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High-Pressure ^{17}O NMR Evidence for a Gradual Mechanistic Changeover from I_a to I_d for Water Exchange on Divalent Octahedral Metal Ions Going from Manganese(II) to Nickel(II)[1–3]

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Variable-temperature and pressure ^{17}O NMR studies of the water exchange on $[M(H_2O)_6](ClO_4)_2$ in water, with M = Mn, Fe, Co and Ni, yield the following parameters (k_m^{298} (s^{-1}), ΔH^* (kJ mol^{-1}), ΔS^* (J K^{-1} mol^{-1}), ΔV^* (cm^3 mol^{-1})): Mn^{2+}, 2.1 × 10^7, +32.9, +5.7, +5.4; Fe^{2+}, 4.39 × 10^6, +41.4, +21.2, +3.8; Co^{2+}, 3.18 × 10^6, +46.9, +37.2, +6.1; Ni^{2+}, 3.15 × 10^4, +56.9, +32.0, +7.2. The volumes of activation are obtained by using the full Swift–Connick equations and are found independent of pressure within experimental limits. The results are interpreted as evidence for a gradual changeover of mechanism from an associative interchange I_a for Mn^{2+} to a dissociative interchange I_d for Ni^{2+}. The available information on the rate of complex formation on these four ions is reviewed and is not in contradiction with this evidence. It is shown that the operational definition of an intimate interchange mechanism given by Langford and Gray is not a sufficient criterion for the assignment of mechanisms of complex formation reactions, when "hard" nucleophiles react with "hard" centers, and that the use of the volume of activation is more adequate. An attempt is made to rationalize the trend going from Mn^{2+} to Ni^{2+} in terms of the monotonous decrease in ionic radius which leaves less and less space for the entering ligand to come in and in terms of the increasing occupancy of the t_{2g} orbitals of the cation hindering the approach of the seventh molecule. Prediction is made that the earlier octahedral (O_h) members of the series react associatively. Due to the expected small dependence of rates of associative I_a substitution reactions on aquo ions on the entering ligand, the importance of the usual Eigen–Wilkins approach as a predictive tool for the rate of both dissociative I_d and associative I_a substitution reactions remains effective.

Introduction

The fundamental reaction needed to understand the kinetics of complex formation on both transition and nontransition octahedral hexasolvated metal ions is the symmetric solvent exchange reaction.[4] For the nonlabile trivalent transition-metal ions where the solvent exchange may be studied by using isotopic dilution techniques, the volume of activation proved of great utility in determining whether the exchange occurs via a dissociative or an associative activation mode.[5] Recently, we have begun to measure the volumes of activation of labile solvent exchange on both diamagnetic[2] and paramagnetic ions by using both proton[6–12] and oxygen-17[13] high-pressure NMR, the first such measures of the pressure dependence of these fast symmetrical reactions. The results obtained for the methanol exchange on the first-row divalent transition-metal ion series from Mn^{2+} to Ni^{2+} were particularly surprising. Co^{2+} and Ni^{2+} gave positive values for ΔV^* considerably smaller than the partial molar volume of the solvent and were readily interpretable in terms of a dissociative interchange, I_d, mechanism. However, Fe^{2+} showed an almost zero value, and the value for Mn^{2+} was clearly negative. These results could only be rationalized in terms of a mechanistic changeover along the series with Mn^{2+} showing associative behavior and Ni^{2+} dissociative. Prior to this work nobody had ever seriously questioned the dissociative nature of complex formation reactions on first-row divalent transition-metal ions. The mechanistic assignments for these reactions were based almost exclusively on complex formation rate constants in aqueous solution. We have recently measured the volume of activation of water exchange on Ni^{2+} which is well in accord with an I_d mechanism and it is clearly desirable to extend such measurements to earlier members of the series in order to see if the mechanistic changeover shown by the methanol ^{1}H NMR results also occurs for water.

Experimental Section

Manganese perchlorate hexahydrate ($Mn(ClO_4)_2 \cdot 6H_2O$, Fluka), iron perchlorate hexahydrate ($Fe(ClO_4)_2 \cdot 6H_2O$, Alfa), and cobalt perchlorate hexahydrate ($Co(ClO_4)_2 \cdot 6H_2O$, Fluka) were used without further purification. All samples and blanks were acidified with 60% perchloric acid ($HClO_4$, Merck).

Two $Mn(H_2O)_6^{2+}$ solutions (1.10 × 10^{-3} and 4.31 × 10^{-3} *m* in manganese and 0.06 and 0.10 *m* in $HClO_4$, respectively), four $Fe(H_2O)_6^{2+}$ solutions (0.1123, 0.1115, 0.1354, and 0.2251 *m* in iron and 0.129, 5.46 × 10^{-2}, 9.79 × 10^{-2}, and 0.378 *m* in $HClO_4$, respectively), and four $Co(H_2O)_6^{2+}$ solutions (4.35 × 10^{-2}, 9.01 × 10^{-2}, 9.75 × 10^{-2}, and 0.197 *m* in cobalt and 0.125, 0.183, 2.44 × 10^{-2}, and 8.46 × 10^{-2} *m* in $HClO_4$, respectively) were prepared by direct dissolution of the weighed salt in suitable amount of oxygen-17-enriched water (25.53 atom %, normalized in ^{1}H, Yeda), 3 times distilled in vacuo before use (concentrations: m = mol of solute/kg of solvent or P_m = ratio of the moles of water in the bound site to the total moles of water). The $Fe(H_2O)_6^{2+}$ solutions were prepared in a nitrogen glovebox to prevent oxidation.

The variation of the transverse relaxation time T_2 with temperature was measured by ^{17}O FT NMR at 8.13 MHz under the same conditions as described in an earlier publication.[13]

The line width measurements as a function of pressure were performed up to 250 MPa. The titanium high-pressure bomb used was very similar to the one described earlier,[13,14] except for the thermostating system which was by circulation of heated or cooled gaseous nitrogen. The temperature inside the bomb was determined with a precision of ±0.2 K.[15] The spectrometric parameters were the same as for the variable-temperature study, except the $\pi/2$ pulse

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(1) This is part 11 of the series High-Pressure NMR Kinetics. A preliminary account of some of this work has already been published.[3]

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length which was 4 μs. The real part of the Fourier transformed and phased spectra was transferred to a minicomputer via a floppy disk, and the relaxation time was obtained by nonlinear least-squares fit to a single Lorentzian function. The results are estimated to be accurate to 5%.

