by a Teflon-coated bar driven externally by a magnetic stirrer. Absence of diffusional problems below 1.4×10^{-4} M s^{-1} initial rates was determined by the conversion vs time plot independence of the stirring rate in kinetic experiments randomly selected from Table II. Possible phase separation in the case of system A was checked with UV-vis spectroscopy by analyzing blank solutions (without catalyst) at 350 nm. The concentration of the commercial H_2O_2 solution was checked iodometrically prior to use.

The following general procedures were followed:

System A. In a typical experiment solid (diphoe)Pt(CF_3)(OH) (0.0284 g, 0.042 mmol) was placed in the reactor, which was evacuated and filled with N_2. Dry, N_2-saturated THF (2.5 mL) was added under N_2 flow, followed by 1-octene (0.350 mL, 2.23 mmol). After stirring of the mixture for a few minutes, a 34% H_2O_2 solution (0.190 mL, 1.80 mmol) was injected through the septum and time was started. The mixture was vigorously stirred to avoid diffusional problems. Where necessary, appropriate amounts of water, $HClO_4$, or KOH were added to the H_2O_2 solution prior to use.

System B. The sequences of operations was analogous to system A except that the amounts used were different. Typically, the following compounds and amounts were used: [(diphoe)Pt(CF_3)(CH_2Cl_2)]BF_4 (0.0215 g, 0.026 mmol), CH_2Cl_2 (10 mL), 1-octene (2.80 mL, 17.8 mmol), 17% H_2O_2 (1.0 mL, 5.0 mmol). In buffered experiments the buffer solution was diluted 1/1 with 34% H_2O_2 prior to use.

All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the catalyst with LiCl did not show any differences in randomly selected analyses. Separation of the products was performed on a 2-m 10% UCC on Chromosorb W packed column by using a flame ionization detector.

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Registry No. (diphoe)Pt(CF_3)(OH), 70504-87-9; [(diphoe)Pt(CF_3)(CH_2Cl_2)]BF_4, 98839-55-5; 1-octene, 111-66-0.

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Oxygen-17 Nuclear Magnetic Resonance Kinetic Study of Water Exchange on the Lanthanide(III) Aqua Ions[1,2]

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We report a variable-temperature ^{17}O NMR study of aqueous lanthanide solutions. Chemical shift measurements on 0.3 *m* $Ln(ClO_4)_3$/2 *m* $HClO_4$ solutions of 12 paramagnetic lanthanide ions are consistent with a constant hydration number along the series. This observation is reinforced by spectrophotometric measurements in acidified $Nd(ClO_4)_3$ solutions. A critical review of the previously published results on this topic suggests that the hydration number is nine for all lanthanide ions. The study was made on high-field NMR spectrometers, extending the accessible kinetic NMR window toward larger rate constants. By a combination of the chemical shifts and the longitudinal and the transverse relaxation rates, the water exchange activation parameters were obtained for six heavy lanthanide ions. The exchange rate constants calculated at 298.15 K are 5.0×10^8 s^{-1} for Tb^{3+}, 3.9×10^8 s^{-1} for Dy^{3+}, 1.9×10^8 s^{-1} for Ho^{3+}, 1.2×10^8 s^{-1} for Er^{3+}, 8.1×10^7 s^{-1} for Tm^{3+}, and 4.1×10^7 s^{-1} for Yb^{3+}. Unsuccessful attempts were made to study the water exchange on Nd^{3+} and Eu^{3+}. The regular decrease of the k^{298} value with ionic radius and the fairly constant negative activation entropies are interpreted as grounds for a similar exchange mechanism for the six ions successfully kinetically characterized.

Introduction

The tripositive lanthanides constitute the longest series of chemically similar metal ions. As their 4f orbitals are shielded by the electrons of the filled 5s and 5p orbitals, ligand field effects or ligand π-orbital back-bonding are very weak. The stability and kinetic behavior of the lanthanide complexes are thus mainly governed by steric and electrostatic factors. The high coordination number and the absence of crystal field stabilization energy are responsible for the considerable lability of the lanthanide complexes.

The behavior of lanthanide(III) ions in aqueous solution remains quite an open question, and many papers concerning the hydration of these ions have already been published. However, as shown by Lincoln's recent review,[3] it is not firmly established whether or not there is a change in coordination number (nine to eight) along the series.

Much has been published about complex formation on these ions, but knowledge of the water exchange kinetics is still very poor. Southwood-Jones et al.[4] reported a variable temperature study of water exchange on Gd^{3+}. For this ion, reliable kinetic characterization was made possible by a combination of ^{17}O NMR and EPR data. In an older ^{17}O NMR study Reuben and Fiat,[5] limited by the low magnetic field (1.4 T) then available, determined only lower limits for the water exchange rates at ambient temperature on the ions Tb^{3+} to Tm^{3+}. As the chemical shift scale and the accessible NMR time scale are extended with an increase of magnetic field, we have performed a variable-temperature kinetic study with high-field (4.7 and 8.5 T) spectrometers. By combining the chemical shifts and the longitudinal and the transverse relaxation rates, we were able to characterize the water exchange kinetics on six heavy lanthanide ions. Moreover, the interpretation of the chemical shifts of water in paramagnetic lanthanide solutions and the results of spectrophotometric measurements gave us useful information about the coordination number of these ions in water.

Experimental Section

A. Materials and Solution Preparation. The lanthanide perchlorates were obtained by dissolving slight excesses of lanthanide oxides (Nucor, 99.99%; Apache Chemical, 99.9%) in 30% perchloric acid (Merck, p.a.). The resulting solutions were filtered and acidified to pH 3 with dilute $HClO_4$, in order to avoid the formation of hydroxo species, and were then evaporated at reduced pressure and the remaining solids were dried under vacuum. Further handling of these hygroscopic salts was always done in a dry glovebox. The hydration of the salts (6–8 mol of water/lanthanide ion) was calculated from the metal content, determined by titration with EDTA.[6] Solutions were prepared by weight with 2 *m* $HClO_4$ as solvent, in order to avoid hydrolysis. Solutions for the spectrophotometric measurements were made with normal water, while those

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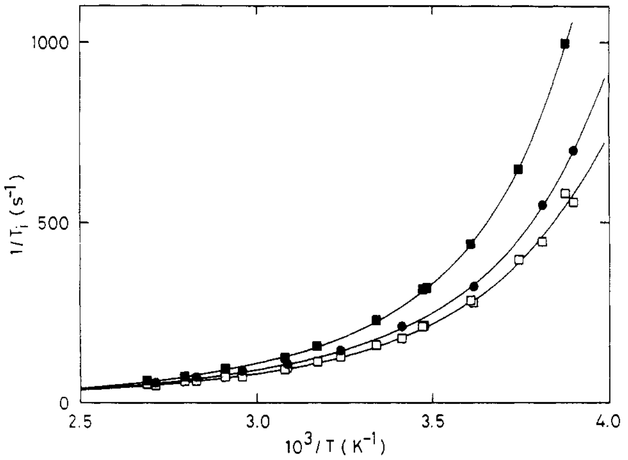

Figure 1. Example of relaxation data obtained at variable temperature in a 0.2994 *m* $Ho(ClO_4)_3$/1.911 *m* $HClO_4$ solution: (□) $1/T_1$ at 4.67 and 8.48 T; (●) $1/T_2$ at 4.67 T; (■) $1/T_2$ at 8.48 T.

for ^{17}O NMR measurements were made with ^{17}O enriched water (Yeda, ^2H normalized, 5–10 atom % ^{17}O). A complete description of the sample compositions is given in the supplementary material (Table S1).

