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Article

Octahedral–Tetrahedral Equilibrium and Solvent Exchange of Cobalt(II) Ions in Primary Alkylamines

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The enthalpy differences ($\Delta H°$) of the equilibrium between the octahedral and tetrahedral solvated cobalt(II) complexes were obtained in some primary alkylamines such as propylamine (pa, 36.1 ± 2.3 kJ $\mathrm{mol^{-1}}$), *n*-hexylamine (ha, 34.9 ± 1.0 kJ $\mathrm{mol^{-1}}$), 2-methoxyethylamine (meea, 44.8 ± 3.1 kJ $\mathrm{mol^{-1}}$), and benzylamine (ba, 50.1 ± 3.6 kJ $\mathrm{mol^{-1}}$) by the spectrophotometric method. The differences in the energy levels between the two geometries of the cobalt(II) complexes in the spherically symmetric field ($\Delta E_{\mathrm{spher}}$) were estimated from the values of $\Delta H°$ by offsetting the ligand field stabilization energies. It was indicated that the value of $\Delta E_{\mathrm{spher}}$ is the decisive factor in determining the value of $\Delta H°$ and is largely dependent on the electronic repulsion between the d-electrons and the donor atoms and the interelectronic repulsion in the d orbitals. The comparison between activation enthalpies ($\Delta H^{\ddagger}$) for the solvent exchange reactions of octahedral cobalt(II) ions in pa and meea revealed that the unexpectedly large rate constant and small $\Delta H^{\ddagger}$ in pa are attributed to the strong electronic repulsion in the ground state and removal of the electronic repulsion in the dissociative transition state, which can give the small $\Delta E_{\mathrm{spher}}$ between the ground and transition states. Differences in the solvent exchange rates and the $\Delta H^{\ddagger}$ values of the octahedral metal(II) ions in some other solvents are discussed in connection with the electronic repulsive factors.

Introduction

The thermodynamic stability and reaction rates for transition metal complexes often have been discussed with reference to the ligand field stabilization energy (LFSE).[1] The ligand field splitting ($10Dq$) of the first-row transition series is generally greater for nitrogen donors such as amines than for oxygen donors because of the stronger σ donation of the former.[2] Considering the greater $10Dq$ values for the octahedral complexes ($10Dq_{\mathrm{oct}}$) compared with those for the tetrahedral ones ($10Dq_{\mathrm{tet}}$), that is, $Dq_{\mathrm{oct}} = (9/4)Dq_{\mathrm{tet}}$ supposing the metal ion is surrounded with equivalent donor atoms and their bond distances are equal in both geometries,[2] we assume that the stabilization of the octahedral geometry compared with the tetrahedral one ($10Dq_{\mathrm{oct}} - 10Dq_{\mathrm{tet}} = (50/9)Dq_{\mathrm{oct}}$) is greater in the case of the nitrogen donors than the oxygen ones because of the greater Dq_{oct} values for the former. Recently, however, it was revealed that the octahedral and tetrahedral solvated cobalt(II) ions coexist in equilibrium in a neat *n*-propylamine (pa) solution[3] though the oxygen donors without steric restraint selectively form the octahedral complexes.[4] Furthermore, it was found that the solvent exchange rate on the octahedral cobalt(II) ion, which is dissociatively activated,[5] is much faster in pa[3] than in the weaker σ-donor solvents such as methanol, acetonitrile, and water,[1] because of the much smaller activation enthalpy ($\Delta H^{\ddagger}$) in pa. This result is inconsistent with the expectation that the stabilization of the octahedral ground state compared with the dissociative transition state is greater in the stronger donor solvents with large $10Dq_{\mathrm{oct}}$ than in the weaker donor ones, unless the empirical fitting parameter depending on

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(1) Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems*; Oxford University Press: New York, 1991; Chapter 3 and references cited therein.