Data Treatment and Results

Variable Temperature. For the analysis of the variable-temperature data, the full Swift and Connick equation[16] had to be used, because, for Co^{2+}, Fe^{2+}, and Mn^{2+}, the water exchange as a function of pressure was studied at various temperatures in the intermediate region as well as in the exchange controlled region. The equations used to interpret the data have been given elsewhere.[13] The relaxation time of the bound water molecule (T_{2m}) was defined as a function of a mean electronic correlation time τ_e. A more complete treatment involves two different correlation times, τ_{e1} and τ_{e2}, for this relaxation process, and has the form[17] in eq 1, where

$$\frac{1}{T_{2m}} = C\left(\tau_{e1} + \frac{\tau_{e2}}{1+\tau_{e2}^2\omega_e^2}\right) \qquad (1)$$

the constant C is proportional to the coupling constant A (eq 2) and τ_{e1} and τ_{e2} are given by eq 3 and 4. In eq 3 and 4,

$$C = \frac{4\pi^2}{3}S(S+1)\left(\frac{A}{h}\right)^2 \qquad (2)$$

$$\frac{1}{\tau_{e1}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}} \qquad (3)$$

$$\frac{1}{\tau_{e2}} = \frac{1}{\tau_m} + \frac{1}{T_{2e}} \qquad (4)$$

T_{1e} and T_{2e} refer to the longitudinal and transverse relaxation times of the electron, and τ_m is the exchange lifetime of the nucleus. For Ni^{2+}, Co^{2+}, and Fe^{2+}, the relationship between T_{1e} and T_{2e} is unknown, and thus, it is generally assumed that they are equal[18,19] (eq 5) and obey an Arrhenius dependence (eq 6). For Mn^{2+}, where T_{1e} and T_{2e} are much longer than

$$T_{1e} = T_{2e} = \tau_e \qquad (5)$$

$$\tau = \tau^{298}\exp\left[\frac{E}{R}(1/T - 1/298.15)\right] \qquad (6)$$

for Ni^{2+}, Co^{2+}, or Fe^{2+}, we do not need to make this assumption since McLachlan[20] has developed equations (eq 7 and 8) to relate T_{1e} and T_{2e} in the case where T_{2e} is much

$$\frac{1}{T_{1e}} = \frac{32}{25}\Delta^2\left(\frac{\tau_v}{1+\tau_v^2\omega_e^2} + \frac{4\tau_v}{1+4\tau_v^2\omega_e^2}\right) \qquad (7)$$

$$\frac{1}{T_{2e}} = \frac{32}{50}\Delta^2\left(3\tau_v + \frac{5\tau_v}{1+\tau_v^2\omega_e^2} + \frac{2\tau_v}{1+4\tau_v^2\omega_e^2}\right) \qquad (8)$$

greater than τ_v (which is the case for Mn^{2+}[21]). In these equations, Δ is a measure of the amplitude of modulation of the zero-field splitting and τ_v is the correlation time for this modulation, which is assumed to have an Arrhenius behavior, according to eq 6.

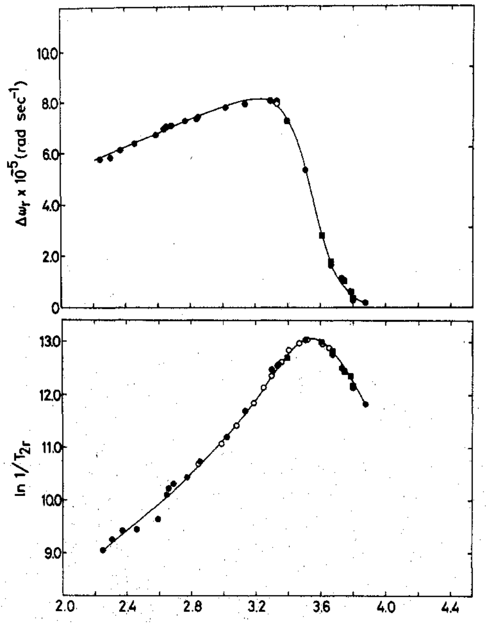

Figure 1. $\Delta\omega_r$ and ln $(1/T_{2r})$ for $[Co(H_2O)_6](ClO_4)_2$ bulk water as a function of reciprocal temperature. The curve through the experimental points is the result of a simultaneous fit of all the data: (○), $P_m = 4.20 \times 10^{-3}$; (■) $P_m = 1.04 \times 10^{-2}$; (●) $P_m = 2.10 \times 10^{-2}$.

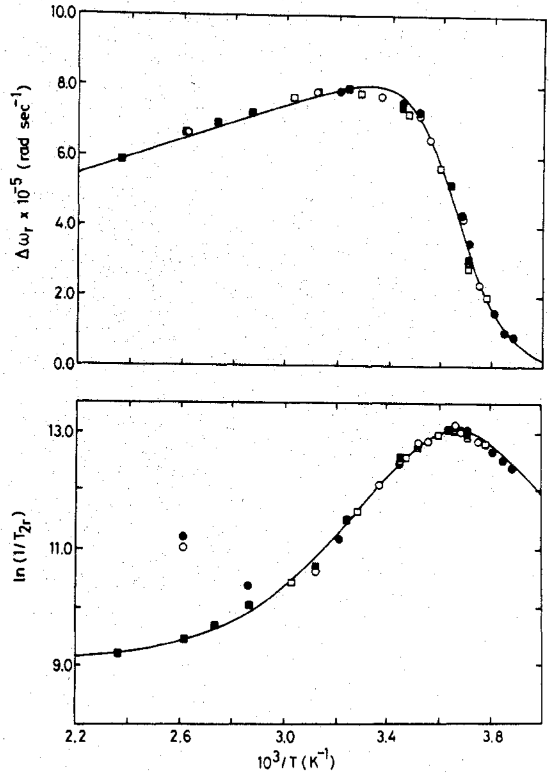

Figure 2. $\Delta\omega_r$ and ln $(1/T_{2r})$ for $[Fe(H_2O)_6](ClO_4)_2$ bulk water as a function of reciprocal temperature. The curve through the experimental points (except the three circles at high temperature, see text) is the result of a simultaneous fit of all the data: (□), $P_m = 1.202 \times 10^{-2}$; (○), $P_m = 1.211 \times 10^{-2}$; (■), $P_m = 1.211 \times 10^{-2}$ with ascorbic acid added (see text); (●), $P_m = 2.400 \times 10^{-2}$.

The experimental relaxation and chemical shift data are shown on Figure 1 for the water exchange on Co^{2+} and on Figure 2 for the water exchange on Fe^{2+}. On both figures, the solid line through the points is a nonlinear least-squares simultaneous computer fit using the full Swift and Connick equations for both T_2 and shift. The parameters optimized were ΔH^*, ΔS^*, A/h, τ_e, and E_e. The value of k_m^{298}, the value

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Table I. Kinetic and NMR Parameters Derived from Relaxation and Chemical Shifts of $Co(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{2+}$ Bulk Water as a Function of Temperature[a]

cation	$10^{-6}k_m^{298}$, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	A/h, MHz	$10^{12}\tau_e^{298}$, s	E_e, kJ mol^{-1}	ref
Co^{2+}	1.35	+33.4	−17.1	14.8	<5		16
	2.38 (300 K)	+43.5	+22.1	17.0	0.5 (456 K)		22
	2.45 ± 0.1	+49.7 ± 3.0	+44.3[b]	13.5	0.9		23, 24
	2.24 ± 0.05	+43.0 ± 0.8	+21.3 ± 2.4	12.0 ± 0.2			19[c]
	3.18 ± 0.17	+46.9 ± 1.2	+37.2 ± 3.7	15.7 ± 0.1	5.2 ± 0.8	20 ± 2	this work
Fe^{2+}	3.2	+32.2	−12.5	11.9	<14		16
	4.39 ± 0.25	+41.4 ± 1.2	+21.2 ± 4.8	9.4 ± 0.1	1.0 ± 0.5	3 ± 5	this work

[a] Errors quoted are standard deviations. [b] Calculated. [c] 2 M in NH_4NO_3, pH 4.2.