B. Spectrophotometric Measurements. The visible spectra were recorded on a Perkin-Elmer Hitachi 340 spectrophotometer with a 0.1 nm band-pass. The variable-temperature measurements were carried out with 5-cm path length thermostated cells for the dilute solution and with 1-mm path length cells for the concentrated one.

C. NMR Measurements. The variable-temperature Fourier transform ^{17}O NMR spectra were obtained with Bruker WH 360 (fitted with a selective probehead) and CXP 200 (fitted with a high power multinuclear probehead, saddle coil system) instruments, operating at 48.79 and 27.11 MHz respectively, without lock. The solutions were sealed in spherical sample cells,[7] in order to eliminate the chemical shift contribution due to the magnetic susceptibility. Sweep widths varied from 1 to 50 kHz, depending on the linewidth of the unique signal observed. The $\pi/2$ pulse lengths were approximately 50 and 10 μs on WH 360 and CXP 200, respectively. The temperature was controlled by the substitution technique,[8] using a 100 Ω Pt resistance. The longitudinal relaxation rates were measured by the inversion–recovery method.[9] As it is very difficult to avoid field inhomogeneities in an NMR cell containing a highly paramagnetic lanthanide solution, we did not measure the full width at half-height to determine the transverse relaxation rate, but instead we used a modified Carr–Purcell–Meiboom–Gill pulse sequence.[9b] The number of refocusing echoes was set to a constant value of 2, and the relaxation delay between the pulses was taken as a variable. In order to check the reliability and the accuracy of our relaxation measurements, we studied an 0.3 *m* $La(ClO_4)_3$/2.0 *m* $HClO_4$ solution at variable temperature. In this diamagnetic solution, the ^{17}O relaxation is governed by a quadrupolar mechanism, thus $1/T_1$ and $1/T_2$ have to be equal. This was experimentally verified: the difference between $1/T_1$ and $1/T_2$ was smaller than 5% over the whole temperature range studied (253–372 K).

Kinetic Data Treatment

The Swift and Connick[10] approach has proven very convenient for the determination of solvent exchange kinetics in dilute paramagnetic systems. The relevant equations have been previously presented[11] but are repeated here for convenience. The transverse relaxation time T_2 and the chemical shift $\Delta\omega_s$ between free and coalesced solvent can be related to the mean life time τ_m of a solvent molecule bound to metal by eq 1 and 2.

$$1/T_2 - 1/T_{2A}{}^0 = P_m\left[(1/\tau_m)\frac{(1/\tau_m + 1/T_{2m})/T_{2m} + (\Delta\omega_m)^2}{(1/\tau_m + 1/T_{2m})^2 + (\Delta\omega_m)^2} + 1/T_{2os}\right] \quad (1)$$

$$\Delta\omega_s = P_m\left[\frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m{}^2(\Delta\omega_m)^2} + \Delta\omega_{os}\right] \quad (2)$$

$T_{2A}{}^0$ is the relaxation time of pure solvent, T_{2m} and T_{2os} are those of coordinated and outer-sphere solvent respectively, P_m is the partial molar fraction of solvent bound to metal, $\Delta\omega_m$ is the chemical shift difference between free and bound solvent and $\Delta\omega_{os}$ is the one between pure and bulk solvent. Zimmermann and Brittin[12] expressed the solvent exchange influence on the observed longitudinal relaxation rate $1/T_1$. Equation 3 is obtained by adding a term taking the outer-sphere processes into account. $T_{1A}{}^0$, T_{1m}, and T_{1os} are the longitudinal relaxation times of pure, bound, and outer-sphere solvent.

$$1/T_1 - 1/T_{1A}{}^0 = P_m[1/(\tau_m + T_{1m}) + 1/T_{1os}] \quad (3)$$

The lanthanide(III) aqua ions are very labile. The application of the fast-exchange hypotheses ($1/T_{1m}$ and $1/T_{2m} \ll 1/\tau_m$; $\Delta\omega_m{}^2 \ll 1/\tau_m{}^2$) to eq 1–3 leads to their simplified forms (eq 4–6).

$$1/T_1 - 1/T_{1A}{}^0 = P_m[1/T_{1m} + 1/T_{1os}] \quad (4)$$

$$1/T_2 - 1/T_{2A}{}^0 = P_m[(\Delta\omega_m)^2\tau_m + 1/T_{2m} + 1/T_{1os}] \quad (5)$$

$$\Delta\omega_s = P_m[\Delta\omega_m + \Delta\omega_{os}] \quad (6)$$

These hypotheses will be demonstrated later. The relaxation of pure water is mainly governed by a quadrupolar relaxation mechanism. $1/T_{1A}{}^0$ and $1/T_{2A}{}^0$ are thus equal under the extreme narrowing condition. Subtraction of eq 4 from eq 5 gives eq 7.

$$1/T_2 - 1/T_1 = P_m[(\Delta\omega_m)^2\tau_m + 1/T_{2m} - 1/T_{1m} + 1/T_{2os} - 1/T_{1os}] \quad (7)$$

By the use of two more a priori simplifications ($1/T_{2m} - 1/T_{1m}$ and $1/T_{2os} - 1/T_{1os} \ll (\Delta\omega_m)^2\tau_m$, justified later), eq 7 was further simplified to give eq 8.

$$(1/T_2 - 1/T_1)/P_m = (\Delta\omega_m)^2\tau_m \quad (8)$$

As $\Delta\omega_m$ and $\Delta\omega_{os}$ have the same temperature dependence, it is impossible to evaluate their respective importance in eq 6. Previous work on other metals ions (Ni^{2+} and Ti^{3+})[13] in water showed that $\Delta\omega_{os}$ is small (less than ±4%) compared to $\Delta\omega_m$, so we further considered $\Delta\omega_{os}$ as negligible relative to $\Delta\omega_m$ and eq 6 was simplified to eq 9.