(2) Douglas, B. E.; Hollingsworth, C. A. *Symmetry in Bonding and Spectra*; Academic Press: San Diego, CA, 1985; Chapter 9.

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

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

(5) Merbach, A. E. In *High-Pressure Chemistry and Biochemistry*; van Eldik, R., Jonas, J., Eds.; D. Reidel Publishing: Dordrecht, The Netherlands, 1987; pp 311−331.

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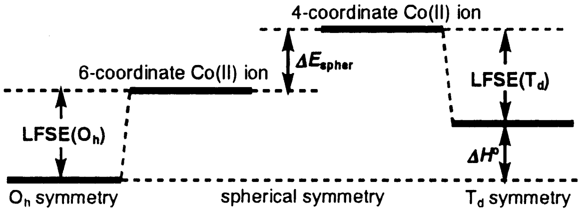

Figure 1. Relative energy levels in the octahedral (O_h)−tetrahedral (T_d) equilibrium.

solvents is introduced as reported by Jordan et al.[6] To resolve such contradictions, it is necessary to consider a spherically symmetrical field[7] in which metal ions are spherically surrounded by homogeneous negative charges of the donor atoms and are not subjected to the ligand field splitting. The energy levels in the spherically symmetrical field are determined simply by the electrostatically attractive and electronically repulsive interactions which are usually much greater than the LFSE and can be decisive factors in determining the stability. Because there is an inevitable difference in the total attractive and repulsive forces between two geometries with different coordination numbers in the spherically symmetrical field (ΔE_{spher}), it is essential to compare the ΔE_{spher} values for the sake of discussion of the octahedral−tetrahedral equilibrium and the reaction rates for the dissociative or associative reaction mechanisms.

In this study, we evaluated the values of ΔE_{spher} for the unique octahedral−tetrahedral equilibrium of the solvated cobalt(II) ion using the difference in enthalpy ($\Delta H°$) and LFSE for each geometry (Figure 1) which were systematically obtained in several primary alkylamine derivatives with different basicities such as pa, *n*-hexylamine (ha), 2-methoxyethylamine (meea), and benzylamine (ba). By comparison of these results, we revealed the main factor that determines the relative energy levels for the octahedral and tetrahedral geometries in the alkylamines. Furthermore, we also discuss the differences in the $\Delta H^{\ddagger}$ values and rate constants of the solvent exchange reactions for the cobalt(II) ion in connection with the differences in energy levels between the ground state and dissociative transition state in the spherically symmetrical field.

Experimental Section

Reagents. The primary alkylamine solvents, *n*-propylamine (pa, Wako, Special Gr.), *n*-hexylamine (ha, Aldrich, 99%), 2-methoxyethylamine (meea, Aldrich, 99%), and benzylamine (ba, Aldrich, 99.5%), were purified by a procedure similar to that described for pa.[3] Anhydrous cobalt(II) trifluoromethanesulfonate (triflate) was prepared from basic cobalt(II) carbonate (Wako, Pr. Gr.) by a procedure similar to that reported previously.[3]

Sample Preparation and Measurements. Because the Co(II) ion is highly oxygen and moisture sensitive in the amine solutions, the samples for the absorption spectral measurements were prepared on a vacuum line by vacuum distillation of the purified amine solvents into twice-fused quartz cuvettes containing known amounts of anhydrous cobalt(II) triflate that were then flame-sealed after degassing. The NMR sample preparation for the solvent exchange measurements was similarly carried out on a vacuum line, using 5 mm o.d. NMR tubes.

