.

The variable-pressure ^{14}N NMR experiments for the tn exchange of Ni(II), Fe(II), and Mn(II) ions have been performed at 367.4, 294.4, and 278.4 K, respectively, where $(T_{2P}P_M)^{-1}$ is equal to k_{ex}, as is apparent from Fig. 1. From the transition-state theory, the activation volume, $\Delta V^\ddagger$, is given by the relation, $(\partial \ln k_{ex}/\partial P)_T = -\Delta V^\ddagger/RT$. Because the plot of $\ln(k_{ex}/k_0)$ vs. P is linear within experimental errors (Fig. 2 and Table S4 as supporting data) where k_0 is the exchange rate constant at 0 MPa, the $\Delta V^\ddagger$ values were determined from the slopes. The activation parameters and rate constants at 298 K for the three amine (en,[1,2] tn, and pa) exchanges on Ni(II), Co(II),[3] Fe(II), and Mn(II) ions are summarized in Table 2.

The $\Delta V^\ddagger$ values range from 7.2 to 0.1 cm^3 mol^{-1} along the series from Ni(II) to Mn(II) ions in tn as in en (see Table 2). Thus we can expect the mechanism from dissociative to dissociative-interchange for the tn exchange along this metal(II) series, as previously discussed for the en exchange.[2] On the other hand, judging from change in the $\Delta S^\ddagger$ values from positive to negative for the pa exchange as well as the tn exchange, the mechanistic changeover from dissociative to associative-interchange along the series from Ni(II) to Mn(II) is acceptable, as is general for monodentate solvent exchanges.[20] The relatively large rate constants (k_{ex}) for the pa exchange compared with the other monodentate solvent exchanges,[20,21] especially those for the metal(II) ions with higher d-orbital occupancy such as Ni(II) and Co(II) ions (1.3×10^7 and 2.0×10^8 s^{-1} at 25 °C), may be attributed to the greater d-electronic repulsion in the metal ions[22] caused by the amine nitrogens. Such destabilization of the ground state is responsible for the relatively small $\Delta H^\ddagger$ values for the pa exchange of Ni(II) and Co(II) ions (37.1 and 36.2 kJ mol^{-1}) compared to the other dissociatively activated monodentate solvent exchanges (50—70 kJ mol^{-1}).[20,21]

It is worthwhile to discuss the kinetic results of the en, tn, and pa exchanges for each of the Ni(II), Co(II), and Fe(II) ions, because the reaction mechanism is comparable among the three amine exchanges of each metal(II) ion. The order of increase in the k_{ex} values of the three amine exchanges, en < tn < pa, is unchanged for the respective metal(II) ions. The difference in k_{ex} for the three amine exchanges comes from the difference in $\Delta H^\ddagger$, especially in the case of Ni(II) and Fe(II) (see Table 2). We have pointed out that the elongation of the M–N bond for the en chelate in the transition state causes angular distortion around the leaving amine nitrogen due to chelate strain. Such a 'kinetic' chelate strain effect enthalpically highly activates the chelate ring opening

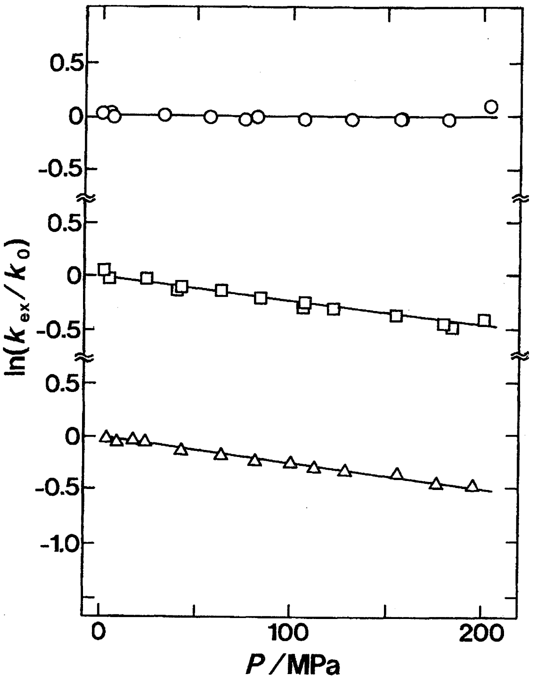

Fig. 2. Pressure dependence of $\ln(k_{ex}/k_0)$ for the tn exchange on Ni(II) ion at 367.4 K (△), Fe(II) ion at 294.4 K (□), and Mn(II) ion at 278.4 K (○).

