

# Inorganic and Bioinorganic Solvent Exchange Mechanisms

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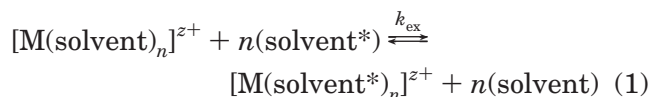
## 1. Introduction

### 1.1. Scope of This Review

The simplest reaction on a metal ion in aqueous or nonaqueous solution is the exchange of a solvent molecule between the first and second coordination

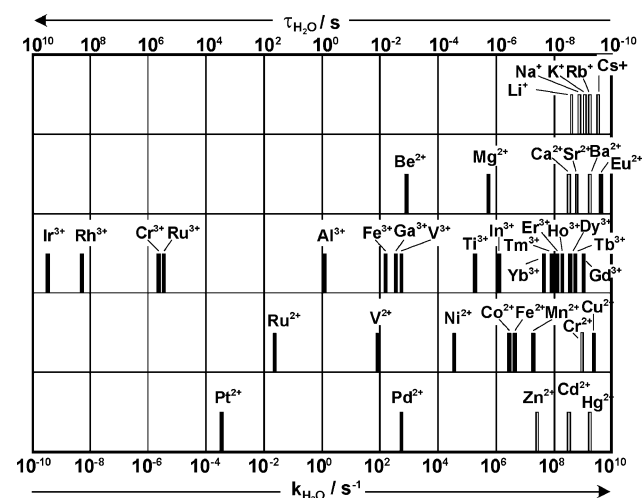
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shells (eq 1). This reaction is fundamental in under-



standing not only the reactivity of metal ions in chemical and biological systems but also the interaction between the metal ion and the solvent molecule. The replacement of a solvent molecule from the first coordination shell represents an important step in complex-formation reactions of metal cations and in many redox processes.<sup>1</sup>

In solvent exchange reactions there is no net reaction and the Gibbs free energy change,  $\Delta G^\circ$ , of the reaction is zero because the reagents and the products are identical. The measured rates of solvent exchange vary extensively with the nature of the metal ion and, to a lesser extent, with that of the solvent. Figure 1 shows that  $k_{\text{H}_2\text{O}}$ , the exchange rate constant for water molecules, covers nearly 20 orders of magnitude. A water molecule stays, in mean, nearly 300 years ( $9 \times 10^9$  s at 298 K) in the first coordination shell of  $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$  (ref 2) before it is replaced by another one coming from bulk solvent. The mean lifetime of  $\text{H}_2\text{O}$  bound to  $[\text{Eu}(\text{H}_2\text{O})_7]^{2+}$  is, however, only about 200 ps ( $2 \times 10^{-10}$  s at 298 K).<sup>3,4</sup> Astonishingly, both exchange processes follow an



**Figure 1.** Mean lifetimes,  $\tau_{\text{H}_2\text{O}}$ , of a particular water molecule in the first coordination shell of a given metal ion and the corresponding water exchange rate  $k_{\text{H}_2\text{O}}$  at 298 K. The filled bars indicate directly determined values, and the empty bars indicate values deduced from ligand substitution studies.

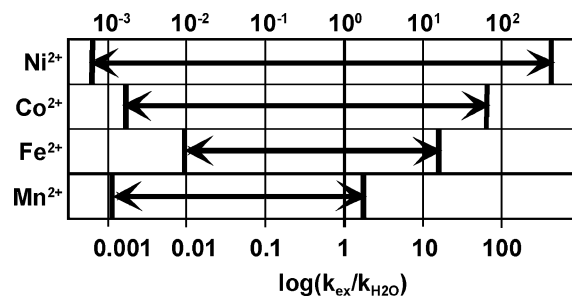


Lothar Helm was born in Gernsbach (Germany) in 1952. He studied physics at the University of Karlsruhe (Germany) and obtained his diploma degree in 1977. He remained in Karlsruhe for his Ph.D. research with Prof. H. G. Hertz and received his degree in physical chemistry in 1980. In 1980 he joined the laboratories of Prof. André Merbach at the University of Lausanne, Switzerland. From 1983 to 2001 he was maître d'enseignement et de recherche at the Faculty of Science of the University of Lausanne. In 2001 he moved, together with the whole chemistry department, from the University of Lausanne to the Ecole Polytechnique Fédérale de Lausanne (EPFL). His main research interest is in the study of reaction mechanisms in coordination chemistry using multinuclear and high-pressure NMR and computer simulation techniques.



Originating from Pully (Switzerland), André E. Merbach was born in 1940. He studied at the Polytechnical School of the University of Lausanne and obtained a degree in chemical engineering in 1962. In 1964, he was awarded his Ph.D. in inorganic chemistry from the University of Lausanne. He then had a Postdoctoral Fellowship in the Lawrence Radiation Laboratory at the University of California, Berkeley, where he studied the ionization of strong electrolytes by NMR. Upon his return, in 1965, to the Institute of Inorganic and Analytical Chemistry at the University of Lausanne, he accepted a teaching and research position in coordination chemistry. In 1973, the Swiss Chemical Society awarded him the Werner Prize and Medal for his work studying the structure, the stability, and the dynamics of metal halogen adducts by NMR and he was nominated Professor in Inorganic and Analytical Chemistry. He was a member of the Research Council of the NSF (1985–1996) and has chaired the European Technical Committee (COST) for chemical research (1998–2000). He organized the XXIXth International Conference in Coordination Chemistry (ICCC) in Lausanne in 1992. He was awarded an honorary doctorate (Honoris Causa) from the University of Lajos Kossuth in Debrecen (Hungary) in 1993 for his work on elucidating reaction mechanisms in coordination chemistry utilizing high-pressure NMR and from the University of Geneva in 2003. He was called at the presidency of the Swiss Chemical Society (2001–2004). Since 2001 he has been Professor of inorganic chemistry at EPFL.

associative activation mode, which means that for both hydration complexes the transition state or intermediate encountered during the exchange reaction has an increased coordination number.



**Figure 2.** Ranges of solvent exchange rate constants,  $k_{ex}$ , with respect to that of water,  $k_{H_2O}$ , for selected divalent transition metal ions (from Table 5).

The dependence on solvents is, however, less pronounced, as shown in different reviews.<sup>5,6</sup> Figure 2 shows the ranges of solvent exchange rate constants with respect to water for four divalent d-transition metal ions. Even if the range for  $Ni^{2+}$  spans nearly 6 orders of magnitude, the discussion of solvent exchange is most conveniently divided into categories of metal ions. A first category is formed by ions of main group elements. These ions have filled electron shells, and they differ mainly in electric charge and ionic radius. The number of solvent molecules in the first shell around the ion, commonly called the coordination number, CN, ranges from 4 up to 10.<sup>7</sup> A second category is formed by the d-transition metal ions, which are, in general, hexacoordinated, with the exception of  $Pd^{2+}$  and  $Pt^{2+}$ , which are four-coordinated (square planar),  $Sc^{3+}$ , which is suggested to be coordinated by seven water molecules,<sup>8</sup> and  $Cu^{2+}$ , where there is some evidence that the aqua ion could be five-coordinated.<sup>9</sup> The solvent exchange rate constants of d-transition metal ions are strongly influenced by the occupancy of the d-orbitals. A third category involves the f-shell ions, which have coordination numbers ranging from six for bulky non-aqueous solvents to eight or nine for water molecules. Their kinetic behavior is mainly influenced by the decrease in ionic radius along the series and by the coordination equilibrium observed along the series.

Replacing some of the first shell water molecules by one or more ligands, which are kinetically inert, can have a strong influence on the rate and the mechanism of exchange of the remaining solvent molecule(s). Metal ion complexes still having one or more solvent molecules directly bound are important in catalysis,<sup>10</sup> as active centers in biomolecules,<sup>11</sup> and, in the special case of gadolinium(III), as contrast agents in medical magnetic resonance imaging.<sup>12</sup>

Solvent exchange reactions have been reviewed several times in the last few years. Lincoln and Merbach published in 1995 a comprehensive review of substitution reactions of solvated metal ions.<sup>5</sup> A follow-up of this review concentrating on solvent exchange was published in 2003.<sup>6</sup> The use of high pressure to elucidate mechanisms of water exchange reactions has been treated in a book chapter published in 2002.<sup>13</sup> This review is a comprehensive compilation of solvent exchange rate constants and reaction mechanisms for solvated metal ions in solution and for metal ion complexes with one or several solvent molecules in the first coordination sphere. Research on contrast agents for medical

magnetic resonance imaging (MRI) has led to an important field of fundamental and applied research in bioinorganic chemistry.<sup>12</sup> We therefore include a special section on water exchange on lanthanides, mainly gadolinium, complexes.

## 1.2. Classification of Exchange Mechanisms

Langford and Gray proposed in 1965<sup>14</sup> a mechanistic classification for ligand substitution reactions, which is now generally accepted and summarized here for convenience. In their classification, they divided ligand substitution reactions into three categories of *stoichiometric mechanisms*: associative (**A**), where an intermediate of increased coordination number can be detected, dissociative (**D**), where an intermediate of reduced coordination number can be detected, and interchange (**I**), where there is no kinetically detectable intermediate. Langford and Gray furthermore distinguished two categories of *intimate mechanisms*: those with an associative activation mode (**a**) and those with a dissociative activation mode (**d**). In the first case the reaction rate is sensitive to the nature of the entering group, whereas in the second case the reaction rate is not sensitive to the variation of the entering group (Figure 3). All **A** mechanisms must be associatively activated, and all **D** mechanisms must be dissociatively activated. The interchange mechanisms (**I**) include a continuous spectrum of transition states where the degree of bond making between the entering ligand and the complex ranges from very substantial (**I<sub>a</sub>** mechanism) to negligible (**I<sub>d</sub>** mechanism) and inversely for bond breaking.<sup>15,16</sup> For a solvent exchange reaction, the forward and backward reaction coordinates must be symmetrical. For an **I<sub>a</sub>** mechanism, both the entering and the leaving solvent molecule must have considerable bonding to the metal ion at the transition state. Inversely, for an **I<sub>d</sub>** mechanism with weak bond making to the entering solvent molecule, the leaving one is also weakly bound.

The assignment of a substitution reaction mechanism is mainly based on the response of the reaction

	evidence for an intermediate of <b>lower</b> coordination number	no evidence for an intermediate		evidence for an intermediate of <b>higher</b> coordination number
stoichiometric mechanism	<b>D</b>	<b>I</b>		<b>A</b>
intimate mechanism	<b>D</b>	<b>I<sub>d</sub></b>	<b>I<sub>a</sub></b>	<b>A</b>
sensitivity of rate to nature of entering group	rate <i>independent</i> of nature of entering group		rate <i>dependent</i> of nature of entering group	

Figure 3. Classification of substitution reactions.

Table 1. Evolution with Time of Exchange Rate Constants and Activation Parameters<sup>a</sup> for  $[\text{Ni}(\text{CH}_3\text{CN})_6]^{2+}$  in  $\text{CH}_3\text{CN}$  Determined by  $^1\text{H}$  and  $^{14}\text{N}$  NMR<sup>a</sup>

year	$10^{-3}k_1$ (298K)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	nucleus	ref
1967	2.8	49	-15		$^1\text{H}$	18
1967	3.9	46	-37		$^1\text{H}$	19
1967	2.1	49	-16		$^1\text{H}$	20
1971	2.9	67	+43		$^1\text{H}$	21
1971	3.0	63.2	+41.8		$^{14}\text{N}$	21
1973	2.0	68	+50		$^{14}\text{N}$	22
1973	3.6	60	+23		$^1\text{H}$	22
1973	14.5	39.5	-32.6		$^{14}\text{N}$	23
1979	2.9	64.6	+37.9	+9.6	$^1\text{H}$	24
1980	3.1	60.8	+25.8	+6.3	$^{14}\text{N}$	25
1989	6.2	41.4	-30	+12.0	$^{14}\text{N}$	26

<sup>a</sup> Units are as follows:  $k_1(298\text{K})$ ,  $\text{s}^{-1}$ ;  $\Delta H^\ddagger$ ,  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$ ,  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $\Delta V^\ddagger$ ,  $\text{cm}^3 \text{mol}^{-1}$ .

rate to the variation of chemical and physical parameters such as the nature and concentration of the entering ligand, temperature, and pressure. The rate law for solvent exchange reactions can be determined using an inert diluent,<sup>17</sup> a technique which is often used for nonaqueous solvents but which cannot be used for water due to the lack of an adequate diluent. The variation of the enthalpy and entropy of activation,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , respectively, obtained from variable temperature experiments, within a series of similar ligand substitution systems can give a guide to a mechanistic change. Thus **d**-activated reactions tend to have greater  $\Delta H^\ddagger$  values than do **a**-activated reactions, and  $\Delta S^\ddagger$  tends to be positive for **d**-activated reactions and negative for **a**-activated reactions. However, the magnitudes of the contributions to these two parameters arising from interactions that occur beyond the first coordination shell can be uncertain and the determination of  $\Delta S^\ddagger$  is often prone to systematic errors, especially if the temperature range for experimental determination of  $k_{\text{ex}}$  is small. Table 1 shows how  $\Delta S^\ddagger$  has evolved with time and experimental method from  $-37$  to  $+50 \text{ J mol}^{-1} \text{ K}^{-1}$  for the same reaction.

The pressure dependence of the exchange rate constant leads to the activation volume,  $\Delta V^\ddagger$ , which has become the major tool for the experimental determination of solvent exchange mechanisms.<sup>16,27-30</sup> This is mainly due to the direct connection between the sign of  $\Delta V^\ddagger$  and the intimate mechanism for solvent exchange.

The volume of activation,  $\Delta V^\ddagger$ , is defined as the difference between the partial molar volumes of the transition state for the reaction and the reactants and is related to the pressure variation of the rate constant at a constant temperature  $T$  by eq 2:<sup>31-33</sup>

$$\left(\frac{\partial \ln(k)}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (2)$$

An approximate solution of the above differential equation (eq 2) is eq 3:

$$\ln\left(\frac{k_P}{k_0}\right) = -\frac{\Delta V_0^\ddagger P}{RT} + \frac{\Delta \beta^\ddagger P^2}{2RT} \quad (3)$$



**Table 2. Volume Changes  $-\Delta V_{elec}^{\ddagger}$  (in  $\text{cm}^3 \text{mol}^{-1}$ ) Arising from Creation of an Electric Charge, a Dipole Moment, or a Quadrupole Moment in Different Solvents<sup>31,35</sup>**

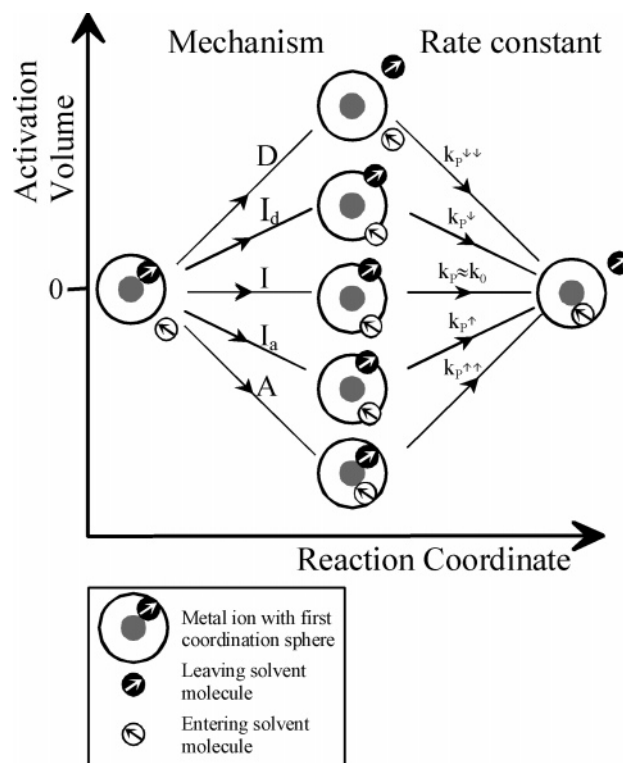
solvent	$-\Delta V_{elec}^{\ddagger}$ from		
	charge <sup>a</sup>	dipole moment <sup>b</sup>	quadrupole moment <sup>c</sup>
water	1.3	1.8	1.4
methanol	4	6	4
acetone	7	10	7
benzene	27	39	28

<sup>a</sup>  $1e = 1.6 \times 10^{-19} \text{ C}$ . <sup>b</sup>  $10 \text{ D} = 33 \times 10^{-30} \text{ C m}$ . <sup>c</sup>  $6.4 \times 10^{-39} \text{ C m}^2$ .

where  $k_P$  and  $k_0$  are the rate constants at pressures  $P$  and 0, respectively,  $\Delta V_0^{\ddagger}$  is the activation volume at  $P = 0$ , and  $\Delta\beta^{\ddagger}$  is the compressibility coefficient of activation.<sup>33</sup> For exchange reactions with water, a highly electrostricted solvent, the quadratic term in eq 2 is small compared to the linear one for pressures generally applied in kinetic studies (typically 0–200 MPa), and therefore, in aqueous solution  $\Delta V^{\ddagger} \cong \Delta V_0^{\ddagger}$ .<sup>34</sup>

The interpretation of the activation volume for solvent exchange reactions on metal ions is based on the transition state theory.<sup>31,32</sup> The experimentally determined activation volume is considered to be the sum of an intrinsic contribution,  $\Delta V_{int}^{\ddagger}$ , and a solvent contribution,  $\Delta V_{solv}^{\ddagger}$ .<sup>33–35</sup> The intrinsic activation volume results from changes in internuclear distances and angles within the reactants during the formation of the transition state and can therefore be used in assignment of reaction mechanisms. The volume changes due to solvent effects are usually associated with electrostriction, which means the very strong electrostatic forces of attraction exerted by charges or electric dipole and quadrupole moments on surrounding solvent molecules. More precisely,  $\Delta V_{solv}^{\ddagger}$  arises from changes in the electrostriction between the transition state and the reactants and can be important for substitution reactions when ions or electric dipoles (or even quadrupoles) are formed or neutralized at the transition state (Table 2). For solvent exchange processes, where the charge of the complex does not change,  $\Delta V_{solv}^{\ddagger}$  is small and  $\Delta V^{\ddagger} \cong \Delta V_{int}^{\ddagger}$ . Therefore, the measured activation volume is a direct measure of the degree of bond formation and bond breaking on going to the transition state.

Figure 4 visualizes the pressure induced changes of the measured exchange rate constants and the underlying solvent exchange reaction mechanism. In a **d**-activated exchange process, the approach to the transition state is characterized mainly by *bond breaking* and results in an increase in volume, which means a decrease in the observed reaction rate constant,  $k_P$  (eq 2). In an **a**-activated exchange process, however, the approach to the transition state is characterized mainly by *bond formation* and results in a decrease in volume, which means an increase in  $k_P$ . Briefly,  $\Delta V^{\ddagger} > 0$  is indicative of dissociatively activated processes, and  $\Delta V^{\ddagger} < 0$  is indicative of associatively activated processes. However, it is less easy to decide on the basis of activation volumes if the mechanism is a limiting associative mechanism, **A** (or dissociative, **D**), or an interchange



**Figure 4.** Solvent exchange processes: volume profiles connected to the transition states.

with a relatively strong contribution of the entering solvent molecule, **I<sub>a</sub>** (or with a negligible contribution of the entering solvent molecule, **I<sub>d</sub>**). The absolute value of the activation volume,  $|\Delta V^{\ddagger}|$ , can serve as a guideline: the larger  $|\Delta V^{\ddagger}|$ , the closer the mechanism is to a limiting **A** or **D**. For octahedral 3d metal transition ions in water, Swaddle<sup>36,37</sup> developed a semiempirical model to estimate the limiting volumes by linking the partial molar volumes of hydrated metal ions to their ionic radii,  $r_M$ . Following Shannon,<sup>38</sup>  $r_M$  values for a specific metal depend on the charge of the ion and on its coordination number. Swaddle's model gives similar limiting values of  $|\Delta V^{\ddagger}| = 13.5 \text{ cm}^3 \text{mol}^{-1}$  for **A** and **D** processes on +2 and +3 octahedral 3d-transition metal ions. Exceptions to this guideline are, however, observed, and therefore, each case has to be considered individually.

### 1.3. Experimental Methods

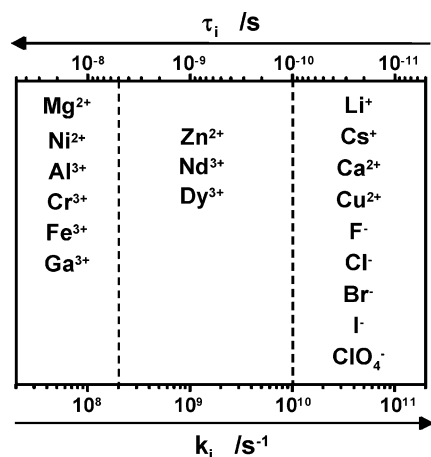
Only a few experimental techniques allow us to measure solvent exchange rate constants directly. The measurement of solvent exchange rates in solution is today almost exclusively performed by NMR, which itself offers a variety of different methods, such as line shape analysis, methods based on relaxation time measurements, or methods based on isotopic labeling.<sup>39,40</sup>

As mentioned above, the pressure dependence of the exchange rate constant has become the major tool for the experimental determination of solvent exchange mechanisms. Consequently, high-pressure, high-resolution NMR probes were developed which allow the application of the variety of NMR techniques to pressures up to several hundreds of megapascals.<sup>40–43</sup>

## 2. Solvent Exchange on Main Group Metal Ions

Main group metal ions are diamagnetic, which limits the possibility to study solvent exchange by NMR to only a few di- and trivalent ions:  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , and  $\text{In}^{3+}$ . All other ions are too labile, due to the low surface charge density and the absence of ligand field stabilization effects.

The technique of high-resolution incoherent quasi-elastic neutron scattering (IQENS) can be used to get information on water–proton binding times in concentrated aqueous ionic solutions. The observation time scale ( $\tau_{\text{obs}} \sim 10^{-9}$  s) of the IQENS method is long enough for Fick's law of translational diffusion to apply but is short enough, when compared with the cation to solvent–proton binding time in some divalent and trivalent metal ion solutions, for two distinct proton populations to be observed.<sup>44</sup> Limits of water–proton binding times obtained by IQENS are given in Figure 5.



**Figure 5.** Ion–water proton binding times,  $\tau_i$ , obtained from IQENS experiments on concentrated aqueous ionic solution at  $\sim 298$  K.<sup>45</sup>

### 2.1. Divalent Main Group Metal Ions

The only divalent main group ions where solvent exchange rates and mechanisms are experimentally available are  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ .  $\text{Be}^{2+}$  forms predominantly tetrahedral complexes, whereas  $\text{Mg}^{2+}$  is in general hexacoordinated.

Beryllium(II) is the smallest metal ion ( $r = 27$  pm) and is the only one where solvent exchange on tetrahedral complexes could be studied in a dozen solvents (Table 3). The general rate law for solvent exchange on  $[\text{Be}(\text{solvent})_4]^{2+}$  can be expressed as given in eq 4.

$$k_{\text{obs}} = k_1 + k_2[\text{solvent}] \quad (4)$$

$k_1$  and  $k_2$  typify **d**- and **a**-activated pathways, respectively. For solvent exchange on  $\text{Be}^{2+}$  in non-aqueous solvents, the bulkiness of solvent molecules becomes an important parameter for solvent exchange mechanisms. A crossover from **a**- to **d**-activation is observed as the steric hindrance at the metal center increases with increasing size of the solvent molecules. For the small solvents DMSO, TMP, DMMP, and MMPP, the second-order term,  $k_2$ , dominates and either an **A** or an **I<sub>a</sub>** mechanism

**Table 3.** Rate Constants and Activation Parameters for Solvent Exchange on Alkaline Earth Ions<sup>f</sup>

solvent	$k_1$ (298K) <sup>a</sup>	$k_2$ (298K) <sup>a</sup>	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>[Be(solvent)<sub>4</sub>]<sup>2+</sup></b>							
$\text{H}_2\text{O}^b$	730	13.2 <sup>c</sup>	59.2	+8.4	-13.6	<b>A</b>	17
DMSO <sup>d</sup>		213	35.0	-83.0	-2.5	<b>A, I<sub>a</sub></b>	17
		140	51.1	-32.3		<b>A, I<sub>a</sub></b>	46
		4.2	43.5	-87.1	-4.1	<b>A, I<sub>a</sub></b>	17
TMP <sup>d</sup>		1.5	56.0	-54.0		<b>A, I<sub>a</sub></b>	47
		0.81	60.2	-44.4		<b>A, I<sub>a</sub></b>	47
DMMP <sup>d</sup>		0.22	68.7	-26.1		<b>A, I<sub>a</sub></b>	48
DMF <sup>d</sup>		16	52.0	-47.5	-3.1	<b>A, I<sub>a</sub></b>	17
	0.2		74.9	-7.3		<b>D</b>	17
NMA <sup>d</sup>		8.5	58.1	-32.0		<b>A, I<sub>a</sub></b>	49
	0.1		83.6	+16.3		<b>D</b>	49
DMA <sup>d</sup>		0.32	76.8	+3.1		<b>A, I<sub>a</sub></b>	49
	0.23		71.5	-17.3		<b>D</b>	49
DEA <sup>d</sup>		0.34	66.7	-30.1		<b>A, I<sub>a</sub></b>	49
	0.38		56.9	-62.1		<b>D</b>	49
DMADMP <sup>d</sup>		0.044	76.4	-14.6		<b>D</b>	48
	0.0073		89.1	+12.6		<b>D</b>	47
TMU <sup>d</sup>		1.0	79.6	+22.3	+10.5	<b>D</b>	17
	1.4		77.1	+16.4		<b>D</b>	46
DMPU <sup>d</sup>	0.1		92.6	+47.5	+10.3	<b>D</b>	17
<b>[Mg(solvent)<sub>6</sub>]<sup>2+</sup></b>							
$\text{H}_2\text{O}^b$	$6.7 \times 10^5$		49.1	+31.1	+6.7	<b>D, I<sub>d</sub></b>	50
MeOH <sup>b</sup>	$4.7 \times 10^3$		69.9	+59		<b>D, I<sub>d</sub></b>	51
EtOH <sup>b</sup>	$2.8 \times 10^6$		74.1	+126		<b>D, I<sub>d</sub></b>	52
DMF <sup>d</sup>	$4.3 \times 10^5$		54.8	+46.8	+8.5	<b>D, I<sub>d</sub></b>	53
DMF <sup>e</sup>	$6.2 \times 10^6$		77.8	+146		<b>D, I<sub>d</sub></b>	54
TMP <sup>e</sup>	$7.4 \times 10^5$		51.3	+39.5		<b>D, I<sub>d</sub></b>	55

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Neat solvent. <sup>c</sup> In  $\text{kg mol}^{-1} \text{s}^{-1}$ , which corresponds to  $730 \text{ s}^{-1}/55.5 \text{ mol kg}^{-1}$ . <sup>d</sup> In  $d_3$ -nitromethane diluent. <sup>e</sup> In  $d_2$ -dichloromethane diluent. <sup>f</sup> Units are as follows:  $k_1(298\text{K})$ ,  $\text{s}^{-1}$ ;  $k_2(298\text{K})$ ,  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ;  $\Delta H^\ddagger$ ,  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$ ,  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $\Delta V^\ddagger$ ,  $\text{cm}^3 \text{mol}^{-1}$ .

operates. Negative activation volumes (Table 3) measured for DMSO and TMP support this assignment. Both the  $k_1$  and the  $k_2$  terms apply for DMF, NMA, DMA, and DEA, consistent with a parallel operation of **d**- and **a**-activated mechanisms. For the most bulky solvents, DMADMP, TMU, and DMPU, a **D** mechanism dominates: only the  $k_1$  term operates and the measured  $\Delta V^\ddagger$  values are very positive (Table 3).