The electronic absorption spectra at various temperatures were recorded on Shimadzu UV-3100PC and UV-265FW spectrophotometers. The ^{14}N NMR measurements at various temperatures were performed on a JEOL-GX 270 FT-NMR spectrometer operating at 19.52 MHz. The flame-sealed NMR tube was coaxially mounted in a 10 mm o.d. NMR tube containing deuterated acetone as a lock solvent. The temperature was controlled within ±0.1 K, and measured by a substitution technique with a thermistor (D641, Takara Thermistor Co.). For the equilibrium experiments on the basis of the temperature dependence of the absorption spectra, the unit of the concentration of the sample solutions, mol kg^{-1}, was converted to mol dm^{-3} with knowledge of the densities of the amine solvents at various temperatures which were measured with an Anton Paar DMA 60 digital density meter.

Results

Equilibrium Study. Each color of the ha, meea, and ba solutions of cobalt(II) triflate in the flame-sealed cuvettes changed reversibly from pale pink to deep purple as the temperature was raised. The absorption spectral changes are quite similar to that of the pa solution,[3] and can be reasonably attributed to the geometrical change from the octahedral solvated cobalt(II) complexes to the tetrahedral one which was demonstrated for the pa solution by means of electronic absorption and EXAFS spectroscopies.[3] The thermodynamic parameters of the octahedral−tetrahedral equilibrium in each amine (eq 1) were determined by analyzing the change in absorbance (A) at a given wavelength as a function of temperature, using eqs 2 and 3,

$$[\mathrm{Co(amine)_6}]^{2+} \rightleftarrows [\mathrm{Co(amine)_4}]^{2+} + 2\ \mathrm{amine} \tag{1}$$

$$A = (\epsilon_{\text{oct}}[\mathrm{Co}]_{\mathrm{T}} + K\epsilon_{\text{tet}}[\mathrm{Co}]_{\mathrm{T}})/(K + 1) \tag{2}$$

$$K = \exp(-\Delta H°/RT + \Delta S°/R) \tag{3}$$

where $[\mathrm{Co}]_{\mathrm{T}}$ is the total concentration of Co(II) ions, K is the equilibrium constant, $K = [\mathrm{Co(amine)_4}^{2+}]/[\mathrm{Co(amine)_6}^{2+}]$, considering that the activity of the solvent is close to unity in such diluted solutions. and ϵ_{oct} and ϵ_{tet} are the respective molar absorption coefficients. The cobalt(II) concentration at each temperature was corrected to the molar scale by using each density of the amine solvents at the corresponding temperatures obtained from the linear dependence of the density on temperature.[8] Each change in the absorbance with temperature was analyzed by using eqs 2 and 3 to provide a good fit to the calculated curve as shown in Figure 2. The thermodynamic parameters listed in Table 1 were determined

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[6] Rusnak, L. L.; Yang, E. S.; Jordan, R. B. *Inorg. Chem.* **1978**, *17*, 1810.

[7] Johnson, D. A.; Nelson, P. G. *Inorg. Chem.* **1995**, *34*, 3253.

[8] The densities of the present amines are 0.781, 0.771, 0.765, 0.756, 0.747, 0.739, and 0.731 g cm^{-3} at 1.1, 11.2, 20.8, 31.0, 41.4, 50.6, and 60.1 °C, respectively, for ha, 0.879, 0.868, 0.858, 0.847, 0.837, and 0.827 g cm^{-3} at 14.3, 24.9, 35.0, 45.3, 55.3, and 64.3 °C, respectively, for meea, and 0.987, 0.978, 0.970, 0.961, 0.953, 0.944, and 0.936 g cm^{-3} at 15.1, 25.1, 35.1, 45.0, 55.4, 64.2, and 72.0 °C, respectively, for ba. The linear regression equations of density (d/g cm^{-3}) as a function of temperature (T/°C) were expressed as $d = (-8.47 \times 10^{-4})T + 0.782$ for ha, $d = (-1.03 \times 10^{-3})T + 0.894$ for meea, and $d = (-8.82 \times 10^{-4})T + 1.001$ for ba. The temperature dependence of density for pa was described in ref 3.