Table 2. Kinetic Parameters for Solvent Exchange of Mn(II), Fe(II), Co(II), and Ni(II) Ions in en, tn, and pa

	Solvent	Mn(II)	Fe(II)	Co(II)	Ni(II)
${k_{ex}}^{298}/s^{-1}$	en	1.7×10^{6} a)	4.3×10^{4} a)	5.4×10^{3} a)	$2.0\times10^{b)}$
	tn	2.5×10^{6}	3.9×10^{5}	2.9×10^{5} c)	3.1×10^{3}
	pa	3.7×10^{7}	6.9×10^{7}	2.0×10^{8} c)	1.3×10^{7}
$\Delta H^{\ddagger}$/kJ mol^{-1}	en	24.7 ± 1.6 a)	46.3 ± 1.4 a)	56.5 ± 3.3 a)	69 ± 3 b)
	tn	21.9 ± 1.5	47.9 ± 1.2	49.3 ± 0.9 c)	61.3 ± 2.1
	pa	26.2 ± 0.6	32.4 ± 1.4	36.2 ± 1.2 c)	37.1 ± 0.1
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	en	-43 ± 5 a)	-1 ± 4 a)	16 ± 10 a)	10 ± 11 b)
	tn	-50 ± 4	23 ± 4	25 ± 3 c)	28 ± 6
	pa	-13 ± 3	14 ± 1	35 ± 6 c)	16 ± 2
$\Delta V^{\ddagger}$/cm^{3} mol^{-1}	en	-0.6 ± 0.5 a,d)	-1.2 ± 0.8 a,e)	0.9 ± 0.9 a,f)	11.4 ± 2.0 b,g)
	tn	0.1 ± 0.5 h)	5.8 ± 0.4 i)	6.6 ± 0.3 c,j)	7.2 ± 0.3 k)

a) Ref. 2. b) Ref. 1. c) Ref. 3. The kinetic parameters for the pa exchange correspond to those for the octahedral Co(II) complex. d) At 278.4 K. e) At 324.5 K. f) At 332.4 K. g) At 383 K. h) At 278.4 K. i) 294.4 K. j) At 302.1 K. k) At 367.4 K.

process for the en exchange because of a decrease in the overlap of the σ orbitals to which the metal–nitrogen (M–N) bond strength is sensitive.[2,23] The present results indicate that the degree of the 'kinetic' chelate strain effect is in the order of pa<tn<en for each metal(II) ion in common, because the six-membered tn chelate can flexibly elongate the M–N bond to form a less distorted M–N–C angle compared to the five-membered en chelate; such a distortion does not take place in the case of the dissociation of the monodentate pa solvent.

The difference in k_{ex} and $\Delta H^{\ddagger}$ between the en and tn exchanges for the respective metal(II) ions is reduced with a decrease in the atomic number from Ni(II) to Fe(II) (Fig. 3), because the variation in k_{ex} and $\Delta H^{\ddagger}$ from a Ni(II) to Fe(II) is more drastic for the en exchange compared to the tn exchange. The difference in variation of k_{ex} and $\Delta H^{\ddagger}$ between the en and tn exchanges is not interpreted by the electronic properties of the amine solvents and/or the metal(II) ions. Judging from the regular sp^3 angle of Ni(II)–N–C in $[Ni(en)_3]^{2+}$ (107.7—108.3°),[13—15] we find that the Ni(II)–N distances are in a range suitable for the five-membered en chelate where the ground state is relatively stabilized;[2] the six-membered tn chelate is obviously large for the Ni(II)–N distance and destabilizes the ground state, considering that the Cr–N–C angles (116.4—122.0°) in $[Cr(tn)_3]^{3+}$[24] are appreciably larger than those for the regular sp^3 amine nitrogen where the Cr–N distances are comparable to those for the $[Ni(N)_6]$-type complexes.[13—15] The en chelate complexes are destabilized with an increase in the ion radius due to the chelate strain in the ground state, where the distortion of the metal–nitrogen–carbon (M–N–C) angle decreases the over-