Water exchange on  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  is characterized by the very negative activation volume  $\Delta V^\ddagger = -13.6 \text{ cm}^3 \text{mol}^{-1}$ , which is close to the calculated limiting contribution for an **A** mechanism,  $\Delta V_{\text{lim}}^\ddagger = -12.9 \text{ cm}^3 \text{mol}^{-1}$ , for 3d octahedral metal ions.<sup>17</sup> This suggests the operation of a limiting **A** mechanism for the exchange of the very small  $\text{H}_2\text{O}$  molecule on  $\text{Be}^{2+}$ .

The hexacoordinated  $\text{Mg}^{2+}$ -solvate complexes are much more labile compared to the tetracoordinated  $\text{Be}^{2+}$  (Table 3). The rate laws determined in non-aqueous solvents are first order for all solvent exchange reactions on  $[\text{Mg}(\text{solvent})_6]^{2+}$ , and activation volumes measured for  $\text{H}_2\text{O}$  and DMF are positive. This indicates the operation of **d**-activated mechanisms.

### 2.2. Trivalent Main Group Metal Ions

The  $\text{Al}^{3+}$  ( $r = 54$  pm),  $\text{Ga}^{3+}$  (62 pm), and  $\text{In}^{3+}$  (80 pm) ions are most conveniently discussed together

**Table 4. Rate Constants and Activation Parameters for Solvent Exchange on Trivalent Main Group Ions<sup>d</sup>**

[M(solvent) <sub>n</sub> ] <sup>3+</sup>	<i>k</i> <sub>1</sub> (298K) <sup>a</sup>	<i>k</i> <sub>2</sub> (298K) <sup>a</sup>	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>Al<sup>3+</sup></b>							
[Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+ b</sup>	1.29		84.7	+41.6	+5.7 +5.6 (ab initio)	<b>I<sub>d</sub></b> <b>D</b>	57 58
[Al(OH)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	3.1 × 10 <sup>4</sup>		36.4	-36.4			59
[Al(F)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	1.1 × 10 <sup>2</sup>		79	+60			60
[Al(F)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	2.3 × 10 <sup>2</sup>		65	+19			61
[Al(F) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup>	1.71 × 10 <sup>4</sup>		66	+57			61
[Al(F) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup>	1.96 × 10 <sup>4</sup>		69	+70			60
[Al(C <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup>	1.09 × 10 <sup>2</sup>		68.9	+25.3			62
[Al(mMal)(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup>	6.6 × 10 <sup>2</sup>		66	+31			63
[Al(mMal) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>	6.9 × 10 <sup>3</sup>		55	+12.8			63
[Al(ma)(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	3.4 × 10 <sup>2</sup>		63	+14			64
[Al(ma) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	1.95 × 10 <sup>3</sup>		49	-19			64
[Al(Sal)(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup>	4.9 × 10 <sup>3</sup>		35	-57			65
[Al(sSal)(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup>	3.0 × 10 <sup>3</sup>		37	-54			65
[AlO <sub>4</sub> Al <sub>12</sub> (OH) <sub>24</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>7+</sup>	1.1 × 10 <sup>3</sup>		53	-7			66, 67
[GeO <sub>4</sub> Al <sub>12</sub> (OH) <sub>24</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>7+</sup>	2.3 × 10 <sup>2</sup>		63	29			68
[GeO <sub>4</sub> Al <sub>12</sub> (OH) <sub>24</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>8+</sup>	1.9 × 10 <sup>2</sup>		56	20			69
[Al(DMSO) <sub>6</sub> ] <sup>3+ c</sup>	0.30		82.6	+22.3	+15.6	<b>D</b>	70, 71
[Al(DMF) <sub>6</sub> ] <sup>3+ c</sup>	0.05		88.3	+28.4	+13.7	<b>D</b>	70, 71
[Al(TMP) <sub>6</sub> ] <sup>3+ c</sup>	0.78		85.1	+38.2	+22.5	<b>D</b>	15
[Al(TMP) <sub>6</sub> ] <sup>3+ c</sup>	0.38		98.3	+76.1		<b>D</b>	72
[Al(DMMP) <sub>6</sub> ] <sup>3+ c</sup>	5.1		79.5	+33.0		<b>D</b>	72
[Al(HMPA) <sub>4</sub> ] <sup>3+ c</sup>		4.8 × 10 <sup>3</sup>	32.2	-42.7		<b>A</b>	72
<b>Ga<sup>3+</sup></b>							
[Ga(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+ b</sup>	4.0 × 10 <sup>2</sup>		67.1	+30.1	+5.0 +4.8 (ab initio)	<b>I<sub>d</sub></b> <b>D</b>	73 58
[Ga(OH)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	1 × 10 <sup>5</sup>		58.9		+6.2	<b>I<sub>d</sub></b>	73
[Ga(DMSO) <sub>6</sub> ] <sup>3+ c</sup>	1.87		72.5	+3.5	+13.1	<b>D</b>	70, 71
[Ga(DMF) <sub>6</sub> ] <sup>3+ c</sup>	1.72		85.1	+45.1	+7.9	<b>D</b>	70, 71
[Ga(TMP) <sub>6</sub> ] <sup>3+ c</sup>	6.4		76.5	+27.0	+20.7	<b>D</b>	15
	5.0		87.9	+63.2		<b>D</b>	74
<b>Sc<sup>3+</sup></b>							
[Sc(TMP) <sub>6</sub> ] <sup>3+ b</sup>		1.2 × 10 <sup>2</sup>	37.4	-60.5	-20.1	<b>A, I<sub>a</sub></b>	75
[Sc(TMP) <sub>6</sub> ] <sup>3+ c</sup>		38.4	21.2	-143.5	-18.7	<b>A, I<sub>a</sub></b>	15
[Sc(TMP) <sub>6</sub> ] <sup>3+ c</sup>		45.3	26.0	-126		<b>A, I<sub>a</sub></b>	76
[Sc(DMMP) <sub>6</sub> ] <sup>3+ c</sup>		13.2	29.7	-124		<b>A, I<sub>a</sub></b>	77
[Sc(TMU) <sub>6</sub> ] <sup>3+ c</sup>	0.21		91.2	+47.8		<b>D</b>	78
<b>In<sup>3+</sup></b>							
[In(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+ b</sup>	4.0 × 10 <sup>4</sup> >3 × 10 <sup>4</sup>		19.2	-96		<b>A, I<sub>a</sub></b>	79
					-5.2 (ab initio)	<b>A</b>	58
[In(TMP) <sub>6</sub> ] <sup>3+ c</sup>		7.6	32.8	-118	-21.4	<b>A, I<sub>a</sub></b>	15
[In(TMP) <sub>6</sub> ] <sup>3+ c</sup>		7.2	35.6	-109		<b>A, I<sub>a</sub></b>	74

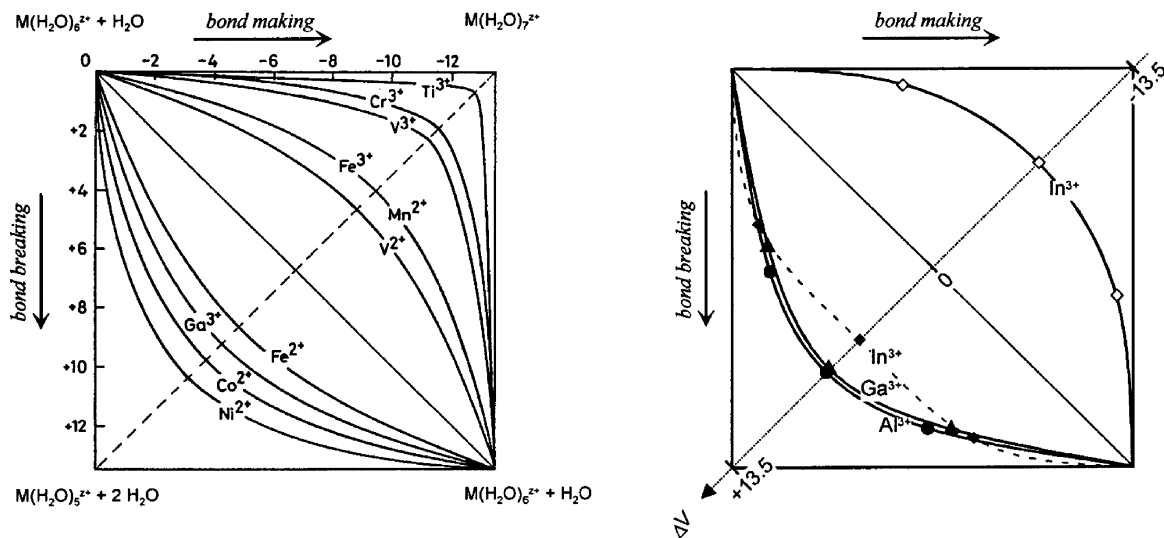
<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Neat solvent. <sup>c</sup> In *d*<sub>3</sub>-nitromethane diluent. <sup>d</sup> Units are as follows: *k*<sub>1</sub>(298K), s<sup>-1</sup>; *k*<sub>2</sub>(298K), dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>;  $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>;  $\Delta S^\ddagger$ , J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta V^\ddagger$ , cm<sup>3</sup> mol<sup>-1</sup>.

with Sc<sup>3+</sup> (75 pm), which also has a closed shell electronic configuration. These four ions together allow studying the influence of metal ion size on solvent exchange on octahedral trivalent metal ions. For the two smallest ions, Al<sup>3+</sup> and Ga<sup>3+</sup>, the solvent exchange follows a dissociative mechanism (first-order rate law, positive activation volume), and the rate of exchange increases from Al<sup>3+</sup> to Ga<sup>3+</sup>, as expected, with the decrease of the surface charge density (Table 4). For the two larger, Sc<sup>3+</sup> and In<sup>3+</sup>, ions, an increase in coordination number becomes possible at the transition state and the solvent exchange mechanism becomes associative (second-order rate law, negative activation volume). For TMP exchange on all four ions, the measured activation volumes (cm<sup>3</sup> mol<sup>-1</sup>) change from +22.5 (Al<sup>3+</sup>) and +20.7 (Ga<sup>3+</sup>) to -18.7 (Sc<sup>3+</sup>) and -21.4 (In<sup>3+</sup>). The thermodynamic reaction volume,  $\Delta V$ , for the addition of one TMP molecule to [Nd(TMP)<sub>6</sub>]<sup>3+</sup> (ionic radius of six coordinated Nd<sup>3+</sup> ions = 98 pm)<sup>38</sup> has been measured by visible spectroscopy to be -23.8 cm<sup>3</sup>

mol<sup>-1</sup>.<sup>56</sup> This suggests the operation of limiting (or close to limiting) mechanisms for TMP exchange on these ions: **D** and **A**, respectively. The change of activation from **d**-activation for the small Al<sup>3+</sup> and Ga<sup>3+</sup> to **a**-activation for the larger In<sup>3+</sup> and Sc<sup>3+</sup> has been generalized for all solvents, including H<sub>2</sub>O.

The water exchange mechanisms on the hexaaqua ions of Al<sup>3+</sup>, Ga<sup>3+</sup>, and In<sup>3+</sup> in aqueous solution have been modeled using ab initio calculations at the Hartree-Fock level.<sup>58</sup> The calculations confirmed the change in activation mode and gave a closer insight on the relation between exchange mechanism and activation volume. To illustrate the interpretation of  $\Delta V^\ddagger$  for H<sub>2</sub>O exchange on aqueous [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, Swaddle used a square whose sides represent M-X and M-Y bond order changes from 0 to 1 for a reaction ML<sub>n</sub>X + Y → ML<sub>n</sub>Y + X, scaled to the physical parameter volume (Figure 6). The scaling was done using a semiempirical description of the partial molar volume of a metal ion for a symmetrical H<sub>2</sub>O exchange reaction.<sup>5</sup> The change of volume dur-





**Figure 6.** Interpretation of activation volumes for water exchange on hexaqua metal ions in terms of contributions from bond making and bond breaking: (left) Swaddle's scaled More-O'Ferrall diagram assuming a continuum of interchange mechanisms; (right) calculated curves for  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , and  $\text{In}^{3+}$  using Connolly volumes.

ing the exchange reaction is given by the sum of the coordinates. Swaddle has argued<sup>80</sup> that all water exchange reactions should be regarded as having interchange, **I**, mechanisms, spanning a continuum in which the degree of bond making by the incoming solvent molecule ranges from very substantial to negligible. For an interchange mechanism, the transition state would necessarily lie on the dashed diagonal (Figure 6, left) and the measured activation volume would allow scaling of the volume curves for exchange reactions of different metal ions. It has been stressed that in this model the **A** and **D** mechanisms are considered as the limiting cases for the interchange mechanistic continuum and are therefore following the edges of the square diagram with "transition states/intermediates" located at the corners of the square diagram. If, however, intermediates with lower and higher coordination numbers can be identified, as, for example, by quantum mechanical calculations, a different view of the diagram has to be defined. For a mechanism where the exchange proceeds via a transition state and an intermediate, this latter lies on the diagonal, but not necessarily on the corner of the square. The two transition states lie symmetrically off the diagonal. The calculations performed on  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , and  $\text{In}^{3+}$  allowed us to draw such a diagram (Figure 6, right).<sup>58</sup> From the calculated volumes, it follows that for these ions the transition states are about halfway between the reactant and the intermediate. For a nonconcerted **A** or **D** mechanism, measured  $\Delta V^\ddagger$  values can be quite far from the limiting values, estimated by Swaddle to be  $-13.5$  or  $+13.5 \text{ cm}^3 \text{ mol}^{-1}$ ,<sup>37</sup> respectively.

The deprotonation of a water molecule on  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  ( $\text{M} = \text{Al}, \text{Ga}$ ) to form  $[\text{M}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  increases the lability of the other water ligands substantially. This increase in lability is larger by 2 orders of magnitude for  $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  ( $2.4 \times 10^4 \text{ s}^{-1}$ ) if compared to  $[\text{Ga}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  ( $2.5 \times 10^2 \text{ s}^{-1}$ ) (Table 4). For  $\text{Al}^{3+}$  the effect is among the largest measured for trivalent metal ions and even much larger than that for the isoelectronic  $[\text{AlF}(\text{H}_2\text{O})_5]^{2+}$  ( $0.9 \times 10^2 \text{ s}^{-1}$ ) (Table 4).<sup>59</sup> For water exchange on

$[\text{Ga}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  an activation volume could be determined which is more positive than that for the hexaqua ion,<sup>57</sup> indicating a more dissociative character of the water exchange reaction. For  $\text{H}_2\text{O}$  exchange on  $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  there are no variable pressure data. But, despite the negative  $\Delta S^\ddagger$  observed from variable temperature measurements,<sup>59</sup> a more dissociative character of the exchange process, if compared to the case of the aqua ion, is also expected.

Water exchange on  $\text{Al}^{3+}$  is also progressively enhanced by several orders of magnitude in substituting first shell water molecules by  $\text{F}^-$ , malonate, methylmalonate, or salicylate (Table 4) and for  $\text{H}_2\text{O}$  exchange on polycations.<sup>66–69,81,82</sup>

### 3. Solvent Exchange on d-Transition Metal Ions

#### 3.1. Hexasolvated d-Transition Metal Ions

In contrast to the cases of metal ions with closed shell electronic configurations, the lability and the exchange mechanisms of d-transition metal ions are strongly affected by the occupancy of their d-orbitals. The order of reactivity on divalent 3d-transition metal ions, for example, is  $\text{V}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+} < \text{Cu}^{2+}$  and is independent of the mechanism. Simple calculations of ligand field activation energies, LFAEs, were performed already thirty years ago for **D** and **A** exchange mechanisms of  $[\text{M}(\text{H}_2\text{O})_6]^{2+/3+}$  complexes.<sup>6,16,83</sup> Correlations were found between LFAEs and water exchange rate constants but not for exchange mechanisms. The important influence of the ligand field activation energies is nicely demonstrated from the labilities of  $\text{V}^{2+}$  and  $\text{V}^{3+}$ . The smaller LFAE of  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  as compared to  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  explains why water exchange is about six times faster on the more highly charged trivalent vanadium.

In general, the solvent exchange rate constants on  $[\text{M}(\text{solvent})_6]^{2+/3+}$  increase in the sequence  $\text{MeOH} < \text{MeCN} < \text{DMF} < \text{H}_2\text{O}$ , independent of the nature of the transition metal ion. This sequence cannot be readily linked to solvent specific characteristics such

**Table 5. Rate Constants and Activation Parameters for Solvent Exchange on Divalent First Row Transition Metal Ions<sup>e</sup>**

[M(solvent) <sub>6</sub> ] <sup>2+</sup>	d-electron config	<i>k</i> <sub>1</sub> (298K) <sup>a</sup>	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>V<sup>2+</sup></b>							
[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>3</sup>	8.7 × 10 <sup>1</sup>	61.8	-0.4	-4.1	I <sub>a</sub>	84
<b>Cr<sup>2+</sup></b>							
[Cr(MeOH) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>1</sup>	1.2 × 10 <sup>8</sup>	31.6	+16.6		I <sub>d</sub> <sup>c</sup>	85
<b>Mn<sup>2+</sup></b>							
[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>2</sup>	2.1 × 10 <sup>7</sup>	32.9	+5.7	-5.4	I <sub>a</sub>	86
[Mn(MeOH) <sub>6</sub> ] <sup>2+</sup>		3.7 × 10 <sup>5</sup>	25.9	-50.2	-5.0	I <sub>a</sub>	87, 88
[Mn(DMF) <sub>6</sub> ] <sup>2+</sup>		2.2 × 10 <sup>6</sup>	34.6	-7.4	+2.4	I <sub>d</sub>	89
		2.7 × 10 <sup>6</sup>	35.8	-2	+1.6	I <sub>d</sub>	90
		6.3 × 10 <sup>5</sup>	17.5	-75.1	+4.2	I <sub>d</sub>	91
[Mn(DMSO) <sub>6</sub> ] <sup>2+</sup>		6.3 × 10 <sup>6</sup>	31	-10			92
[Mn(NMBuL) <sub>6</sub> ] <sup>2+</sup>		2.4 × 10 <sup>4</sup>	39	-25			93
Mn(HMPA) <sub>6</sub> <sup>2+</sup>		1.0 × 10 <sup>7</sup>	51	+43			93
[Mn(HOAc) <sub>6</sub> ] <sup>2+</sup>		1.6 × 10 <sup>7</sup>	29	-10	+0.4		94, 95
[Mn(MeCN) <sub>6</sub> ] <sup>2+</sup>		1.4 × 10 <sup>7</sup>	29.6	-8.9	-7.0	I <sub>a</sub>	96
		1.3 × 10 <sup>7</sup>	28.6	-13	-5.8	I <sub>a</sub>	97
		1.2 × 10 <sup>7</sup>	30.3	-8		I <sub>a</sub>	98
		3.1 × 10 <sup>7</sup>	35.9	+19		I <sub>a</sub>	99
[Mn(EtCN) <sub>6</sub> ] <sup>2+</sup>		1.3 × 10 <sup>7</sup>	29.6	-10	-2.1	I <sub>a</sub>	97
[Mn(PrCN) <sub>6</sub> ] <sup>2+</sup>		9.9 × 10 <sup>6</sup>	31.3	-6	-5.0	I <sub>a</sub>	97
[Mn(Pr <sup>i</sup> CN) <sub>6</sub> ] <sup>2+</sup>		1.1 × 10 <sup>7</sup>	40.0	+24	-2.5	I <sub>a</sub>	97
[Mn(Bu <sup>i</sup> CN) <sub>6</sub> ] <sup>2+</sup>		9.3 × 10 <sup>6</sup>	35.6	+8	+0.6	I	97
[Mn(PhCN) <sub>6</sub> ] <sup>2+</sup>		1.2 × 10 <sup>7</sup>	36.9	+14			97
[Mn(DMTF) <sub>6</sub> ] <sup>2+</sup>		3.9 × 10 <sup>7</sup>			+11.5	I <sub>d</sub>	91
[Mn(HOAc) <sub>6</sub> ] <sup>2+</sup> <sup>b</sup>		1.6 × 10 <sup>7</sup>	29	-10	+0.4	I <sub>d</sub>	95
[Mn(OAc) <sub>2</sub> (HOAc) <sub>4</sub> ] <sup>b</sup>		4.8 × 10 <sup>7</sup>	32	+9	+6.7	I <sub>d</sub>	95
[Mn(en) <sub>3</sub> ] <sup>2+</sup>		1.7 × 10 <sup>6</sup>	24.7	-43	-0.6	I	100
[Mn(tn) <sub>3</sub> ] <sup>2+</sup>		2.5 × 10 <sup>6</sup>	21.9	-50	+0.1	I	101
[Mn(pa) <sub>6</sub> ] <sup>2+</sup>		3.7 × 10 <sup>7</sup>	26.2	-13			101
<b>Fe<sup>2+</sup></b>							
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>2</sup>	4.4 × 10 <sup>6</sup>	41.4	+21.2	+3.8	I <sub>d</sub>	86
[Fe(MeOH) <sub>6</sub> ] <sup>2+</sup>		5.0 × 10 <sup>4</sup>	50.2	+12.6	+0.4	I	87, 88
[Fe(MeCN) <sub>6</sub> ] <sup>2+</sup>		6.6 × 10 <sup>5</sup>	41.4	+5.3	+3.0	I <sub>d</sub>	96
[Fe(DMF) <sub>6</sub> ] <sup>2+</sup>		9.7 × 10 <sup>5</sup>	43.0	+13.8	+8.5	I <sub>d</sub>	89
[Fe(en) <sub>3</sub> ] <sup>2+</sup>		4.3 × 10 <sup>4</sup>	46.3	-1	-1.2	I <sub>a</sub>	100
[Fe(tn) <sub>3</sub> ] <sup>2+</sup>		3.9 × 10 <sup>5</sup>	47.9	+23	+5.8		101
[Fe(pa) <sub>6</sub> ] <sup>2+</sup>		6.9 × 10 <sup>7</sup>	32.4	+14			101
<b>Co<sup>2+</sup></b>							
[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>2</sup>	3.2 × 10 <sup>6</sup>	46.9	+37.2	+6.1	I <sub>d</sub>	86
[Co(MeOH) <sub>6</sub> ] <sup>2+</sup>		1.8 × 10 <sup>4</sup>	57.7	+30.1	+8.9	I <sub>d</sub>	87, 102
[Co(AcOH) <sub>6</sub> ] <sup>2+</sup>		1.3 × 10 <sup>6</sup>	37	-6			94
[Co(MeCN) <sub>6</sub> ] <sup>2+</sup>		3.4 × 10 <sup>5</sup>	49.5	+27.1	+8.1 <sup>d</sup>	I <sub>d</sub>	25, 87, 103
[Co(DMF) <sub>6</sub> ] <sup>2+</sup>		3.9 × 10 <sup>5</sup>	56.9	+52.7	+6.7	I <sub>d</sub>	87, 104
[Co(DMSO) <sub>6</sub> ] <sup>2+</sup>		4.5 × 10 <sup>5</sup>	49	+28			105
[Co(TMU) <sub>4</sub> ] <sup>2+</sup>		1.7 × 10 <sup>7</sup>	26	-20		I <sub>a</sub>	106
[Co(en) <sub>3</sub> ] <sup>2+</sup>		5.4 × 10 <sup>3</sup>	56.5	+16	+0.9	I <sub>d</sub>	100
[Co(tn) <sub>3</sub> ] <sup>2+</sup>		2.9 × 10 <sup>5</sup>	49.3	+25	+6.6	I <sub>d</sub>	107
[Co(pa) <sub>6</sub> ] <sup>2+</sup>		2.0 × 10 <sup>8</sup>	36.2	+35		I <sub>d</sub>	107
[Co(meea) <sub>6</sub> ] <sup>2+</sup>		1.1 × 10 <sup>7</sup>	46.6	+46			108
<b>Ni<sup>2+</sup></b>							
[Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup>	3.2 × 10 <sup>4</sup>	56.9	+32.0	+7.2	I <sub>d</sub>	86
[Ni(MeOH) <sub>6</sub> ] <sup>2+</sup>		1.0 × 10 <sup>3</sup>	66.1	+33.5	+11.4	I <sub>d</sub>	87, 102
[Ni(MeCN) <sub>6</sub> ] <sup>2+</sup>		2.8 × 10 <sup>3</sup>	64.3	+37	+8.5	I <sub>d</sub>	25, 87
		6.2 × 10 <sup>3</sup>	41.4	-30	+12.0	I <sub>d</sub>	26
[Ni(EtCN) <sub>6</sub> ] <sup>2+</sup>		1.3 × 10 <sup>4</sup>	42.0	-25	+13.7	I <sub>d</sub>	26
[Ni(PrCN) <sub>6</sub> ] <sup>2+</sup>		1.0 × 10 <sup>4</sup>	43.3	-23	+13.1	I <sub>d</sub>	26
[Ni(Pr <sup>i</sup> CN) <sub>6</sub> ] <sup>2+</sup>		1.6 × 10 <sup>4</sup>	43.3	-19	+12.4	I <sub>d</sub>	26
[Ni(Bu <sup>i</sup> CN) <sub>6</sub> ] <sup>2+</sup>		1.0 × 10 <sup>4</sup>	47.1	-10	+14.4	I <sub>d</sub>	26
[Ni(PhCN) <sub>6</sub> ] <sup>2+</sup>		9.4 × 10 <sup>3</sup>	51.6	+4	+13.1	I <sub>d</sub>	26
[Ni(DMF) <sub>6</sub> ] <sup>2+</sup>		3.8 × 10 <sup>3</sup>	62.8	+33.5	+9.1	I <sub>d</sub>	102, 104, 109
		6.9 × 10 <sup>3</sup>	54.4	+25.0		I <sub>d</sub>	110
		7.7 × 10 <sup>3</sup>	39.3	-37.7		I <sub>d</sub>	111
		3.7 × 10 <sup>3</sup>	59.3	+22.3		I <sub>d</sub>	112
[Ni(DMTF) <sub>6</sub> ] <sup>2+</sup>		8.7 × 10 <sup>6</sup>	57.4	+80.5	+20.6/+21.8	D	91
[Ni(en) <sub>3</sub> ] <sup>2+</sup>		2.0 × 10 <sup>1</sup>	69	+10	+11.4	I <sub>d</sub>	100
[Ni(tn) <sub>3</sub> ] <sup>2+</sup>		3.1 × 10 <sup>3</sup>	61.3	+28	+7.2	I <sub>a</sub>	101
[Ni(pa) <sub>6</sub> ] <sup>2+</sup>		1.3 × 10 <sup>7</sup>	37.1	+16			101



Table 5 (Continued)

[M(solvent) <sub>6</sub> ] <sup>2+</sup>	d-electron config	<i>k</i> <sub>1</sub> (298K) <sup>a</sup>	Δ <i>H</i> <sup>‡</sup>	Δ <i>S</i> <sup>‡</sup>	Δ <i>V</i> <sup>‡</sup>	mech	ref
			<b>Cu<sup>2+</sup></b>				
[Cu(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	d <sup>9</sup>	5.7 × 10 <sup>9</sup>					9
[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>		4.4 × 10 <sup>9</sup>	11.5	−21.8	+2.0	I <sub>d</sub> <sup>c</sup>	113
[Cu(MeOH) <sub>6</sub> ] <sup>2+</sup>		3.1 × 10 <sup>7</sup>	17.2	−44.0	+8.3	I <sub>d</sub> <sup>c</sup>	114
[Cu(DMF) <sub>6</sub> ] <sup>2+</sup>		9.1 × 10 <sup>8</sup>	24.3	+8.1	+8.4	I <sub>d</sub>	115
[Cu(en) <sub>3</sub> ] <sup>2+</sup>		1.4 × 10 <sup>7</sup>	9.2	−77		I <sub>d</sub>	116

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> 0.02 M HClO<sub>4</sub> in *d*<sub>2</sub>-dichloromethane diluent. <sup>c</sup> Tetragonal distortion. <sup>d</sup> Average of +9.9, +6.7, and +7.7 cm<sup>3</sup> mol<sup>−1</sup>. <sup>e</sup> Units are as follows: *k*<sub>1</sub>(298K), s<sup>−1</sup>; Δ*H*<sup>‡</sup>, kJ mol<sup>−1</sup>; Δ*S*<sup>‡</sup>, J K<sup>−1</sup> mol<sup>−1</sup>; Δ*V*<sup>‡</sup>, cm<sup>3</sup> mol<sup>−1</sup>.

as size, dielectric constant, and donor number. It seems to depend on the combined effect of several such properties of the solvent.