Table 1. Thermodynamic Parameters for the Octahedral−Tetrahedral Equilibrium of Solvated Cobalt(II) Complexes in Primary Alkylamines

solvent	K^{298}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
pa[a]	1.12	36.1 ± 2.3	122 ± 8
ha	0.99	34.9 ± 1.0	117 ± 3
meea	0.141	44.8 ± 3.1	134 ± 10
ba	0.265	50.1 ± 3.6	157 ± 11

[a] Reference 3.

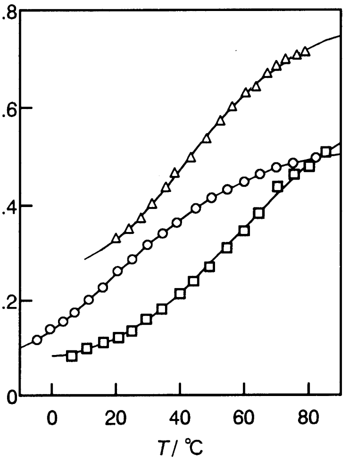

Figure 2. Temperature dependence of absorbance for solvated cobalt(II) complexes in ha at 560 nm (○) (C_{Co} = 2.4 × 10^{-3} mol dm^{-3}), in meea at 550 nm (□) (C_{Co} = 2.8 × 10^{-3} mol dm^{-3}), and in ba at 560 nm (△) (C_{Co} = 4.7 × 10^{-3} mol dm^{-3}). The solid lines are depicted by using the obtained values of the thermodynamic parameters and molar absorption coefficients.

by using the large absorbance change in the d−d transition bands (Figures 2 and 3).

It is seen from the thermodynamic parameters that the octahedral solvated cobalt(II) complex is almost quantitatively formed in meea below 270 K and the d−d absorption bands for the tetrahedral complex are dominantly observed just below the boiling point of 368 K due to their large molar absorption coefficients compared with those for the octahedral complex (Figure 3b). Because the octahedral or tetrahedral complex was not quantitatively formed in the measurable temperature ranges for the equilibria in the ha and ba solutions, the absorption spectra of both geometries were obtained from ϵ_{oct} and ϵ_{tet} determined at each wavelength (Figure S3a,c). The absorption bands for the octahedral and tetrahedral complexes can be assigned to the transitions from $^4T_{1g}$ to $^4T_{2g}$, $^4A_{2g}$, and $^4T_{1g}(P)$ for the former and those from $^4A_2$ to $^4T_1(F)$ and $^4T_1(P)$ for the latter as assigned for the pa solution (Table 2).[9] The crystal field strength, $10Dq$, and the Racah parameter, B, for each complex were estimated from the electronic transition energies,[9] and then the ligand field stabilization energies (LFSE) were calculated from the values of $10Dq$ and B by using the expressions of the ground-state energy levels, $-3Dq + 7.5B - {}^1\!/_2(225B^2 + 100Dq^2 + 180DqB)^{1/2}$ for $^4T_{1g}$ and $-12Dq$ for $^4A_2$, respectively (Table 3).