$$\Delta\omega_s/P_m = \Delta\omega_m \quad (9)$$

In the lanthanide solutions, $\Delta\omega_m$ for ^{17}O is principally due to a contact (or scalar) interaction with the metal ion.[14] According to the same authors,[14] this contact shift is proportional to the inverse of temperature (eq 10), except for Sm^{3+} and Eu^{3+}. ω_0 is the spectrometer frequency,

$$\Delta\omega_m/\omega_0 = \frac{2\pi g_L(g_L - 1)J(J + 1)\mu_B}{3k_BT\gamma_1}A/h + \frac{B_2}{T^2} \quad (10)$$

A/h is the hyperfine coupling constant, γ_I is the gyromagnetic ratio of the nucleus I, g_L is the Landé factor of the metal ion and μ_B is the Bohr magneton. A second empirical term B_2/T^2 has been added in eq 10 in order to obtain an appropriate description of the measured chemical shifts. According to Bleaney,[15] this term describes the pseudocontact (or dipolar) interaction with the ion. However Horrocks[16] has shown that the dipolar shift does not vary rigorously with $1/T^2$. We have thus used eq 10 for our data treatment without trying to explain the meaning of the small B_2/T^2 contribution to $\Delta\omega_m$ (5–10% in our case).

The variable-temperature dependence of the residence time τ_m is related to the pseudo-first-order reaction rate constant k for the exchange of a particular coordinated water molecule. Its temperature dependence, given in eq 11, was taken from the

$$k = 1/\tau_m = k_BT/h\ \exp(\Delta S^*/R - \Delta H^*/RT) \quad (11)$$

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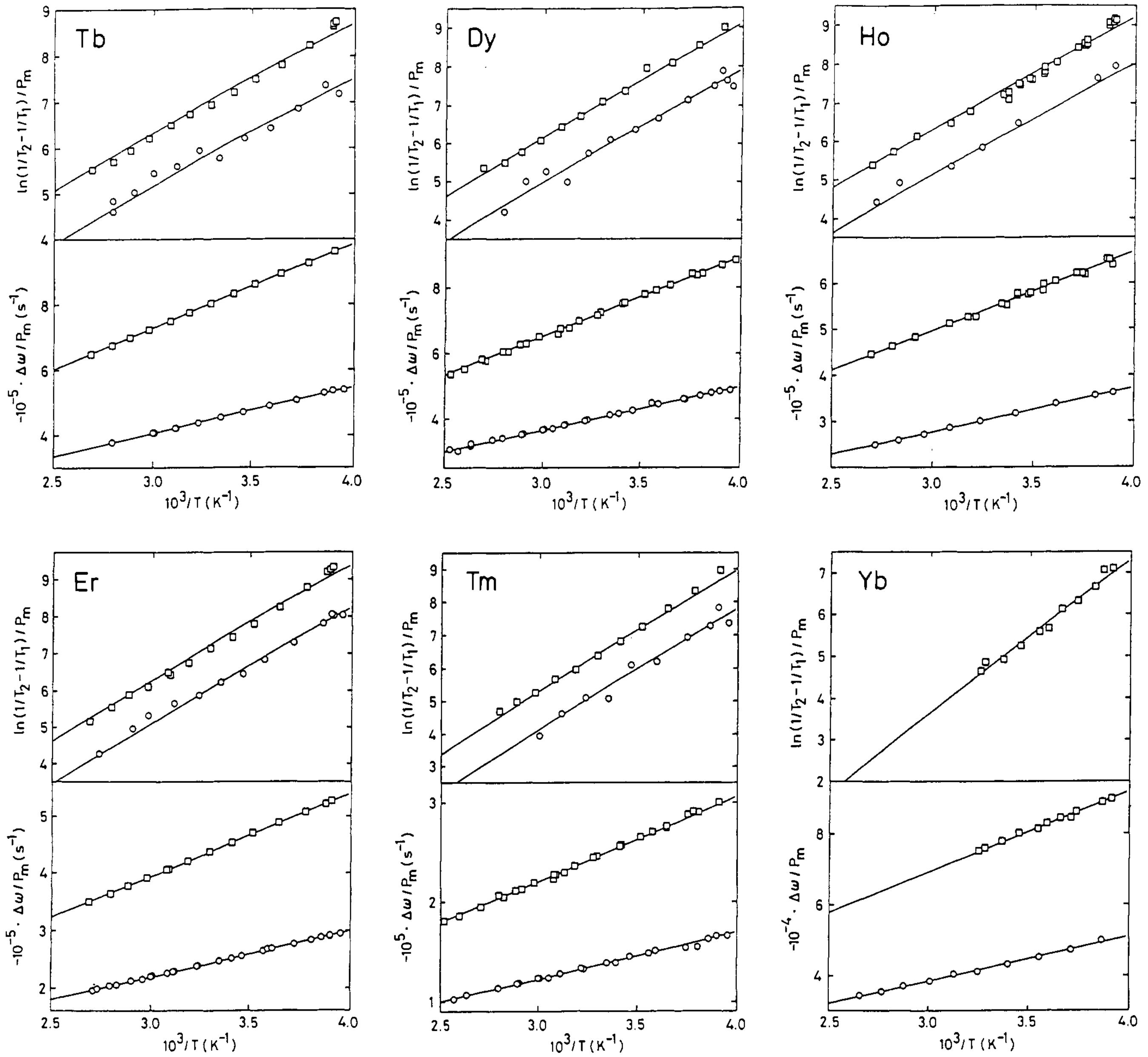

Figure 2. Variable-temperature ^{17}O NMR data for acidified $[Ln(H_2O)_9]^{3+}$ solutions: ln $[(1/T_2 - 1/T_1)/P_m]$ and reduced chemical shift versus reciprocal temperature at 48.79 MHz (□) and 27.11 MHz (○). $[Ln(ClO_4)_3]$ and $[HClO_4]$ are typically equal to 0.3 and 2.0 *m*, respectively, except for Ho^{3+} solutions (see Table II).

