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Ligand Exchange on Hexakis(1,1,3,3-tetramethylurea) Complexes of Trivalent Lanthanides. Proton Nuclear Magnetic Resonance Study

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Abstract

A ^{1}H NMR study of the kinetics of exchange of 1,1,3,3-tetramethylurea (tmu) on six-coordinated $[Ln(tmu)_6]^{3+}$ in CD_3CN is reported for Ln = Tb, Dy, Ho, Er and Yb. When Ln = Er and Yb, the rate of ligand exchange = $k6[Ln(tmu)_6{}^{3+}]$, and k (298.2 K) = 214 ± 2 and 65.5 ± 0.9 s^{-1}, $\Delta H^{\neq} = 35.5 \pm 0.5$ and 38.3 ± 1.0 kJ mol^{-1}, and $\Delta S^{\neq} = -81.3 \pm 1.7$ and -81.8 ± 3.1 J K^{-1} mol^{-1}, respectively. Although overall ligand exchange rate laws have not been determined for Ln = Tb, Dy and Ho, observed first order exchange rate constants, k = 1380, 1290 and 510 s^{-1} (298.2 K) have been determined. From these data, and that previously published, it is clear that a dominant factor determining the rate of ligand exchange on $[Ln(tmu)_6]^{3+}$ is the ionic radius of Ln^{3+}. The lability of $[Ln(tmu)_6]^{3+}$ towards ligand exchange is several orders of magnitude less than is the case for eight-coordinated $[Ln(dmf)_8]^{3+}$ and nine-coordinated $[Ln(H_2O)_9]^{3+}$, and this is attributed to an increase in Ln^{3+}–ligand dipole attraction as the coordination number decreases.

Introduction

The variation of the coordination number of the trivalent lanthanide ions (Ln^{3+}) from 6 to 10, depending on the nature of the ligands in the first coordination sphere, and the absence of significant ligand field and directional bonding effects, render these ions fascinating subjects for the study of the factors controlling the lability and mechanism of ligand substitution processes [1]. While there have been numerous studies of multidentate ligand substitution on Ln^{3+}, direct solvent and monodentate ligand exchange studies, which should provide the basis for understanding the mechanisms of ligand substitution on Ln^{3+}, require substantial access to high field NMR spectrometers and in consequence have only been undertaken quite recently [2–9].

The coordination number, n, of the $[LnL_n]^{3+}$ species varies with the nature of the monodentate ligand, L. Thus when L is water, the coordination number is 9 in the solid state [10] (although there has been debate over the existence of equilibria between eight- and nine-coordinated species in solution [1], and recent neutron diffraction studies show Dy^{3+} and Yb^{3+} to be eight coordinated in water [11]). When L is dimethylformamide (dmf), a coordination number of 8 applies to all Ln^{3+} in solution, but for the lighter lanthanides $[Ln(dmf)_9]^{3+}$ also appears in equilibrium with $[Ln(dmf)_8]^{3+}$ [3, 4]. This tendency for n to decrease with increasing size of L continues for 1,1,3,3-tetramethylurea (tmu) as demonstrated by the observation of $[Lu(tmu)_6]^{3+}$ and $[Tm(tmu)_6]^{3+}$ in solution, and $[Er(tmu)_6]^{3+}$ in the solid state [7, 8, 12]. This decrease in coordination number also appears to be characterised by a decrease in the lability of $[LnL_n]^{3+}$ towards ligand exchange as exemplified by $[Tm(H_2O)_9]^{3+}$ [4] and $[Tm(tmu)_6]^{3+}$ [8], for which ligand exchange rate constants, k (298.2 K) = 8.1×10^7 and 1.45×10^2 s^{-1}, respectively.

In order to increase the range of kinetic data available for monodentate ligand exchange on six-coordinated Ln^{3+} species, and thereby better assess the generality of the influence of coordination number on lability, we have extended our earlier studies of $[Tm(tmu)_6]^{3+}$ [8] and $[Lu(tmu)_6]^{3+}$ [7] to the remaining $[Ln(tmu)_6]^{3+}$ species amenable to dynamic ^{1}H NMR studies.