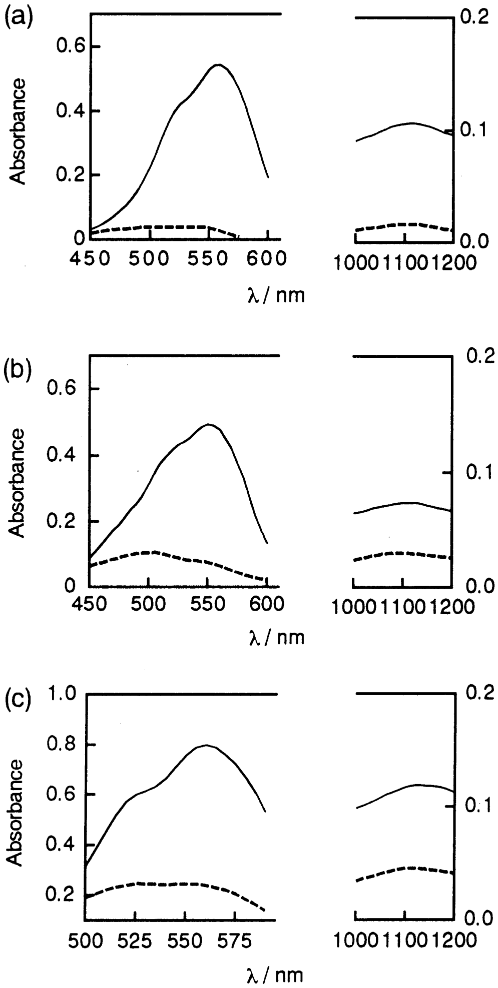

Figure 3. Absorption spectra of the octahedral (- - -) and tetrahedral (—) solvated cobalt(II) complexes in ha (a) (C_{Co} = 2.4 × 10^{-3} mol dm^{-3}, calcd), meea (b) (C_{Co} = 2.8 × 10^{-3} mol dm^{-3}, obsd at 270 K for the octahedral complex and at 363 K for the tetrahedral complex), and ba (c) (C_{Co} = 4.7 × 10^{-3} mol dm^{-3}, calcd).

NMR Study. The NMR line-broadening of the solvent molecules in the bulk due to the paramagnetic cobalt(II) ions is expressed as $T_{2P}^{-1} = \pi(\Delta\nu_{obsd} - \Delta\nu_{solv})$, where T_{2P}^{-1} is the transverse relaxation rate and $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ are the half-height widths of the NMR signals of the solvent molecules in the bulk in the presence and absence, respectively, of the paramagnetic ions. The T_{2P}^{-1} value was normalized by dividing by the molar fraction of the bound solvent molecules, P_M. The NMR line-broadening data were analyzed by using the modified Swift−Connick equation:[10,11]

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M}\frac{T_{2M}^{-2} + (\tau_M T_{2M})^{-1} + (\Delta\omega_M)^2}{(\tau_M^{-1} + T_{2M}^{-1})^2 + (\Delta\omega_M)^2} + \frac{1}{T_{2o}} \tag{4}$$

in which the symbols have their usual meanings.[12] Figure 4 shows the temperature dependence of $(T_{2P}P_M)^{-1}$ for the ^{14}N nucleus of meea, and it is apparent that the τ_M^{-1} and $\tau_M(\Delta\omega_M)^2$ terms dominate the relaxation over the present temperature range and T_{2M}^{-1} and T_{2o}^{-1} are small compared to the other relaxation terms. Thus, eq 4 is reduced to

$$(T_{2P}P_M)^{-1} = (\tau_M^{-1}(\Delta\omega_M)^{-2} + \tau_M)^{-1} \tag{5}$$

where the solvent exchange rate constant, k_{ex}, is equal to

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[9] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1984.

Table 2. Absorption Spectral Data for d−d Transitions of Octahedral and Tetrahedral Solvated Cobalt(II) Complexes in Primary Alkylamines

	d−d transition $\sigma/10^3$ cm^{-1}				
complex	$^4T_{1g} \rightarrow {}^4T_{2g}$	$^4T_{1g} \rightarrow {}^4A_{2g}$	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	$^4A_2 \rightarrow {}^4T_1(F)$	$^4A_2 \rightarrow {}^4T_1(P)$
$[Co(pa)_6]^{2+}$ [a]	8.55	17.76	19.49		
$[Co(ha)_6]^{2+}$	9.05	18.35	20.00		
$[Co(meea)_6]^{2+}$	9.19	18.45	19.80		
$[Co(ba)_6]^{2+}$	9.01	18.02	19.05		
$[Co(pa)_4]^{2+}$ [a]				8.40	17.67, 18.66sh
$[Co(ha)_4]^{2+}$				8.97	17.92, 18.87sh
$[Co(meea)_4]^{2+}$				9.03	18.12, 19.08sh
$[Co(ba)_4]^{2+}$				8.85	17.86, 18.87sh

[a] Reference 3.