### 3.1.1. Divalent First Row *d*-Transition Metal Ions

Solvent exchange on octahedral first row transition metals is by far the most extensively studied and has been reviewed several times. For small solvent molecules such as H<sub>2</sub>O, MeOH, and MeCN, the mechanism for solvent exchange changes from I<sub>a</sub> to I<sub>d</sub> as the number of *d*-electrons increases and the ionic radius decreases. This changeover of mechanism, manifested in a change of sign for the activation volumes (Table 5), has been explained with a combination of three effects: (a) the increase of the *t*<sub>2g</sub> orbital occupancy disfavors the approach of the entering nucleophilic solvent molecule on a trigonal face of the octahedron in an *a*-activated mechanism; (b) *e*<sup>\*</sup><sub>g</sub> electron occupancy increases, which favors breaking of the metal–solvent bond in a *d*-activated mechanism; and (c) to a lesser extent, the decrease of *r*<sub>M</sub> favors dissociation over association due to steric crowding. [V(solvent)<sub>6</sub>]<sup>2+</sup> and [Mn(solvent)<sub>6</sub>]<sup>2+</sup> exchange first shell solvent molecules through an *a*-activated mechanism, while their Fe<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> analogues show *d*-activated mechanisms.

The effect of bulkiness of solvent molecules on exchange processes has been studied on Mn<sup>2+</sup> (ref 97) and Ni<sup>2+</sup> (ref 26) using the six nitriles MeCN, EtCN, PrCN, Pr<sup>*i*</sup>CN, PhCN, and Bu<sup>*t*</sup>CN, listed here with increasing molar volumes, *V*<sub>0</sub>. The donor numbers of these solvent molecules differ only slightly (between 11.9 for PhCN and 16.6 for Bu<sup>*t*</sup>CN),<sup>97</sup> but *V*<sub>0</sub> increases from 52.9 cm<sup>3</sup> mol<sup>−1</sup> for MeCN to 104.6 cm<sup>3</sup> mol<sup>−1</sup> for Bu<sup>*t*</sup>CN.<sup>26</sup> The exchange rate constants for the six nitriles studied are very similar within the two series (Table 5). Positive activation volumes (+12.0 to +14.4 cm<sup>3</sup> mol<sup>−1</sup>) were measured for all six Ni<sup>2+</sup> complexes, and a similar dissociative I<sub>d</sub> mechanism was assigned. The observed increase in Δ*S*<sup>‡</sup> has been attributed to changes in solvent–solvent interactions due to the decrease in electric dipole moment. On Mn<sup>2+</sup>, the exchange of MeCN, the smallest molecule of the six nitriles, proceeds via an I<sub>a</sub> pathway, as concluded from negative Δ*V*<sup>‡</sup> and Δ*S*<sup>‡</sup> values.<sup>97</sup> The activation enthalpies and entropies, Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup>, both increase gradually in the order MeCN < EtCN < PrCN < Bu<sup>*t*</sup>CN < PhCN < Pr<sup>*i*</sup>CN, and the reaction mechanism is concluded to be less associative with increasing bulkiness, but it never becomes as positive as that with the sterically hindered solvent DMF.

The last member of the series of divalent *d*-transition metal ions, Cu<sup>2+</sup>, shows solid-state Jahn–Teller distortion: the four ligands in the equatorial plane have shorter metal–ligand bonds than the two axial ligands.<sup>117–119</sup> In solution this effect is expected to be dynamic: the distortion axis jumps very rapidly, and on average, all ligands become, in time, axial and equatorial. The axial ligands are only loosely bound to the metal ion, which partially explains the very high lability of all copper solvates (Table 5). Slightly positive Δ*V*<sup>‡</sup> values have been measured for MeOH and DMF,<sup>115</sup> indicating that these solvent molecules exchange via a *d*-activation mode: molecules at the axial position can easily dissociate. On the basis of the commonly accepted assumption that Cu<sup>2+</sup>, in analogy to the case of the solid state, is also six-coordinated in aqueous solution,<sup>120</sup> the water exchange rate constant and a characteristic time for the inversion of the tetragonal distortion (~5 ps at 298 K) have been determined by <sup>17</sup>O NMR.<sup>113</sup> The Δ*V*<sup>‡</sup> measured is relatively small (+2.0 ± 1.5 cm<sup>3</sup> mol<sup>−1</sup>),<sup>115</sup> and in agreement with the results on MeOH and DMF, a *d*-activation mode was proposed for water exchange. However, a complementary experimental and computational study performed by double difference neutron diffraction and by first principles molecular dynamics, respectively, showed evidence that the coordination number of Cu<sup>2+</sup> could be five in aqueous solution.<sup>9</sup> It is interesting to note that in two recent EXAFS papers contradictory results with CN = 6<sup>121</sup> and CN = 5<sup>122</sup> have been found. From the Car–Parrinello molecular dynamics study, an equilibrium between square pyramid and trigonal bipyramid structures was proposed with a rapid exchange between them. Oxygen-17 experimental data showed the presence of two time constants, a fast one of ~5 ps and a slower one of ~230 ps, which were in the original paper interpreted as the time constant for the rapid reorientation of the Jahn–Teller distortion axis and the lifetime of a water molecule in the first coordination shell of Cu<sup>2+</sup>, respectively.<sup>113</sup> In a five-coordinated complex the experimental data could be reinterpreted with the time constants τ<sub>1</sub> ~ 5 ps for the mean lifetime of square pyramid and trigonal bipyramid structures and τ<sub>M</sub> = 175 ps for the lifetime of a water molecule in the first shell.<sup>9</sup>

### 3.1.2. Trivalent First Row *d*-Transition Metal Ions

The lability and mechanism for solvent exchange on the trivalent [M(solvent)<sub>6</sub>]<sup>3+</sup> transition metal ions vary with *d*-electronic configuration in a similar

**Table 6. Rate Constants and Activation Parameters for Solvent Exchange on Trivalent First Row Transition Metal Ions<sup>c</sup>**

[M(solvent) <sub>6</sub> ] <sup>3+</sup>	d-electron config	<i>k</i> <sub>1</sub> (298K) <sup>a</sup>	Δ <i>H</i> <sup>‡</sup>	Δ <i>S</i> <sup>‡</sup>	Δ <i>V</i> <sup>‡</sup>	mech	ref
[Sc(TMP) <sub>6</sub> ] <sup>3+</sup>	<i>t</i> <sub>2g</sub> <sup>0</sup>	1.21 × 10 <sup>3</sup>	37.4	−60.5	−20.1	<b>I<sub>a</sub></b>	75
[Ti(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	<i>t</i> <sub>2g</sub> <sup>1</sup>	1.8 × 10 <sup>5</sup>	43.4	+1.2	−12.1	<b>A, I<sub>a</sub></b>	124
[Ti(DMF) <sub>6</sub> ] <sup>3+</sup>		6.6 × 10 <sup>4</sup>	23.6	−73.6	−5.7	<b>I<sub>a</sub></b>	125
[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	<i>t</i> <sub>2g</sub> <sup>2</sup>	5.0 × 10 <sup>2</sup>	49.4	−27.8	−8.9	<b>I<sub>a</sub></b>	123
[V(DMSO) <sub>6</sub> ] <sup>3+</sup>		1.31 × 10 <sup>1</sup>	38.5	−94.5	−10.1	<b>I<sub>a</sub></b>	126
[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	<i>t</i> <sub>2g</sub> <sup>3</sup>	2.4 × 10 <sup>−6</sup>	108.6	+11.6	−9.6	<b>I<sub>a</sub></b>	127
[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	(2nd sphere)	7.8 × 10 <sup>9</sup>	21.3	+16.2			128
[Cr(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>	(2nd sphere)	6.9 × 10 <sup>9</sup> <sup>b</sup>					129
[Cr(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>		1.8 × 10 <sup>−4</sup>	111.0	+55.6	+2.7	<b>I</b>	127
[Cr(DMSO) <sub>6</sub> ] <sup>3+</sup>		3.1 × 10 <sup>−8</sup>	96.7	−64.5	−11.3	<b>I<sub>a</sub></b>	130
[Cr(DMF) <sub>6</sub> ] <sup>3+</sup>		3.3 × 10 <sup>−7</sup>	97.1	−43.5	−6.3	<b>I<sub>a</sub></b>	131
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	<i>t</i> <sub>2g</sub> <sup>3</sup> <i>e</i> <sub>g</sub> <sup>2</sup>	1.6 × 10 <sup>2</sup>	64.0	+12.1	−5.4	<b>I<sub>a</sub></b>	132, 133
[Fe(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>		1.2 × 10 <sup>5</sup>	42.4	+5.3	+7.0	<b>I<sub>d</sub></b>	132, 133
[Fe(DMSO) <sub>6</sub> ] <sup>3+</sup>		9.3	62.5	−16.7	−3.1	<b>I<sub>a</sub></b>	134
[Fe(DMF) <sub>6</sub> ] <sup>3+</sup>		6.3 × 10 <sup>1</sup>	42.3	−69.0	−0.9	<b>I</b>	134

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> By molecular dynamics technique. <sup>c</sup> Units are as follows: *k*<sub>1</sub>(298K), s<sup>−1</sup>; Δ*H*<sup>‡</sup>, kJ mol<sup>−1</sup>; Δ*S*<sup>‡</sup>, J K<sup>−1</sup> mol<sup>−1</sup>; Δ*V*<sup>‡</sup>, cm<sup>3</sup> mol<sup>−1</sup>.

manner to that for their divalent analogues (Table 6). The important influence of the ligand field activation energy is nicely demonstrated on the labilities of V<sup>2+</sup> and V<sup>3+</sup>. The LFAE of *t*<sub>2g</sub><sup>2</sup> [V(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is smaller than that of *t*<sub>2g</sub><sup>3</sup> [V(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, making water exchange of the trivalent ion about six times faster than that for the divalent ion, despite the smaller formal charge (Tables 5 and 6). Both exchange processes are **a**-activated with negative volumes of activation of −8.9 cm<sup>3</sup> mol<sup>−1</sup> (V<sup>3+</sup>)<sup>123</sup> and −4.1 cm<sup>3</sup> mol<sup>−1</sup> (V<sup>2+</sup>).<sup>84</sup>

Cr<sup>3+</sup> forms the most inert solvent complexes of first row, high spin transition metal ions as a consequence of the large ligand field difference contributing to the activation energy.<sup>6</sup> Furthermore, Cr<sup>3+</sup> interacts so strongly with first shell water molecules that even second shell water molecules are relatively strongly bound. A lifetime of more than 100 ps has been measured and was nicely confirmed by a classical molecular dynamics simulation.<sup>128,129</sup>

Values of activation volumes measured on [M(solvent)<sub>6</sub>]<sup>3+</sup> become less negative on going along the series from Ti<sup>3+</sup> to Fe<sup>3+</sup> (Table 6). If Ga<sup>3+</sup>, which is not a transition metal but which is in the same row in the periodic table, is added, the activation volumes become even positive (Table 4). This changeover in mechanism from associative to dissociative activation mode for solvent exchange along the series of trivalent transition metal ions is similar to that observed for the divalent ions. The Δ*V*<sup>‡</sup> value of −12.1 cm<sup>3</sup> mol<sup>−1</sup> for water exchange on Ti<sup>3+</sup> (ref 124) is markedly more negative than the following ones, and it is close to the limiting value estimated by Swaddle (−13.5 cm<sup>3</sup> mol<sup>−1</sup>)<sup>36,37</sup> for a limiting **A** mechanism. The assignment of a limiting **A** mechanism for [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> was also confirmed by quantum mechanical computational studies.<sup>135,136</sup>

### 3.1.3. Second and Third Row *d*-Transition Metal Ions

Experimental studies of solvent exchange on octahedral second and third row transition metal ions are rather limited. Water exchange has been studied on Ru<sup>2+</sup>, Ru<sup>3+</sup>, Rh<sup>3+</sup>, and Ir<sup>3+</sup> whereas acetonitrile exchange has only been studied on Ru<sup>2+</sup> (Table 7). From the arguments developed above for first row transition metals (hindered nucleophilic attack), one would expect a dissociative activation mode for water exchange on the low spin *t*<sub>2g</sub><sup>6</sup> hexaaqua ions [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, [Rh(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, and [Ir(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. In a study of the mechanism of substitution on [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, it was shown that the rate constants for the anation reactions by Cl<sup>−</sup>, Br<sup>−</sup>, and I<sup>−</sup> were very similar, indicating identical steps to reach the transition state by dissociation of a water molecule.<sup>137</sup> An extension to a large variety of ligands possessing different charges and different nucleophilicities clearly demonstrated that the rate of formation of the monocomplex is independent of the entering ligand, and an **I<sub>d</sub>** mechanism was therefore attributed for substitution reactions on [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>.<sup>10,138</sup> In a variable pressure study of water exchange on this ion, an activation volume of −0.4 cm<sup>3</sup> mol<sup>−1</sup> has been observed and an **I** mechanism without predominant **a**- or **d**-character was assigned.

The aqua ions of Rh<sup>3+</sup> and Ir<sup>3+</sup> have been even more intriguing. From virtually identical rate constants and Δ*H*<sup>‡</sup> values for substitution of H<sub>2</sub>O by Cl<sup>−</sup> and Br<sup>−</sup> on [Rh(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, a dissociative **D** mechanism was assigned.<sup>144–146</sup> However, from negative Δ*V*<sup>‡</sup> values for water exchange on aqua ions of Rh<sup>3+</sup> and Ir<sup>3+</sup>, an associative interchange mechanism **I<sub>a</sub>** was concluded.<sup>2,142</sup>

Final attributions of mechanisms operating for water exchange on Ru<sup>2+</sup>, Rh<sup>3+</sup>, and Ir<sup>3+</sup> have been made from quantum chemical calculations. All attempts to calculate a transition state for an inter-

**Table 7. Rate Constants and Activation Parameters for Solvent Exchange on Second and Third Row Transition Metal Ions<sup>b</sup>**

[M(solvent) <sub>6</sub> ] <sup>2+</sup>	d-electron config	<i>k</i> <sub>1</sub> (298K) <sup>a</sup>	Δ <i>H</i> <sup>‡</sup>	Δ <i>S</i> <sup>‡</sup>	Δ <i>V</i> <sup>‡</sup>	mech	ref
			<b>Ru<sup>2+</sup></b>				
[Ru(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	t <sub>2g</sub> <sup>6</sup>	1.8 × 10 <sup>-2</sup>	87.8	+16.1	-0.4	<b>I</b>	139
[Ru(MeCN) <sub>6</sub> ] <sup>2+</sup>		8.9 × 10 <sup>-11</sup>	140.3	+33.3	+0.4	<b>I</b>	139, 140
			<b>Ru<sup>3+</sup></b>				
[Ru(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	t <sub>2g</sub> <sup>5</sup>	3.5 × 10 <sup>-6</sup>	89.8	-48.3	-8.3	<b>I<sub>a</sub></b>	139
[Ru(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>		5.9 × 10 <sup>-4</sup>	95.8	+14.9	+0.9	<b>I</b>	139
			<b>Rh<sup>2+</sup></b>				
[Rh <sub>2</sub> (MeCN) <sub>10</sub> ] <sup>4+</sup>	d <sup>7</sup>	3.1 × 10 <sup>-5</sup> (eq)	66	-111	-4.9		141
			<b>Rh<sup>3+</sup></b>				
[Rh(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	t <sub>2g</sub> <sup>6</sup>	2.2 × 10 <sup>-9</sup>	131	+29	-4.2	<b>I<sub>a</sub></b>	142
[Rh(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>		4.2 × 10 <sup>-5</sup>	103		+1.5	<b>I</b>	142
			<b>Re<sup>2+</sup></b>				
[Re <sub>2</sub> (MeCN) <sub>10</sub> ] <sup>4+</sup>	d <sup>5</sup>	3.1 × 10 <sup>-7</sup> (eq)	109	+6			143
			<b>Ir<sup>3+</sup></b>				
[Ir(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	t <sub>2g</sub> <sup>6</sup>	1.1 × 10 <sup>-10</sup>	130.5	+2.1	-5.7	<b>I<sub>a</sub></b>	2
[Ir(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>		5.6 × 10 <sup>-7</sup>			-0.2	<b>I</b>	2

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Units are as follows: *k*<sub>1</sub>(298K), s<sup>-1</sup>; Δ*H*<sup>‡</sup>, kJ mol<sup>-1</sup>; Δ*S*<sup>‡</sup>, J K<sup>-1</sup> mol<sup>-1</sup>; Δ*V*<sup>‡</sup>, cm<sup>3</sup> mol<sup>-1</sup>.

change mechanism for [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> failed, and a **D** mechanism without excluding **I<sub>d</sub>** was assigned.<sup>147</sup> In a second study, it was shown that the **I<sub>a</sub>** pathway with retention of the configuration of the spectator ligands is energetically clearly preferred over the **D** pathway.<sup>148</sup> In the same paper, it has also been shown that for **d**- and **a**-activated mechanisms the volume change due to changes in bond lengths between the Ir<sup>3+</sup> ion and the spectator water molecules is negligible: -1.8 cm<sup>3</sup> mol<sup>-1</sup> and -0.9 cm<sup>3</sup> mol<sup>-1</sup> for the **D** and the **I<sub>a</sub>** mechanism, respectively. This finding is important because it clarifies the debate about interpretation of activation volumes.<sup>148</sup>

The low spin t<sub>2g</sub><sup>5</sup> aqua ion of Ru<sup>3+</sup> is 4 orders of magnitude less labile than the t<sub>2g</sub><sup>6</sup> aqua ion of Ru<sup>2+</sup> and exchanges H<sub>2</sub>O molecules by an **I<sub>a</sub>** mechanism (Table 7). Both exchange rate constants are relatively slow, allowing, therefore, a direct observation of the electron exchange of the [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>3+/2+</sup> couple in aqueous solution (*k*<sub>ex</sub><sup>298</sup> = 20 M<sup>-1</sup> s<sup>-1</sup>).<sup>149</sup>

Solvent exchange of acetonitrile on Ru<sup>2+</sup> is 8 orders of magnitude slower than water exchange (Table 6).<sup>139</sup> This is mainly a consequence of a strong increase of Δ*H*<sup>‡</sup> (by more than 50 kJ mol<sup>-1</sup>) which arises probably from a strong back-bonding from the electron rich Ru<sup>2+</sup> into the MeCN π\* orbitals. In Fe<sup>2+</sup> this back-bonding is much less important and the change in lability between [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and [Fe(MeCN)<sub>6</sub>]<sup>2+</sup>, both high spin, is less than 1 order of magnitude (Table 5).

## 3.2. Effect of Spectator Ligands on Solvent Exchange

### 3.2.1. First Row Transition Oxometal Ions

The monomeric first row transition oxometal ions TiO<sup>2+</sup> and VO<sup>2+</sup> provide an opportunity to study the effect of the oxo ligand on the lability of the axial and equatorial ligands. Exchange rates of equatorial solvent molecules on [VO(solvent<sub>eq</sub>)<sub>4</sub>(solvent<sub>ax</sub>)]<sup>2+</sup> increase in the order H<sub>2</sub>O ~ CH<sub>3</sub>OH ~ DMF < DMSO

**Table 8. Rate Constants and Activation Parameters for Axial and Equatorial Solvent Exchange on First Row Transition Oxometal Ions [MO(eq-solvent)<sub>4</sub>(ax-solvent)]<sup>2+</sup> <sup>c</sup>**

[MO(solvent) <sub>5</sub> ] <sup>2+</sup>	<i>k</i> <sub>1</sub> (298K) <sup>a</sup>	Δ <i>H</i> <sup>‡</sup>	Δ <i>S</i> <sup>‡</sup>	Δ <i>V</i> <sup>‡</sup>	ref
			<b>TiO<sup>2+</sup></b>		
[TiO(DMSO) <sub>5</sub> ] <sup>2+</sup> <sup>b</sup>	161 (eq)	57.5	-9.9	+4.8	153
	6100 (ax)	59.8	+28.3	+1.6	153
			<b>VO<sup>2+</sup></b>		
[VO(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	500 (eq)	87.8	+16.1	-0.4	154, 155
	≈10 <sup>9</sup> (ax)			+1.9	154, 156
[VO(MeOH) <sub>5</sub> ] <sup>2+</sup>	565 (eq)	39.6	-59.4		157
[VO(MeCN) <sub>5</sub> ] <sup>2+</sup>	2850 (eq)	29.5	-83.7	-1.0	156, 157
[VO(DMSO) <sub>5</sub> ] <sup>2+</sup>	1760 (eq)	60.1	+18.5	-5.3	158, 159
[VO(DMF) <sub>5</sub> ] <sup>2+</sup>	575 (eq)	30.3	-87.7		160
	200 (eq)	54.8	-17.2	-6.8	156, 161
	46000 (ax)	64	+58.0		161
[VO(DMA) <sub>5</sub> ] <sup>2+</sup>	4700 (eq)	42.3	-33.1	-9.7	156, 161

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Studied in *d*<sub>3</sub>-nitromethane diluent. <sup>c</sup> Units are as follows: *k*<sub>1</sub>(298K), s<sup>-1</sup>; Δ*H*<sup>‡</sup>, kJ mol<sup>-1</sup>; Δ*S*<sup>‡</sup>, J K<sup>-1</sup> mol<sup>-1</sup>; Δ*V*<sup>‡</sup>, cm<sup>3</sup> mol<sup>-1</sup>.

< CH<sub>3</sub>CN < DMA (Table 8). Exchange of axial solvent molecules is much faster and could only be measured for H<sub>2</sub>O and DMF. A similar observation was made for [TiO(DMSO<sub>eq</sub>)<sub>4</sub>(DMSO<sub>ax</sub>)]<sup>2+</sup>, the only titanil complex where solvent exchange has been studied up to now. In water the exchange of the oxo ligand on the vanadyl complex (*k*<sub>O</sub><sup>298</sup>(VO) = 2.4 × 10<sup>-5</sup> s<sup>-1</sup>)<sup>150</sup> is much slower than that on the titanil complex (*k*<sub>O</sub><sup>298</sup>(TiO) = 1.6 × 10<sup>4</sup> s<sup>-1</sup>).<sup>151</sup> This huge difference cannot be assigned to electronic effects alone. Whereas the oxygen exchange on VO<sup>2+</sup> is base catalyzed,<sup>152</sup> a [H<sup>+</sup>] dependence of the oxygen exchange rate on titanil has been observed,<sup>151</sup> showing that the oxo ligand on TiO<sup>2+</sup> is easily protonated and thereby labilized.