Table II. Kinetic and NMR Parameters Derived from Relaxation of the $Mn(H_2O)_6^{2+}$ Bulk Water as a Function of Temperature[a]

$10^{-7}k_m^{298}$, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	A/h, MHz	$10^{12}\tau_v^{298}$, s	$10^{-18}\Delta^2$, s^{-2}	E_v, kJ mol^{-1}	$10^8 T_{1e}^{298}$, s	ref
3.1	+33.9	+12.2	9.2			4.2[b]	0.38	16
2.2	+32.2 ± 0.4	+3.8 ± 1.7	5.4 ± 0.3				1.4	21
2.1 ± 0.1	+32.9 ± 1.3	+5.7 ± 5.0	5.3 ± 0.5	3.3[b]	5.6 ± 3.0	16.3[b]	1.25	this work

[a] Errors quoted are standard deviations. [b] Fixed value.

of the rate constant at 298.15 K, is obtained by repeating the curve fit with use of the modified Eyring equation to express the temperature dependence of τ_m (eq 9). At convergence,

$$\frac{1}{\tau_m} = k_m = \frac{T}{298.15}k_m^{298}\exp\left[-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \qquad (9)$$

all the other parameters and their standard deviations are identical with the ΔH^*, ΔS^* fit. The values of the parameters and their standard deviations are given in Table I, together with previously reported values from literature.[16,19,22-24] A small amount of ascorbic acid was added to one of the Fe^{2+} solutions. This was done to prevent any oxidation of Fe^{2+} at high temperature by traces of oxygen which are difficult to avoid. Below 333 K, the line widths and shifts of this solution are in very good agreement with the line widths and shifts of the other solutions used. They are also reproducible at a given temperature over the course of the variable-temperature experiment, even after heating of the solution at 423 K. Conversely, the line widths of the samples containing no ascorbic acid are abnormally broadened above 333 K and are slightly too narrow at room temperature after this treatment. This suggests that these samples have undergone some oxidation to Fe^{3+}. The water exchange on hydrolyzed Fe^{3+}, slower than the corresponding exchange on Fe^{2+}, is in the slow-exchange region of the Swift–Connick curve at temperatures around 370 K.[25] Therefore, any oxidation, even small, of the Fe^{2+} will result in a substantial broadening of the lines. This is well shown in Figure 2, by the three relaxation data at high temperature which are in total disaccord with the other experimental points. These data have not been introduced in the fitting procedure.

For the water exchange on the Mn^{2+} ion, the chemical shifts are very much smaller than the line widths and are thus not easily measurable. Figure 3 shows the experimental relaxation data together with the curve calculated by using the full Swift–Connick equation. The parameters optimized were ΔH^*, ΔS^*, Δ^2, and A/h and are given together with k_m^{298} (obtained as above) in Table II. In the same table are also shown previously published results from other laboratories.[16,21] The contribution of T_{1e} to the overall relaxation time is only small (see below), and it is thus clear that the data cannot define well all three parameters (Δ^2, τ_v^{298}, and E_v) of T_{1e}. We have thus fixed E_v at 16.3 kJ mol^{-1}, the value obtained in the ^1H NMR study of Bloembergen and Morgan.[26] The kinetic parameters are very insensitive to changes in this value. We have also fixed τ_v^{298} at 3.3×10^{-12} s^{-1}, the value obtained from an EPR study[27] which is also close to the values obtained by ^1H NMR studies (3.2×10^{-12} [28] and 2.4×10^{-12} s^{-1} [26]).

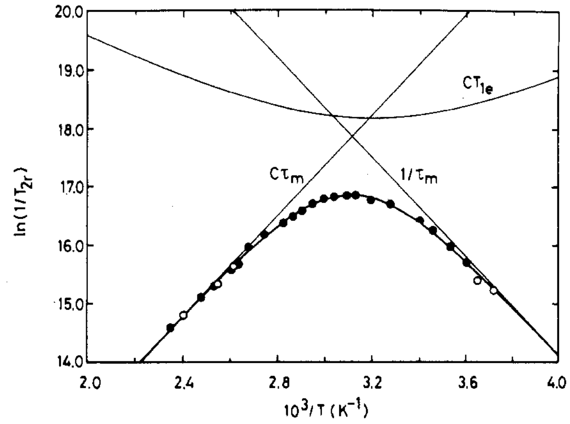

Figure 3. ln $(1/T_{2r})$ for $[Mn(H_2O)_6](ClO_4)_2$ bulk water as a function of reciprocal temperature. The curve through the experimental points is the result of a simultaneous fit of all the data: (●), $P_m = 1.2 \times 10^{-4}$; (○), $P_m = 4.7 \times 10^{-4}$.

In order to explore the contribution of T_{1e} to the overall relaxation rate, we may note that for Mn^{2+}, $\Delta\omega_m^2$ is very much less than T_{2m}^{-2} or $(T_{2m}\tau_m)^{-1}$ and the Swift and Connick equation reduces to eq 10.[16]

$$\frac{1}{T_{2r}} = 1\bigg/\left[\tau_m + \frac{1}{C}\left(\frac{1}{\tau_m} + \frac{1}{T_{1e}}\right)\right] \qquad (10)$$

The three contributions to T_{2r} in eq 10 are also shown in Figure 3. The maximum contribution of the CT_{1e} term is about 25% but at the temperatures where the high-pressure experiments were performed (see below). The contribution is only about 6%.

Variable Pressure. High-pressure $1/T_2$ measurements were performed at two temperatures in the slow-exchange-controlled region (263.3 and 264.6 K for Co^{2+}, 268.0 and 268.8 K for

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Fe^{2+}, and 277.9 and 279.1 K for Mn^{2+}), at one temperature in the intermediate-exchange region for Co^{2+} and Mn^{2+} (307.8 K for Co^{2+} and 376.3 K for Mn^{2+}), and at three temperatures in the intermediate-exchange region for Fe^{2+} (284.6, 286.8, and 292.0 K). The natural line width of pure acidified water was substracted from the measured line width, taking into account its slight pressure dependence.[13]

For the Co^{2+} ion, the pressure dependence of the chemical shift was studied at 307.8 K, the temperature of the variable-pressure relaxation measurement in the intermediate-exchange region. We observed no pressure dependence of the bulk water chemical shift in this region where the exchange is fast enough to make the chemical shift independent of the exchange rate. This gives us confidence that the scalar coupling constant A/h is not strongly pressure dependent.[8] On the other hand, in the temperature range where the relaxation rate is at its maximum, a change in rate constant should be reflected by a large change in bulk water chemical shift. A study of the pressure dependence of the shift at 286.6 K, a temperature close to that of maximum relaxation rate, was carried out in addition to the relaxation measurements, resulting in another way of measuring the volume of activation for this particular solvent exchange process.