Table 3. Values of 10*Dq*, *B*, and LFSE of Solvated Cobalt(II) Complexes in Primary Alkylamines

complex	$10Dq/10^3$ cm^{-1}	$B/10^3$ cm^{-1}	LFSE/10^3 cm^{-1} (kJ mol^{-1})
$[Co(pa)_6]^{2+}$	9.21[a]	0.77[a]	−6.38 (−76.3)
$[Co(ha)_6]^{2+}$	9.30	0.75	−6.37 (−76.2)
$[Co(meea)_6]^{2+}$	9.29	0.71	−6.38 (−76.4)
$[Co(ba)_6]^{2+}$	9.01	0.67	−6.34 (−75.8)
$[Co(pa)_4]^{2+}$	4.90	0.79	−5.88 (−70.3)
$[Co(ha)_4]^{2+}$	5.26	0.77	−6.31 (−75.5)
$[Co(meea)_4]^{2+}$	5.29	0.78	−6.35 (−75.9)
$[Co(ba)_4]^{2+}$	5.18	0.77	−6.22 (−74.4)

[a] Reference 3.

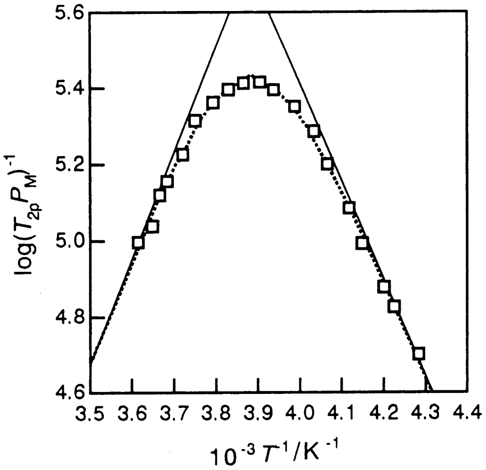

Figure 4. Temperature dependence of $\log(T_{2P}P_M)^{-1}$ for a 19.52-MHz ^{14}N NMR of meea solution of cobalt(II) ions ($P_M = 7.27 \times 10^{-3}$). The solid lines with negative and positive slopes indicate the contribution of τ_M^{-1} and $\tau_M\Delta\omega_M^2$ terms, respectively.

Table 4. Kinetic Parameters for Solvent Exchange of Octahedral Cobalt(II) Ions in pa and meea

solvent	k_{ex}^{298}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}
pa[a]	2.0×10^8	36.2 ± 1.2	35 ± 6
meea	1.1×10^7	46.6 ± 0.7	46 ± 3

[a] Reference 3.

Table 5. Values of $\Delta H°$ and ΔE_{Spher} of Solvated Cobalt(II) Complexes in Primary Alkylamines

solvent	$\Delta H°$/kJ mol^{-1}	ΔE_{spher}/kJ mol^{-1}
pa	36.1[a]	30.1
ha	34.9	34.2
meea	44.8	44.3
ba	50.1	48.7

[a] Reference 3.

$\tau_M^{-1} = (k_BT/h)\exp(-\Delta H^‡/RT + \Delta S^‡/R)$ and the temperature dependence of $\Delta\omega_M$ is expressed as $\Delta\omega_M = -C_\omega/T$. The sufficient solvent exchange region in which the τ_M^{-1} term is dominant was not observed in ha or ba because of the relatively higher freezing points. On the basis of the results of the equilibrium experiments (vide supra), it is confirmed that the octahedral cobalt(II) species predominantly exists (>97%) in the present temperature range for the NMR measurements, and furthermore the octahedral species is formed almost quantitatively (>99.8%) in the chemical exchange region below 240 K. The activation parameters obtained by a least-squares fitting according to eq 5 and the rate constant at 298 K for the octahedral cobalt(II) ion in meea are listed in Table 4 together with those in pa.