### 3.2.2. Effect of Spectator Ligands on Solvent Exchange

Partial substitution of the coordinated solvent molecules by other ligands, which are kinetically inert and commonly denoted as spectator ligands, can

**Table 9. Effect of Spectator Ligands on the Solvent Exchange Rate Constants on First Row Divalent Transition Metal Ions<sup>f</sup>**

complex	$k_1(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	ref
<b>Mn<sup>2+</sup></b>					
[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$2.1 \times 10^7$	32.9	+5.7	-5.4	86
[Mn(EDTA-BOM)(H <sub>2</sub> O)] <sup>2+</sup>	$9.3 \times 10^7$	43.1	+53 <sup>b</sup>		162
[Mn(EDTA-BOM <sub>2</sub> )(H <sub>2</sub> O)] <sup>2+</sup>	$1.3 \times 10^8$	38.4	+39 <sup>b</sup>		162
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup>	19	68.0	+7.7	-4.5	163
[Mn(DMF) <sub>6</sub> ] <sup>2+</sup>	$2.2 \times 10^6$	34.6	-7.4	+2.4	89
[Mn(Me <sub>6</sub> tren)(DMF)] <sup>2+</sup>	$2.7 \times 10^6$	18.0	-61.2	-6	164
<b>Co<sup>2+</sup></b>					
[Co(MeCN) <sub>6</sub> ] <sup>2+</sup>	$3.4 \times 10^5$	49.5	+27.1	+8.1	25, 87, 103
[Co(dmgH) <sub>2</sub> (MeCN) <sub>2</sub> ] <sup>2+</sup>	$2.3 \times 10^5$	30.3	-41		165
[Co(dmg) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> (MeCN) <sub>2</sub> ] <sup>2+</sup>	$1.4 \times 10^5$	18.1	-86		165
[Co(MeOH) <sub>6</sub> ] <sup>2+</sup>	$1.8 \times 10^4$	57.7	+30.1	+8.9	87, 102
[Co(dmgH) <sub>2</sub> (MeOH) <sub>2</sub> ] <sup>2+</sup>	$2.8 \times 10^4$	58.2	+35		165
[Co(dpgH) <sub>2</sub> (MeOH) <sub>2</sub> ] <sup>2+</sup>	$7.2 \times 10^5$	14.0	-86		165
[Co(dpgH) <sub>2</sub> (acetone) <sub>2</sub> ] <sup>2+</sup>	$3.5 \times 10^5$	14.2	-91		165
[Co(Me <sub>6</sub> tren)(DMF)] <sup>2+</sup>	51.4	52.4	-36.5	-2.7	164
<b>Ni<sup>2+</sup></b>					
[Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$3.15 \times 10^4$	56.9	+32.0	+7.2	86
[Ni(NH <sub>3</sub> )(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	$25 \times 10^4$	44.4	+8		166
[Ni(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	$61 \times 10^4$	32.7	-25		166
[Ni(NH <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	$250 \times 10^4$	42.7	21		166
[Ni(en)(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	$44 \times 10^4$	42	+42		167
[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	$540 \times 10^4$	38	+10.9		167
[Ni(dien)(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	$120 \times 10^4$	23.0	-51 <sup>b</sup>		168
[Ni(trien)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	$290 \times 10^4$	29.3	-23 <sup>b</sup>		168
[Ni(tren)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+ c</sup>	$82/900 \times 10^4$	33.5	-19/+1 <sup>c</sup>		169
[Ni(cyclen)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	$2100 \times 10^4$	32.7	15		170
[Ni(Me <sub>4</sub> cyclam)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+ d</sup>	$16 \times 10^8$	37.4	+38		171
[Ni(Me <sub>4</sub> cyclam)(H <sub>2</sub> O)] <sup>2+ e</sup>	$1.6 \times 10^7$	24.7	-24		171
[Ni(bpy)(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	$4.9 \times 10^4$	52.8	+22		172
[Ni(bpy) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	$6.6 \times 10^4$	57.4	+38		172
[Ni(tpy)(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	$5.2 \times 10^4$	44.8	-4		173
[Ni(H <sub>2</sub> O) <sub>5</sub> Cl] <sup>+</sup>	$14 \times 10^4$	33.5	-34 <sup>c</sup>		174
[Ni(H <sub>2</sub> O) <sub>2</sub> (NCS) <sub>4</sub> ] <sup>2-</sup>	$110 \times 10^4$	25.1	-45 <sup>c</sup>		175
[Ni(H <sub>2</sub> O)(EDTA)] <sup>2-</sup>	$70 \times 10^4$	33.5	-29		176
[Ni(H <sub>2</sub> O)(HEDTA)] <sup>-</sup>	$20 \times 10^4$	41	-6		176
[Ni(DMF) <sub>6</sub> ] <sup>2+</sup>	$3.7 \times 10^3$	59.3	+33.5	+9.1	109, 112
[Ni(DMF) <sub>5</sub> Cl] <sup>2+</sup>	$5.3 \times 10^5$	42.4	+6.7		112
[Ni(pyMa)(DMF)] <sup>2+</sup>	$3.3 \times 10^3$	36.3	-55.8	+10.6	177
[Ni(Me <sub>4</sub> cyclam)(DMF) <sub>2</sub> ] <sup>2+ d</sup>	$33 \times 10^7$	38.3	+47		171
[Ni(Me <sub>4</sub> cyclam)(DMF)] <sup>2+ e</sup>	$1.5 \times 10^7$	30.1	-6.4		171
[Ni(MeCN) <sub>6</sub> ] <sup>2+</sup>	$2.8 \times 10^3$	64.3	+37	+8.5	26
[Ni(pyMa)(MeCN)] <sup>2+</sup>	$3.8 \times 10^2$	68.9	+35.6	-3.5	177
[Ni(Me <sub>4</sub> cyclam)(MeCN) <sub>2</sub> ] <sup>2+ d</sup>	$1.5 \times 10^7$	41.5	+32		171
[Ni(Me <sub>4</sub> cyclam)(MeCN)] <sup>2+ e</sup>	$0.56 \times 10^7$	20.3	-47		171
<i>trans</i> -[Ni(tren)(MeCN) <sub>2</sub> ] <sup>2+</sup>	$16.5 \times 10^4$	45	+6		178
<i>cis</i> -[Ni(tren)(MeCN) <sub>2</sub> ] <sup>2+</sup>	$>2 \times 10^6$				178
<b>Cu<sup>2+</sup></b>					
[Cu(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	$5.7 \times 10^9$				9
[Cu(tmpa)(H <sub>2</sub> O)] <sup>2+</sup>	$8.6 \times 10^6$	43.0	+32	-3.0	179
[Cu(tren)(H <sub>2</sub> O)] <sup>2+</sup>	$2.4 \times 10^6$	26.4	-34.4	-4.7	180
[Cu(tpy)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	$6.6 \times 10^8$	20.7	-6.6	0.0	181
[Cu(fz) <sub>2</sub> (H <sub>2</sub> O)] <sup>2+</sup>	$3.5 \times 10^5$	25.9	-52	-4.7	179
[Cu(tren)(MeCN)] <sup>2+</sup>	$1.7 \times 10^6$	45	+26		182
[Cu(DMF) <sub>6</sub> ] <sup>2+</sup>	$9.1 \times 10^8$	24.3	+8.1	+8.4	115
[Cu(Me <sub>6</sub> tren)(DMF)] <sup>2+</sup>	$5.6 \times 10^2$	43.3	-47.0	+6.5	164, 183

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Calculated from  $k_1(298\text{K})$  and  $\Delta H^\ddagger$ . <sup>c</sup> The two inequivalent H<sub>2</sub>O atoms exchange at different rates. <sup>d</sup> *RSSR* form of the macrocycle. <sup>e</sup> Five coordinate *RSRS* form of the macrocycle. <sup>f</sup> Units are as follows:  $k_1(298\text{K})$ , s<sup>-1</sup>;  $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>;  $\Delta S^\ddagger$ , J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta V^\ddagger$ , cm<sup>3</sup> mol<sup>-1</sup>.

substantially alter the lability of the remaining solvent molecules. The influence of such spectator ligands on solvent exchange is illustrated by the series of Ni<sup>2+</sup> complexes given in Table 9.

Substitution by NH<sub>3</sub> and by polyamines labilizes the remaining water molecules roughly in proportion to the number of coordinating nitrogen atoms (Table 9). The source of this labilization is the greater electron donation through  $\sigma$ -bonding to the metal

center.<sup>168</sup> It appears, however, that although bpy and tpy may also donate electron density to the metal center through  $\sigma$ -bonding, electron withdrawal through the  $\pi$ -bonding system of these ligands results in only modest changes in lability.<sup>172</sup>

The effects of temperature and pressure on the water exchange reaction of the five-coordinate complexes [Cu(tmpa)(H<sub>2</sub>O)]<sup>2-</sup> and [Cu(fz)<sub>2</sub>(H<sub>2</sub>O)]<sup>2-</sup> resulted in  $k_1$  values which are several orders of



magnitude less than that published for the Cu(II) aqua ion ( $k_1 \sim 5 \times 10^9 \text{ s}^{-1}$ ; Table 5).<sup>113</sup> This drastic decrease in lability has been explained by the absence of Jahn–Teller distortion for the five-coordinated species.<sup>179</sup> The mechanism of water exchange is of associative character, and the overall charge on the complex does not seem to have a specific effect on the water exchange mechanism. The rates of exchange on the five-coordinate complexes depend less on the particular ligand and appear not to be very markedly influenced by the particular five-coordinate geometry with the exception of the case of  $[\text{Cu}(\text{tpy})(\text{H}_2\text{O})_2]^{2+}$ , for which water exchange is very rapid.<sup>181</sup>

The presence of sterically constraining ligands such as  $\text{Me}_6\text{tren}$  can have substantial effects on lability and mechanism on the remaining solvent molecule. DMF exchange on the five-coordinated  $[\text{M}(\text{Me}_6\text{tren})(\text{DMF})]^{2+}$  is substantially decreased for  $\text{M} = \text{Co}$  or  $\text{Cu}$  but decreased very little when  $\text{M} = \text{Mn}$ .<sup>164</sup>  $\Delta V^\ddagger$  values are consistent with a change in activation mode from associative when  $\text{M} = \text{Mn}$  and  $\text{Co}$  to dissociative when  $\text{M} = \text{Cu}$  (Table 9). The origin of these variations has been attributed to the somewhat interconnected causes of stereochemical and d-orbital occupancy variations.

Solvent exchange on trivalent metal ions with amines in the first coordination shell has widely been studied (Table 10). When steric crowding of the metal center is increased on going from  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  to  $[\text{M}(\text{CH}_3\text{NH}_2)_5(\text{H}_2\text{O})]^{3+}$ , the rate of water exchange is decreased ( $\text{M} = \text{Cr}$ ), increased ( $\text{M} = \text{Co}$ ), or nearly unchanged ( $\text{M} = \text{Rh}$ ) (Tables 10 and 11).<sup>184</sup> The changes in  $k_{\text{ex}}$  are consistent with **a**- and **d**-activated mechanisms operating for  $\text{Cr}$  and  $\text{Co}$ , respectively. The activation volumes become more positive as steric crowding increases for all three  $\text{M}$ , indicating a change to either a more dissociative or a less associative mode of activation (Figure 7).

Regarding  $\text{Ru}^{2+}$  and  $\text{Rh}^{3+}$ , both water and acetonitrile are greatly labilized by  $\pi$ -acceptor spectator ligands (Table 11). The increase in lability by more than 10 orders of magnitude along the sequence  $[\text{Ru}(\text{MeCN})_6]^{2+} < [\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+} < [\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3]^+$  is a consequence of a corresponding decrease in activation enthalpy and the last complex having the largest  $\Delta S^\ddagger$ . Along the sequence, the  $\text{Ru}-\text{N}$  distance becomes longer and the activation mode becomes more dissociative, as indicated by  $\Delta S^\ddagger$  increasing from +0.4 to +2.4 and +11.1  $\text{cm}^3 \text{ mol}^{-1}$ .<sup>201</sup> Thus, the kinetic *trans* effect correlates with the structural *trans* influence. The labilization of  $\text{H}_2\text{O}$  in  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$  is also attributed to the *trans* labilizing effect of the  $\pi$ -acid ( $\eta^6\text{-C}_6\text{H}_6$ ), but there is no corresponding structural influence reflected in the  $\text{Ru}-\text{O}$  distances, which are 212 pm in both complexes. The overall range of lability is 12 and 14 orders of magnitude within the series of  $\text{Ru}^{2+}$  and  $\text{Rh}^{3+}$  complexes in which  $\text{H}_2\text{O}$ ,  $\text{MeCN}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{C}_5\text{H}_5$  are coordinated.

### 3.2.3. Solvent Exchange on $\text{MX}_x\text{L}_{6-x}$ ( $\text{M} = \text{Ti}, \text{Zr}, \text{Nb}, \text{Sn}, \text{Sb}, \text{Hf}, \text{and Ta}$ ) Adducts

Solvent exchange reactions for a variety of Lewis bases  $\text{L}$  have been studied, in inert solvents, on

octahedral adducts of the form  $\text{MX}_5\cdot\text{L}$  with  $\text{M} = \text{Nb}(\text{V}), \text{Sb}(\text{V}), \text{and Ta}(\text{V})$  and of the form  $\text{MX}_4\cdot 2\text{L}$  with  $\text{M} = \text{Ti}(\text{IV}), \text{Zr}(\text{IV}), \text{Sn}(\text{IV}), \text{and Hf}(\text{IV})$  ( $\text{X} = \text{F}^-, \text{Cl}^-$ , and  $\text{Br}^-$ ), and the results are summarized in Table 12.

The  $\text{MX}_5\cdot\text{L}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) show an interesting solvent  $\text{L}$  controlled dissociative–associative crossover for the substitution mechanism. The complete neutrality along the reaction profile allows the neglect of electrostriction effects. Moreover, an unusually large number of kinetic facts are available for mechanistic assignments: rate laws,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ,  $\Delta V^\ddagger$  and  $\Delta\beta^\ddagger$ , steric effects, free energy relationships, and nucleophilic sequences. The exchange reactions proceed via a **D** mechanism when  $\text{L}$  is a nitrile, ether, or phosphoryl ligand and via an **I<sub>a</sub>** or **A** mechanism when  $\text{L}$  is a dimethyl sulfide, dimethyl selenide, or dimethyl telluride. Going from the first set of ligands to the second, the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  decrease abruptly, with a change in sign for the latter parameter. The dissociative and associative reactions are respectively accelerated and slowed when the ligand and the reaction center are sterically hindered. The dissociative reactions fit to a linear free energy relationship of slope near unity, whereas, for the associative reactions, the reaction center exerts discrimination between the various nucleophiles (order of reactivity  $(\text{CH}_3)_2\text{S} < (\text{CH}_3)_2\text{Se} < (\text{CH}_3)_2\text{Te}$ ). Interestingly, the exchange on the  $\text{TaBr}_5\cdot(\text{CH}_3)_2\text{S}$  adduct can proceed via both mechanistic paths. For this exchange, the rate law is second order below 300 K, but a first-order term appears at higher temperatures. This temperature-dependent mechanism crossover is not surprising if one considers the large differences in  $\Delta H^\ddagger$  between the two paths. Positive activation volumes ranging from +15.2 to +30.5  $\text{cm}^3 \text{ mol}^{-1}$  have been determined for limiting dissociative (**D**) reactions when  $\text{L} = (\text{CH}_3)_2\text{O}, \text{CH}_3\text{CN}, (\text{CH}_3)_3\text{CCN}, (\text{CH}_3\text{O})\text{Cl}_2\text{PO}, \text{and } ((\text{CH}_3)_2\text{N})_3\text{PS}$ .<sup>221,225</sup> Negative values of  $\Delta V^\ddagger$  range between  $-10.7$  and  $-19.8 \text{ cm}^3 \text{ mol}^{-1}$  for associative-interchange reactions (**I<sub>a</sub>**) when  $\text{L} = (\text{CH}_3)_2\text{S}, (\text{CH}_3)_2\text{Se}, \text{and } (\text{CH}_3)_2\text{Te}$ . From a simple model based on hard and incompressible spherical or cylindrical molecules, volumes for octahedral complexes and five-coordinated intermediates in a **D** mechanism have been calculated. The volume differences obtained were close to the measured positive  $\Delta V^\ddagger$ , confirming the limiting **D** mechanism for ligands with  $\text{O}$  and  $\text{N}$  as binding atoms.<sup>221</sup> A crossover in mechanism is observed for ligands with the soft binding atoms  $\text{S}, \text{Se}, \text{and Te}$ . Application of the molecular model to an **A** mechanism would give an absolute volume of  $|\Delta V^\ddagger|$  at least equal to that of the  $\text{Me}_2\text{O}$  **D** reaction. Considering the very crowded first coordination sphere of the adducts, the addition of a seventh ligand without substantial modification of bond lengths and angles of the six present ligands seems to be impossible. The relatively small negative  $\Delta V^\ddagger$  values of  $-10$  to  $-20 \text{ cm}^3 \text{ mol}^{-1}$  lead, therefore, to the suggestion of an **I<sub>a</sub>** mechanism for  $(\text{CH}_3)_2\text{S}, (\text{CH}_3)_2\text{Se}, \text{and } (\text{CH}_3)_2\text{Te}$  without excluding an **A** mechanism with a substantial elongation of the five  $\text{MX}$  bonds.

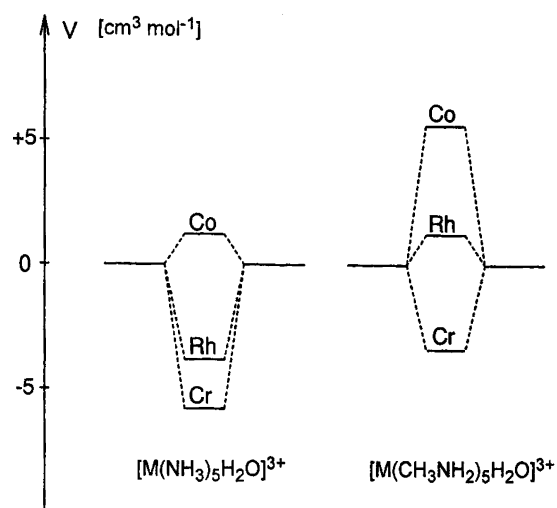
**Table 10. Effect of Spectator Ligands on the Solvent Exchange Rate Constants on First Row Trivalent Transition Metal Ions<sup>c</sup>**

complex		$k_1(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>Cr<sup>3+</sup></b>							
[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>		$2.4 \times 10^{-6}$	108.6	+11.6	-9.6		127
[Cr(NCS)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	<i>trans</i>	$6 \times 10^{-6}$	122	+63			185
	<i>cis</i>	$3 \times 10^{-6}$	104	-1.3			
[Cr(Cl)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	<i>trans</i>	$5 \times 10^{-5}$	109	+38			185
	<i>cis</i>	$2.9 \times 10^{-6}$	105	+0.8			
[Cr(Br)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	<i>trans</i>	-					185
	<i>cis</i>	$3 \times 10^{-6}$					
[Cr(NH <sub>3</sub> ) <sub>4</sub> <sup>eq</sup> (NH <sub>3</sub> ) <sub>1</sub> <sup>ax</sup> (H <sub>2</sub> O*) <sup>ax</sup> ] <sup>3+</sup>		$5.75 \times 10^{-5}$	99.1	+7			186, 187
		$5.8 \times 10^{-5}$	97.1	0	-5.8		188
[Cr(NH <sub>3</sub> ) <sub>4</sub> <sup>eq</sup> (H <sub>2</sub> O*) <sub>2</sub> <sup>ax</sup> ] <sup>3+</sup>		$1.17 \times 10^{-5}$	98.5	-9			186, 187
[Cr((NH <sub>3</sub> ) <sub>3</sub> H <sub>2</sub> O) <sup>eq</sup> (NH <sub>3</sub> ) <sup>ax</sup> (H <sub>2</sub> O*) <sup>ax</sup> ] <sup>3+</sup>		$5.92 \times 10^{-5}$	95.1	-7			186, 187
[Cr((NH <sub>3</sub> ) <sub>3</sub> H <sub>2</sub> O) <sup>eq</sup> (H <sub>2</sub> O*) <sub>2</sub> <sup>ax</sup> ] <sup>3+</sup>		$1.23 \times 10^{-5}$					186, 187
[Cr( <i>cis</i> -(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ) <sup>eq</sup> (NH <sub>3</sub> ) <sup>ax</sup> (H <sub>2</sub> O*) <sup>ax</sup> ] <sup>3+</sup>		$5.78 \times 10^{-5}$	95.1	-7			186, 187
[Cr( <i>cis</i> -(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ) <sup>eq</sup> (H <sub>2</sub> O*) <sub>2</sub> <sup>ax</sup> ] <sup>3+</sup>		$1.02 \times 10^{-5}$	105	+13			186, 187
[Cr( <i>trans</i> -(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ) <sup>eq</sup> (NH <sub>3</sub> ) <sup>ax</sup> (H <sub>2</sub> O*) <sup>ax</sup> ] <sup>3+</sup>		$7.6 \times 10^{-5}$					186, 187
[Cr( <i>trans</i> -(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ) <sup>eq</sup> (H <sub>2</sub> O*) <sub>2</sub> <sup>ax</sup> ] <sup>3+</sup>		$0.997 \times 10^{-5}$	97.0	-15			186, 187
[Cr(NH <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ) <sup>eq</sup> (NH <sub>3</sub> ) <sup>ax</sup> (H <sub>2</sub> O*) <sup>ax</sup> ] <sup>3+</sup>		$4.9 \times 10^{-5}$	101	+11			186, 187
[Cr(NH <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ) <sup>eq</sup> (H <sub>2</sub> O*) <sub>2</sub> <sup>ax</sup> ] <sup>3+</sup>		$0.449 \times 10^{-5}$					186, 187
[Cr(H <sub>2</sub> O) <sub>4</sub> <sup>eq</sup> (NH <sub>3</sub> ) <sup>ax</sup> (H <sub>2</sub> O*) <sup>ax</sup> ] <sup>3+</sup>		$2.8 \times 10^{-5}$					186, 187
[Cr(CH <sub>3</sub> NH <sub>2</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>		$4.1 \times 10^{-6}$	98.5	-17.5	-3.8		184
(H <sub>2</sub> O) <sub>4</sub> Cr( $\mu$ -OH) <sub>2</sub> Cr(H <sub>2</sub> O) <sub>4</sub> <sup>4+</sup>	<i>trans</i>	$3.58 \times 10^{-4}$	80.5	-40			189
	<i>cis</i>	$0.66 \times 10^{-4}$	97	0			
	bridging	$1.14 \times 10^{-5}$	99.5	-10			
[(H <sub>2</sub> O) <sub>3</sub> (OH)Cr( $\mu$ -OH) <sub>2</sub> Cr(OH)(H <sub>2</sub> O) <sub>3</sub> ] <sup>4+</sup>	<i>trans</i>	$1.24 \times 10^{-2}$	125.3	139			189
	<i>cis</i>	$4.75 \times 10^{-2}$	82.8	-12			
	bridging	$1.47 \times 10^{-3}$	126.7	125			
<b>Fe<sup>3+</sup></b>							
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>		$1.6 \times 10^2$	64.0	+12.1	-5.4		132, 133
[Fe(CDTA)(H <sub>2</sub> O)] <sup>-</sup>		$1.3 \times 10^7$	27	-18	+4.0		190
[Fe(EDTA)(H <sub>2</sub> O)] <sup>-</sup>		$7.2 \times 10^7$	24.3	-13	+2.2		190
[Fe(HEDTA)(H <sub>2</sub> O)]		$7.8 \times 10^7$	22	-20	+2.1		190
[Fe(EDDS)(H <sub>2</sub> O)] <sup>-</sup>		$4.3 \times 10^5$	48	+24	-14.4		190
[Fe(PhDTA)(H <sub>2</sub> O)] <sup>-</sup>		$1.2 \times 10^7$	26	-22	+4.6		191
[Fe( $\alpha$ -EDDADP)(H <sub>2</sub> O)] <sup>- b</sup>		$2.3 \times 10^8$	36	+36	+3.0		190
		$2.5 \times 10^6$	24	-42			
[Fe(TPPS)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3-</sup>		$2.0 \times 10^6$	67	99	+7.9		192
		$1.4 \times 10^7$	57.3	84.5			193
[Fe(TMPyP)(H <sub>2</sub> O) <sub>2</sub> ] <sup>5+</sup>		$4.5 \times 10^5$	71	100	+7.4		192
		$7.8 \times 10^5$	57.7	61.5			193
[Fe(TMPS)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3-</sup>		$2.1 \times 10^7$	61	100	+11.9		192
[Fe(DMF) <sub>6</sub> ] <sup>3+</sup>		$6.3 \times 10^1$	42.3	-69.0	-0.9		134
[Fe(PhDTA)(DMF)] <sup>-</sup>		$3.4 \times 10^7$	18	-40	+10		191, 194
<b>Co<sup>3+</sup></b>							
di-aqua							
<i>cis</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		$7.5 \times 10^{-6}$					195
<i>trans</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		$1.1 \times 10^{-5}$					195
[Co(tren)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		$3.7 \times 10^{-5}$ (p)					196
		$8.7 \times 10^{-6}$ (t)					
[Co(cyclen)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		$2 \times 10^{-4}$					196
[Co( <i>N</i> -Mecyclen)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		$2 \times 10^{-4}$					196
mono-aqua							
[Co(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>		$5.7 \times 10^{-6}$	111.3	+28	+1.2	<b>I<sub>d</sub></b>	27
[Co(CH <sub>3</sub> NH <sub>2</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>		$7.0 \times 10^{-4}$	99.0	+26.7	+5.7	<b>I<sub>d</sub></b>	184
<i>cis</i> -[Co(en) <sub>2</sub> (NH <sub>3</sub> )(H <sub>2</sub> O)] <sup>3+</sup>		$1.1 \times 10^{-6}$					197
<i>p</i> -[Co(tren)(NH <sub>3</sub> )(H <sub>2</sub> O)] <sup>3+</sup>		$1.1 \times 10^{-5}$					196
<i>t</i> -[Co(tren)(NH <sub>3</sub> )(H <sub>2</sub> O)] <sup>3+</sup>		$1.2 \times 10^{-5}$					196
[Co(cyclen)(NH <sub>3</sub> )(H <sub>2</sub> O)] <sup>3+</sup>		$<1.4 \times 10^{-4}$					198
mono-hydroxo							
[Co(NH <sub>3</sub> ) <sub>5</sub> (OH)] <sup>3+</sup>		$<1.4 \times 10^{-7}$					27
<i>p</i> -[Co(tren)(NH <sub>3</sub> )(OH)] <sup>3+</sup>		$1.7 \times 10^{-4}$					196
<i>t</i> -[Co(tren)(NH <sub>3</sub> )(OH)] <sup>3+</sup>		$<1 \times 10^{-6}$					196
[Co(cyclen)(NH <sub>3</sub> )(OH)] <sup>3+</sup>		8					198
di-hydroxo							
<i>cis</i> -[Co(en) <sub>2</sub> (OH) <sub>2</sub> ] <sup>3+</sup>		$3.0 \times 10^{-5}$					195
<i>trans</i> -[Co(en) <sub>2</sub> (OH) <sub>2</sub> ] <sup>3+</sup>		$2.3 \times 10^{-6}$					195
[Co(tren)(OH) <sub>2</sub> ] <sup>3+</sup>		$9.7 \times 10^{-5}$ (p)					196
		$2.2 \times 10^{-7}$ (t)					

Table 10 (Continued)

complex	$k_1(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>Co<sup>3+</sup></b>						
aqua-hydroxo						
<i>cis</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O)OH] <sup>3+</sup>	$9.3 \times 10^{-4}$					195
<i>trans</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O)OH] <sup>3+</sup>	$1.2 \times 10^{-3}$					195
[Co(tren)(p-OH <sub>2</sub> t-OH)] <sup>3+</sup>	0.05 (p)					196
[Co(tren)(t-OH <sub>2</sub> p-OH)] <sup>3+</sup>	0.03 (p), 0.01 (t)					196
[Co(cyclen)(H <sub>2</sub> O)OH] <sup>3+</sup>	12					196
[Co( <i>N</i> -Mecyclen)(H <sub>2</sub> O)OH] <sup>3+</sup>	15					196
[Co( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	60					199
[Co(CN) <sub>5</sub> (H <sub>2</sub> O)] <sup>2-</sup>	$5.9 \times 10^{-4}$	90.2	-4			200
[Co( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(bpy)(H <sub>2</sub> O)] <sup>2+</sup>	0.6	70.5		-6		199

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Two exchange processes observed. <sup>c</sup> Units are as follows:  $k_1(298\text{K})$ , s<sup>-1</sup>;  $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>;  $\Delta S^\ddagger$ , J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta V^\ddagger$ , cm<sup>3</sup> mol<sup>-1</sup>.