The volume of activation ΔV_0^* was obtained as discussed elsewhere[8] by nonlinear least-squares fitting of the data to the full relaxation or shift equation. The values of the NMR parameters needed for the analysis were taken from the variable-temperature study and kept at their ambient pressure values. The pressure dependence of the rate constants was allowed to vary according to eq 11, where k_P and k_0 are the

$$\ln k_P = \ln k_0 - \frac{\Delta V_0^* P}{RT} + \frac{\Delta\beta^* P^2}{2RT} \qquad (11)$$

rate constants at pressure P and zero, respectively, $\Delta\beta^*$ is the compressibility coefficient of activation, and ΔV_0^* is the zero pressure volume of activation. The k_0 value for each data set was a parameter which was also optimized.[10] In the case of Mn^{2+} water exchange, because the contribution of the T_{1e} term to the relaxation time is only of about 6%, we could reasonably assume that any change in T_{1e} with pressure would not affect the value of ΔV_0^* significantly. For each metal ion, a simultaneous quadratic fit of all variable-pressure relaxation experiments was made. For Co^{2+}, it yielded a volume of activation of $\Delta V_0^* = +6.8 \pm 0.8$ cm^3 mol^{-1} with a compressibility coefficient of activation $10^{-2}\Delta\beta^* = +0.6 \pm 0.8$ cm^3 mol^{-1} MPa^{-1}. For Fe^{2+}, the obtained values were $\Delta V_0^* = +3.8 \pm 0.7$ cm^3 mol^{-1} and $10^{-2}\Delta\beta^* = +0.0 \pm 0.6$ cm^3 mol^{-1} MPa^{-1}, whereas for Mn^{2+}, the obtained values were $\Delta V_0^* = -5.8 \pm 0.5$ cm^3 mol^{-1} and $10^{-2}\Delta\beta^* = -0.4 \pm 0.4$ cm^3 mol^{-1} MPa^{-1}. The suppression of the $\Delta\beta^*$ term never altered significantly the sum of the residuals, and therefore, this term was set to zero and a linear expression used in all calculations. The values of the volume of activation became $\Delta V^* = +6.1 \pm 0.2$ cm^3 mol^{-1} for the Co^{2+} water exchange, $\Delta V^* = +3.8 \pm 0.2$ cm^3 mol^{-1} for the Fe^{2+} water exchange, and $\Delta V^* = -5.4 \pm 0.1$ cm^3 mol^{-1} for the Mn^{2+} water exchange. For Co^{2+}, we were also able to fit the chemical shift data together with all the relaxation data. This latter fit produced the same values of ΔV_0^*, $\Delta\beta^*$, and ΔV^* as the relaxation data alone, showing that the shift data are well in accord with the relaxation data.

To take into account any temperature dependence of the volume of activation, we have introduced the thermal expansivity of activation $\Delta\alpha^*$,[29] according to eq 12, where ΔV^*_{298}

$$\Delta V^* = \Delta V^*_{298} + \Delta\alpha^* \Delta V^*_{298}(T - 298.15) \qquad (12)$$

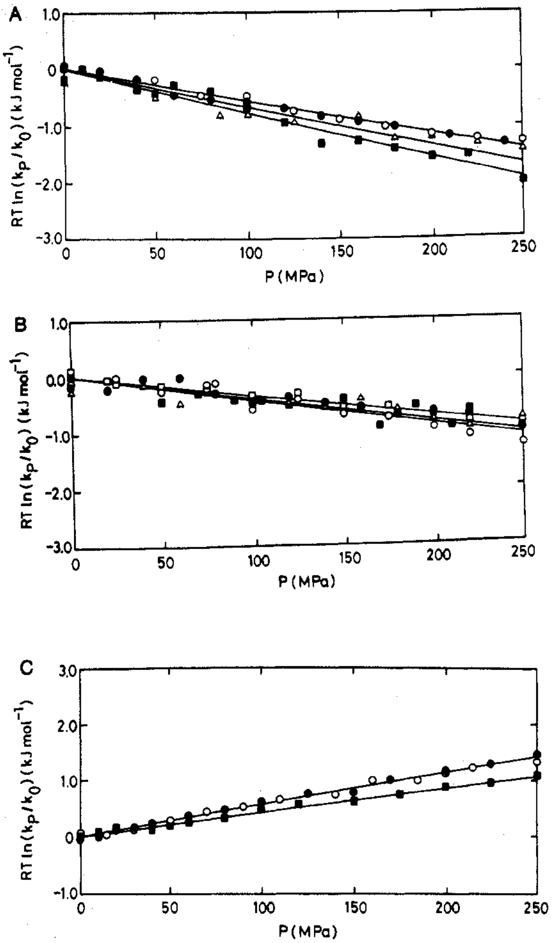

Figure 4. Experimental values of $RT \ln (k_p/k_0)$ as a function of pressure. The solid lines are calculated from a simultaneous fit of all the data by taking into account the temperature dependence of ΔV^*. (A) $[Co(H_2O)_6](ClO_4)_2$ water exchange: (●), $P_m = 1.00 \times 10^{-2}$, $T = 263.3$ K; (○), $P_m = 8.9 \times 10^{-3}$, $T = 264.6$ K; (△), $P_m = 1.04 \times 10^{-2}$, $T = 286.6$ K (chemical shifts); (■), $P_m = 9.6 \times 10^{-3}$, $T = 307.3$ K. (B) $[Fe(H_2O)_6](ClO_4)_2$ water exchange: (□), $P_m = 1.202 \times 10^{-2}$, $T = 268.0$ K; (●), $P_m = 1.202 \times 10^{-2}$, $T = 268.8$ K; (△), $P_m = 1.211 \times 10^{-2}$, $T = 284.6$ K; (■), $P_m = 1.202 \times 10^{-2}$, $T = 286.8$ K; (○), $P_m = 1.460 \times 10^{-2}$, $T = 292.0$ K. (C) $[Mn(H_2O)_6](ClO_4)_2$ water exchange: (○), $P_m = 1.2 \times 10^{-4}$, $T = 277.9$ K; (●), $P_m = 1.2 \times 10^{-4}$, $T = 279.1$ K; (■), $P_m = 1.2 \times 10^{-4}$, $T = 376.3$ K.

is the volume of activation at 298.15 K. For each metal ion, all the data have been fitted simultaneously by using eq 11 and 12. Figure 4 shows the results of the fit together with the experimental data. The values of ΔV^*_{298} and $\Delta\alpha^*$ obtained from this fit are $\Delta V^*_{298} = +7.3 \pm 0.3$ cm^3 mol^{-1} and $\Delta\alpha^* = (+6.8 \pm 0.4) \times 10^{-3}$ K^{-1} for Co^{2+}, $\Delta V^*_{298} = +4.5 \pm 0.4$ cm^3 mol^{-1} and $\Delta\alpha^* = (+7.8 \pm 4.4) \times 10^{-3}$ K^{-1} for Fe^{2+}, and $\Delta V^*_{298} = -5.5 \pm 0.1$ cm^3 mol^{-1} and $\Delta\alpha^* = (-2.7 \pm 0.2) \times 10^{-3}$ K^{-1} for Mn^{2+}.