Experimental

Materials

$[Ln(tmu)_6](ClO_4)_3$ and $[Ln(tmu)_6](CF_3SO_3)_3$ were prepared by literature methods [13, 14] and the analyses in Table 1 were obtained. An ion-exchange technique [15] was used to determine Ln^{3+} as a trivalent cation, and other elemental analyses were carried out by the Australian Microanalytical Service, Melbourne. (**Caution**: Perchlorate salts of metal complexes may be explosive under some conditions

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TABLE 1. Elemental analyses for $[Ln(tmu)_6](ClO_4)_3$ and $[Ln(tmu)_6](CF_3SO_3)_3$

Complex		Ln (%)	C (%)	N (%)	H (%)
$[Yb(tmu)_6](ClO_4)_3$	found	15.1	30.7	14.7	6.3
	calc.	14.8	30.8	14.4	6.2
$[Er(tmu)_6](ClO_4)_3$	found	14.3	30.9	14.3	6.4
	calc.	14.4	31.0	14.5	6.3
$[Ho(tmu)_6](ClO_4)_3$	found	14.4	31.1	14.8	6.3
	calc.	14.2	31.1	14.5	6.3
$[Dy(tmu)_6](ClO_4)_3$	found	14.3	30.1	14.5	6.1
	calc.	14.0	31.1	14.5	6.2
$[Tb(tmu)_6](ClO_4)_3$	found	13.8	31.1	14.6	6.3
	calc.	13.8	31.2	14.6	6.3
$[Pr(tmu)_6](ClO_4)_3$	found	12.7	31.5	15.2	6.3
	calc.	12.4	31.7	14.9	6.4
$[Er(tmu)_6](CF_3SO_3)_3$	found	12.8	29.8	12.5	5.4
	calc.	12.8	30.2	12.8	5.5
$[Ho(tmu)_6](CF_3SO_3)_3$	found	12.6	30.1	12.8	5.5
	calc.	12.6	30.3	12.8	5.6

and should be handled with care. No explosion hazard was encountered during the course of this study.) The infrared spectra of the complexes in nujol mulls exhibited no absorptions attributable to coordinated perchlorate or the presence of trace amounts of water. Hydrated trivalent lanthanide perchlorates were obtained through the reaction of the trivalent lanthanide oxides (Spex) with the stoichiometric amount of concentrated perchloric acid. Hydrated trivalent lanthanide trifluoromethanesulfonates were similarly prepared using concentrated trifluoromethanesulfonic acid (Aldrich). Tmu (Fluka) and CD_3CN (99% deuterated, Aldrich) were distilled and stored over Linde A4 molecular sieves prior to use. Solutions of $[Ln(tmu)_6](ClO_4)_3$ or $[Ln(tmu)_6](CF_3SO_3)_3$ and tmu in CD_3CN were prepared in a dry nitrogen flushed glove box, and were sealed under vacuum in 5 mm NMR tubes.

NMR Spectroscopy

Variable temperature 300.13 MHz ^1H NMR studies were carried out on a Bruker CXP 300 spectrometer. Depending on the concentration and temperature of the sample, up to 1200 transients were collected and stored as 8192 datum point blocks prior to Fourier transformation and complete lineshape analysis [16] on a Nicolet BNC-12 computer. It was only with the $[Er(tmu)_6]^{3+}$ and $[Yb(tmu)_6]^{3+}$ systems that the variation of the linewidths and chemical shifts of coordinated and free tmu were separately observed over a sufficient temperature range, in the absence of chemical exchange induced modification, to permit extrapolation of these magnitudes into the higher temperature range, where chemical exchanged induced resonance coalescence occurred, as required for the complete lineshape analysis. (The temperature dependences of linewidth and chemical shift of the coordinated tmu incorporate the temperature dependence of the paramagnetic effect of the lanthanide ion.) Such extrapolations were not possible for the other three lanthanide ions (Tb^{3+}, Dy^{3+} and Ho^{3+}) and accordingly the averaged temperature dependences observed for $[Er(tmu)_6]^{3+}$ and $[Yb(tmu)_6]^{3+}$ were assumed to apply in the treatment of these three ions, as is described below.

Probe temperature control was ±0.03 K and the Bruker B-VT 1000 temperature controller was calibrated with a copper-constantan thermocouple.