**Figure 7.** Volume profiles for the water exchange on  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  and  $[\text{M}(\text{CH}_3\text{NH}_2)_5(\text{H}_2\text{O})]^{3+}$  for three inert metal ions. A shift to more positive (less negative) volumes of activation is observed with the bulkier methylamine groups.

For the  $\text{SbCl}_5 \cdot \text{L}$  adducts, the solvent exchange reactions studied in  $\text{CH}_2\text{Cl}_2$  and  $(\text{CHCl}_2)_2$  as diluent show first-order rate laws, positive activation entropies ranging from +31 to +108 J K<sup>-1</sup> mol<sup>-1</sup>, positive activation volumes from +18.2 to +30.0 cm<sup>3</sup> mol<sup>-1</sup>, and a linear free energy relationship of slope -1.08 for a series of nitriles, ethers, and -PO donor solvents. It is concluded that a limiting dissociative **D** mechanism exists for the whole series of solvent exchange reactions studied.

Octahedral  $\text{MX}_4 \cdot 2\text{L}$  adducts can exist in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  in the *cis* form, in the *trans* form, or as an equilibrium of both *cis* and *trans* isomers.<sup>226–229</sup> On the 3d<sup>0</sup>  $\text{TiCl}_4 \cdot 2\text{L}$  and on the 4d<sup>10</sup>  $\text{SnCl}_4 \cdot 2\text{L}$  adducts, *cis/trans* isomerization and intermolecular exchange of L on the *cis* isomer have been observed with first-order rate laws and positive activation volumes.<sup>217,223,224,230</sup> **D** mechanisms with five-coordinated intermediates were concluded for the intermolecular *cis* substitution, which was found to be faster than *cis/trans* isomerization.<sup>224</sup>

Interestingly, the soft solvent  $\text{Me}_2\text{S}$  and  $\text{Me}_2\text{Se}$  do exchange dissociatively on the d<sup>0</sup> and d<sup>10</sup> tetrachlorides, contrary to the associative behavior observed for Nb(V) and Ta(V) pentahalide analogues. In the case of adducts with larger Zr(IV) and Hf(IV) ions,

the exchange behavior differs completely: the fastest process is the *cis/trans* isomerization, and the slowest processes are the intermolecular solvent exchanges on the *cis* and *trans* isomers.<sup>218</sup> The intermolecular exchanges are now second order with very negative  $\Delta S^\ddagger$  values and, when measured, a negative  $\Delta V^\ddagger$  value too (-11.5 cm<sup>3</sup> mol<sup>-1</sup> for *trans*- $\text{ZrCl}_4 \cdot 2(\text{CH}_3\text{O})_3\text{PO}$ ). The two 2D <sup>1</sup>H NMR exchange correlation spectra (Figure 8) obtained at 0.1 and 198 MPa exemplify this behavior for  $\text{ZrCl}_4 \cdot 2(\text{CH}_3\text{O})_3\text{PO}$ .<sup>231</sup> The intermolecular processes show an important increase in rate with pressure (large negative  $\Delta V^\ddagger$  values), whereas for the intramolecular isomerization the effect is much smaller (small  $\Delta V^\ddagger$  value). This is typical of **I<sub>a</sub>/A** behaviors and an intramolecular process. The striking differences in reaction mechanism from Ti(IV) and Sn(IV) to Zr(IV) and Hf(IV) metal chloride adducts,  $\text{MCl}_4 \cdot 2\text{L}$ , is due to the increase in ionic radius, which favors the changeover from a bond breaking to a bond making mechanism.

### 3.3. Square Planar Complexes

Square planar stereochemistry is mostly confined to the d<sup>8</sup> transition metal ions, and Pd<sup>2+</sup> and Pt<sup>2+</sup> metal centers are the most studied ones. The vast majority of solvent exchange reactions on square planar complexes undergo an **a**-activated mechanism, which is most probably a consequence of the coordinatively unsaturated four-coordinate 16 outer shell electron complex achieving noble gas configuration in the five-coordinate transition states or reactive intermediate.<sup>232</sup>

Solvent exchange on Pd<sup>2+</sup> and Pt<sup>2+</sup> complexes shows a variation in lability of about 16 orders of magnitude and is generally characterized by activation volumes which are either negative or close to zero (Table 13). Exchange reactions of nonaqueous solvents have been studied in inert diluents and were found to have a second-order rate dependence on free solvent concentration, underlining their associative character. The size of the solvent molecules has an important effect on the lability. Replacing  $\text{Me}_2\text{S}$  by the more sterically hindered  $\text{Et}_2\text{S}$  decreases the exchange rate constant by more than 400 times. Even more, solvent exchange on  $[\text{Pd}(\text{DMA})_4]^{2+}$  is slower than that on  $[\text{Pd}(\text{DMF})_4]^{2+}$ , despite the stronger nucleophilicity of DMA, as shown by the Gutmann donor numbers of 27.8 and 27.0 for DMA and DMF, respectively. Such steric influence on reaction rates

**Table 11. Effect of Spectator Ligands on the Solvent Exchange Rate Constants on Second and Third Rows Transition Metal Ions<sup>e</sup>**

complex	$k_1(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref	
<b>monovalent</b>							
[Re <sup>I</sup> (CO) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup>	$5.5 \times 10^{-3}$	90	+14			202	
[Re <sup>I</sup> (CO) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> (OH)]	27					202	
<b>divalent</b>							
[Ru(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$1.8 \times 10^{-2}$	87.8	16.1	-0.4	<b>I<sub>d</sub></b>	139	
[Ru( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup> <sup>b</sup>	11.5	75.9	29.9	+1.5	<b>I<sub>d</sub></b>	203	
[Ru( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )(bpy)(H <sub>2</sub> O)] <sup>2+</sup>	$6.8 \times 10^{-2}$	69	-27		<b>I<sub>d</sub></b>	199	
[Ru( $\eta^6$ -C <sub>6</sub> Me <sub>6</sub> )(bpy)(H <sub>2</sub> O)] <sup>2+</sup>	$10.2 \times 10^{-2}$	67.5	-31		<b>I<sub>d</sub></b>	199	
[Ru( $\eta^6$ -cymene)(bpy)(H <sub>2</sub> O)] <sup>2+</sup>	$8.5 \times 10^{-2}$	66.4	-33		<b>I<sub>d</sub></b>	199	
[Ru(DPMe <sub>2</sub> )(tpmm)(H <sub>2</sub> O)] <sup>2+</sup>	$7.0 \times 10^{-5}$					204	
[Ru(DPPro) <sub>2</sub> (tpmm)(H <sub>2</sub> O)] <sup>2+</sup>	66					204	
[Ru(MeCN)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	$1.5 \times 10^{-3}$					205	
	eq					205	
	ax	$3.9 \times 10^{-4}$ <sup>d</sup> / $7.2 \times 10^{-3}$				205	
[Ru(DMSO)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	eq	$1.9 \times 10^{-5}$	112.9	+43.2		205	
	ax	$6.8 \times 10^{-2}$ <sup>d</sup>				205	
[Ru(H <sub>2</sub> C=CH <sub>2</sub> )(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	eq	$2.8 \times 10^{-4}$	106.6	+44.6	+6.1	205	
	ax	2.9	85.2	+49.5	+6.5	205	
[Ru(F <sub>2</sub> C=CH <sub>2</sub> )(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	eq	$9.3 \times 10^{-6}$ <sup>c</sup>				205	
	ax	4.3	73.0	+12.1		205	
[Ru(CO)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	eq	$2.54 \times 10^{-6}$	111.6	22.4		206	
	ax	$3.54 \times 10^{-2}$	81			206	
<i>cis</i> -[Ru(CO) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	eq	$1.58 \times 10^{-7}$	120.3	28.4		206	
	ax	$4.53 \times 10^{-4}$	97.9	19.3		206	
[Ru(CO) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	$10^{-4} < k_{\text{ex}} < 10^{-3}$					206	
[Ru(CO) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> (OH)] <sup>+</sup>	0.053 ( $k_{\text{OH}}$ at 262 K)					206	
[Ru(MeCN) <sub>6</sub> ] <sup>2+</sup>	$8.9 \times 10^{-11}$	140.3	+33.3	+0.4	<b>I</b>	140	
[Ru( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )(MeCN) <sub>3</sub> ] <sup>2+</sup> <sup>b</sup>	$4.07 \times 10^{-5}$	102.5	+15.0	+2.4	<b>I</b>	201	
[Ru( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(MeCN) <sub>3</sub> ] <sup>+</sup> <sup>b</sup>	5.6	86.5	+59.6	+11.1	<b>D</b>	201	
[Ru(Tp)(MeCN) <sub>3</sub> ] <sup>+</sup> <sup>b</sup>	$1.2 \times 10^{-8}$	155.9	+126.5			207	
[Os( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup> <sup>b</sup>	11.8	66	-5	+2.9	<b>I<sub>d</sub></b>	203	
<i>trans</i> -[Os(en) <sub>2</sub> ( $\eta^2$ -H <sub>2</sub> )(H <sub>2</sub> O)] <sup>2+</sup>	1.59	72.4	+1.7	-1.5	<b>I<sub>d</sub>, D</b>	208	
<i>trans</i> -[Os(en) <sub>2</sub> ( $\eta^2$ -H <sub>2</sub> )(MeCN)] <sup>2+</sup>	$2.74 \times 10^{-4}$	98.0	+15.6	-0.5	<b>I<sub>d</sub>, D</b>	208	
<b>trivalent</b>							
[Ru(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$3.5 \times 10^{-6}$	90	-48	-8	<b>I<sub>a</sub></b>	139	
[Ru(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>	$2.3 \times 10^{-4}$					209	
[Rh(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$2.2 \times 10^{-9}$	131	29	-4.2	<b>I<sub>a</sub></b>	142	
[Rh(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>	$8.6 \times 10^{-6}$	103.0	+3	-4.1	<b>I<sub>a</sub></b>	188	
<i>cis</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>	$7.5 \times 10^{-6}$	105.4	+11			210	
<i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>	$7.2 \times 10^{-9}$	143.1	+78			210	
<i>cis</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>	$2.38 \times 10^{-5}$	102.9	+12			210	
<i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>	$3.38 \times 10^{-5}$	99.2	+3			210	
[Rh(CH <sub>3</sub> NH <sub>2</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>	$1.06 \times 10^{-5}$	112.7	+37.8	+1.2	<b>I<sub>d</sub></b>	184	
[Rh( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	$1.6 \times 10^5$	65.6	75.3	+0.6	<b>I<sub>d</sub></b>	199	
[Rh( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(bpy)(H <sub>2</sub> O)] <sup>2+</sup>	$1.6 \times 10^3$	47.9	-18			199	
[(H <sub>2</sub> O) <sub>4</sub> Rh( $\mu$ -OH) <sub>2</sub> Rh(H <sub>2</sub> O) <sub>4</sub> ] <sup>4+</sup>	<i>trans</i>	$0.85 \times 10^{-6}$	150	+141	+8.5	<b>D</b>	211
		$1.26 \times 10^{-6}$	118.8	+41		212	
	<i>cis</i>	$0.54 \times 10^{-6}$	159	+168	+10.1	<b>D</b>	211
		$0.49 \times 10^{-6}$	64.2	-150		212	
[(H <sub>2</sub> O) <sub>3</sub> (OH)Rh( $\mu$ -OH) <sub>2</sub> Rh(OH)(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	<i>trans</i>	$3.44 \times 10^{-6}$	145.9	+140		212	
	<i>cis</i>	$2.68 \times 10^{-6}$	102.0	-9		212	
[Rh( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(MeCN) <sub>3</sub> ] <sup>2+</sup>	$3.7 \times 10^1$	76.7	+42	+0.8	<b>D</b>	213	
[Rh( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(DMSO) <sub>3</sub> ] <sup>2+</sup>	$3.6 \times 10^3$	54.6	+6.4	+3.3	<b>D</b>	213	
[Ir(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$1.1 \times 10^{-10}$	130.5	+2.1	-5.7	<b>I<sub>a</sub></b>	2	
[Ir(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>3+</sup>	$6.4 \times 10^{-8}$	118	+11	-3.2	<b>I<sub>a</sub></b>	214	
<i>trans</i> -[Ir(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>	$1.1 \times 10^{-11}$	162	+90			215	
<i>trans</i> -[Ir(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>	$4.4 \times 10^{-7}$	110	+3			215	
<i>trans</i> -[Ir(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)(OH)] <sup>2+</sup>	$7.2 \times 10^{-6}$	93	-31			215	
[Ir( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	$2.5 \times 10^4$	54.9	+23.6	+2.4	<b>I<sub>d</sub></b>	199	
[Ir( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(bpy)(H <sub>2</sub> O)] <sup>2+</sup>	$2.2 \times 10^2$	59.1	+4		<b>I<sub>d</sub></b>	199	
[Ir( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(MeCN) <sub>3</sub> ] <sup>2+</sup>	$8.8 \times 10^{-2}$	85.9	+23	+1.5	<b>D</b>	213	
[Ir( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(DMSO) <sub>3</sub> ] <sup>2+</sup>	$2.5 \times 10^3$	60.3	+22	+2.8	<b>D</b>	213	

<sup>a</sup> Rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> All three H<sub>2</sub>O or MeCN are equivalent. <sup>c</sup> At 308.4 K. <sup>d</sup> At 279 K. <sup>e</sup> Units are as follows:  $k_1(298\text{K})$ , s<sup>-1</sup>;  $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>;  $\Delta S^\ddagger$ , J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta V^\ddagger$ , cm<sup>3</sup> mol<sup>-1</sup>.

is consistent with the operation of an **a**-activated mechanism.

On Pd<sup>2+</sup>, second-order exchange rate constants on solvent molecules with hard donor atoms, like H<sub>2</sub>O, MeCN, DMF, and DMA, differ by less than a factor of 15, whereas solvents with much softer binding

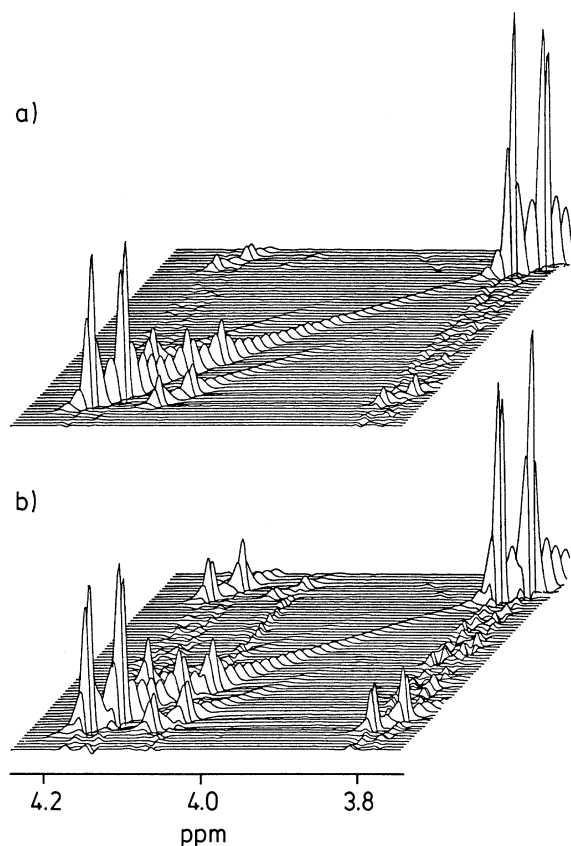
atoms, like MeS<sub>2</sub> and MeNC, have much faster exchange rates. In the case of MeNC, this may be due to the formation of a five-coordinate intermediate stabilized by  $\pi$  back-bonding from the metal center to MeNC. This dependence on the softness of the binding atom is nicely demonstrated by the DMSO



**Table 12. Kinetic Parameters for Solvent Exchange for  $\text{MX}_x\text{L}_{6-x} + \text{L}^* \rightleftharpoons \text{MX}_x\text{L}_{6-x}^* + \text{L}$  in  $\text{CH}_2\text{Cl}_2^f$** 

complex	$k_1(298\text{K})^a$	$k_2(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>Ti(V)</b>							
<i>cis</i> -TiF <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> O <sup>d</sup>		$1.7 \times 10^5$	52.3	+30.5	-		216, 217
<i>cis</i> -TiCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> O	$2.8 \times 10^7$		61.3	+103.1		<b>D</b>	217
<i>cis</i> -TiCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> S	$3.5 \times 10^6$		56.9	+1.1	+24.4	<b>D</b>	217
<i>cis</i> -TiCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> Se	$8.9 \times 10^5$		56.1	+7.1	+26.1	<b>D</b>	217
<i>cis</i> -TiCl <sub>4</sub> ·2(CH <sub>3</sub> O) <sub>2</sub> ClPO <sup>b</sup>	$5.5 \times 10^4$		56.6	+5.7	-	<b>D</b>	217
<i>cis</i> -TiCl <sub>4</sub> ·2TMPA <sup>b</sup>	$5.6 \times 10^2$		60.1	+0.3	+17.5	<b>D</b>	217
<i>cis</i> -TiBr <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> S	$2.4 \times 10^6$		50.2	+5.5		<b>D</b>	217
<i>cis</i> -TiBr <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> Se	$7.2 \times 10^5$		53.8	+7.7		<b>D</b>	217
<b>Zr(IV)</b>							
<i>cis</i> -ZrCl <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> O		$4.3 \times 10^{-3}$	28.1	-100.3			218
<i>cis</i> -ZrCl <sub>4</sub> ·2Cl <sub>2</sub> (CH <sub>3</sub> N)PO <sup>b</sup>	0.843		58.9	-48.8			218
		78	34.5	-93.0			
<i>cis</i> -ZrCl <sub>4</sub> ·2(CH <sub>3</sub> O) <sub>2</sub> ClPO <sup>b</sup>		110	27.6	-113.2			218
<i>trans</i> -ZrCl <sub>4</sub> ·2(CH <sub>3</sub> O) <sub>3</sub> PO <sup>b</sup>		276	30.2	-96.9	-11.1		218
<i>trans</i> -ZrCl <sub>4</sub> ·2(Cl(CH <sub>3</sub> ) <sub>2</sub> N)PO <sup>c</sup>		70	33.5	-97.3			218
<b>Nb(V)</b>							
NbF <sub>5</sub> ·((CH <sub>3</sub> ) <sub>2</sub> N) <sub>3</sub> PO		0.16	33.5	-147		<b>I<sub>d</sub></b>	219
NbF <sub>5</sub> ·((CH <sub>3</sub> O) <sub>3</sub> ) <sub>3</sub> PO		$2.5 \times 10^5$	17.2	-84		<b>I<sub>d</sub></b>	219
NbCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> O <sup>b</sup>	810		61.5	+17	+28.7	<b>D</b>	220, 221
NbCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> S		$3.0 \times 10^4$	15.9	-106		<b>I<sub>a</sub></b>	220
NbCl <sub>5</sub> ·CH <sub>3</sub> CN <sup>b</sup>	550		71.1	+46	+19.5	<b>D</b>	221, 222
NbCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>3</sub> CCN <sup>b</sup>	280		71.6	+42	+15.2	<b>D</b>	221, 222
NbCl <sub>5</sub> ·BrCH <sub>2</sub> CN <sup>b</sup>	$1.6 \times 10^4$		66.6	+59		<b>D</b>	222
NbCl <sub>5</sub> ·ClCH <sub>2</sub> CN <sup>b</sup>	$3.2 \times 10^4$		71.2	+80		<b>D</b>	222
NbCl <sub>5</sub> ·FCH <sub>2</sub> CN <sup>b</sup>	$6.4 \times 10^4$		66.1	+71		<b>D</b>	222
NbCl <sub>5</sub> ·Cl(CH <sub>3</sub> O) <sub>2</sub> PO <sup>b</sup>	3.4		83.7	+46		<b>D</b>	219
NbCl <sub>5</sub> ·Cl <sub>2</sub> (CH <sub>3</sub> O)PO <sup>b</sup>	300		64.0	+17	+20.5	<b>D</b>	219, 221
NbCl <sub>5</sub> ·Cl <sub>3</sub> PO <sup>b</sup>	$1.3 \times 10^4$		67.0	+58.6		<b>D</b>	219
NbCl <sub>5</sub> ·((CH <sub>3</sub> ) <sub>2</sub> N) <sub>3</sub> PS	14		59	+65	+17.7	<b>D</b>	219, 221
NbBr <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> O	$3.9 \times 10^4$		66.5	66		<b>D</b>	220
NbBr <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> S		$6.4 \times 10^3$	21.8	-99	-12.1	<b>I<sub>a</sub></b>	220, 221
<b>Sn(IV)</b>							
<i>cis</i> -SnCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> CO	$2.2 \times 10^8$		51.3	+87		<b>D</b>	223
<i>cis</i> -SnCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> S	$1.2 \times 10^7$		66.6	+114.3	+38.4	<b>D</b>	224
<i>cis</i> -SnCl <sub>4</sub> ·2TMPA	$8.1 \times 10^6$		62.0	+38		<b>D</b>	223
<i>trans</i> -SnCl <sub>4</sub> ·2TMPA	5.3		80.4	+39		<b>D</b>	223
<b>Sb(V)</b>							
SbCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> O	$1.9 \times 10^3$		75.5	+71	+27.2	<b>D</b>	225
SbCl <sub>5</sub> ·(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O	$1.2 \times 10^4$		96.2	+156	+30.0	<b>D</b>	225
SbCl <sub>5</sub> ·CH <sub>3</sub> CN	$1.5 \times 10^5$		66.5	+77	+24.7	<b>D</b>	225
SbCl <sub>5</sub> ·CH <sub>3</sub> SCN	$1.6 \times 10^5$		57.1	+46		<b>D</b>	225
SbCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>3</sub> CCN	$1.5 \times 10^5$		70.1	+89	+18.2	<b>D</b>	225
SbCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> CO	$3.8 \times 10^3$		69.9	+58	+28.1	<b>D</b>	225
SbCl <sub>5</sub> ·Cl(CH <sub>3</sub> ) <sub>2</sub> NPO <sup>e</sup>	$5.9 \times 10^{-5}$		111.5	+48		<b>D</b>	225
SbCl <sub>5</sub> ·Cl <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> NPO	340		70.8	+41	+23.0	<b>D</b>	225
SbCl <sub>5</sub> ·(CH <sub>3</sub> O) <sub>3</sub> PO <sup>e</sup>	$3.2 \times 10^{-3}$		113.8	+89		<b>D</b>	225
SbCl <sub>5</sub> ·Cl(CH <sub>3</sub> O) <sub>2</sub> PO <sup>b</sup>	86		74.3	+41		<b>D</b>	225
SbCl <sub>5</sub> ·Cl <sub>2</sub> (CH <sub>3</sub> O)PO	$7.8 \times 10^3$		60.1	+31		<b>D</b>	225
SbCl <sub>5</sub> ·TMU <sup>e</sup>	$2.3 \times 10^{-4}$		120.9	+91		<b>D</b>	225
SbCl <sub>5</sub> ·DMA <sup>e</sup>	$2.5 \times 10^{-4}$		125.8	+108		<b>D</b>	225
SbCl <sub>5</sub> ·DMF <sup>e</sup>	$1.5 \times 10^{-4}$		124.7	+100		<b>D</b>	225
SbCl <sub>5</sub> ·THF <sup>e</sup>	4.9		101.0	+107		<b>D</b>	225
SbCl <sub>5</sub> ·POCl <sub>3</sub> <sup>e</sup>	$1.0 \times 10^6$		56.9	+61		<b>D</b>	225
<b>Hf(IV)</b>							
<i>cis</i> -HfCl <sub>4</sub> ·2Cl <sub>2</sub> (CH <sub>3</sub> N)PO <sup>b</sup>	1.5		76.1	+13.4		<b>D</b>	218
		130	37.2	-79.5		<b>I<sub>a</sub></b>	
<i>cis</i> -HfCl <sub>4</sub> ·2Cl(CH <sub>3</sub> O)PO <sup>b</sup>		260	20.1	-131.4		<b>I<sub>a</sub></b>	218
<i>trans</i> -HfCl <sub>4</sub> ·2Cl(CH <sub>3</sub> O)PO <sup>b</sup>		970	26.4	-99.2		<b>I<sub>a</sub></b>	218
<i>trans</i> -HfCl <sub>4</sub> ·2(CH <sub>3</sub> O) <sub>2</sub> PO <sup>b</sup>		53	43.1	-67.4		<b>I<sub>a</sub></b>	218
<b>Ta(V)</b>							
TaF <sub>5</sub> ·((CH <sub>3</sub> ) <sub>2</sub> N) <sub>2</sub> (CH <sub>3</sub> O)PO		$6.3 \times 10^3$	23.9	-92		<b>I<sub>d</sub></b>	219
TaF <sub>5</sub> ·((CH <sub>3</sub> ) <sub>2</sub> N)(CH <sub>3</sub> O) <sub>2</sub> PO		$2.6 \times 10^4$	18.0	-100		<b>I<sub>d</sub></b>	219
TaF <sub>5</sub> ·(CH <sub>3</sub> O) <sub>3</sub> PO		$1.8 \times 10^5$	18.0	-84		<b>I<sub>d</sub></b>	219
TaCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> O	19		83.3	+59	+27.8	<b>D</b>	220, 221
TaCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> S		$2.4 \times 10^3$	21.8	-107	-19.8	<b>I<sub>a</sub></b>	220, 221
TaCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> Se		$3.1 \times 10^3$	25.1	-94	-18.7	<b>I<sub>a</sub></b>	220, 221
TaCl <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> Te		$3.8 \times 10^3$	24.3	-95	-10.7	<b>I<sub>a</sub></b>	220, 221
TaBr <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> O	960		74.5	+62	+30.5	<b>D</b>	220, 221
TaBr <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> S		250	28.9	-102	-12.6	<b>I<sub>a</sub></b>	220, 221
TaBr <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> Se		$1.1 \times 10^3$	33.1	-76	-13.6	<b>I<sub>a</sub></b>	220, 221
TaBr <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> Te		$2.0 \times 10^3$	31.8	-75	-16.4	<b>I<sub>a</sub></b>	220, 221

<sup>a</sup> Calculated from activation parameters. <sup>b</sup> In CHCl<sub>3</sub>. <sup>c</sup> In 1,1,1,2,2-tetrachloroethane. <sup>d</sup> In SO<sub>2</sub>. <sup>e</sup> In (CHCl<sub>2</sub>)<sub>2</sub>. <sup>f</sup> Units are as follows:  $k_1(298\text{K})$ , s<sup>-1</sup>;  $k_2(298\text{K})$ , m<sup>-1</sup> s<sup>-1</sup>;  $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>;  $\Delta S^\ddagger$ , J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta V^\ddagger$ , cm<sup>3</sup> mol<sup>-1</sup>.