Table III summarizes the kinetic parameters for the water exchange on the divalent metal ions studied to date. We have repeated two variable-pressure measurements on Ni^{2+} with the bomb used for Co^{2+}, Fe^{2+}, and Mn^{2+} and obtained a significant reduction in the scatter of the data. The revised value of $\Delta V^* = +7.2 \pm 0.3$ cm^3 mol^{-1} is almost identical with the previously reported value, $\Delta V^* = +7.1 \pm 0.2$ cm^3 mol^{-1}. The values of $\Delta\beta^*$ can be neglected (see Table III), and we thus compare only the volumes of activation obtained from the linear forms of eq 11. The values of $\Delta\alpha^*$ are small but significant. It is interesting to note that, for the three cations, the sign of $\Delta\alpha^*$ is such as to make the ΔV^* become more

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(29) Some other authors use the quantity $\Delta\gamma^* = \Delta\alpha^* \Delta V^*_{298}$. We have used $\Delta\alpha^*$ to be consistent with the thermodynamic definition of thermal expansivity: $\alpha = 1/V(\partial V/\partial T)_P$.

Table III. Kinetic Parameters for Water Exchange on Divalent Metal Ions[a]

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
k_m^{298}, s^{-1}	(2.1 ± 0.1) × 10^7	(4.39 ± 0.25) × 10^6	(3.18 ± 0.17) × 10^6	(3.15 ± 0.08) × 10^4 [b]
ΔH^*, kJ mol^{-1}	+32.9 ± 1.3	+41.4 ± 1.2	+46.9 ± 1.2	+56.9 ± 0.8[b]
ΔS^*, J K^{-1} mol^{-1}	+5.7 ± 5.0	+21.2 ± 4.8	+37.2 ± 3.7	+32.0 ± 3.0[b]
ΔV^*, cm^3 mol^{-1} [c]	−5.4 ± 0.1	+3.8 ± 0.2	+6.1 ± 0.2	+7.2 ± 0.3[d]
$10^2\Delta\beta^*$, cm^3 mol^{-1} MPa^{-1} [e]	−0.4 ± 0.4	+0.0 ± 0.6	+0.6 ± 0.8	+0.7 ± 0.8[d]
$10^3\Delta\alpha^*$, K^{-1} [f]	−2.7 ± 0.2	+7.8 ± 4.4	+6.8 ± 0.4	

[a] Errors quoted are standard deviations. [b] Reference 13. [c] Obtained by assuming $\Delta\beta^* = 0$ and $\Delta\alpha^* = 0$. The temperature ranges of the measurements are as follows: for Mn^{2+}, 277.9–376.4 K; for Fe^{2+}, 268.0–292.0 K; for Co^{2+}, 263.3–307.3 K; for Ni^{2+}, 309.1–314.4 K. If each dataset is fitted separately, the values of ΔV^* (cm^3 mol^{-1}) are as follows: for Mn^{2+}, −6.0 ± 0.6 at 277.9 K, −6.3 ± 0.5 at 279.1 K, −4.3 ± 0.4 at 376.3 K; for Fe^{2+}, +3.6 ± 0.3 at 268.0 K, +3.6 ± 0.3 at 268.8 K, +3.2 ± 0.7 at 284.6 K, +3.4 ± 0.5 at 286.8 K, +5.0 ± 0.4 at 292.0 K; for Co^{2+}, +7.4 ± 0.5 at 263.3 K, +4.9 ± 1.4 at 264.6 K, +7.4 ± 1.5 at 307.8 K, +6.1 ± 1.6 at 286.6 K (shifts). [d] These data make this value slightly different from the previously published value.[13] See text. [e] Obtained by assuming $\Delta\alpha^* = 0$. [f] Obtained by assuming $\Delta\beta^* = 0$.

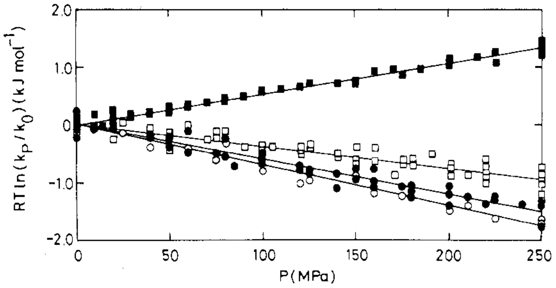

Figure 5. Experimental and calculated values of $RT \ln (k_P/k_0)$ as a function of pressure at 298 K for the water exchange on Mn(II) (■), Fe(II) (□), Co(II) (●), and Ni(II) (○, new data).

positive as the temperature increases. For comparison, the thermal expansivity of pure water is about 0.5 × 10^{-3} K^{-1}. However, in view of the lack of interpretation of this parameter coupled with the fact that it may be very sensitive to nonrandom errors in the data, we choose to restrict discussion to values of ΔV^* obtained with $\Delta\alpha^*$ set to zero. The value of $\Delta\alpha^*$ is anyway small enough not to change significantly the value of ΔV^*. Figure 5 shows the variation of rate constant with pressure for the four systems.

Discussion

The values of the volumes of activation for solvent exchange on the first-row divalent transition-metal ion series in both aqueous and nonaqueous solvents are summarized in Table IV. For Ni^{2+} and Co^{2+}, the values are always positive but considerably less than the solvent partial molar volume. The negative values for both water and methanol exchange on Mn^{2+}, and the small values for exchange of these solvents on Fe^{2+}, give us confidence that the change in sign of ΔV^* along the series is a general trend and is not due to some solvent anomaly. This trend is given added credence from the fact that the values for Co^{2+} are always slightly less than for Ni^{2+}. The detailed arguments whereby volumes of activation may be used as mechanistic criteria for solvent exchange have been given recently,[3,12] and we will thus restrict discussion to certain key points.

Table IV. Volumes of Activation ΔV^* (cm^3 mol^{-1}) for Solvent Exchange on Divalent Metal Ions

solvent	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	ref
H_2O	−5.4 (298 K)	+3.8 (298 K)	+6.1 (298 K)	+7.2 (298 K)	this work
CH_3OH	−5.0 (279 K)	+0.4 (255 K)	+8.9 (279 K)	+11.4 (307 K)	12
CH_3CN			+7.7 (286 K)[a]	+9.6 (294 K)	10
DMF			+6.7 (296 K)	+9.1 (297 K)	10

[a] The value obtained by ^1H NMR was $\Delta V^* = +9.9$ (260 K).[10] This more accurate value of ΔV^* has recently been obtained by using ^{13}C NMR.[30] A value of $\Delta V^* = +6.7$ (between 265.4 and 272.3 K) has been obtained recently by ^{14}N NMR by T. W. Swaddle and co-workers (personal communication).

The mechanistic classification most frequently used in the discussion of substitution reactions at metal centers is due to Gray and Langford.[31] These authors differentiate three mechanistic pathways: associative A, dissociative D, and interchange I. Their criteria are in principle very simple and are based on kinetic tests which may be applied to give evidence for "long-lived" intermediates; "long-lived" implies long enough for the intermediate and its solvation shell to relax, i.e., lose memory of its precursors and hence exhibit the properties of the intermediate. An intermediate of increased coordination number implies an A mechanism and one of reduced coordination a D mechanism. If no evidence can be found for an intermediate, in effect, if the intermediate does not exist long enough to manifest its properties, or if there is truly no minimum in the reaction coordinate, then the mechanism is classified as interchange I. These mechanistic criteria are thus structural in nature although evidence for the structure is based on kinetic grounds. For the interchange mechanism, a further subdivision is made on whether the reaction rate is much more sensitive to variation of the leaving group than to variation of the entering group (dissociative interchange I_d) or if it is approximately as sensitive, or more sensitive, to variations of the entering group as to variations of the leaving group (associative interchange I_a). This latter subdivision is thus made on kinetic grounds rather than on the structure of the transition state.