Table I. Kinetic and NMR Parameters Determined at Variable Temperature for Water Exchange on $Ln(H_2O)_9{}^{3+}$[a]

metal ion	$10^{-8}k^{298}$, s^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	A/h, MHz	B_2, K^2
Gd^{3+}[b]	10.6 ± 0.9	12.0 ± 1.4	−31.9 ± 4.3		
Tb^{3+}	4.96 ± 0.12	12.08 ± 0.48	−37.9 ± 1.6	0.619 ± 0.020	11.6 ± 7.1
Dy^{3+}	3.86 ± 0.09	16.57 ± 0.47[c]	−25.0 ± 1.5	0.595 ± 0.012	21.3 ± 3.9
Ho^{3+}	1.91 ± 0.03	16.36 ± 0.39	−31.5 ± 1.3	0.600 ± 0.015	5.5 ± 3.9
Er^{3+}	1.18 ± 0.02	18.37 ± 0.34	−28.8 ± 1.1	0.663 ± 0.013	11.7 ± 2.2
Tm^{3+}	0.81 ± 0.02	22.68 ± 0.58	−17.4 ± 1.9	0.642 ± 0.016	10.6 ± 1.5
Yb^{3+}	0.41 ± 0.01	23.29 ± 0.94	−21.0 ± 3.3	0.782 ± 0.023	−0.3 ± 7.2

[a] Errors quoted correspond to 1 standard deviation in the calculations. [b] Values taken from ref 4. [c] Lower limit from ref 5: $\Delta H^{\ddagger} < 21$ kJ mol^{-1}.

transition state theory. We measured $\Delta\omega_s$, $1/T_2$ and $1/T_1$ in solutions of Nd^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+}. An example of experimental relaxation results is reported in Figure 1 for a Ho^{3+} solution. The differences $1/T_2 - 1/T_1$ were significant (more than 5% of measured relaxation rate values) only for the ions going from Tb^{3+} to Yb^{3+}. The absence of a significant effect for the light lanthanide Nd^{3+} ion only allows calculation of a lower exchange rate limit. The greatest difference $1/T_2 - 1/T_1$ for this ion is less than 5% of the measured relaxation rates. Introducing this value and $\Delta\omega_m$ estimated at 298.15 K in eq 8, we found that k^{298} was larger than 1×10^9 s^{-1} for Nd^{3+}. For the ions going from Tb^{3+} to Yb^{3+}, nonlinear fits were made of $(1/T_2 - 1/T_1)/P_m$ and $\Delta\omega_m/P_m$ versus reciprocal temperature by using eq 8–11. The adjustable parameters were $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ or k^{298}, A/h, and B_2. Calculations were made by using a P_m value corresponding to a coordination number of nine. This choice will be justified in the discussion. The experimental results and the calculated functions are illustrated in Figure 2. The corresponding kinetic and NMR parameters are reported in Table I. We also did calculations corresponding to a coordination number of eight. For each ion,

Table II. Influence of Metal and Acid Concentrations on Water Exchange on $Ho(H_2O)_9^{3+}$ [a]

$[Ho(ClO_4)_3]$, *m*	$[HClO_4]$, *m*	$10^{-8}k^{258}$, s^{-1}	$10^{-8}k^{298}$, s^{-1}	A/h, MHz
0.0987	1.980	0.57 ± 0.03	2.06 ± 0.05	*b*
0.1945	1.942	0.48 ± 0.02	2.25 ± 0.05	0.63 ± 0.02
0.2994	1.911	0.59 ± 0.03	1.86 ± 0.05	0.60 ± 0.02
0.3593	1.892	0.53 ± 0.03	2.29 ± 0.15	0.65 ± 0.06
0.2958	0.9831	0.51 ± 0.01	2.62 ± 0.06	0.61 ± 0.02
0.2815	0.4587	0.50 ± 0.02	2.27 ± 0.08	*b*
c		0.59 ± 0.02	1.91 ± 0.03	0.60 ± 0.02

[a] Errors quoted correspond to 1 standard deviation in the calculations. [b] No chemical shift measurements were made. A/h was taken equal to 0.600 MHz for the rate constants calculation. [c] The data of all solutions analyzed simultaneously.

ΔH^{*} does not change, ΔS^{*} increases by 1.0 J K^{-1} mol^{-1}, and k^{298}, A/h, and B_2 are multiplied by a factor of 9/8.

Various solutions of Ho^{3+} were measured in order to reveal a possible influence of the metal and proton concentrations on the kinetic or NMR parameters. Measurements were made at low temperature (258–300 K), where the kinetic contributions are large for all the samples studied. Values of $(1/T_2 - 1/T_1)/P_m$ and $\Delta\omega_s/P_m$ were the same within experimental error for all the samples. Table II gives the calculated values of A/h and the exchange rate at 258.15 and 298.15 K for each solution. No significant difference is observed, and we conclude the absence of metal and proton concentration influences on our results in Ho^{3+} solutions. This conclusion was extended to all metal ions studied.

The simplifications used for the relaxation data treatment must now be verified. To obtain eq 8, it was assumed that $1/T_{2m} - 1/T_{1m} \ll \Delta\omega_m^2\tau_m$. $1/T_{1m}$ and $1/T_{2m}$ are each the sum of three contributions due to the interaction of the nuclear quadrupole moment with the electric field gradient and to dipolar and scalar interactions with the electron spin of the metal ion. The dipolar and scalar contributions have been expressed by Alsaadi et al.,[17] leading to eq 12 and 13. $1/T_{1m}^{Q}$ and $1/T_{2m}^{Q}$ are the quadrupolar

$$1/T_{1m} = 1/T_{1m}^{Q} + \frac{J(J+1)\gamma_I^2\gamma_s^2\hbar^2}{15r^6}\left(6\tau_s + \frac{14\tau_s}{1+\omega_s^2\tau_s^2}\right) + \frac{4\pi^2}{3}J(J+1)\left(\frac{A}{h}\right)^2\left(\frac{2\tau_s}{1+\omega_s^2\tau_s^2}\right) \quad (12)$$

$$1/T_{2m} = 1/T_{2m}^{Q} + \frac{J(J+1)\gamma_1^2\gamma_s^2\hbar^2}{15r^6}\left(7\tau_s + \frac{13\tau_s}{1+\omega_s^2\tau_s^2}\right) + \frac{4\pi^2}{3}J(J+1)\left(\frac{A}{h}\right)^2\left(\tau_s + \frac{\tau_s}{1+\omega_s^2\tau_s^2}\right) \quad (13)$$

contributions to $1/T_{1m}$ and $1/T_{2m}$, τ_s is the electron spin relaxation time of metal ion, and γ_s and ω_s are the gyromagnetic ratio and Larmor frequency of the metal electronic spin. Other symbols have been defined in eq 10. Under the extreme narrowing condition,[18] the quadrupole contributions to $1/T_{1m}$ and $1/T_{2m}$ are equal. Equation 14 is obtained by subtracting eq 12 from eq 13.

$$1/T_{2m} - 1/T_{1m} = J(J+1)\left(\tau_s - \frac{\tau_s}{1+\omega_s^2\tau_s^2}\right)\left[\frac{\gamma_I^2\gamma_s^2\hbar^2}{15r^6} + \frac{4\pi^2}{3}\left(\frac{A}{h}\right)^2\right] \quad (14)$$

This difference depends on the magnetic field. We then calculated it at the two fields used in this study, and we compared it with $\Delta\omega_m^2\tau_m$, taken from our results. For these calculations, *r* was taken as the mean of the metal–oxygen distances measured in solid nonahydrates,[20–22] A/h was taken from our results, and τ_s was calculated from the data of Alsaadi et al.[17] at the extreme temperatures used in this study. Results of the calculations are listed in Table III. $1/T_{2m} - 1/T_{1m}$ is always small compared to $\Delta\omega_m^2$ τ_m, (less than 5%). The effect of neglecting this difference in eq 7 will thus be less than the experimental errors on the kinetic parameters. $1/T_{2m} - 1/T_{1m}$ is therefore negligible compared to $\Delta\omega_m^2$ τ_m for all the ions under study.