**Figure 8.** 400 MHz 2D  $^1\text{H}$  NMR exchange correlation spectra (a) at 0.1 MPa and (b) at 198 MPa for the intermolecular exchange between free  $(\text{CH}_3\text{O})_3\text{PO}$  and both *cis*- and *trans*-coordinated solvent in  $\text{ZrCl}_4 \cdot 2(\text{CH}_3\text{O})_3\text{PO}$  and for the intramolecular *cis/trans* isomerization (at 256 K in  $\text{CHCl}_3/\text{CDCl}_3$  as diluent).

exchange on *cis*- $[\text{Pd}(\text{Me}_2\text{SO})_2(\text{Me}_2\text{SO})_2]^{2+}$ , where two  $\text{Me}_2\text{SO}$  groups are *S*-bonded and two are *O*-bonded.<sup>240</sup> The soft donor  $\text{Me}_2\text{SO}$  exerts a strong *trans* effect on

the hard donor  $\text{Me}_2\text{SO}$ , which is a good leaving ligand, and vice versa. As a consequence,  $\text{Me}_2\text{SO}$  exchanges much more rapidly than  $\text{Me}_2\text{S}$ . The relative labilities of  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  complexes vary with the nature of the solvent molecules (Table 13). Exchange rates of soft solvents, with the exception of 1,4-dithiane and  $\text{Me}_2\text{S}$ , are very similar for both metal ions, whereas hard solvents exchange 6 orders of magnitude more slowly on  $\text{Pt}^{2+}$  than on  $\text{Pd}^{2+}$ .

Mechanistic interpretation of activation volumes on square planar complexes is complicated by the geometry. The sterically less crowded complexes may have two loosely bound solvent molecules occupying the axial sites above and below the plane.<sup>241</sup> Replacing them in the formation of a five-coordinated transition state or intermediate may result by compensation in relatively small volume effects. It is therefore difficult to distinguish between **I<sub>a</sub>** and **A** mechanisms from the value of the activation volume. Nevertheless, the  $\Delta V^\ddagger$  values are negative and, together with the second-order rate laws observed, point to an **a**-activation for those solvent exchange reactions.

The operation of a **d**-activated mechanism with the formation of a three-coordinate intermediate is, however, favored by strong  $\sigma$ -donor ligands such as phenyl and methyl.<sup>242</sup> The exchange rate of DMSO on  $[\text{PtPh}_2(\text{DMSO})_2]^{2+}$  is nearly independent of the free DMSO concentration in the diluent  $\text{CDCl}_3$ , and positive activation volumes on complexes of the form  $[\text{PtR}_2\text{S}_2]^{2+}$  ( $\text{R} = \text{Ph}, \text{Me}; \text{S} = \text{Me}_2\text{SO}, \text{Me}_2\text{S}$ ) have been measured.<sup>243</sup> The overall mechanistic picture has been taken as the first clear-cut evidence for the operation of a **D** mechanism involving a 3-coordinate 14-electron intermediate for simple ligand substitution on square planar complexes (Table 14).

**Table 13. Rate Constants and Activation Parameters for Solvent Exchange on Square Planar Transition-Metal Ions<sup>j</sup>**

complex	$k_2(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	ref
<b><math>\text{Pd}^{2+}</math></b>					
$[\text{Pd}(\text{NH}_3)_4]^{2+ b}$	0.016	67.3	-54.1		233
$[\text{Pd}(\text{Et}_2\text{S})_4]^{2+ c}$	5.0	50.4	-62.8	-11.6	234
$[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$	10.2 <sup>d</sup>	49.5	-60	-2.2	235
	560 <sup>e</sup>	49.5	-26	-2.2	235
$[\text{Pd}(\text{DMA})_4]^{2+ c}$	34.8	43.2	-76.2	-2.8	234
$[\text{Pd}(\text{MeCN})_4]^{2+ c}$	48.8	45.4	-60.1	-0.1	234
$[\text{Pd}(\text{DMF})_4]^{2+ c}$	153	41.9	-62.3	-0.2	234
$[\text{Pd}(\text{Me}_2\text{S})_4]^{2+ c}$	2140	31.9	-74.3 <sup>f</sup>	-9.4	234
$[\text{Pd}(1,4\text{-dithiane})_2]^{2+ c}$	9780	22.9	-91.6	-9.8	236
$[\text{Pd}(\text{MeNC})_4]^{2+ g}$	$1.06 \times 10^6$	16.4	-74.5	-3.1	234
<b><math>\text{Pt}^{2+}</math></b>					
$[\text{Pt}(\text{NH}_3)_4]^{2+ b}$	$9.5 \times 10^{-10} d$	125	+4		237
$[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$	$7.1 \times 10^{-6} d$	89.7	-43	-4.6	238
	$3.9 \times 10^{-4} e$	89.7	-9	-4.6	238
$[\text{Pt}^{\text{IV}}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$	$7.0 \times 10^{-6} d$	115	+42		239
$[\text{Pt}(\text{Me}_2\text{S})_4]^{2+ c}$	1.54	42.1	-100.2	-22.0	236
<i>cis</i> - $[\text{Pt}(\text{Me}_2\text{SO})_2(\text{Me}_2\text{SO})_2]^{2+ c, h}$	2	47	-74	-5	240
<i>cis</i> - $[\text{Pt}(\text{Me}_2\text{SO})_2(\text{Me}_2\text{SO})_2]^{2+ c, i}$	3200	32.8	-62.0	-2.5	240
$[\text{Pt}(1,4\text{-dithiane})_2]^{2+ c}$	28.8	32.9	-106	-12.6	236
$[\text{Pt}(\text{MeNC})_4]^{2+ g}$	$6.2 \times 10^5$	13.8	-87.9	-3.7	234

<sup>a</sup> Second-order rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> In aqueous solution. <sup>c</sup> Studied in *d*<sub>3</sub>-nitromethane diluent. <sup>d</sup> Units are  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . <sup>e</sup> First-order rate constant for the exchange of a particular water molecule.<sup>5</sup> <sup>f</sup> Misprint in ref 234 corrected in ref 236. <sup>g</sup> Studied in *d*<sub>3</sub>-acetonitrile diluent. <sup>h</sup> Sulfur bonded. <sup>i</sup> Oxygen bonded. <sup>j</sup> Units are as follows:  $k_2(298\text{K})$ ,  $\text{kg mol}^{-1} \text{s}^{-1}$ ;  $\Delta H^\ddagger$ ,  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$ ,  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $\Delta V^\ddagger$ ,  $\text{cm}^3 \text{mol}^{-1}$ .

**Table 14. Effect of Spectator Ligands on the Rate Constants and Activation Parameters for Solvent Exchange on Square Planar Transition Metal Ions<sup>j</sup>**

complex	$k_2(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	ref
<b>Pd<sup>2+</sup></b>					
[Pd(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	10.2 <sup>b</sup>	49.5	-60	-2.2	235
	560 <sup>c</sup>	49.5		-2.2	
[Pd(dien)(H <sub>2</sub> O)] <sup>2+</sup>	93 <sup>b</sup>	38	-80	-2.8	244
[Pd(Me <sub>5</sub> dien)(H <sub>2</sub> O)] <sup>2+</sup>	3.4 <sup>b</sup>	62	-27	-7.2	245
[Pd(Et <sub>5</sub> dien)(H <sub>2</sub> O)] <sup>2+</sup>	0.053 <sup>b</sup>	63	-58	-7.7	245
<i>trans</i> -[PdCl <sub>2</sub> ((CH <sub>3</sub> ) <sub>2</sub> S) <sub>2</sub> ] in CHCl <sub>3</sub>	260	38.5	-69.7	-7.1	246
in CH <sub>2</sub> Cl <sub>2</sub>	300	33.4	-85.6	-8.4	
in <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	624	36.1	-70.2	-7.2	
in C <sub>6</sub> H <sub>5</sub> CN	393	38.1	-67.4	-5.4	
<b>Pt<sup>2+</sup></b>					
[Pt(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	7.1 × 10 <sup>-6 b</sup>	89.7	-43	-4.6	238
	3.9 × 10 <sup>-4 c</sup>	89.7	-9	-4.6	238
[Pt{C <sub>6</sub> H <sub>3</sub> (CH <sub>2</sub> NMe <sub>2</sub> ) <sub>2</sub> -2,6}(H <sub>2</sub> O)] <sup>2+</sup>	130 <sup>b</sup>	47.4	-45	-9.2	247
[Pt(Me <sub>2</sub> S) <sub>4</sub> ] <sup>2+ d</sup>	1.54	42.1	-100.2	-22.0	236
<i>cis</i> -[PtPh <sub>2</sub> (Me <sub>2</sub> S) <sub>2</sub> ] <sup>2+ e</sup>	0.21 (in s <sup>-1</sup> )			+4.7	243
<i>cis</i> -[PtMe <sub>2</sub> (Me <sub>2</sub> S) <sub>2</sub> ] <sup>2+ d</sup>	1.38 (in s <sup>-1</sup> )			+4.9	243
<i>cis</i> -[PtPh <sub>2</sub> (DMSO) <sub>2</sub> ] <sup>2+ h</sup>	1.24 (in s <sup>-1</sup> )			+5.5	243
<i>cis</i> -[PtMe <sub>2</sub> (DMSO) <sub>2</sub> ] <sup>2+ d</sup>	1.12 (in s <sup>-1</sup> )	84.0	-0.5	+4.9	243
<i>cis</i> -[Pt(Me <sub>2</sub> SO) <sub>2</sub> (Me <sub>2</sub> SO) <sub>2</sub> ] <sup>2+ d,f</sup>	2	47	-74	-5	240
<i>cis</i> -[Pt(Me <sub>2</sub> SO) <sub>2</sub> (Me <sub>2</sub> SO) <sub>2</sub> ] <sup>2+ d,g</sup>	3200	32.8	-62.0	-2.5	240
[Pt(en)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	9.5 × 10 <sup>-6</sup>				248
[Pt(Me <sub>4</sub> en)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	1.15 × 10 <sup>-6</sup>				248
[Pt(2-ampy)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	3.5 × 10 <sup>-3</sup>				248
[Pt(dps)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	1.0 × 10 <sup>-2</sup>				248
<i>cis</i> -[Pt(py) <sub>2</sub> (CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	1.6 × 10 <sup>-2</sup>				248
[Pt(Me <sub>4</sub> phen)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	2.7 × 10 <sup>-2</sup>				248
[Pt(dipy)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	5.3 × 10 <sup>-2</sup>				248
[Pt(Ph <sub>2</sub> phen)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	1.0 × 10 <sup>-1</sup>				248
[Pt(bpy)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	1.6 × 10 <sup>-1</sup>				248
[Pt(phen)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	1.8 × 10 <sup>-1</sup>				248
[Pt(NO <sub>2</sub> phen)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	3.3 × 10 <sup>-1</sup>				248
[Pt(cy <sub>2</sub> dim)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	9.2 × 10 <sup>-1</sup>	45.5	-93		248
[Pt(pr <sup>2</sup> dim)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	7.9 × 10 <sup>-1</sup>	46.2	-91		248
[Pt(Me <sub>2</sub> phen)(CH <sub>3</sub> )(DMSO)] <sup>+ i</sup>	3.81 × 10 <sup>4</sup>				248

<sup>a</sup> Second-order rate constant for the exchange of a particular coordinated solvent molecule. <sup>b</sup> Units are dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup> First-order rate constant for the exchange of a particular water molecule.<sup>5</sup> <sup>d</sup> Studied in *d*<sub>3</sub>-nitromethane diluent. <sup>e</sup> Studied in benzene diluent. <sup>f</sup> Sulfur bonded. <sup>g</sup> Oxygen bonded. <sup>h</sup> Studied in *d*<sub>3</sub>-chloroform diluent. <sup>i</sup> Studied in *d*<sub>6</sub>-acetone diluent. <sup>j</sup> Units are as follows:  $k_2(298\text{K})$ , kg mol<sup>-1</sup> s<sup>-1</sup>;  $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>;  $\Delta S^\ddagger$ , J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta V^\ddagger$ , cm<sup>3</sup> mol<sup>-1</sup>.

A series of monoalkyl square planar complexes of the type [Pt(N–N)(CH<sub>3</sub>)(Me<sub>2</sub>SO)]PF<sub>6</sub>, where N–N represents chelating diamines or diimines of widely different steric and electronic characteristics, were tailored to offer only one site of exchange to a neutral molecule, that is, DMSO, in a noncoordinating solvent (Table 14).<sup>248</sup> The lability of dimethyl sulfoxide in the complexes depends in a rather unexpected and spectacular way upon the nature of the coordinate N–N ligands, the difference in reactivity between the first Me<sub>4</sub>en,  $k_2^{298} = 1.15 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$ , and the last Me<sub>2</sub>phen,  $k_2^{298} = 3.81 \times 10^4 \text{ mol}^{-1} \text{ s}^{-1}$ , members of the series being greater than 10 orders of magnitude, as a result of a well-known phenomenon of steric retardation (for the first complex) and an unprecedented case of steric acceleration (for the last complex). Other factors of primary importance in controlling the reactivity are (i) the presence of an extensive  $\pi$  system on the ligand N–N, (ii) the ease with which this  $\pi$  system interacts with nonbonding d electrons of the metal, and (iii) the flexibility and ease of elongation of the chelate bite distance. The basicity plays a somewhat minor role, except in the restricted range of the same class of compounds such as substituted phenanthrolines.

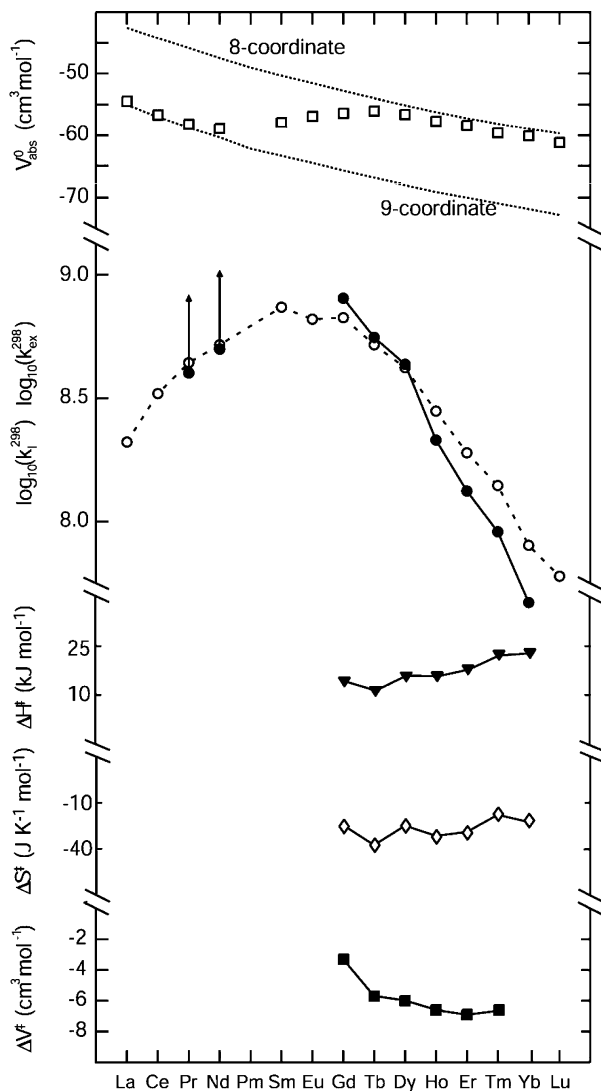
## 4. Solvent Exchange on Lanthanides and Actinides

### 4.1. Solvent Exchange on Trivalent Lanthanides

The fifteen trivalent lanthanide ions La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Pm<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup>, and Lu<sup>3+</sup>, which are commonly denoted as Ln<sup>3+</sup>, represent the most extended series of chemically similar metal ions. The filling of the 4f orbitals from La<sup>3+</sup> to Lu<sup>3+</sup> is accompanied by a smooth decrease in atomic radius of 18.4 pm for nine-coordinate ionic radii and of 18.3 pm for eight-coordinate ionic radii.<sup>38</sup> As a consequence of the shielding of the 4f orbitals by the filled 5s and 6p orbitals, the ligand field effects on Ln<sup>3+</sup> ions are very small by comparison with those for first row transition metal ions. The geometry of the first coordination shell is mainly determined by the electrostatic attraction of the strongly charged ion on polar solvent molecules and by electrostatic and steric repulsion between the solvent molecules.

#### 4.1.1. Water Exchange on Ln<sup>3+</sup> Aqua Ions

The hydration number of the trivalent lanthanide ions has been extensively addressed by various



**Figure 9.** Absolute partial molar volumes,  $V_{\text{abs}}^{\circ}$ , of  $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$  in aqueous  $\text{Ln}(\text{ClO}_4)_3$  solutions ( $\square$ ), compared with calculated values for  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$  and  $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$  (upper and lower dotted lines, respectively). Interchange rate constants,  $k_i$ , for substitution of  $\text{SO}_4^{2-}$  on  $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$  are shown as  $\circ$ , and water exchange rate constants (at 298 K) for  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$  are shown as  $\bullet$ . Activation enthalpies,  $\Delta H^{\ddagger}$ , activation entropies,  $\Delta S^{\ddagger}$ , and activation volumes,  $\Delta V^{\ddagger}$ , are shown as  $\blacktriangledown$ ,  $\diamond$ , and  $\blacksquare$ , respectively.

techniques such as neutron scattering,<sup>249,250</sup> X-ray scattering, extended X-ray absorption<sup>251,252</sup> fine structure (EXAFS),<sup>253</sup> and density<sup>254,255</sup> and by spectrophotometric ones.<sup>256</sup> The change in coordination number, CN, from nine for the lighter ions  $\text{La}^{3+}$  to  $\text{Nd}^{3+}$  to eight for the heavier ions  $\text{Gd}^{3+}$  to  $\text{Lu}^{3+}$  is now well established. This change in CN is a direct consequence of the lanthanide contraction and is nicely reflected in the evolution of the absolute partial molar volumes,  $V_{\text{abs}}^{\circ}$ , along the  $\text{Ln}^{3+}$  series (Figure 9).<sup>254,255</sup>

The change of hydration number across the  $\text{Ln}^{3+}$  series has significant consequences for the kinetics of water exchange between the first coordination shell of the lanthanide ions and the bulk of the solution. As can be seen from Figure 9,  $k_{\text{ex}}$  decreases from  $\text{Gd}^{3+}$  to  $\text{Yb}^{3+}$  along the series with the systematic decrease of the ionic radius. Both  $\Delta S^{\ddagger}$  and  $\Delta V^{\ddagger}$  are negative, but the activation volume is far

**Table 15. Rate Constants and Activation Parameters for Water Exchange on Lanthanide Aqua Ions<sup>c</sup>**

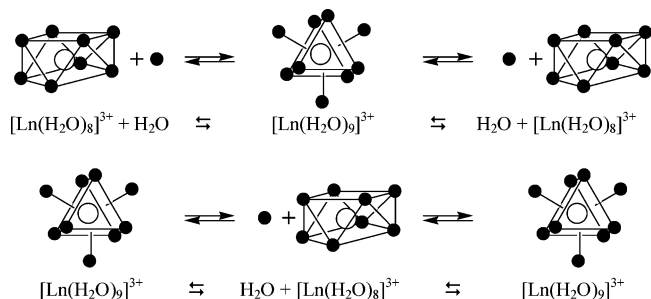
complex	$r_M^a$	$k_1$ (298K) <sup>a</sup>	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V^{\ddagger}$	mech	ref
<b>Eu<sup>2+</sup></b>							
$[\text{Eu}(\text{H}_2\text{O})_7]^{2+}$		500 <sup>b</sup>	15.7	-7.0	-11.3	<b>I<sub>a</sub>, A</b>	3, 4, 260
<b>Ln<sup>3+</sup></b>							
$[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$		$\geq 50$					259
$[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$		$\geq 40$					259
$[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$		83.0	14.9	-24.1	-3.3	<b>I<sub>a</sub></b>	261
$[\text{Tb}(\text{H}_2\text{O})_8]^{3+}$		55.8	12.1	-36.9	-5.7	<b>I<sub>a</sub></b>	262, 263
$[\text{Dy}(\text{H}_2\text{O})_8]^{3+}$		43.4	16.6	-24.0	-6.0	<b>I<sub>a</sub></b>	262, 263
$[\text{Ho}(\text{H}_2\text{O})_8]^{3+}$		21.4	16.4	-30.5	-6.6	<b>I<sub>a</sub></b>	262, 263
$[\text{Er}(\text{H}_2\text{O})_8]^{3+}$		13.3	18.4	-27.8	-6.9	<b>I<sub>a</sub></b>	262, 263
$[\text{Tm}(\text{H}_2\text{O})_8]^{3+}$		9.1	22.7	-16.4	-6.0	<b>I<sub>a</sub></b>	262, 263
$[\text{Yb}(\text{H}_2\text{O})_8]^{3+}$		4.7	23.3	-21.0			262, 263

<sup>a</sup> First-order rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> The value originally published for CN = 8 in ref 260 was corrected for CN = 7 in ref 4. <sup>c</sup> Units are as follows:  $r_M$ , pm;  $k_1(298\text{K})$ ,  $10^7 \text{ s}^{-1}$ ;  $\Delta H^{\ddagger}$ ,  $\text{kJ mol}^{-1}$ ;  $\Delta S^{\ddagger}$ ,  $\text{J K}^{-1} \text{ mol}^{-1}$ ;  $\Delta V^{\ddagger}$ ,  $\text{cm}^3 \text{ mol}^{-1}$ .

from the value of  $-12.9 \text{ cm}^3 \text{ mol}^{-1}$  calculated with Swaddle's semiempirical model for the reaction volume for  $\text{CN}8 \rightarrow \text{CN}9$  on lanthanides<sup>36</sup> (see dotted lines in Figure 9) and from the value of  $-11 \text{ cm}^3 \text{ mol}^{-1}$  measured by variable pressure UV-vis experiments on the equilibrium  $[\text{Ce}(\text{H}_2\text{O})_8]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Ce}(\text{H}_2\text{O})_9]^{3+}$ .<sup>257</sup> Therefore, an **I<sub>a</sub>** mechanism has been assigned for water exchange on  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$ . The increase of the exchange rate constants from  $\text{Yb}^{3+}$  up to  $\text{Gd}^{3+}$  is understandable: according to an **I<sub>a</sub>** mechanism, the transition state for water exchange is close to an ennea-coordinate  $\text{Ln}^{3+}$ , which is more and more favored for the larger ions (Table 15). The same increase is observed for the interchange rate constants,  $k_i$ , between an inner sphere water molecule and a  $\text{SO}_4^{2-}$  ion from the outer sphere.<sup>258</sup> For the light lanthanides, the kinetic effect is not sufficient to enable the determination of  $k_{\text{ex}}$  by  $^{17}\text{O}$  transverse NMR relaxation rate measurements at 9.4 T. For  $[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$  and  $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$ , which have the most favorable chemical shifts in the beginning of the lanthanide series, measurements at 14.1 T allowed the determination of lower limits of  $k_{\text{ex}}$  (see the arrows in Figure 9).<sup>259</sup> For the three other lighter paramagnetic lanthanides ions,  $\text{Ce}^{3+}$ ,  $\text{Pm}^{3+}$ , and  $\text{Sm}^{3+}$ , the kinetic effect and the chemical shifts are too small to enable the determination of the water exchange rate by  $^{17}\text{O}$  NMR relaxation rate measurements.

The eight- and nine-coordinate  $\text{Ln}^{3+}$  aqua ions adopt in aqueous solution a square antiprism geometry (SAP) and a tricapped trigonal prism geometry (TTP), respectively.<sup>250,264</sup> Consequently, the transition state,  $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ , in an **I<sub>a</sub>** water exchange mechanism on  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$  is proposed to have a TTP geometry, similar to the one observed in the solid state for the whole series. This leads to the possible mechanistic path for water exchange on  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$  illustrated in Figure 10. It can be well understood by taking the reverse case of an exchange on  $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$  (case of the early lanthanides) that the transition state should have a metal center with lower CN, like  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$ . In this latter case, the water exchange should proceed through an **I<sub>d</sub>** mech-





**Figure 10.** Possible mechanistic paths for water exchange on eight- and nine-coordinate lanthanides.

anism with a transition state that adopts SAP geometry. This change in mechanism has been supported by a computational study using classical molecular dynamics simulation.<sup>265</sup>

#### 4.1.2. Nonaqueous Solvents

The only nonaqueous solvents studied over the series on  $\text{Ln}^{3+}$  are DMF and TMU (Table 16). Exchange of DMF has been studied in neat solvent and in the diluent  $\text{CD}_3\text{NO}_2$ .<sup>266</sup> For the light lanthanides  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Nd}^{3+}$ , an equilibrium between eight- and nine-coordination is observed at low temperature.<sup>56</sup> The reaction volume for addition of a DMF molecule to  $[\text{Nd}(\text{DMF})_8]^{3+}$  was determined spectrophotometrically to be  $-9.8 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>56</sup> Kinetic parameters for DMF exchange were measured by  $^1\text{H}$  NMR for the heavier lanthanides from  $\text{Tb}^{3+}$  to  $\text{Yb}^{3+}$ .<sup>266</sup> The exchange process is characterized by a systematic increase of  $\Delta H^\ddagger$ , by a change from negative to positive  $\Delta S^\ddagger$ , and by positive  $\Delta V^\ddagger$  as the ionic radius decreases (Table 16). **d**-Activation has been assigned for these exchange processes with a mechanistic crossover from **I<sub>d</sub>** to limiting **D** at  $\text{Er}^{3+}$ .<sup>267</sup>

**Table 16.** Rate Constants and Activation Parameters for Nonaqueous Solvent Exchange on Trivalent Lanthanides<sup>d</sup>

$\text{M}^{3+}$	$r_{\text{M}}^a$	$k_1$ (298K) <sup>b</sup>	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	mech	ref
<b>[Ln(DMF)<sub>8</sub>]<sup>3+</sup></b>							
$\text{Tb}^{3+}$	104.0	$19 \times 10^6$	14.1	-58	+5.2	<b>I<sub>d</sub></b>	266
$\text{Dy}^{3+}$	102.7	$6.3 \times 10^6$	13.8	-69	+6.1	<b>I<sub>d</sub></b>	266
$\text{Ho}^{3+}$	101.5	$3.6 \times 10^6$	15.3	-68	+5.2	<b>I<sub>d</sub></b>	266
$\text{Er}^{3+}$	100.4	$13 \times 10^6$	23.6	-30	+5.4	<b>D</b> and <b>I<sub>d</sub></b>	266
$\text{Tm}^{3+}$	99.4	$31 \times 10^6$	33.2	+10	+7.4	<b>D</b>	266
$\text{Yb}^{3+}$	98.5	$99 \times 10^6$	39.3	+40	+11.8	<b>D</b>	266
<b>[Ln(DMSO)<sub>8</sub>]<sup>3+</sup></b>							
$\text{Gd}^{3+}$	105.3	$6.2 \times 10^6$	32.8	-4.7	+8.2	<b>I<sub>d</sub></b>	268
<b>[Ln(TMU)<sub>6</sub>]<sup>3+</sup> c</b>							
$\text{Tb}^{3+}$	92.3	1380	38.2	-56.7	-	<b>D</b>	269
$\text{Dy}^{3+}$	91.2	1290	38.6	-56.0	-	<b>D</b>	269
$\text{Ho}^{3+}$	90.1	510	40.9	-55.9	-	<b>D</b>	269
$\text{Y}^{3+}$	90.0	253	27.1	-108	-	<b>D</b>	270
$\text{Er}^{3+}$	89.0	214	35.5	-81.3	-	<b>D</b>	269
$\text{Tm}^{3+}$	88.0	145	29.3	-105	-	<b>D</b>	271
$\text{Yb}^{3+}$	86.8	65.5	38.3	-81.8	-	<b>D</b>	269
$\text{Lu}^{3+}$	86.1	41.9	41.7	-74	-	<b>D</b>	272
$\text{Sc}^{3+}$	74.5	0.90	68.6	-15.7	-	<b>D</b>	78

<sup>a</sup> Eight- and six-coordinate ionic radii from ref 38. <sup>b</sup> First-order rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>c</sup> In  $\text{CD}_3\text{CN}$  diluent. <sup>d</sup> Units are as follows:  $r_{\text{M}}$ , pm;  $k_1(298\text{K})$ ,  $10^7 \text{ s}^{-1}$ ;  $\Delta H^\ddagger$ ,  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$ ,  $\text{J K}^{-1} \text{ mol}^{-1}$ ;  $\Delta V^\ddagger$ ,  $\text{cm}^3 \text{ mol}^{-1}$ .