For symmetric solvent-exchange reactions, it is clear that these kinetic tests are not operational since the nature of the entering group cannot be varied. However, we do wish to reiterate the argument given previously that, for solvent exchange reactions, symmetry requires that, at the transition state, the extent of bonding to both entering and leaving solvent molecules must be identical. This is nothing other than the principle of microscopic reversibility. However, for a metal ion reacting via an I_d mechanism, where there is, by definition, only weak bonding to the entering solvent, there must also only be weak bonding to the leaving solvent. Conversely, for an I_a mechanism, where there is, also by definition, considerable bonding to the entering solvent, there must also be considerable bonding to the leaving solvent. From a structural viewpoint, the difference between an I_d and an I_a reaction is the degree of expansion of the transition state. ΔV^*, the difference between the volumes of the transition state and reactants, is a direct measure of this degree of expansion. A corollary of this idea is that one may envisage a continuous spectrum of transition states ranging from the highly compact, very asso-

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Table V. Comparison of the Rates of the Interchange Step for the MSO_4 Formation ($k_I(SO_4)$)[a] and for Water Exchange ($k_I(H_2O)$) Reactions at 298 K

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	ref
$k_I(H_2O)$, s^{-1}	2.1×10^7	4.39×10^6	3.18×10^6	3.15×10^4	this work
$k_I(SO_4)$, s^{-1}	2.4×10^7	2.4×10^6	1.1×10^6	2.4×10^4	37[b]
$k_I(SO_4)/k_I(H_2O)$	1.1	0.6	0.4	0.8	
$k_I(SO_4)$, s^{-1}	4.8×10^7		1.8×10^6		38
$k_I(SO_4)/k_I(H_2O)$	2.3		0.6		

[a] Obtained by ultrasonic absorption. [b] Latest values from the Eigen and Tamm research groups.

ciative I_a (or A) mechanism, right through to the highly noncompact, very dissociative I_d (or D) mechanism. We have recently shown that bond length changes in the nonexchanging ligands between reactants and transition state are generally fairly small and that the changes in sign of ΔV^* going from Mn^{2+} to Ni^{2+} could only be explained in terms of a gradual changeover of mechanism from I_a to I_d.[3,32]

One could imagine that the small values of the volumes of activation for both water and methanol exchanges on Fe^{2+} do not arise from a single interchange process with expanded transition state but from the simultaneous existence of two kinetic pathways, one with dissociative character and the other with associative character. In other words, a mechanistic *crossover* would occur along the series, from an associative favored pathway for Mn^{2+} to a dissociative favored pathway for Ni^{2+}. Should this crossover effectively be taking place, it would be reflected by an important variation of the volumes of activation for Fe^{2+} solvent exchange with temperature and pressure. The thermal expansivity of activation $\Delta\alpha^*$ and the compressibility coefficient of activation $\Delta\beta^*$, respectively, describe the temperature and pressure dependence of ΔV^*, and these two parameters have been shown to be very small or negligible. We can therefore reject the idea of crossover and reaffirm the idea of a mechanistic *changeover* going from Mn^{2+} to Ni^{2+}.

Prior to the advent of the variable-pressure NMR studies of solvent exchange on the series Mn^{2+} to Ni^{2+}, it had been generally accepted that complex formation reactions on all octahedral divalent metal ions proceeded via I_d mechanisms. This idea, first put forward by Eigen[33] and Wilkins[34] arose from the simultaneous availability of NMR-derived water-exchange rates on the labile first-row transition-metal ions by Swift and Connick[16] and ultrasonic relaxation studies on aqueous metal sulfates by Eigen and Tamm.[35] Although there was subsequent controversy[36] over whether three relaxation processes (as Eigen postulated) were involved, or two, the overall interpretation of the ultrasonic results was not in dispute: the first relaxation process(es) involve(s) the fast formation of an outer-sphere complex (frequently referred to as an encounter complex) followed by a slow-interchange step between a solvent molecule in the first coordination sphere and the SO_4^{2-} ligand. Thus, the scheme of the reaction may be formulated (by neglecting charges and with $L = SO_4$) as in eq 13.

$$M(H_2O)_6 + L \underset{}{\overset{K_{os}}{\rightleftharpoons}} M(H_2O)_6{\cdot}L \xrightarrow{k_I(L)} M(H_2O)_5L + H_2O \qquad (13)$$

The close similarity between the rate of the interchange step $k_I(L)$ in reaction scheme 13, and the rate of water exchange $k_I(H_2O)$ ($=k_m$) led Eigen and Wilkins to the conclusion that $k_I(L)$ may be identified with $k_I(H_2O)$ and, hence, is independent of the nature of the entering ligand (I_d mechanism). The early study of Eigen and Tamm has been repeated since,[36-38] and we have listed the most recent data in Table V, where the water-exchange rates from this work are also given. We have calculated the ratio of $k_I(SO_4)$ to $k_I(H_2O)$, which should be independent of the metal center if an I_d mechanism is assumed. One may notice that for Mn^{2+}, the values are larger than the corresponding values for the other cations (3 to 4 times the Co^{2+} values). The variation of the ratio along the series is not large by kinetic standards, and the scatter of the data is important. If the replacement of a water molecule by a sulfate on Mn^{2+} proceeds via an associative I_a mechanism, the resulting effect on $k_I(SO_4)$ may well be small. For this reason, we believe that the results obtained so far by ultrasonic absorption are not incompatible with the concept of changeover in the series, even if the evidence is not striking.

The ultrasonic absorption method should be the method of choice to study complex formation reactions, since it gives directly the rate of the interchange step. However, because of the technical problems inherent to this method, most studies have involved either stopped-flow or temperature-jump techniques where the *overall* rate of complex formation is obtained. It may readily be shown that the observed pseudo-first-order rate constant k_{obsd} is related to the constants appearing in reaction scheme 13 by eq 14. For virtually all cases, $K_{os}[L]$

$$k_{obsd} = K_{os}k_I(L)[L]/(1 + K_{os}[L]) \qquad (14)$$

$\ll 1$, and the overall second-order rate constant k_f is given by eq 15. In order to compare the rate constants for complex

$$k_f = K_{os}k_I(L) \qquad (15)$$

formation on Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, we have used the recent compilation by Margerum and co-workers.[39] In this tabulation, one can observe large discrepancies between the results emerging from different research groups. For this reason, we have decided to restrict discussion to the results obtained by groups which have made comparative studies on two or more of the four cations. For Co^{2+} and Ni^{2+}, there are nearly 50 values to compare, among them, four involving monodentate ligands, whereas for Mn^{2+} and Fe^{2+}, the data are extremely sparse: there are only eight Mn^{2+} and four Fe^{2+} complex formation studies which are readily comparable with their Co^{2+} and Ni^{2+} analogues. We have summarized, in Table VI, the rate constants for complex formation reactions of the four cations in the series with all the monodentate ligands studied and with the multidentate ligands for which a comparative study involving all, or at least three, of the cations exists. The stability constants quoted by the authors of these studies have also been included in the table. From an examination of this table, there is evidence that the formation rate constants often depend on the nature of the incoming ligand, especially for Mn^{2+} complexes. There are too many superimposed effects to question the validity of the Eigen–Wilkins mechanism at this stage. The first complication arises from the fact that the measured rate constant is not $k_I(L)$ but k_f. In order to obtain $k_I(L)$, according to eq 15, it