Relaxation of the outer-sphere water is governed by the same mechanisms as for water bound directly to the metal. However, scalar coupling with the metal electron spin will be smaller, and the dipole–dipole contribution will be negligible because this parameter depends on the reciprocal sixth power of the distance to the metal ion. The difference $1/T_{2os} - 1/T_{1os}$ will then be smaller than the difference $1/T_{2m} - 1/T_{1m}$ and is negligible compared to $\Delta\omega_m^2$ τ_m in eq 7.

In order to demonstrate the fast-exchange hypotheses (see eq 4–6), we have measured $1/T_{1A}^{0}$ in a 1.913 *m* $HClO_4$ solution as a function of temperature. Following Hindmann,[23] we used a double exponential function (eq 15) to fit the longitudinal relaxation rate of our acidified water. The following parameters were found:

$$1/T_{1A}^{0} = A_1 \exp(E_1/RT) + A_2 \exp(E_2/RT) \quad (15)$$

$A_1 = (1.92 \pm 1.82) \times 10^{-2}$ s^{-1}; $E_1 = 21.4 \pm 1.9$ kJ mol^{-1}; $A_2 = 9.15 \pm 17.3$ s^{-1}; $E_2 = 2.40 \pm 6.80$ kJ mol^{-1}. Equation 15 was then used to calculate $1/T_{1A}^{0}$ at the extreme temperatures reached in this study. Using eq 4 and the measured $1/T_1$ value, we were able to estimate $1/T_{1m} + 1/T_{1os}$, listed in Table III. This sum is always smaller (at least 3 orders of magnitude) than $1/\tau_m$, and $1/T_{1m} \ll 1/\tau_m$. As was shown above, $1/T_{2m} - 1/T_{1m}$ is small, which implies that $1/T_{2m}$ is of the same order of magnitude as $1/T_{1m}$, and that $1/T_{2m} \ll 1/\tau_m$. Finally, Table III shows that $1/\tau_m^2$ is always at least 1000 times larger than $(\Delta\omega_m)^2$ at the lowest temperatures. All hypotheses leading to eq 11 and 12 are thus justified.

Results and Discussion

A. Coordination Number. Knowledge of the coordination number (hereafter CN) of the rare-earth-metal trivalent ions in solution is of primary importance for the interpretation of the thermodynamic and kinetic properties of complexes of such elements. In the solid state, diffraction studies on hydrated lanthanide salts with noncoordinating anions show various CN values. The perchlorate salts crystallize with six water molecules in an octahedral geometry around the metal ion.[24] A dodecahedral geometry has recently been established for hydrated complexes of Y^{3+}, Gd^{3+}, and Lu^{3+} with a crown ether, where eight water molecules are close to the metal ion.[25] These crystals were

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[18] The extreme narrowing condition is respected if $(\omega_0\tau_c)^2 \ll 1$. τ_c is the molecular reorientation correlation time, defined by the Stokes–Einstein equation: $\tau_c = 4\pi a^3\eta/3k_BT$, where *a* is the radius of the investigated species and η is the viscosity of the solution. Lanthanide aqua complexes are rather large species and it is not obvious that the extreme narrowing condition is obeyed, especially at low temperature. Taking 400 pm (radius of a Ln(III) aqua complex) for *a* and 5×10^{-3} kg s^{-1} m^{-1} (viscosity of water at 253 K) for η, we calculated an approximate value of 4×10^{-10} s for τ_c at 253 K (the lowest temperature investigated in this study.). This value is reasonable when compared to that of 1.1×10^{-10} s for the smaller Mn^{2+} aqua complex, calculated at the same temperature by using the results of Pfeifer.[19] In our study, the highest value of ω_0 for ^{17}O was 3.07×10^{8} s^{-1} (at 8.48 T). The maximum value of $(\omega_0\tau_c)^2$ is therefore 0.015; thus, the extreme narrowing condition is fulfilled for the lanthanide aqua complexes.

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Table III. Useful Parameters for the Discussion of the Hypotheses Used in the Data Treatment

				at 4.67 T		at 8.48 T					
metal ion	r, pm	T, K	$10^{13}\tau_s$, s	$(1/T_{2m} - 1/T_{1m})$, s^{-1}	$(\Delta\omega_m)^2\tau_m$, s^{-1}	$(1/T_{2m} - 1/T_{1m})$, s^{-1}	$(\Delta\omega_m)^2\tau_m$, s^{-1}	$10^{-7}1/\tau_m$ s^{-1}	$(1/T_{1m} + 1/T_{1os})$, s^{-1}	$10^{-14}(1/\tau_m^2)$, s^{-2}	$10^{-11}(\Delta\omega_m)^2$, s^{-2}
Nd^{3+}	251.3	255.7	1.82	0.05	<9	0.15	<28	>90	835	>8100	0.3
		307.3	1.34	0.02	<2	0.06	<6	>270	219	>73000	0.2
Tb^{3+}	240.9	256.0	2.51	1.5	1484	4.6	4893	19.17	2314	367	9.2
		371.8	2.19	1.0	79.8	3.1	263	163.1	214	26600	4.2
Dy^{3+}	239.6	253.0	3.84	5.6	2209	16.6	7284	10.91	3061	119	7.8
		371.8	3.15	3.2	57.5	9.6	190	180.0	304	32400	3.4
Ho^{3+}	238.2	256.2	2.35	1.3	2353	4.2	7759	5.58	2925	31.1	4.3
		371.8	2.04	0.9	68.9	2.8	227	88.18	302	7780	2.0
Er^{3+}	236.9	253.0	3.38	3.8	3293	11.6	10858	2.66	2625	7.1	2.8
		371.8	2.28	1.2	59.5	3.7	197	63.38	224	4060	1.2
Tm^{3+}	235.8	255.8	6.69	16.1	1784	42.9	5882	1.54	3023	2.4	0.9
		371.8	2.74	1.2	18.8	3.7	62.0	62.22	194	3870	0.4
Yb^{3+}	234.8	255.7	2.93	0.77	335	2.4	1103	0.745	2732	5.6	0.08
		307.3	1.45	0.01	31.1	0.30	103	5.583	364	31.2	0.06

obtained from a low water content solvent mixture (six H_2O per rare-earth-metal ion). However, a CN of 9 for hydrated lanthanide salts seems to be the rule, since lanthanide bromate,[20] ethyl sulfate,[21] and trifluoromethanesulfonate[22] crystallize spontaneously in aqueous solution with nine water molecules arranged in a tricapped trigonal prism around the metal ion.