Exchange of TMU on  $[\text{Ln}(\text{TMU})_6]^{3+}$  has been studied in  $\text{CD}_3\text{CN}$  diluent, and  $k_{\text{ex}}$  was found to be independent of TMU concentration, consistent with the operation of a **D** mechanism (Table 16).<sup>78,269,270,272</sup> The decrease in coordination number results in a decrease in lability by several orders of magnitude.

Exchange of DMSO on lanthanides has only been studied on  $[\text{Gd}(\text{DMSO})_8]^{3+}$  so far (Table 16).<sup>268</sup> The rate constant measured is more than 2 orders of magnitude slower than that for water exchange. Comparison of the positive  $\Delta V^\ddagger$  measured on  $[\text{Gd}(\text{DMSO})_8]^{3+}$  with the negative one found for  $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$  shows that activation modes for solvent exchange are different: DMSO exchange follows a **d**-activation mode like that for DMF on  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  in contrast to  $\text{H}_2\text{O}$  exchange, which proceeds with an **a**-activation mode.

#### 4.2. Water Exchange on Trivalent Lanthanide Complexes

Studies of water exchange on lanthanide and especially on  $\text{Gd}^{3+}$  complexes with one to several  $\text{H}_2\text{O}$  molecules bound in the first coordination shell of the ion have become an important research issue in the past decade. Very stable complexes of  $\text{Gd}^{3+}$  with multidentate ligands are commonly used as contrast agents in medical magnetic resonance imaging (MRI), and optimizing water exchange on those complexes is a key to higher relaxivity agents.<sup>273</sup> Because these studies deal with solvent exchange on a metal ion, which is the subject of this review, we have included data on  $\text{H}_2\text{O}$  exchange on complexes of the form  $[\text{Ln}(\text{L})(\text{H}_2\text{O})_n]^{z+/}$  (Table 17).

Before discussing some general observations on lability and water exchange mechanisms on these complexes, we would like to comment on experimental determination of  $k_{\text{ex}}$  and its activation parameters. A direct way to determine water exchange rate constants as a function of temperature and pressure is  $^{17}\text{O}$  NMR.<sup>40</sup> Measuring the temperature dependence of the increase of transverse  $^{17}\text{O}$  NMR relaxation rates of bulk water,  $1/T_{2r}$ , induced by the presence of the paramagnetic complex  $[\text{Ln}(\text{L})(\text{H}_2\text{O})_n]^{z+/}$  gives access to  $k_{\text{ex}}$ .<sup>274</sup> For  $\text{Gd}^{3+}$  complexes such as  $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$ ,  $[\text{Gd}(\text{DTPA-BMA})(\text{H}_2\text{O})]$ , or  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ , several independent  $^{17}\text{O}$  NMR relaxation and chemical shift studies were performed showing that exchange rate constants can be determined with an accuracy of  $\pm 20\%$ . In the case of extremely fast water exchange processes with  $k_{\text{ex}} > 10^8 \text{ s}^{-1}$ , exchange rate constants can be determined if besides  $1/T_{2r}$  the chemical shift changes,  $\Delta\omega_r$ , of the bulk water  $^{17}\text{O}$  NMR signal are measured, which allows the determination of the scalar coupling constant  $A/\hbar$ .<sup>40</sup> The accuracy of  $k_{\text{ex}}$  measurement depends in this case on the difference between  $k_{\text{ex}}$  and the relaxation of the  $^{7/2}$  electron spin of  $\text{Gd}^{3+}$ .<sup>261</sup> In principle,  $^1\text{H}$  relaxation measured over a wide range of magnetic field, leading to nuclear magnetic relaxation dispersion (NMRD) profiles, is also influenced by water and/or water proton exchange.<sup>275,276</sup> Because  $^1\text{H}$  relaxation is enhanced not only via first shell water molecules but also by second shell and outer sphere relaxation, it is by far less reliable to

**Table 17. Effect of Spectator Ligands on the Rate Constants and Activation Parameters for Water Exchange on Gd<sup>3+</sup> and Eu<sup>2+</sup> Complexes**

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / 10 <sup>6</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
<b>Ln<sup>3+</sup></b>						
[Gd(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup>		830 <sup>b</sup>	14.9	-24.1	-3.3	261
		804 <sup>c</sup>	15.3	-23.1		277
		682 <sup>d</sup>	18.2	-30.0		278
<b>Acyclic ligands</b>						
[Gd(DTPA)(H <sub>2</sub> O)] <sup>2-</sup>		4.1 <sup>b</sup>	52.0	+56.2	+12.5	279
		3.3 <sup>c</sup>	51.6	+53		277
		4.0 <sup>d</sup>	52	+56 <sup>e</sup>		280
		3.1 <sup>f</sup>	51.5	+52.1		283,290
[Gd(DTPA-BA)(H <sub>2</sub> O)]		0.42	43.3	+8.2	+6.3	281
		R <sub>1</sub> = R <sub>2</sub> = H				
[Gd(DTPA-BMA)(H <sub>2</sub> O)]		0.43	46.6	+18.9	+7.3	282
		0.45 <sup>c</sup>	47.6	+23		277
		0.48 <sup>f</sup>	48	+24.9		290
		R <sub>1</sub> = CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BEA)(H <sub>2</sub> O)]		0.50	46.8	+21.2	+7.3	281
		R <sub>1</sub> = CH <sub>2</sub> CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BnPA)(H <sub>2</sub> O)]		0.55	47.2	+23.4		281
		R <sub>1</sub> = CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BnBA)(H <sub>2</sub> O)]		0.64	48.5	+29.2	+7.0	281
		R <sub>1</sub> = (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BAA)(H <sub>2</sub> O)]		0.79	48.4	+20.4	+7.1	281
		R <sub>1</sub> = (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BHA)(H <sub>2</sub> O)]		0.70	45.7	+20.5	+6.5	281
		R <sub>1</sub> = (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BHeptA)(H <sub>2</sub> O)]		0.71	45.7	+20.5		281
		R <sub>1</sub> = (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> ; R <sub>2</sub> = H				
[Gd(DTPA-BBMPA)(H <sub>2</sub> O)]		0.73	48.9	+31.5		281
		R <sub>1</sub> = CH <sub>3</sub> ; R <sub>2</sub> = CH <sub>3</sub>				
[Gd(DTPA-BBEA)(H <sub>2</sub> O)]		0.70	48.3	+29.2		281
		R <sub>1</sub> = CH <sub>2</sub> CH <sub>3</sub> ; R <sub>2</sub> = CH <sub>2</sub> CH <sub>3</sub>				
[Gd(DTPA-BBnPA)(H <sub>2</sub> O)]		0.75	42.3	+9.4		281
		R <sub>1</sub> = (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> ; R <sub>2</sub> = (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>				

Table 17 (Continued)

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / $10^6$ s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
[Gd(DTPA-BtBA)(H <sub>2</sub> O)]	 R <sub>1</sub> = t-But.; R <sub>2</sub> = H	0.65	52.6	+42.9		281
[Gd(DTPA-BiPA)(H <sub>2</sub> O)]	 R <sub>1</sub> = i-prop ; R <sub>2</sub> = H	0.74	44.2	+15.8		281
[Gd(DTPA-(R,S)BHPA)(H <sub>2</sub> O)]	 R <sub>1</sub> =  ; R <sub>2</sub> = H	0.44	43.2	+8.1		281
[Gd(DTPA-(BzA) <sub>2</sub> (H <sub>2</sub> O))]	 R <sub>1</sub> =  ; R <sub>2</sub> = H	1.7 <sup>f</sup>	40.6	+10.6		283
[Gd(DTPA-(BzE) <sub>2</sub> (H <sub>2</sub> O))]		3.2 <sup>f</sup>	53.4	+58.6		283
[Gd(BOPTA)(H <sub>2</sub> O)] <sup>2-</sup>		3.45				288
[Gd((S)-EOB-DTPA)(H <sub>2</sub> O)] <sup>2-</sup>		3.6 5.1 <sup>f</sup>	49.1 53.5	+45.2 +63	+12.3	289 283,290
[Gd(EOB-DTPA-BMA)(H <sub>2</sub> O)] <sup>2-</sup>		1.1	43.9	+17.6		290
[Gd((S)-C <sub>4</sub> -bz-DTPA)(H <sub>2</sub> O)] <sup>2-</sup>		5.3 <sup>f</sup>	50.1	+51.8		283
[Gd((R)-C <sub>4</sub> -bz-DTPA)(H <sub>2</sub> O)] <sup>2-</sup>		3.9 <sup>f</sup>	54.5	+64.4		283
[Gd(C <sub>4</sub> -bz-DTPA-BMA)(H <sub>2</sub> O)] <sup>2-</sup>		1.2	37.1	-3.54		290
[Gd(L)(H <sub>2</sub> O)] <sup>-</sup>		1.9	50.6	+40.2	+10.6	289
[Gd(L)(H <sub>2</sub> O)] <sup>-</sup>		1.3	48.6	+35.7	+12.7	289
[Gd(MP-2269)(H <sub>2</sub> O)] <sup>4-</sup>		4.20	51.6	55		292
[Gd(COPTA)(H <sub>2</sub> O)] <sup>2-</sup>		3.40				293
[Gd(DTPA-N-MA)(H <sub>2</sub> O)] <sup>-</sup>		1.30	48.6	36	+12.7	289

Table 17 (Continued)

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / 10 <sup>6</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
[Gd(DTPA-N'-MA)(H <sub>2</sub> O)] <sup>-</sup>		1.90	50.6	40	+10.6	289
[Gd(DTPA-BA)(H <sub>2</sub> O)(CH <sub>2</sub> ) <sub>n</sub> ] <sub>x</sub> n=6		0.43	50.2	32	+9.6	294
[Gd(DTPA-BA)(H <sub>2</sub> O)(CH <sub>2</sub> ) <sub>n</sub> ] <sub>x</sub> n=10		0.66	40.0	2		294
[Gd(DTPA-BA)(H <sub>2</sub> O)(CH <sub>2</sub> ) <sub>n</sub> ] <sub>x</sub> n=12		0.50	49.8	31		294
[Gd(DTPA-BA)(H <sub>2</sub> O)-PEG] <sub>x</sub>		0.48	47.0	22	+9.2	295
[Gd(DTPA-BMEA)(H <sub>2</sub> O)]		0.39	49.8	27	+7.4	296
[Gd(DTPA-BGLUCA)(H <sub>2</sub> O)]		0.38	47.6	22	+6.8	297
[Gd(DTPA-BENGALAA)(H <sub>2</sub> O)]		0.22	42.5	0	+5.6	297
[Gd(EGTA)(H <sub>2</sub> O)] <sup>-</sup>		31	42.7	42	+10.5	298
[Gd(EPTPA)(H <sub>2</sub> O)] <sup>2-</sup>		330	22.1	-9.1	+6.6	285
		94.3				299
[Gd((S)-4-bz-EPTPA)(H <sub>2</sub> O)] <sup>2-</sup>		435				287
[Gd(EPTPA-bz-NO <sub>2</sub> )(H <sub>2</sub> O)] <sup>2-</sup> diastereomer A		150	27.9	+11.0		285
diastereomer B		140				286
		260				286
[Gd(EPTPA-bz-NH <sub>2</sub> )(H <sub>2</sub> O)] <sup>2-</sup> diastereomer A		198				286
diastereomer B		180				286
		440				286
[Gd(EPDPA-PY)(H <sub>2</sub> O)] <sup>2-</sup>		80.0				299
[Gd(EPDPA-HP)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		149				299
[Gd(EPDPA-H1P)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		141				299
[Gd(EPDPA-H2P)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		110				299
[Gd(DTTA-prop)(H <sub>2</sub> O)] <sup>2-</sup>		31	30.8	+2.0		285



Table 17 (Continued)

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / 10 <sup>6</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
[Gd(H-TTAHA)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2-</sup>		8.6	40.4	23	+2.9	300
[Gd(PDTA)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		102	11.0	-54.6	-1.5	261
[Gd(tris(2-hydroxymethyl)-TREN-Me-2,3-HOPO)(H <sub>2</sub> O) <sub>2</sub> ]		62.5	2.6			301
[Gd(TREN-HOPO-TAM)(H <sub>2</sub> O) <sub>2</sub> ]		130				302
[Gd(TREN-HOPO-TAM-PEG-2000)(H <sub>2</sub> O)]		53				302
[Gd(TREN-HOPO-TAM-PEG-5000)(H <sub>2</sub> O)]		32				302
[Gd(TREN-bis(6-Me-HOPO)-TAM-TRI(H <sub>2</sub> O) <sub>2</sub> )]		53	25.9		-5	303
[Gd(TREN-Me <sub>2</sub> -5,4-HOPY)(H <sub>2</sub> O) <sub>2</sub> ]		490	1.0			304
[Gd(L)(H <sub>2</sub> O)]		5.0	40.1	17.8		305
[Gd <sub>2</sub> (pi(DTTA) <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		1.1	45.0			291
[Gd <sub>3</sub> (H <sub>3</sub> taci) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>		11.0	59.8	-89	-12.7	306
[Nd(DTPA-BMA)(H <sub>2</sub> O)]		0.53	43.4	+10.2	-0.8	284
[Eu(DTPA-BMA)(H <sub>2</sub> O)]		0.66	49.2	+31.5	+8.5	284

Table 17 (Continued)

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / 10 <sup>6</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
[Gd(DTPA-BMA)(H <sub>2</sub> O)]	$R_1 = \text{CH}_3; R_2 = \text{H}$ 	0.43	46.6	+18.9	+7.3	282
		0.45 <sup>c</sup>	47.6	+23		277
	$R_1 = \text{CH}_3; R_2 = \text{H}$ 	0.48 <sup>f</sup>	48	+24.9		290
[Tb(DTPA-BMA)(H <sub>2</sub> O)]	$R_1 = \text{CH}_3; R_2 = \text{H}$ 	1.61	50.3	42.6	+9.8	284
[Dy(DTPA-BMA)(H <sub>2</sub> O)]	$R_1 = \text{CH}_3; R_2 = \text{H}$ 	3.53	48.9	44.4	+7.3	284
[Ho(DTPA-BMA)(H <sub>2</sub> O)]	$R_1 = \text{CH}_3; R_2 = \text{H}$ 	5.98	54.2	66.6	+9.4	284
<b>Cyclic ligands</b>						
[Gd(DOTA)(H <sub>2</sub> O)] <sup>-</sup>		4.8 <sup>b</sup>	48.8	+46.6	+10.5	279
		4.1 <sup>c</sup>	49.8	+48.5		277
		5.4 (M) / 500 (m) <sup>d</sup>	55 / 50			280
[Gd(DO2A)(H <sub>2</sub> O) <sub>3</sub> ] <sup>-</sup>		10	21.3	-39		307
[Gd(DO3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		11	33.6	+2.4		308
[Gd(THP)(H <sub>2</sub> O)] <sup>-</sup>		18.9				309
[Gd(L)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		0.66	17	-92 <sup>e</sup>		310
[Gd(L)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		1.7	11	-104 <sup>e</sup>		310
[Gd(L)(H <sub>2</sub> O)]		5.56	44.0	+17		311
[Gd(L)(H <sub>2</sub> O)]	$n=2; R=n\text{-C}_4\text{H}_9$ 	4.63	49.0	+32		311
[Gd(L)(H <sub>2</sub> O)]	$n=6; R= \text{CH}_3$ 	2.00	50.1	+28		311
[Gd(L)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		1.30	56.0	+45		311

Table 17 (Continued)

complex	ligand in protonated form	$k_1(298\text{K})^a$ / $10^6 \text{ s}^{-1}$	$\Delta H^\ddagger$ /kJ $\text{mol}^{-1}$	$\Delta S^\ddagger$ /J $\text{K}^{-1}$ $\text{mol}^{-1}$	$\Delta V^\ddagger$ / $\text{cm}^3$ $\text{mol}^{-1}$	ref
[Gd(L)(H <sub>2</sub> O) <sub>2</sub> ]		55.56	40.8	+25		311
[Gd(L)(H <sub>2</sub> O)]		110	21			312
[Gd(TRITA)(H <sub>2</sub> O)] <sup>-</sup>		270	17.5	-25	-1.5	285,313
[Gd(TRITA-bz-NO <sub>2</sub> )(H <sub>2</sub> O)] <sup>-</sup>		120	35.5	+20		313
[Gd(NO <sub>2</sub> PhDO3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		7.4	33.8			314
[Gd(NH <sub>2</sub> PhDO3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>		17.6	36.2			314
[Gd(p-NO <sub>2</sub> -Bn-DOTA)S-RRRR-1)(H <sub>2</sub> O)] <sup>-</sup>		8.3				315
[Gd(p-NO <sub>2</sub> -Bn-DOTA)(S-SSSS-1)(H <sub>2</sub> O)] <sup>-</sup>		67				315
[Gd(DOTASA)(H <sub>2</sub> O)] <sup>-</sup>		6.3	45.5	38		316
[Gd(DO3A-bz-NO <sub>2</sub> )(H <sub>2</sub> O)] <sup>-</sup>		1.6	40.9	11	7.7	317
[G3(N{CS}N-bz-Gd{DO3A}{H <sub>2</sub> O}) <sub>23</sub> ]		1.0	28.8	-30		317
[G4(N{CS}N-bz-Gd{DO3A}{H <sub>2</sub> O}) <sub>30</sub> ]		1.3	27.7	-31		317
[G5(N{CS}N-bz-Gd{DO3A}{H <sub>2</sub> O}) <sub>52</sub> ]		1.5	24.0	-43		317
[Gd(DOTASA-C <sub>18</sub> )(H <sub>2</sub> O)] <sup>-</sup> monomer		4.8	42.7	+27		318
[Gd(DOTASA-C <sub>18</sub> )(H <sub>2</sub> O)] <sup>-</sup> (micelle)		4.8	45.5	+35.4		319

Table 17 (Continued)

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / 10 <sup>6</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
[Gd(DOTA-C <sub>10</sub> )(H <sub>2</sub> O)] <sup>-</sup> (micelle)		4.9	49	+45		319
[Gd(DOTA-C <sub>12</sub> )(H <sub>2</sub> O)] <sup>-</sup> (micelle)		4.9	52	+67		319
[Gd(DOTA-C <sub>14</sub> )(H <sub>2</sub> O)] <sup>-</sup> (micelle)		4.9	48.9	+47.5		319
Gadomer-17		1.0	24.7	-47.4		320
[Gd(DOTTA)(H <sub>2</sub> O)]		0.128				321
[Gd(DTMA)(H <sub>2</sub> O)]		0.059				321
[Gd(BO(DO3A)(H <sub>2</sub> O)) <sub>2</sub> ] <sup>-</sup>		1.0	30.0	-29	0.5	324
[Gd <sub>2</sub> (pip(DO3A) <sub>2</sub> (H <sub>2</sub> O)) <sub>2</sub> ] <sup>-</sup>		1.5	34.2	-12		277
[Gd <sub>2</sub> (bisoxa(DO3A) <sub>2</sub> (H <sub>2</sub> O)) <sub>2</sub> ] <sup>-</sup>		1.4	38.5	+2	2.3	277
[Gd <sub>2</sub> (en(DO3A) <sub>2</sub> (H <sub>2</sub> O)) <sub>2</sub> ] <sup>-</sup>		1.3	35.2			291
[Gd(DOTMA)(H <sub>2</sub> O)]		15				325
[Gd((RRRR)-L)(H <sub>2</sub> O)]		14.7	73	+137 <sup>e</sup>		325
[Gd((RSRS)-L)(H <sub>2</sub> O)]		7.1	66	+108 <sup>e</sup>		325



Table 17 (Continued)

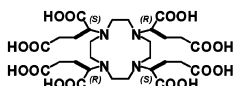
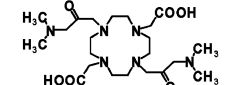
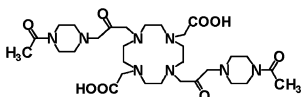
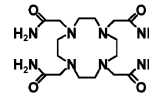
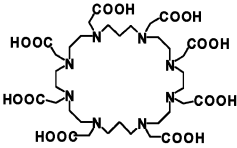
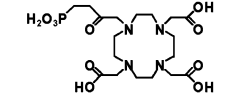
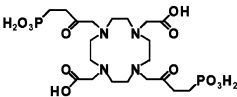
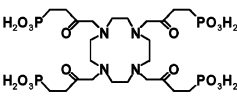
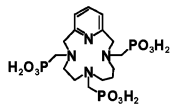
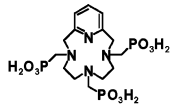
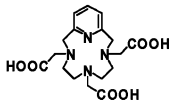
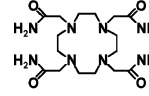
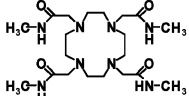
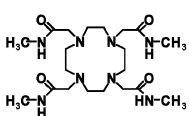
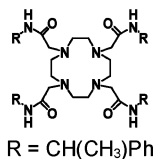
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[Gd((RSRS)-L)(H <sub>2</sub> O)] <sup>-</sup>		3.7	64	+96 <sup>e</sup>		325
[Gd(DOTA-2DMA)(H <sub>2</sub> O)] <sup>+</sup>		0.74 (M) / 70 (m)				326
[Gd(DOTA-2APA)(H <sub>2</sub> O)] <sup>+</sup>		0.43 (M) / 330 (m)				326
[Gd(DOTAM)(H <sub>2</sub> O)] <sup>3+</sup>		0.05				321
[Gd <sub>2</sub> (OHEC)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2-</sup>		0.40	30.9	-34	+7.3	331
[Gd(DOTA-1AmP)(H <sub>2</sub> O)] <sup>2-</sup>		0.77 (M)	329			332
[Gd(DOTA-2AmP)(H <sub>2</sub> O)] <sup>3-</sup>		0.16 (M)				332
[Gd(DOTA-4AmP)(H <sub>2</sub> O)] <sup>5-</sup>		0.04 (M)				332
[Gd(PCTP-13)(H <sub>2</sub> O)] <sup>3+</sup>		125	58	105		333
[Gd(PCTP-12)(H <sub>2</sub> O)] <sup>3+</sup>		170	14	-40		334
[Gd(PCTA-12)(H <sub>2</sub> O) <sub>2</sub> ]		14	45	43		334
[Eu(DOTAM)(H <sub>2</sub> O)] <sup>3+</sup> <sup>i</sup>		0.008 (M) 0.33 (m)	53.1 44.2	+8.4 +8.8	+4.9 -	327
[Eu(DOTMA)(H <sub>2</sub> O)] <sup>3+</sup> <sup>i</sup>		0.008 (M) 0.33 (m)	59.7 46.7	+30.3 +18.0	+6.9 -	328
[Eu(DOTMA)(H <sub>2</sub> O)] <sup>3+</sup> <sup>i</sup>		0.008 (M) 0.33 (m)	59.7 / 46.7	+30.3 +18.0	+6.9 -	328
[Eu(L)(H <sub>2</sub> O)] <sup>3+</sup> <sup>k</sup>		0.0036 (M)				329

Table 17 (Continued)

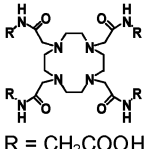
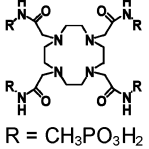
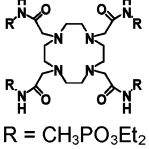
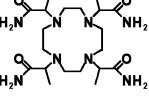
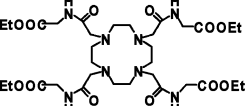
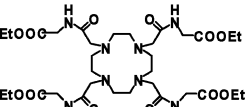
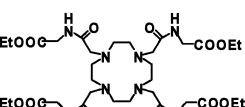
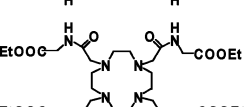
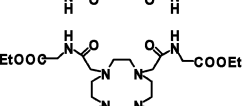
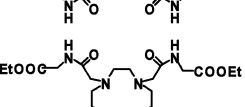
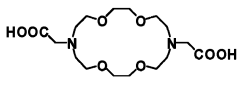
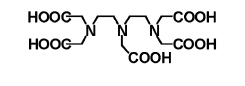
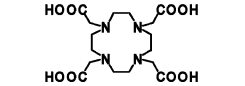
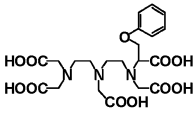
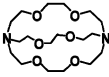
complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / $10^6 \text{ s}^{-1}$	$\Delta H^\ddagger$ /kJ $\text{mol}^{-1}$	$\Delta S^\ddagger$ /J $\text{K}^{-1}$ $\text{mol}^{-1}$	$\Delta V^\ddagger$ / $\text{cm}^3$ $\text{mol}^{-1}$	ref
[Eu(DOTAM-Gly)(H <sub>2</sub> O)] <sup>-</sup>	 R = CH <sub>2</sub> COOH	0.025 (M)				330
[Eu(L)(H <sub>2</sub> O)] <sup>-</sup>	 R = CH <sub>3</sub> PO <sub>3</sub> H <sub>2</sub>	0.015 (M)				323
[Eu(L)(H <sub>2</sub> O)] <sup>-k</sup>	 R = CH <sub>3</sub> PO <sub>3</sub> Et <sub>2</sub>	$7.7 \times 10^{-4}$ (M)				323
[Eu(DOTMAM)(H <sub>2</sub> O)] <sup>3+ k</sup>		0.011 (M) - (m)	57.2 / - - (m)	+24.4 -		328
[Pr(L)(H <sub>2</sub> O)] <sup>3+</sup>		0.022 <sup>g</sup>	36	-39		322
[Nd(L)(H <sub>2</sub> O)] <sup>3+</sup>		0.0059 <sup>g</sup>	48	+1		322
[Sm(L)(H <sub>2</sub> O)] <sup>3+</sup>		0.0015 <sup>g</sup>	45	-12		322
[Eu(L)(H <sub>2</sub> O)] <sup>3+</sup>		0.0013 <sup>g</sup> 0.0026 <sup>h</sup>	62	+47		322 323
[Y(L)(H <sub>2</sub> O)] <sup>3+</sup>		0.017 <sup>g</sup>	46	-5		322
[Er(L)(H <sub>2</sub> O)] <sup>3+</sup>		0.056 <sup>g</sup>	31	-56		322
[Eu(H <sub>2</sub> O) <sub>7</sub> ] <sup>2+</sup>	<b>Ln<sup>2+</sup></b>	5'000 <sup>m</sup>	15.7	-7.0	-11.3	3,4,260
[Eu(ODDA)(H <sub>2</sub> O)]		430	22.5	-4.0	-3.9	335
[Eu(DTPA)(H <sub>2</sub> O)] <sup>3-</sup>		1300 1250	26.3	+18.3	+4.5	336 337
[Eu(DOTA)(H <sub>2</sub> O)] <sup>2-</sup>		2'460	21.4	+6.9	+0.1	335

Table 17 (Continued)

complex	ligand in protonated form	$k_1$ (298K) <sup>a</sup> / $10^6$ s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ /cm <sup>3</sup> mol <sup>-1</sup>	ref
[Eu(BOPTA)(H <sub>2</sub> O)] <sup>3-</sup>		1250				337
[Eu(2.2.2)(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>		310	30.6	+20.5	+1	338

<sup>a</sup> First-order rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Analysis of <sup>17</sup>O NMR data only. <sup>c</sup> Combined analysis of EPR and <sup>1</sup>H and <sup>17</sup>O NMR data (Solomon–Bloembergen–Morgan theory<sup>277</sup>). <sup>d</sup> Combined analysis of EPR and <sup>1</sup>H and <sup>17</sup>O NMR data (EPR relaxation following Rast et al.<sup>339,340</sup>). <sup>e</sup> Calculated from  $k^{298}$  and  $\Delta H^\ddagger$ . <sup>f</sup> Calculated from  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . <sup>g</sup> From <sup>17</sup>O relaxation in CH<sub>3</sub>CN solution. <sup>h</sup> From <sup>17</sup>O relaxation in H<sub>2</sub>O solution. <sup>i</sup> From combined <sup>17</sup>O and <sup>1</sup>H NMR analysis in CD<sub>3</sub>CN solution. <sup>k</sup> From <sup>1</sup>H NMR in CD<sub>3</sub>CN solution. <sup>m</sup> The value originally published for CN = 8 in ref 260 was corrected for CN = 7 in ref 4.