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Table VI. Rate Constants k_f (M^{-1} s^{-1}) and Stability Constants K (M^{-1}) for Complex Formation on Divalent Aquometal Ions at 298 K

	Mn^{2+}		Fe^{2+}		Co^{2+}		Ni^{2+}			
ligand[a]	k_f	K	k_f	K	k_f	K	k_f	K	techn	ref
NH_3[b]					0.95×10^5	1.3×10^2	3.3×10^3	1.9×10^3	TJ	40
imidazole					1.3×10^5	2.6×10^2	5.0×10^3	1.9×10^3	TJ	41
HF	22×10^5	*c*	14×10^5	*c*	5.5×10^5	*c*	3.1×10^3	*c*	^{19}F NMR	42
F^-	27×10^5	3.7[d]	9.3×10^5	1.6	1.8×10^5	1.8	8.4×10^3	4	^{19}F NMR	42
PADA[e]	$\geqslant 5 \times 10^5$	5			0.4×10^5	6×10^3	4×10^3	$\sim 2 \times 10^4$	TJ	43
phen[f]	1.2×10^5	4×10^3			1.2×10^5	2×10^7	1.2×10^3	3.2×10^8	SF	44
bpy			1.6×10^5	2×10^4	0.63×10^5	1×10^6	1.6×10^3	3.2×10^7	SF	44
terpy	1.1×10^5	5×10^9	0.8×10^5	1.2×10^7	0.24×10^5	2.5×10^8	1.4×10^3	5×10^6	SF	44
murexide$^-$[g]	$\sim 90 \times 10^5$	1.2×10^2			1.5×10^5	2.9×10^2	1.0×10^3	2.4×10^3	TJ	45
β-alanine$^-$[b]	0.5×10^5				0.75×10^5	1×10^4	10×10^3	4×10^4	TJ	46
ATP^{4-}	$>10^9$	$\sim 1 \times 10^5$			9.2×10^7	4.6×10^4	4.1×10^6	1.1×10^5	TJ	47

[a] The following ligand abbreviations have been used: PADA = (pyridine)-2-azo-*p*-dimethylaniline, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine, terpy = 2,2′,2″-terpyridine, ATP^{4-} = adenosine 5′-triphosphate. [b] 293 K. [c] $K' = K(F^-) \times K_a(HF)$; $K_a(HF) = 1.23 \times 10^{-3}$ M. [d] pH > 4. [e] 288 K. [f] 284 K. [g] 283 K.

is necessary to know K_{os} which is, in general, not measurable but is frequently calculated by using the Fuoss equation.[48] The problems inherent in the use of this equation have been frequently discussed: the theory treats the ion and ligand as charged spheres in a dielectric continuum, and thus its use for irregularly shaped, neutral, or dipolar ligands is highly speculative. A further complication in comparing $k_I(L)$ with $k_I(H_2O)$ may be that, in the outer-sphere complex, the exchange of certain water molecules is less likely to bring about complex formation than others due to their unfavorable positions and one may therefore introduce a statistical factor F to take this into account. Thus, for an I_d mechanism, where, apart from the statistical term F, the interchange step $k_I(L)$ may be identified with the water-exchange rate $k_I(H_2O)$, we may write eq 16. In view of the uncertainties in both K_{os} and

$$k_f = K_{os}Fk_I(H_2O) \tag{16}$$

F, agreement within a factor of 10 between the calculated rate constants $k_I(L)$ and the water-exchange rate $k_I(H_2O)$ has been considered acceptable to assign an I_d mechanism.

K_{os} is expected to be virtually independent of ion along the series Mn^{2+} to Ni^{2+}, the only slight change being a monotonous one due to the monotonous change of the ionic radii. One would also expect F to be a constant. Thus, any two cations reacting with the same ligand by the same mechanism should yield similar values for the ratio $k_f/k_I(H_2O)$. From the wealth of data available, at both ambient[39] and high[13] pressure, there is no doubt that the Eigen–Wilkins I_d mechanism is appropriate for Ni^{2+}. Thus, we can introduce the ratio $R(M/Ni)$ defined in eq 17, to compare the other cations with Ni^{2+}. Any

$$R(M/Ni) = \frac{k_f^{M}k_I^{Ni}(H_2O)}{k_f^{Ni}k_I^{M}(H_2O)} \tag{17}$$

change in $R(M/Ni)$ should yield information about differences in mechanism between those and Ni^{2+}. The $R(M/Ni)$ values calculated from the data in Table VI are given in Table VII. Since $R(M/Ni)$ is a composite of four measurements, compounding of errors may be serious, and the absolute values have to be regarded with caution. Nevertheless, it would be unrealistic to conclude that the $R(M/Ni)$ values are equal and close to unity. The other values of $R(M/Ni)$ for Co^{2+}/Ni^{2+}, not given here, show a similar scatter. Many of the data refer to chelating ligands where slow ring closure may affect the rate. This effect should be even more important for faster substituting ions. For example, the very low value of $R(M/Ni)$ for Mn^{2+} with β-alanine may be due to chelation-controlled substitution. Thus, the results with multidentate ligands should be treated with caution. The monodentate ligands should provide more reliable information. Unfortunately, in the only existing study, the scatter and uncertainty are large,[50] and one is really unable to decide whether there is an influence of the entering ligand on the interchange rate or not. At this point of the discussion, we hope to have shown that it is very dubious to use the available complex formation rates, even for the sulfato complex, to prove a constancy in mechanism along the series.

Table VII. Ratios $R(M/Ni) = k_f^{M}k_I^{Ni}(H_2O)/k_I^{M}(H_2O)$ at 298 *K*,[a] Calculated from the Data in Tables III and IV

ligand	R(Mn/Ni)	R(Fe/Ni)	R(Co/Ni)
HF	1.08	3.28	1.77
F^-	0.49	0.81	0.21
PADA[b]	$\geqslant 0.13$		0.09
phen[c]	0.10		0.82
bpy		0.73	0.39
terpy	0.12	0.42	0.17
murexide$^-$[d]	8.18		1.23
β-alanine$^-$[e]	0.007		0.07[f]
ATP^{4-}	>0.4		0.22

[a] When the temperature at which the complex formation has been studied is not 298 K, $k_I^{M}(H_2O)$ is calculated at the same temperature, by using eq 9. [b] 288 K. [c] 284 K. [d] 283 K. [e] 293 K. [f] A ratio of 0.26 is obtained by using more recent k_f values for Co^{2+} and Ni^{2+}, published by the same research group.[49] There is no new value reported for Mn^{2+}.