In solution, one of the main hypotheses concerning CN is due to Spedding and co-workers. They interpreted the absence of regular variations of some physical and thermodynamic properties (mainly the partial molal volumes of the metal ions) of lanthanide (III) chloride,[26] perchlorate,[27] and nitrate[28] solutions by a change in CN in the middle of the series. According to this assumption, the CN is 9 for the lighter elements (La–Nd) and 8 for the heavier ones (Tb–Lu), and an equilibrium occurs between nona- and octahydrated species for Sm, Eu, and Gd. However, in all these studies, changes in the outer sphere structure can also explain these irregular variations, a possibility not envisaged by Spedding et al.

Both X-ray and neutron diffraction techniques have been used for the study of lanthanide solutions. Using X-ray diffraction, Habenschuss and Spedding[29] found a decrease in CN from 9 to 8 along the series. Narten and co-workers[30] confirmed this conclusion by neutron diffraction studies in Nd and Dy solutions. These results add weight to Spedding's assumption based on the interpretation of the partial molal volumes of lanthanide ions in solution. Wertz et al.[31] found a CN of 8 for La, Nd, and Gd ions, taking into account the complexation of chloride at high concentration. More recently, Johansson et al.[32] had to use a CN of 8 for La, Sm, Tb, and Er ions in order to obtain the best theoretical simulation of their X-ray data, obtained in perchlorate solutions. In all of these studies, high metal concentrations (usually more than 1 m) were used, and therefore one cannot exclude anion complexation (usually chloride). This fact could explain different results obtained by various authors for the same lanthanide ions.

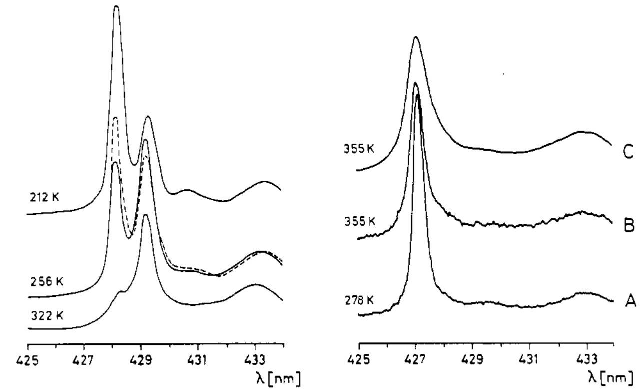

Figure 3. Left: Visible absorption spectra for $Nd(ClO_4)_3$ in DMF at the temperatures indicated. Solid lines represent spectra at ambient pressure; dashed lines show the spectrum at 120 MPa (redrawn from ref 36). Right: Visible absorption spectra for $Nd(ClO_4)_3$ in acidified water: (A, B) 9.97×10^{-2} m Nd^{3+}, 1.96 m H^+; (C) 3.019 m Nd^{3+}, 2.01 m H^+.

Interpretation of the fluorescence lifetimes of Eu^{3+} and Tb^{3+} also allow the determination of the hydration numbers of these ions. The nonradiative deexcitation lifetime is proportional to the number of water molecules bound to the metal. Using this technique, Horrocks and Sudnick[33] found a CN of 9.6 and 9.1 in water for the Eu and Tb ions, respectively. In view of the previously cited results of Spedding's group, they concluded that the CN decreases from 10 to 9 along the lanthanide series. Sinha[34] found lifetimes for Eu^{3+} and Tb^{3+} in solution that are equal to those measured in solid $[Eu(H_2O)_9](CF_3SO_3)_3$ and $[Tb(H_2O)_9](CF_3SO_3)_3$. He concluded to a constant CN of 9 along the whole series.

Using NMR spectroscopy, it is possible to calculate CN by using peak integration if the signals of free and coordinated solvent molecules are well separated. However this is impossible in aqueous lanthanide solutions, because the bound water molecules exchange very rapidly with those of the bulk solvent. In order to split the coalesced signal of the total solvent into two distinguishable ones, an inert diluent has to be added in order to decrease the freezing point of the samples. Some ^1H NMR studies were made at low temperature in water-acetone mixtures[35], of which the most recent and detailed study was done by Brücher et al.[35d] They found CN ≥ 9 for Lu^{3+}, the smallest ion of the lanthanide series.

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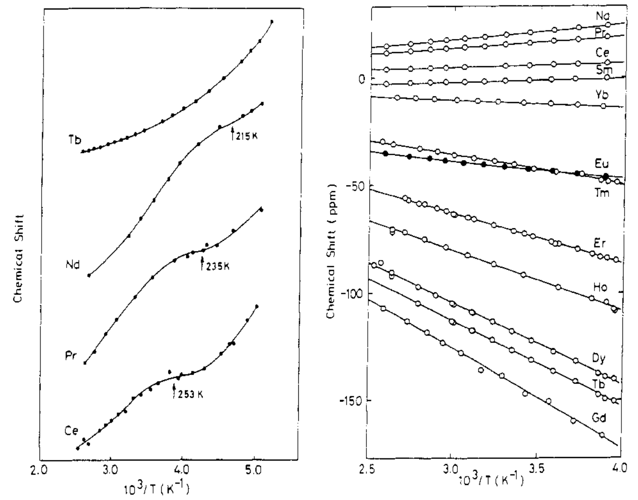

Figure 4. Left: ^1H chemical shift (in arbitrary units) of DMF formyl proton versus reciprocal temperature in $Ln(ClO_4)_3$/DMF solutions (redrawn from ref 36). The approximate temperatures corresponding to the inflection points are indicated. Right: ^{17}O chemical shift of water versus reciprocal temperature in 0.3 *m* $Ln(ClO_4)_3$/2.0 *m* $HClO_4$ aqueous solutions.

In dimethylformamide,[36] the solvation of lanthanide(III) ions has been well established. For the heavy lanthanide ions, a CN of 8 has been determined by ^1H NMR peak integration. No coordination of the perchlorate anion was detected by ^{35}Cl NMR.[36a] A spectrophotometric study[36b] of neodymium solutions at variable temperature and pressure unambiguously shows an equilibria between two solvated species (Figure 3, left). The peak at 429.3 nm increases in intensity with temperature, decreases with pressure, and was attributed to the $[Nd(DMF)_8]^{3+}$ species. The peak at 428.2 nm shows the opposite behavior and was attributed to $[Nd(DMF)_9]^{3+}$. We did similar measurements in aqueous solutions of $Nd(ClO_4)_3$. As shown by the right-hand side of Figure 3, no significant variation occurs when temperature or concentration change. According to Davidenko et al.[37] the unique peak we observed at 427.1 nm was assigned to the $[Nd(H_2O)_9]^{3+}$ species. The absence of temperature effect on the UV–visible spectra was already observed by Geier et al.,[38] not only for Nd^{3+} but also for the other lanthanide ions. These authors interpreted their results by suggesting a constant CN along the series.