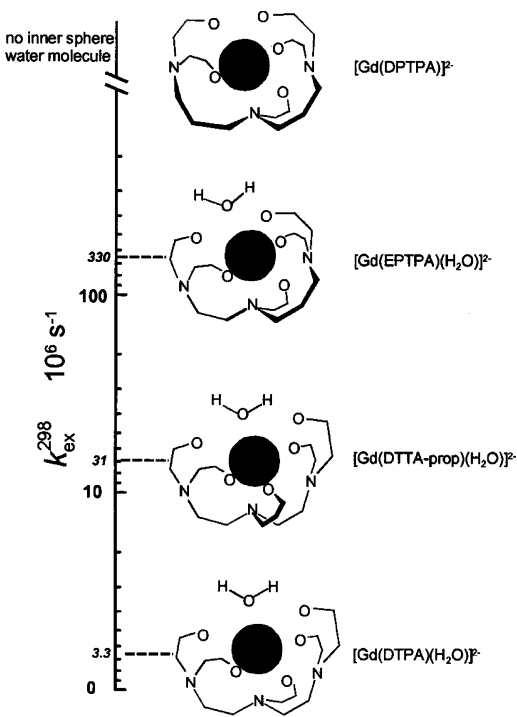
extract exchange rate constants from NMRD profiles than from <sup>17</sup>O relaxation. Therefore, we report in Table 17 data from <sup>17</sup>O NMR studies or from combined analysis of <sup>17</sup>O NMR, <sup>1</sup>H NMRD, and, eventually, EPR studies.

Water exchange rate constants reported for different Gd<sup>3+</sup> complexes cover a range of more than 5 orders of magnitude, from the lowest for [Gd(DOTA-4AmP)(H<sub>2</sub>O)]<sup>5-</sup> ( $k_{\text{ex}} = 4 \times 10^3$  s<sup>-1</sup>)<sup>332</sup> to the highest ( $k_{\text{ex}} = 8 \times 10^8$  s<sup>-1</sup>)<sup>261,277</sup> for the aqua ion itself. When the first water exchange rate constants on Gd<sup>3+</sup> polyaminocarboxylate complexes were measured, it was a great surprise that they were much slower than those on [Gd(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>. For complexes with one water molecule in the first coordination shell, the exchange reaction proceeds, if the ligand is octadentate, through a **d**-activated mechanism, leading to a positive activation volume (Table 17). The mostly observed nine-coordinate geometry does not allow the transition state to accommodate a ten-coordinate geometry due to steric constraints: the coordination cage formed by the polyaminocarboxylate ligands renders the first shell of Gd<sup>3+</sup> very rigid. This is not in favor of rearrangements around the metal center on going to the transition state, as is possible for the aqua ion, for example. Since there is no possibility for an incoming water molecule to help break the bond between the leaving water molecule and the trivalent metal center, the activation energy barrier is high and reduces the water exchange rate constant of polyaminocarboxylate complexes compared to the one on [Gd(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> up to 1 to 4 orders of magnitude.

Steric crowding is an important issue to influence the water exchange rate on polyaminocarboxylate complexes of Gd<sup>3+</sup>, as can be seen from modifications of the commercial acyclic DTPA and cyclic DOTA ligands. Addition of one more CH<sub>2</sub> group, in the macrocyclic or linear amine backbone, to give respectively the TRITA or the EPTPA, generates Gd<sup>3+</sup> complexes with significantly faster water exchange.<sup>285</sup> For the cyclic TRITA, the steric compression also increases the distance between the plane of the carboxylate oxygens and the metal (83 pm in [Gd(TRITA)(H<sub>2</sub>O)]<sup>-</sup> versus 70 pm in [Gd(DOTA)(H<sub>2</sub>O)]<sup>-</sup>). Since the Gd–O<sub>water</sub> distance is similar in

the two complexes (248 pm in TRITA and 245 pm in DOTA), the final result is that the bound water molecule in [Gd(TRITA)(H<sub>2</sub>O)]<sup>-</sup> is much closer to the negatively charged carboxylates, which also facilitates its departure.<sup>285</sup> The water exchange mechanisms assigned from the measured activation volumes are dissociative interchange **I<sub>d</sub>** for [Gd(EPTPA)(H<sub>2</sub>O)]<sup>2-</sup> and interchange **I** for [Gd(TRITA)(H<sub>2</sub>O)]<sup>-</sup>. For the latter there is a strong participation of the incoming water in the rate-determining step which, in addition to the repulsive effect of the close carboxylates on the bound water, contributes to the increase of the water exchange rate. DTTA-prop<sup>5-</sup>, which has an additional CH<sub>2</sub> group on the central acetate, has also been studied. Water exchange on [Gd(DTTA-prop)(H<sub>2</sub>O)]<sup>2-</sup> is 1 order of magnitude faster than that on [Gd(DTPA)(H<sub>2</sub>O)]<sup>2-</sup> but 1 order of magnitude slower than that for [Gd(EPTPA)(H<sub>2</sub>O)]<sup>2-</sup>.<sup>285</sup> This implies that elongation of the amine backbone is more effective to produce a crowding effect on the metal than the elongation of the acetate arms. Adding two CH<sub>2</sub> groups on the backbone of DTPA,<sup>5-</sup> leading to the ligand DTPA<sup>5-</sup>, results in the elimination of the water molecule from the inner sphere (see Figure 11).

While the water exchange rate is strongly affected when coordinating groups or the overall charges are changed, it remains relatively constant on introducing different substituents which do not directly interfere in the inner coordination shell. Very similar rates have been reported for the different bisamide DTPA derivatives DTPA-BA, DTPA-BMA, DTPA-BEA, etc.<sup>281,282,296,297</sup> Likewise, even bulky substituents on the carbon backbone of the DTPA have almost no influence on the water exchange kinetics:  $k_{\text{ex}}$  is similar for the Gd<sup>3+</sup> complexes of DTPA, EOB-DTPA, COPTA, and MP-2269.<sup>279,289,293,341</sup> Therefore, forming dimeric or multimeric species from the same chelating unit does in general not influence to a great extent the lability of bound water molecules.<sup>274</sup> For example,  $k_{\text{ex}}$  values measured on dimers formed with the chelating unit DO3A are, within <10%, the same as that of the monomer [Gd(DO3A-bz-NO<sub>2</sub>)(H<sub>2</sub>O)].<sup>277</sup> Dendrimers based on the same chelating unit DO3A-bz-NO<sub>2</sub> having between 23 and 52 Gd<sup>3+</sup> ions bound



**Figure 11.** Schematic representation of the influence on water exchange rate (at 298.15 K) of the crowding effect around the metal due to the elongation of the acetate arm or the amine backbone of DTPA<sup>5-</sup>.

to their surface, depending on the generation of the dendrimer, also exchange bound water molecules with  $(1.0\text{--}1.6) \times 10^6 \text{ s}^{-1}$ , which is very close to the value measured for the monomer ( $1.6 \times 10^6 \text{ s}^{-1}$ ).<sup>317</sup>

Gadolinium polyaminocarboxylate chelates exist in aqueous solution as a mixture of geometric isomers. In the case of macrocyclic ligands derived from cyclen, two isomers are found: a minor one called *m* (twisted antiprismatic geometry) and a major one called *M* (antiprismatic geometry).<sup>321,325–327</sup> Water exchange rate constants could be measured on both isomers of DOTA-tetraamides and were found to be much larger for the *m* isomer and independent of the ligand within the family of DOTA-tetraamides studied.<sup>328</sup>

Complexes with two water molecules in the first coordination shell,  $q = 2$ , such as  $[\text{Gd}(\text{PDTA})(\text{H}_2\text{O})_2]^-$ ,<sup>261</sup>  $[\text{Gd}(\text{DO3A})(\text{H}_2\text{O})_2]$ ,<sup>308</sup> or  $[\text{Gd}(\text{TREN})\text{-bis}(6\text{-Me-HOPO})\text{-(TAM-TRI)}(\text{H}_2\text{O})_2]^-$ ,<sup>303</sup> can have faster water exchange than those with  $q = 1$ . This is observed for the PDTA and TREN-bis(6-Me-HOPO)-(TAM-TRI) complexes. Activation volumes measured for water exchange on those compounds are negative, indicating an **a**-activated mechanism with a lower energy barrier compared to that for dissociation of  $\text{H}_2\text{O}$ . The value of  $k_{\text{ex}}$  for water exchange on the macrocyclic DO3A complex is, however, only twice as much as that for exchange on  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ . This is commonly explained by the much more rigid structure of the macrocyclid ligand DO3A if compared, for example, to the acyclic PDTA. On the dimeric compound  $[\text{Gd}_2(\text{bisoxa})(\text{DO3A})_2(\text{H}_2\text{O})_2]$  formed from two DO3A subunits, a positive  $\Delta V^\ddagger$  has been measured,<sup>277</sup> illustrating that the rigidity of the chelating unit does not allow substantial participation of an incoming water molecule in the exchange process.

As for aqua ions of lanthanide ions, water exchange on polyaminocarboxylate complexes varies across the lanthanide series. Increasing water exchange rates have been reported for  $[\text{Ln}(\text{DTPA-BMA})(\text{H}_2\text{O})]$  from  $\text{Ln} = \text{Nd}$  to  $\text{Ho}$  (Table 17).<sup>282,284</sup> The measured  $\Delta V^\ddagger$  revealed a change in mechanism for the water exchange reaction from an associative interchange **I<sub>a</sub>** to a dissociative **I<sub>d</sub>** mechanism. A strong change in lability of the bound water molecule along the  $\text{Ln}^{3+}$  series was also observed for complexes of DOTA-tetraamide ligands.<sup>322</sup>

### 4.3. Solvent Exchange on Divalent Lanthanide Ions and Divalent Lanthanide Complexes

Up to now,  $\text{Eu}^{2+}$  is the only divalent aqua ion studied kinetically in solution. The main interest for studying this redox instable ion comes from its potential use as a “smart” contrast agent for MRI. It is relatively stable in oxygen-free solutions, and it is isoelectronic to  $\text{Gd}^{3+}$ .<sup>342</sup> The goal of the research is to synthesize complexes of  $\text{Eu}^{2+}$  which are thermodynamically stable in the divalent and in the trivalent states in order to have a contrast agent responsive to local  $\text{O}_2$  concentration, for example. The coordination number in solution of the aqua complex has been determined to be 7.2 by EXAFS.<sup>4</sup> Water exchange on  $[\text{Eu}(\text{H}_2\text{O})_7]^{2+}$  is faster than that on  $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$  and is the fastest ever directly measured by  $^{17}\text{O}$  NMR (Table 15).<sup>3,260</sup> The value of  $-11.3 \text{ cm}^3 \text{ mol}^{-1}$  measured for  $\Delta V^\ddagger$  is more negative than those determined on trivalent lanthanide aqua ions. This clearly indicates an **a**-activated exchange process with most probably a limiting **A** mechanism. The coordination number of 7.2 indicates an equilibrium between a predominant  $[\text{Eu}(\text{H}_2\text{O})_7]^{2+}$  and a minor  $[\text{Eu}(\text{H}_2\text{O})_8]^{2+}$  species.<sup>4</sup> The presence of such an equilibrium at room temperature indicates that the energy barrier for the water exchange reaction on the major seven-coordinate species is low and the water exchange reaction is very fast.

Complexes of  $\text{Eu}^{2+}$  are normally less redox stable than the aqua ion. Measurements of the redox potentials show that the macrocyclic  $[\text{Eu}(\text{ODDA})(\text{H}_2\text{O})]$ ,  $[\text{Eu}(\text{ODDM})(\text{H}_2\text{O})]^{2-}$ , and  $[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]^{2-}$  complexes are more redox stable than the acyclic  $[\text{Eu}(\text{DTPA})(\text{H}_2\text{O})]^{3-}$ .<sup>342</sup> The  $\text{Eu}^{2+}$  complexes of the macrobicyclic cryptand (2.2.2) are even more stable than the aqua ion.<sup>343</sup> As a consequence of the lower charge and the larger ionic radius of  $\text{Eu}^{2+}$  compared to  $\text{Gd}^{3+}$ , the water exchange constants on  $\text{Eu}^{2+}$  polyaminocarboxylate complexes are of the same order of magnitude as that of  $[\text{Eu}(\text{H}_2\text{O})_7]^{2+}$ . For  $[\text{Eu}(\text{DTPA})(\text{H}_2\text{O})]^{3-}$ , the  $k_{\text{ex}}(298\text{K})$  value is only reduced by a factor of 4,<sup>336</sup> and the water exchange rate on  $[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]^{2-}$  is the highest among all the  $\text{Eu}^{2+}$  complexes and is just about half of the water exchange rate on  $[\text{Eu}(\text{H}_2\text{O})_7]^{2+}$  (Table 17).<sup>344</sup>

The activation mode for water exchange on  $\text{Eu}^{2+}$  chelates depends on the macrocyclic ligand. From the smaller activation volume it was concluded that water exchange on  $[\text{Eu}(\text{DTPA})(\text{H}_2\text{O})]^{3-}$  ( $\Delta V^\ddagger = +4.5 \text{ cm}^3 \text{ mol}^{-1}$ ) proceeds according to an **I<sub>d</sub>** mechanism as compared to a **D** mechanism for  $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$  ( $\Delta V^\ddagger = +12.5 \text{ cm}^3 \text{ mol}^{-1}$ ). This reveals less steric



crowding around the larger and divalent  $\text{Eu}^{2+}$ . The value of  $\Delta V^\ddagger$  measured for water exchange on the 18-membered macrocyclic  $[\text{Eu}(\text{ODDA})(\text{H}_2\text{O})]^{335}$  is slightly negative, and an  $\text{I}_a$  mechanism was assigned (Table 17). The  $[\text{Eu}(\text{ODDA})(\text{H}_2\text{O})]$  complex is peculiar: from analogy to the crystal structure of the corresponding  $\text{Sr}^{2+}$  complex, it is assumed that coordination of the water molecule and the carboxylate groups occurs at opposite sides of the molecule.<sup>335</sup> The water coordinating site, located at the hydrophobic side, is therefore much more open in the  $\text{ODDA}^{2-}$  than in the  $\text{DTPA}^{5-}$  complex, for example. It can therefore accommodate a second water molecule in the inner shell without the preceding departure of the leaving water molecule.

In the cryptate  $[\text{Eu}(2.2.2)(\text{H}_2\text{O})_2]^{2+}$ , the encapsulated metal ion is 10 coordinate and has two inner shell water molecules.<sup>338,344</sup> The exchange rate constant is the lowest of all  $\text{Eu}^{2+}$  chelates measured so far, which is probably due to the positive charge. The value of  $\Delta V^\ddagger$  is close to zero (Table 17), and therefore, an  $\text{I}$  mechanism was assigned for the water exchange process.

#### 4.4. Actinides

Compared to water exchange studies on the lanthanide series, equivalent studies on actinide ions are very scarce. The most studied cation, which is also the most easy to manipulate, is  $\text{UO}_2^{2+}$ . Water exchange on the diamagnetic  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ , which has  $D_{5h}$  geometry, was studied by  $^{17}\text{O}$  NMR using  $\text{Tb}^{3+}$  as chemical shift reagent (Table 18).<sup>345</sup> An  $\text{I}_d$  mechanism was proposed for the water exchange process from comparison of experimental data with quantum chemical calculations. However, Vallet et al. assigned from pure quantum mechanical results an  $\text{I}$  or  $\text{A}$  mechanism for water exchange on  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ .<sup>346</sup> In the same paper an  $\text{A}$  mechanism was assigned to water exchange on  $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ . The geometries calculated for  $\text{A}$  and  $\text{I}$  mechanisms on

**Table 18. Rate Constants and Activation Parameters for Water Exchange on Actinides or Actinyl Aqua Ions<sup>g</sup>**

complex	$k_1(298\text{K})^a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	mech	ref
$[\text{Th}(\text{H}_2\text{O})_{10}]^{4+}$	$>5 \times 10^7$				348
$[\text{Th}(\text{H}_2\text{O})_9]^{4+}$	$2.4 \times 10^9$				349
	(2nd sphere)				
$[\text{U}(\text{H}_2\text{O})_{10}]^{4+}$	$\sim 5 \times 10^6$	$\sim 35$	$\sim 0$		348
$[\text{U}(\text{F})(\text{H}_2\text{O})_9]^{4+}$	$5 \times 10^6$	36	+2.5		348
$[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$	$1.4 \times 10^6$	38	-12		350
	$1.3 \times 10^6$	26.1	-40	$\text{I}$ or $\text{A}^f$	345
$[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$	$11.8 \times 10^3$ <sup>b</sup>	32	-60		347
	$460 \times 10^3$ <sup>c</sup>	31.7	-30		347
$[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$				$\text{A}^f$	346
$[\text{UO}_2(\text{C}_2\text{O}_4)(\text{F})(\text{H}_2\text{O})_2]^-$	$1.8 \times 10^4$	45.4	-11.3		345
$[\text{NpO}_2(\text{H}_2\text{O})_5]^{2+}$	$5.3 \times 10^6$ <sup>d</sup>	20.2	-72		347
$[\text{PuO}_2(\text{H}_2\text{O})_n]^{2+}$	$5.7 \times 10^4$ <sup>e</sup>	12	-115		347

<sup>a</sup> First-order rate constant for the exchange of a particular coordinated solvent molecule.<sup>5</sup> <sup>b</sup> Solution composition:  $\text{MO}_2^{2+}/\text{H}^+/\text{H}_2\text{O}/\text{acetone} = 1/0.57/69.1/177.9$ . <sup>c</sup> Solution composition:  $\text{MO}_2^{2+}/\text{H}^+/\text{H}_2\text{O}/\text{acetone} = 1/4.1/86.9/161.6$ . <sup>d</sup> Solution composition:  $\text{MO}_2^{2+}/\text{H}^+/\text{H}_2\text{O}/\text{acetone} = 1/3.8/78.7/153.4$ . <sup>e</sup> Solution composition:  $\text{MO}_2^{2+}/\text{H}^+/\text{H}_2\text{O}/\text{acetone} = 1/2.2/67.3/174.7$ . <sup>f</sup> By quantum chemical methods. <sup>g</sup> Units are as follows:  $k_1(298\text{K})$ ,  $10^7 \text{ s}^{-1}$ ;  $\Delta H^\ddagger$ ,  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$ ,  $\text{J K}^{-1} \text{ mol}^{-1}$ .

$[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$  and on  $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$  indicate that the entering and the leaving water molecules are located outside the pentagonal plane formed by the spectator ligands.<sup>346</sup> In Table 18 water exchange rate constants measured on  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ ,  $[\text{NpO}_2(\text{H}_2\text{O})_5]^{2+}$ , and  $[\text{PuO}_2(\text{H}_2\text{O})_5]^{2+}$  in  $\text{H}_2\text{O}/\text{acetone}$  mixtures at low temperature and extrapolated to 298 K on are given.<sup>347</sup> As the  $\Delta S^\ddagger$  values become more negative with increasing atomic number, a mechanism with more pronounced associative character was proposed for the compounds with heavier metal centers.

For the tetravalent  $\text{U}^{4+}$  and  $\text{Th}^{4+}$ , the first experimental kinetic studies on water exchange have been conducted recently.<sup>345,348,349</sup> The coordination numbers for these two complexes were determined by EXAFS as  $\text{CN} = 10 \pm 1$ .<sup>351</sup> On the basis of the high coordination number (there are no complexes known with unidentate ligands and coordination numbers larger than 10), a limiting associative mechanism ( $\text{A}$ ) is unlikely and a  $\text{d}$ -activated mechanism is probable. Surprisingly, the coordination of one fluoride or one hydroxide to  $\text{U}(\text{IV})$  had no detectable effect on the water exchange rate.

#### 5. Glossary

2-ampy	2-(aminomethyl)pyridine
AcOH	acetic acid
bpy	2,2'-bipyridine
Bu <sup>t</sup> CN	valeronitrile
CDTA	<i>trans</i> -1,2-diaminocyclohexanetetraacetate
cy <sub>2</sub> dim	<i>N,N'</i> -dicyclohexylethylenediimine
cyclen	1,4,7,10-tetraazacyclododecane
DEA	<i>N,N'</i> -diethylacetamide
dien	diethylenetriamine
dipy	2,2'-dipyridylamine
DMA	<i>N,N'</i> -dimethylacetamide
DMADMP	<i>O,O'</i> -dimethyl- <i>N,N'</i> -dimethylphosphoramidate
DMF	<i>N,N'</i> -dimethylformamide
dmg	dimethylglyoximate
DMMP	dimethyl methylphosphonate
DMPU	dimethylpropyleneurea
DMSO	dimethyl sulfoxide
DMTF	<i>N,N'</i> -dimethylthioformamide
dpgH	diphenylglyoximate
DPMet	di(1-pyrazolyl)methane
DPPPro	di(1-pyrazolyl)propane
dps	2,2'-dipyridylsulfide
EDDS	<i>s,s'</i> -ethylenediaminedisuccinate
EDTA	ethylenediaminetetraacetate
EDTA-BOM	ethylenediaminetetraacetate-benzoyloxymethylene
en	1,2-diaminoethane
Et <sub>5</sub> dien	<i>N,N,N''</i> -pentaethyl-diethylenetriamine
EtCN	propionitrile
EtOH	ethanol
fz	ferrozine = 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine
HMPA	hexamethylphosphoramide
HOAc	acetic acid
ma	maltolate = 3-oxy-2-methyl-4-pyrone
NMBuL	<i>N</i> -methyl- $\gamma$ -butylactam
Me <sub>4</sub> cyclam	<i>N,N,N',N''</i> -tetramethyl-1,4,8,11-tetraazacyclotetradecane
meea	2-methoxyethylamine
Me <sub>4</sub> en	<i>N,N,N',N'</i> -tetramethyl-1,2-diaminoethane
Me <sub>2</sub> phen	2,9-dimethyl-1,10-phenanthroline

Me <sub>4</sub> phen	3,4,7,8-tetramethyl-1,10-phenanthroline
Me <sub>5</sub> dien	<i>N,N,N',N'',N'''</i> -pentamethyl-diethylenetriamine
Me <sub>6</sub> tren	2,2',2''-tri( <i>N,N</i> -dimethylamino)triethylamine
MeCN	acetonitrile
MeOH	methanol
mMal	methylmalonate
MMPP	methyl methylphenylphosphinate
NMA	<i>N</i> -methylacetamide
<i>N</i> -Mecyclen	<i>N</i> -methyl-1,4,7,10-tetraazacyclododecane
NO <sub>2</sub> phen	5-nitro-1,10-phenanthroline
pa	<i>n</i> -propylamine
Ph <sub>2</sub> phen	4,7-diphenyl-1,10-phenanthroline
PhCN	benzonitrile
PhDTA	<i>o</i> -phenylenediamine- <i>N,N,N',N''</i> -tetraazetate
PrCN	butyronitrile
pr <sup>i</sup> <sub>2</sub> dim	<i>N,N'</i> -diisopropylethylenediimine
Pr <sup>i</sup> CN	isobutyronitrile
pyMa	3,7,11-tribenzyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene
Sal	salicylate
sSal	sulfosalicylate
THF	tetrahydrofurane
TMP	trimethyl phosphate
tmpa	tris(2-pyridylmethyl)amine
TMPS	<i>meso</i> -tetrakis(sulfonatomesityl)porphine
TMPyP	<i>meso</i> -tetrakis( <i>N</i> -methyl-4-pyridyl)porphine
TMU	<i>N,N,N',N''</i> -tertramethylurea
tn	1,3-propanediamine
Tp	hydridotris(pyrazolyl)borate
tpmm	tri(2-pyridyl)methoxymethane
TPPS	<i>meso</i> -tetrakis( <i>p</i> -sulfonatophenyl)porphine
tpy	2,2',2''-terpyridine
tren	2,2',2''-triaminotriethylamine
trien	triethylentetramine
α-EDDADP	α-ethylenediaminediacetatedipropionate
η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub>	cyclopentadienyl
η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub>	pentamethylcyclopentadienyl
η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub>	benzene
η <sup>6</sup> -cymene	<i>p</i> -isopropyltoluene

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