Another approach would be to compare the activation parameters of $k_I(H_2O)$ and $k_I(L)$. They are difficult to obtain for K_{os}, since there is considerable uncertainty in the temperature dependence of this constant. Furthermore, in the particular case of the stopped-flow experiment, where the variation of the rate of reaction with temperature is very large, the "kinetic window" is too small to cover a wide temperature range, which is necessary to obtain reliable values for ΔH^* and ΔS^*. The difficulties encountered in using ΔS^* to assign a reaction pathway have been discussed elsewhere.[5,8] The

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Table VIII. Activation Volumes ΔV_I^* for Water Exchange Reaction and the Interchange Step for Complex Formation Reactions in Water[a]

ligand	Co^{2+}	Ni^{2+}	techn	ref
H_2O	+6.1 ± 0.2	+7.2 ± 0.2	^{17}O NMR	this work
NH_3	+4.8 ± 0.7	+6.0 ± 0.3	TJ	52
PADA	+7.2 ± 0.2	+7.7 ± 0.3	TJ	52
glycinate$^-$ [b]	+5 ± 2	+7 ± 1	TJ	53
murexide$^-$ [c]		+8.7 ± 1.5	TJ	54
imidazole		+11.0 ± 1.6	TJ	55

[a] The observed volume of activation ΔV_f^* is the sum of the volume of activation for the interchange step, ΔV_I^*, and the volume of reaction for outer-sphere complexation, ΔV_{os}^0. This later term is assumed equal to zero for uncharged ligands. [b] $\Delta V_{os}^0 = 3.2$ cm^3 mol^{-1}.[53] [c] $\Delta V_{os}^0 = 3.4$ cm^3 mol^{-1}.[54]

factors which affect this parameter are poorly understood and nonrandom errors are often associated with the determination of ΔS^*. The volume of reaction, ΔV_f^*, another measurable parameter, is the sum of two contributions, as shown in eq 18.

$$\Delta V_f^* = \Delta V_{os}^0 + \Delta V_I^*(L) \qquad (18)$$

In this equation, derived by differentiation of eq 15, ΔV_{os}^0 is the volume of outer-sphere complex formation and $\Delta V_I^*(L)$ is the volume of activation for the interchange step in complex formation reactions, which may be identified with the volume of activation for water exchange, $\Delta V_I^*(H_2O)$, when an I_d mechanism is assumed. There are a few variable-pressure studies of complex formation reactions on Co^{2+} and Ni^{2+} to compare with the volume of activation for water exchange. They are listed in Table VIII. Grant[53] has estimated ΔV_{os}^0 to be +3.2 cm^3 mol^{-1} for nickel(II) and cobalt(II) glycinate(1−), and Jost[54] has estimated a value of +3.5 cm^3 mol^{-1} for nickel(II) murexide(1−); for neutral ligands, the value of ΔV_{os}^0 must be negligible. With the sole unexplained exception of imidazole, all the values in Table VIII are well in accord to show that the rate-determining step in these substitution reactions on Co^{2+} and Ni^{2+} is the leaving of a water molecule. The I_d mechanism is also confirmed by the positive sign and the magnitudes of $\Delta V_I^*(L)$. It would be very useful to have the same information for Mn^{2+}. Unfortunately, there is no pressure-dependence study of complex formation reactions with this cation to compare with that of the corresponding $\Delta V_I^*(H_2O)$. Suitable reactions are very difficult to find for Mn^{2+}, but, it is to be hoped that, with the advent of the high-pressure techniques applied to the study of fast reactions, volumes of reactions will now also become accessible for substitution reactions on this ion.

According to the HSAB principle,[51] Mn^{2+} is a "hard" center and will react preferentially with "hard" nucleophiles. The nucleophilic power of potential ligands is related to their polarizability, and thus, the selectivity of Mn^{2+} toward various ligands must be poor, and the influence of a change in ligand on the interchange rate will be small. Therefore, even for substitution reactions where the interchange step has an associative character, the rate $k_I(L)$ will be close to the rate of water exchange.[5] Using the mechanistic criteria of Langford and Gray, one is led to the conclusion that, because of the low sensitivity to entering groups, the mechanism would be described as a dissociative interchange. This is not compatible with the structure of the transition state where the coordination number has increased, and thus, the Langford–Gray operational definition of an intimate interchange mechanism, used as sole criterion, is not sufficient. Fortunately, the volume of activation can be used as another, powerful criterion for the assignment of substitution mechanisms, especially when "hard" nucleophiles react with "hard" centers.

One may try to rationalize the experimentally observed trend toward dissociative behavior: the changeover occurring gradually along the series is paralleled by a monotonous decrease in ionic radius going from Mn^{2+} to Ni^{2+}. The smaller the central cation, the smaller the space left for the entering ligand to come in and the less favorable it is for a seven-coordinate structure to be formed at the transition state. This decrease in ionic radius will thus go along with an increasing dissociative behavior. Additionally, one may suppose that increasing occupancy of the t_{2g} orbitals of the cation going from Mn^{2+} to Ni^{2+} also influences the associative character of substitution reactions on these ions. The approach of the seventh molecule toward the face of the octahedron is not electrostatically favored when the t_{2g} orbitals of the metal ion are highly occupied, and therefore, the formation of a seven-coordinate transition state is less probable for Ni^{2+} than for Mn^{2+}. The next step would be to extend these arguments to predict the behavior of the earlier regular octahedral members of the series, V^{2+} and Ti^{2+}. For V^{2+}, the ionic radius is intermediate between the ionic radii of Fe^{2+} and Mn^{2+}, and the t_{2g} orbital occupancy is the same as for Mn^{2+}. Looking only at these two aspects, we would expect the character of substitution reactions on V^{2+} to be less associative than for that of Mn^{2+}, but, we have also to take the changes in e_g orbital occupancy into account. These orbitals are σ antibonding, and it can be supposed that their filling will produce an increasing dissociative character. For V^{2+}, the e_g orbitals are vacant, whereas for Mn^{2+}, they are partially filled, which means that V^{2+} should react with more associative character than Mn^{2+}. It is thus very difficult to make predictions on whether substitution reactions on this ion will show more associative character than those on Mn^{2+} or less, but one can be sure that it reacts more associatively than Fe^{2+}. For its left neighbor, Ti^{2+}, the vacancy of the e_g orbitals and both the ionic radius and the t_{2g} occupancy arguments predict an increase of the associative character compared to Mn^{2+}. Because of the above-discussed low sensitivity of the substitution rates of these ions to changes in the incoming ligands, confirmation of these predictions will not be easy to obtain, and the ΔV^* method may be the only investigation tool available. Finally, due to the expected small dependence of associative interchange I_a substitution rates to the entering ligand, the importance of the Eigen–Wilkins approach as a predictive tool for the rate of both dissociative I_d and associative I_a substitution reactions remains effective.

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Registry No. $Mn(H_2O)_6^{2+}$, 15365-82-9; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Co(H_2O)_6^{2+}$, 15276-47-8; $Ni(H_2O)_6^{2+}$, 15365-79-4.

Supplementary Material Available: Experimental data for the temperature dependence of the $M(ClO_4)_2$ bulk water relaxation rate ($M = Mn^{2+}, Fe^{2+}, Co^{2+}$) and chemical shifts ($M = Fe^{2+}, Co^{2+}$) (Tables SI to SV) and the pressure dependence of the $M(ClO_4)_2$ bulk water relaxation rate ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}$) and chemical shifts ($M = Co^{2+}$) (Tables SVI to SX) and calculated kinetic parameters from a least-squares fit of variable pressure data (various combinations of data sets) (Tables SXI to SXIV) (20 pages). Ordering information is given on any current masthead page.

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