The lanthanide-induced NMR solvent shifts also provide information about the CN. In their review, Reilley et al.[39] have separated the scalar and dipolar contributions to the ^1H and ^{17}O shifts in aqueous lanthanide solutions. Their calculations, done separately for the light (Ce–Eu) and heavy (Gd–Yb) ions, gave two different sets of results, possibly indicative of a structural change around the metal ions. However, as it was admitted by the authors, the accuracy of their calculations is very poor and their results do not allow distinction between a model in which both the light and heavy ions are 9-coordinate with subtly different structures and one in which the CN decreases along the series.

Variation of the lanthanide-induced shifts with temperature can be used to study possible changes in CN. An irregular variation of $\Delta\omega_s$ versus $1/T$, showing an inflection point, is characteristic of a change in CN with temperature. An example[36b] of such behavior is given in the left-hand side of Figure 4 for DMF solutions of Ce^{3+}, Pr^{3+}, and Nd^{3+}. We have reported the ^{17}O chemical shifts of water, measured in 12 paramagnetic lanthanide solutions, in the right-hand side of Figure 4. No inflection point is detected, which is consistent with an absence of CN change with temperature for each ion studied.

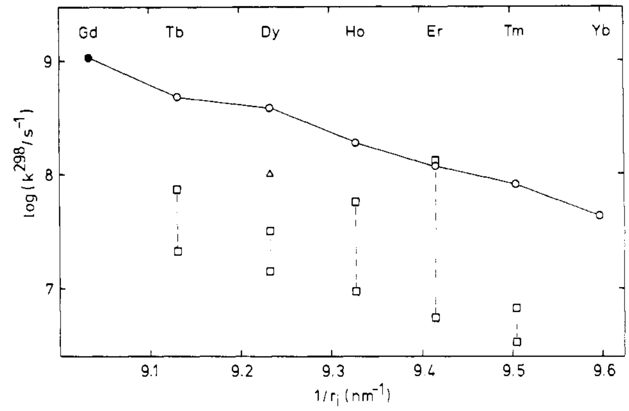

Figure 5. Logarithm of water exchange rates (in s^{-1}) at 298.15 K for $Ln(H_2O)_9^{3+}$ versus reciprocal ionic radii: (●) work of Southwood-Jones et al.[4] (○) this work; (□) upper and lower limits calculated by Reuben and Fiat,[3] (△) work of Granot and Fiat.[40]

In DMF the temperature corresponding to the inflection point of the $\Delta\omega_s$ versus $1/T$ curve increases by 20 K from Nd^{3+} to Pr^{3+}, and by 18 K from Pr^{3+} to Ce^{3+}. When one proceeds from one ion to the next in the series, the change in ionic radius thus induces a decrease by ≈20 K on the temperature of the coordination equilibrium. The chemical shift study in aqueous solution has been made over a wide range of temperature, and it is unlikely that the temperature of the coordination equilibrium jumps from less than 258 K to more than 370 K between two adjacent ions in the series. It is therefore concluded that the CN is constant for all the lanthanide ions in solution. The exact magnitude of this constant CN is open to question but a value of 9 is tenable. Intuitively, CN < 9 is unlikely in light of the fact that stable $Ln(H_2O)_9^{3+}$ species exist for La–Lu in the solid state.[3,20–22] In his recent review, Lincoln favors a CN of 9 for the Ln^{3+} ions in solution.[3] Moreover, the recent fluoresence[34] results in Eu^{3+} and Tb^{3+} solutions and the NMR peak integration study in Lu^{3+} solutions[35d] are also compatible with a CN = 9. Thus it is believed that all the lanthanide ions are surrounded by nine water molecules in dilute aqueous solution.

B. Kinetic Parameters. As Figure 5 shows, the water exchange rates on the lanthanide (III) ions are 1 order of magnitude larger than the previous estimations.[5,40] Reuben and Fiat[5] obtained their results by interpreting the ^{17}O line widths of concentrated (up to 3 *m*) perchlorate solutions. Such high concentrations were used in order to observe a significant kinetic effect on their low-field spectrometer. The rate constants were calculated by two methods. In the first one, the authors considered that the line broadening was due only to the exchange process, which leads to lower rate limits. In the second one, they assigned part of the line broadening to the relaxation of water bound to the metal ion, thus obtaining upper rate limits. However, the line widths are also certainly affected by the field inhomogeneities due to the paramagnetic solutions. Their interpretation of these line widths[5] leads to an overestimation of $1/T_2$ and thus to an underestimation of the exchange rate constants. The various problems experienced by these authors have been avoided in this work. First, the kinetic contribution to the relaxation parameters has been enhanced, even in diluted solutions, by the use of high-field magnets (4.67 and 8.48 T). Second, a Carr–Purcell pulse sequence was applied for the determination of $1/T_2$, thus avoiding the inhomogeneity problems. Third, no contribution due to the bound water relaxation rate $(1/T_{2m})$ appears in the difference $1/T_2 - 1/T_1$. The rate constants determined are therefore real values and not just limits.

The kinetic results concord with the data of Southwood-Jones et al.[4] for Gd^{3+}. The exchange rate decreases regularly along the

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Table IV. Solvent Exchange Rate Constants (10^7 s^{-1}) at 298.15 K for Water and DMF on Heavy Lanthanide Ions

metal ion	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
ionic radius[a]	109.5	108.3	107.2	106.2	105.2	104.2
rate constant $Ln(H_2O)_9^{3+}$	49.6	38.6	19.1	11.8	8.1	4.1
rate constant $Ln(DMF)_8^{3+}$[b]	1.9	0.63	0.36	1.3	3.1	9.9
exchange mechanism	I_d	I_d	I_d	I_d, D	D	D

[a] In pm, taken from ref 45 for CN = 9. [b] From ref 11.

series of heavy lanthanides, following the trend in ionic radii. The water exchange rate constants are very close to the substitution rate of water by sulfate (5.2×10^8 s^{-1} for Tb^{3+} to 0.8×10^8 s^{-1} for Yb^{3+}), determined by ultrasonic absorption.[41] These substituion rates increase from La^{3+} to Sm^{3+} and decrease from Eu^{3+} to Lu^{3+}. Unfortunately, it is impossible to say whether the water exchange rate will follow the same trend, or whether it will continue to increase with the increase of ionic radii for the lighter elements.[42] However, a lower limit value of 10^9 s^{-1} has been determined for the exchange on Nd^{3+} (5.2×10^8 s^{-1} for the sulfate complexation[41]). This tends to indicate that the aqua ions at the beginning of the series are more labile than those at the end.