Discussion

As shown in Table 3, the thermodynamic stability is not attributed to the magnitude of the LFSE because the ligand field splitting (10*Dq*) and the d-electronic repulsion (Racah parameter *B*) complementarily change to give a rather constant LFSE value. The difference in energy levels of the solvated metal ions in the spherically symmetrical field (ΔE_{spher}) is calculated from the $\Delta H°$ value by offsetting the LFSE for each geometry (Figure 1), and it is confirmed that the $\Delta H°$ value depends on the ΔE_{spher} values as in Table 5. The energy level of the metal complex in the spherically symmetrical field is changed from that of the free ion by the following factors: (1) stabilization by electrostatic attraction between the spherically symmetrical metal ion and the surrounding donor atoms, (2) destabilization by electronic repulsion between the d electrons and the donor atoms, and (3) destabilization by the d-electronic repulsion (reduction of the nephelauxetic effect that still remains in the energy levels of any spectral terms after offsetting LFSE).[2] Needless to say, an increase in the charge density of the surrounding donor atoms increases the stabilizing factor (1) and the destabilizing factors (2) and (3), and changes in the respective stabilization and destabilization energies are greater in the six-coordinate complexes than in the corresponding four-coordinate ones. Accordingly, if it is the case that the stabilization of the six-coordinate complexes relative to the four-coordinate ones by factor (1) exceeds the relative destabilization by factors (2) and (3), ΔE_{spher} in Figure 1

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(10) Swift, T.; Connick, R. E. *Chem. Phys.* **1962**, *37*, 307.
(11) Rusnak, L. L.; Jordan, R. B. *Inorg. Chem.* **1976**, *15*, 709.
(12) Hioki, A.; Funahashi, S.; Tanaka, M. *J. Phys. Chem.* **1985**, *89*, 5057.

increases by an increase in the charge density of the donor atoms. On the contrary, if the contribution of the relative destabilization of the six-coordinate complexes is greater than that of the relative stabilization, ΔE_{spher} decreases by an increase in the charge density of the donor atoms. The latter is true for the present case considering that the order of the ΔE_{spher} values, pa < ha < meea < ba (Table 5), agrees with the reverse order of the solvent basicity and the B values for the octahedral complexes,[13] and it is probable that this order is not affected by the difference in the outer-solvation energy between the octahedral and tetrahedral solvated complexes in the present amine solvents. In addition, the B values for the tetrahedral complexes are not much affected by the variation in the donor atoms because of the mixing of the d orbitals with outer p orbitals.

The change in the electronic repulsion within the d orbitals should be emphasized here. The ground term ^4F for the d^7 ion is expressed by the Racah parameters as $21A - 43B + 14C$, where the Racah parameter A is correlated with the other parameters B and C, and is theoretically 2 orders of magnitude over B and Dq.[14] Accordingly, the ΔE_{spher} value is sensitively affected by a slight change in the d-electronic repulsion that is observed as the values of B. It is consistent with the fact that the weak solvents, which cause small $10Dq$ and B values concomitantly, form the octahedral cobalt(II) complexes selectively because the small d-orbital splitting is sufficiently compensated by the small d-electronic repulsion.