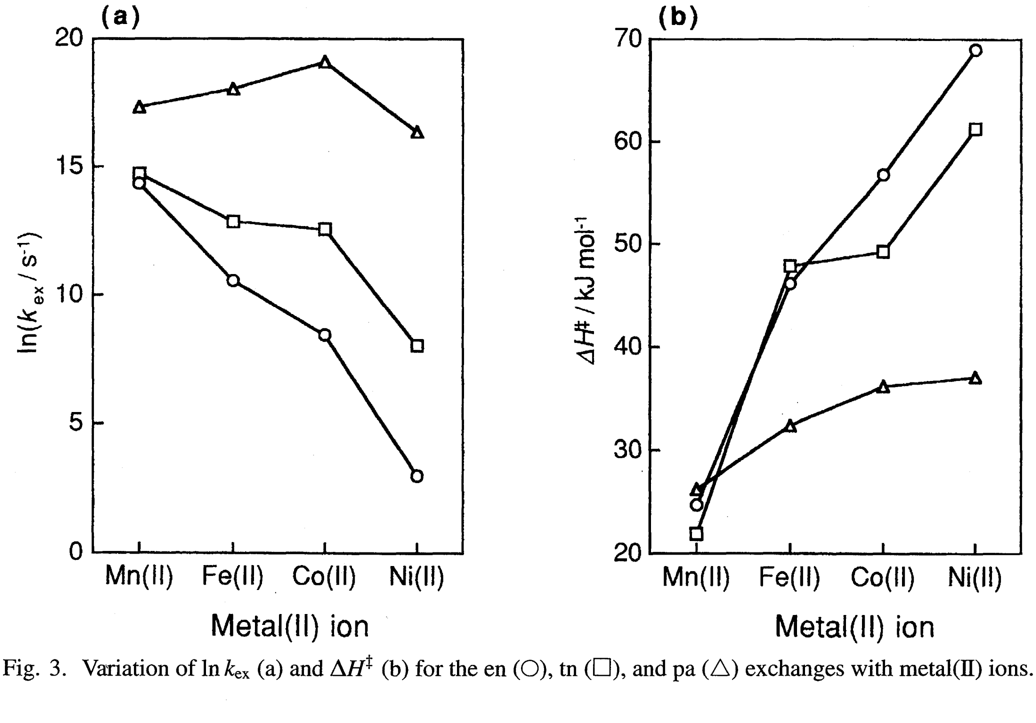

Fig. 3. Variation of ln k_{ex} (a) and $\Delta H^{\ddagger}$ (b) for the en (○), tn (□), and pa (△) exchanges with metal(II) ions.

lap of the σ bonding orbitals as in the transition state.[23] On the other hand, the destabilization of the tn chelate complexes may be reduced for the relatively large metal ion by the fitness of the chelate ring size, as reported for the Co(II) ion where the crystal field strength of $[Co(tn)_3]^{2+}$ is similar to or slightly greater than that of $[Co(en)_3]^{2+}$.[3] The chelate strain effect of en and the fitness of the tn chelate ring size for the relatively large metal(II) ions in the ground state cancel out the difference in the 'kinetic' chelate strain effect between en and tn.

It should be mentioned that the Mn(II) ion with high-spin d^5 configuration has no crystal field stabilization and a fairly ionic character and that consequently the distortion of the chelate bite angle does not affect the crystal field. Therefore, the angular distortion around the amine nitrogen can be relaxed by adjustment of the chelate bite angle. Such an electronic factor reduces the chelate strain both in the ground state and in the activation process. Furthermore, the variation in the geometry or the coordination number in the transition state caused by the difference in the reaction mechanism makes a difference only in the spherically symmetric potential.[22] Such constancy in the crystal field of both the ground state and the transition state for the high-spin Mn(II) ion contributes to the small variation of the k_{ex} and $\Delta H^\ddagger$ values for the present three amine exchanges. This is also the case for the small range of the k_{ex} and $\Delta H^\ddagger$ values for various solvent exchanges on the Mn(II) ion,[20] even if there is some difference in the reaction mechanism.[25]