If water exchange on the aqua ions is very fast, the exchange process will be diffusion-controlled,[43] and it is debatable whether or not a kinetically distinguishable first coordination sphere still exists for such labile species. For the heavy lanthanide ions, the exchange rate is more than 180 times slower (for Gd^{3+}) than the diffusion rate, and it still makes a sense to use the model of an ion surrounded by a well-defined first coordination sphere, characterized by a precise CN.

The kinetic parameters for the exchange of water and DMF are compared in Table IV. In DMF,[11] the exchange rate does not vary regularly along the series, as is the case in water. This could be explained by an increase in steric crowding of the ligands with the decrease in ionic radii, showed by the mechanistic change from I_d to D along the axis. This variation is also reflected by $\Delta S^{\ddagger}$, going from negative to positive values, and by the change from second- to first-order exchange rate laws. Unfortunately, for water no diluent is sufficiently inert to allow a variable-ligand concentration study in order to obtain the exchange rate laws. However, for the water exchange the rate constants decrease regularly and the $\Delta S^{\ddagger}$ values are negative and fairly constant. Even if a precise activation mode cannot be assigned only by interpreting the sign of $\Delta S^{\ddagger}$, these two observations are consistent with an absence of mechanistic change along the series studied.

Acknowledgment. We thank Dr. Deirdre Hugi-Cleary for her linguistic help. This work was financially supported by the Swiss National Science Foundation (Grant No. 2.854-0.85).

Registry No. $Tb(H_2O)_9^{3+}$, 56422-15-2; $Dy(H_2O)_9^{3+}$, 56422-19-6; $Ho(H_2O)_9^{3+}$, 55664-37-4; $Er(H_2O)_9^{3+}$, 56422-25-4; $Tm(H_2O)_9^{3+}$, 56422-23-2; $Yb(H_2O)_9^{3+}$, 56422-17-4.

Supplementary Material Available: Sample compositions (Table S1), temperature dependence of relaxation rates (Table S2), and temperature dependence of chemical shifts (Table S3) (19 pages). Ordering information is given on any current masthead page.

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(42) As shown by eq 8, the kinetic effect is proportional to the square of $\Delta\omega_m$; this parameter is small for light lanthanide ions compared to the heavier ones. Determination of the water exchange rates for the early lanthanides by using the same technique is thus not possible.

(43) In water at 298 K, diffusion processes allow the displacement of the water molecules over a distance of one molecular diameter in 5×10^{-12} s, which corresponds to a diffusion limiting rate of 2×10^{11} s^{-1} (see ref 44).

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Contribution from the Institut für Anorganische und Analytische Chemie, Universität Freiburg, 7800 Freiburg, FRG,
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Dinuclear (Pt,Pt) and Heteronuclear (Pt,Pd) Complexes of Uracil Nucleobases with Identical and Mixed Amine (NH_3, en, bpy) Ligands on the Two Metals. Effects of the Heterometal and Amine on the Oxidizability

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The preparation is reported of a series of dinuclear complexes of composition $[(X_2)PtL_2M(Y_2)]Z{\cdot}nH_2O$ with L = 1-methyluracil anion (1-MeU, $C_5H_5N_2O_2$) or 1-methylthymine anion (1-MeT, $C_6H_7N_2O_2$) bound to Pt via the N^3 position and the second metal M (Pt^{II}, Pd^{II}) coordinated through the two O^4 positions of the L ligands. X_2 and Y_2 are any of the following amines: ammonia, $(NH_3)_2$; ethylenediamine, en; 2,2′-bipyridine, bpy. The complexes were characterized by elemental analysis, by spectroscopic methods (IR, Raman, ^1H NMR, UV), and, in the case of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Pd(en)](NO_3)_2{\cdot}6H_2O$ (**4a**), by X-ray analysis. **4a** crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.698$ (2) Å, $b = 11.796$ (2) Å, $c = 12.965$ (2) Å, $\alpha = 114.94$ (1)°, $\beta = 100.29$ (1)°, $\gamma = 111.69$ (1)°, $V = 1383.5$ $Å^3$, and $Z = 2$. The two 1-MeU ligands adopt a head–head orientation, with *cis*-$Pt(NH_3)_2$ coordination through N^3 and (en)Pd coordination through O^4. The Pt–Pd separation within the cation is 2.927 (1) Å. Dinuclear cations are stacked in such a way that Pt atoms of adjacent dinuclear units face each other (Pt···Pt = 4.553 (1) Å) and likewise Pd atoms are next to each other (Pd···Pd = 3.255 (1) Å). Oxidation of Pt,Pt and Pt,Pd complexes by means of Ce^{IV} in 0.7 M H_2SO_4 has been studied. $[Pt^{II}]_2$ complexes are oxidized without exception to the corresponding $[Pt^{III}]_2$ compounds, whereas $[Pt^{II}Pd^{II}]$ complexes give a mixture of mononuclear $[Pt^{IV}]$ and $[Pd^{II}]$ complexes. With $[Pt^{II}]_2$ complexes, tetranuclear, mixed-valence Pt(2.25) species were observed as intermediates whenever the Y_2 entity was planar ($(NH_3)_2$, bpy), specifically for the following combinations: $X_2 = Y_2 = (NH_3)_2$, $X_2 = Y_2 =$ bpy, $X_2 = (NH_3)_2$ and $Y_2 =$ bpy, $X_2 =$ en and $Y_2 = (NH_3)_2$. In contrast, for $Y_2 =$ en, no Pt(2.25) species were detected by using visible spectroscopy. Standard redox potentials for the respective oxidation steps were determined by use of a standardized Pt electrode. Introduction of en ligands into the dinuclear $[Pt^{II}]_2$ complexes at either side (X_2 and/or Y_2) raised the redox potential for the $[Pt^{II}]_2/[Pt^{III}]_2$ couple relative to that of the $(NH_3)_2$ analogue slightly, while introduction of bpy ligands led to a significant increase in $E°$.

Introduction

Dinuclear Pt^{II} complexes (Chart I, M = Pt) with two bridging cyclic amidate ligands such as deprotonated 1-methylthymine (1-MeT),[2] 1-methyluracil (1-MeU),[3] α-pyridone,[4] α-pyrrolidone,[5] or 1-methylhydantoin[6] in head–head orientations represent suitable

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(1) (a) Universität Freiburg. (b) Technische Universität München.

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