To discuss solvent exchange reactions on the basis of the above concept, we compared the activation parameters for the pa exchange on the octahedral cobalt(II) ion[3] with those for the meea exchange which were obtained in this work (Table 4). The moderately positive $\Delta S^{\ddagger}$ values similar to those for the other solvent exchange reactions on the octahedral cobalt(II) ion are consistent with the dissociative mechanism accepted for the cobalt(II) ion.[1,5] The exchange rate constants are depend on the $\Delta H^{\ddagger}$ values, and the value for meea is larger than that for pa, which is more basic and can give the stronger electronic repulsion than meea. In the case of complexes with strong electronic repulsion in the ground state, the dissociative transition state is relatively stabilized enthalpically because removal of the electronic repulsion in the transition state with the reduced coordination number decreases ΔE_{spher} between the ground state and the activation state (Figure 5a). Contrarily, it is also probable that large $\Delta H^{\ddagger}$ values and small rate constants are observed for complexes with weak electronic repulsion (Figure 5b). Therefore, the enthalpic acceleration of the pa exchange is attributed to the great electronic repulsion. Furthermore, differences in the rate constant at 298 K (k_{ex}^{298}) and $\Delta H^{\ddagger}$ between pa and general solvents such as water, methanol, and acetonitrile become larger with an increase in the number of d electrons of the metal(II) ions as shown in Figure 6. Considering that the electronic repulsion in the ground state caused by the d electrons and the dissociative character of the reaction mechanism are enhanced by the increase in the number of d electrons,[5] the trend shown in Figure 6 is consistent with the above-described view that electronic repulsion between donor atoms and d orbitals and the d-electronic repulsion can be one of the decisive factors determining the difference in stability between the complexes with different coordination numbers.

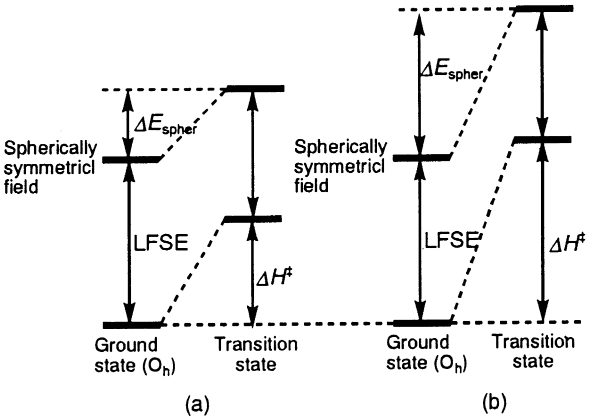

Figure 5. Relative energy levels of the ground state and the dissociative transition state of the solvent exchange reaction with strong (a) and weak (b) electronic repulsions.

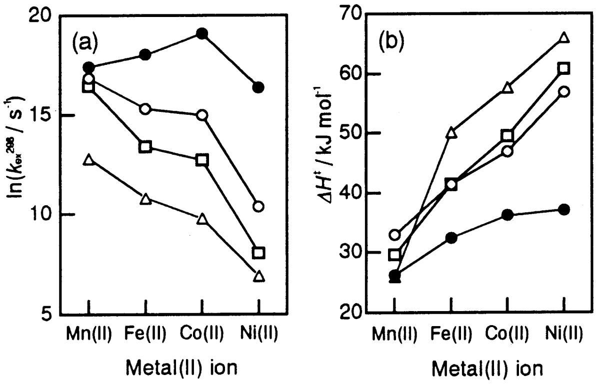

Figure 6. Variation of ln k_{ex} (a) and $\Delta H^{\ddagger}$ (b) for solvent exchange reactions of manganese(II), iron(II), cobalt(II), and nickel(II) ions in pa (●),[3,15] water (○),[1] acetonitrile (□),[1] and methanol (△).[1]

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Supporting Information Available: Temperature dependence of absorbance of solvated cobalt(II) complexes in ha, meea, and ba (Table S1), ^{14}N NMR line broadening data for the meea solution of cobalt(II) ions at various temperatures (Table S2), NMR parameters obtained by a least-squares fitting (Table S3), and temperature dependence of density for ha, meea, and ba (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vol. 2.

(14) The Racah parameters are calculated by the hydrogen model as $A = 11(13Z/576)$, $B = 11/140(13Z/576)$, and $C = 5/16(13Z/576)$ (au), where Z is the effective charge.

(15) Aizawa, S.; Iida, S.; Matsuda, K.; Funahashi, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1593.