Supporting Data. The compositions of the NMR sample solutions (Table S1), the NMR line-broadening data at various temperatures for tn and pa exchange (Table S2), the values of the NMR parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$, C_ω, C_M, E_M, C_0, and E_0) (Table S3), the NMR line-broadening data at various pressures for tn exchange (Table S4), the observed EXAFS oscillations $\chi_{obsd}(k)$ weighted by k^3 (Fig. S1), the Fourier transforms $|G(R)|$ of $k^3\chi_{obsd}(k)$ (Fig. S2) and the Fourier filtered EXAFS oscillations $\chi(k)$ (Fig. S3) for water, tn, and pa solutions (in total 9 pages) are deposited as Document No. 70022 at the Office of the Editor of Bull. Chem. Soc. Jpn. and are also available from the author on request.

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References

1) S. Soyama, M. Ishii, S. Funahashi, and M. Tanaka, *Inorg. Chem.*, **31**, 536 (1992).

2) S. Aizawa, K. Matsuda, T. Tajima, M. Maeda, T. Sugata, and S. Funahashi, *Inorg. Chem.*, **34**, 2042 (1995).

3) S. Aizawa, S. Iida, K. Matsuda, and S. Funahashi, *Inorg. Chem.*, **35**, 1338 (1996).

4) M. Ishii, S. Funahashi, K. Ishihara, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **62**, 1852 (1989).

5) Because of low solubility of the Ni(II) salt in pa, a sufficient EXAFS spectrum was not obtained.

6) S. Funahashi, in "High Pressure Liquids and Solutions," ed by Y. Taniguchi, M. Senoo, and K. Hara, Elsevier, Amsterdam (1994), pp. 31—48.

7) M. Nomura, "KEK Report 85-7," National Laboratory for High Energy Physics, Tsukuba, Japan (1985).

8) Y. Inada, K. Sugimoto, K. Ozutsumi, and S. Funahashi, *Inorg. Chem.*, **33**, 1875 (1994).

9) Y. Inada, S. Funahashi, and H. Ohtaki, *Rev. Sci. Instrum.*, **65**, 18 (1994).

10) Y. Marcus, *Chem. Rev.*, **88**, 1475 (1988).

11) H. Ohtaki and T. Radnai, *Chem. Rev.*, **93**, 1157 (1993).

12) We can expect that the Ni (II) ion in pa has the octahedral geometry as in $[Ni(N)_6]^{2+}$ ($N=NH_3$, CH_3NH_2, 1/2en, and 1/2tn) considering their ligand fields (Ref. 15).

13) M.-U. Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970).

14) G. B. Jameson, R. Schneider, E. Dubler, and H. R. Oswald, *Acta Crystallogr., Sect. B*, **B38**, 3016 (1982).

15) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1858 (1970).

16) A. B. P. Lever, "Inorganic Electronic Spectroscopy," 2nd ed, Elsevier, Amsterdam (1984), Chaps. 3 and 6.

17) T. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

18) L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **15**, 709 (1976).

19) A. Hioki, S. Funahashi, and M. Tanaka, *J. Phys. Chem.*, **89**, 5057 (1985).

20) A. E. Merbach, in "High Pressure Chemistry and Biochemistry," ed by R. van Eldik and J. Jonas, D. Reidel Publishing, Dordrecht, The Netherlands (1987), pp. 311—331.

21) R. B. Jordan, "Reaction Mechanisms of Inorganic and Organometallic Systems," Oxford University Press, New York (1991), Chap. 3. The original references are cited therein.

22) H. L. Schlafer and G. Gliemann, "Basic Principles of Ligand Field Theory," Wiley, London (1969), Part A, Chaps. 1 and 3.

23) B. Douglas and C. A. Hollingsworth, "Symmetry in Bonding and Spectra," Academic Press, San Diego, CA (1985), Chap. 8.

24) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, **10**, 2387 (1974).

25) M. Ishii, S. Funahashi, and M. Tanaka, *Chem. Lett.*, **1987**, 871.