Results and Discussion

[Ln(tmu)$_6$]$^{3+}$ Stoichiometry and Kinetics of Ligand Exchange

The ideal circumstances under which $[LnL_n]^{3+}$ stoichiometries and intermolecular ligand exchange rate laws may be determined by NMR spectroscopic methods occur when the rate of ligand exchange varies from the slow exchange limit of the NMR timescale (where the resonances of the free and coordinated ligand may be separately integrated to yield the complex stoichiometry), through the coalescence region (where the rate of ligand exchange may be determined), to the fast exchange limit of the NMR timescale (where environmental averaging of the free and coordinated ligand resonances occurs) as the temperature is increased. For the $[Ln(tmu)_6]^{3+}$ systems investigated in CD_3CN solution in this study, the above requirements are met when L = Er and Yb, to a lesser extent for Tb and Dy, barely for Ho (Figs. 1 and 2), and not at all for Pr, for which a single tmu ^1H resonance is observed over the accessible temperature range consistent with the chemical shift between free and coordinated tmu being very small, or ligand exchange being in the fast exchange limit, or both.

A well resolved ^1H singlet resonance arising from free tmu appears downfield from the singlet resonance arising from coordinated tmu characterises each of the three solutions of $[Er(tmu)_6]^{3+}$ and tmu in CD_3CN, whose compositions appear in Table 2, in the temperature range 235–260 K. The observations of singlet resonances for tmu in both environments indicates that the rate of rotation about the tmu C–N bond is in the fast exchange limit [17]. Integration and comparison of the two tmu resonance areas yield a coordination number of 6.0 ± 0.1 consistent with $[Er(tmu)_6]^{3+}$ being the greatly predominant Er^{3+} species in solution. (Solutions of $[Er(tmu)_6](CF_3SO_3)_3$ and tmu, studied in a similar manner, yield coordination numbers of 5 and less, depending on concentration. It is concluded that $CF_3SO_3^-$ coordinates under these conditions, and in

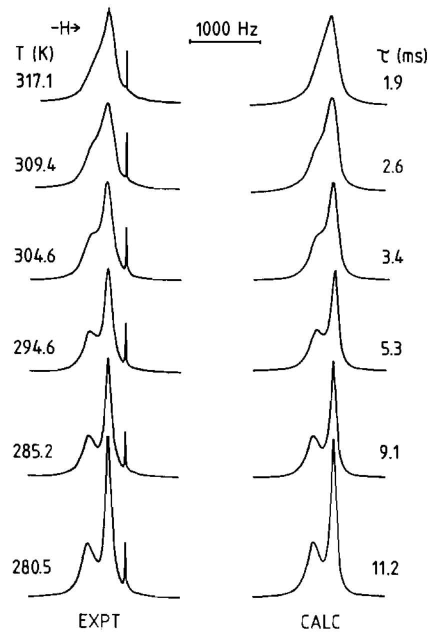

Fig. 1. The temperature dependent ^{1}H (300.13 MHz) NMR spectra of a solution of $[Er(tmu)_6]^{3+}$ (0.1012 mol dm^{-3}) and tmu (0.6681 mol dm^{-3}) in CD_3CN (16.22 mol dm^{-3}). The experimental spectra are shown to the left with the corresponding temperature, and the best-fit calculated lineshapes and corresponding τ values appear to the right. The $[Er(tmu)_6]^{3+}$ resonance appears downfield, and the narrow minor resonance arises from the proton impurity of CD_3CN.

consequence our kinetic studies are confined to $[Ln(tmu)_6](ClO_4)_3$ as there is no evidence for ClO_4^- coordination.)

Complete lineshape analysis [16] of the coalescence of the resonances of free and coordinated tmu at ten temperatures (and shown for selected temperatures in Fig. 1) yields the mean site lifetime of a single tmu coordinated in $[Er(tmu)]^{3+}$, τ, and the corresponding exchange rate constant, k_{ex}, as shown in eqn. (1), in which all other symbols have their usual meaning. The kinetic parameters for the three solutions are collected in Table 2. The small variation of the kinetic parameters with concentration is consistent with a first order tmu exchange process providing the dominant exchange path such that the observed exchange rate constant, k_{ex}, $= k$, the overall first order exchange rate constant.

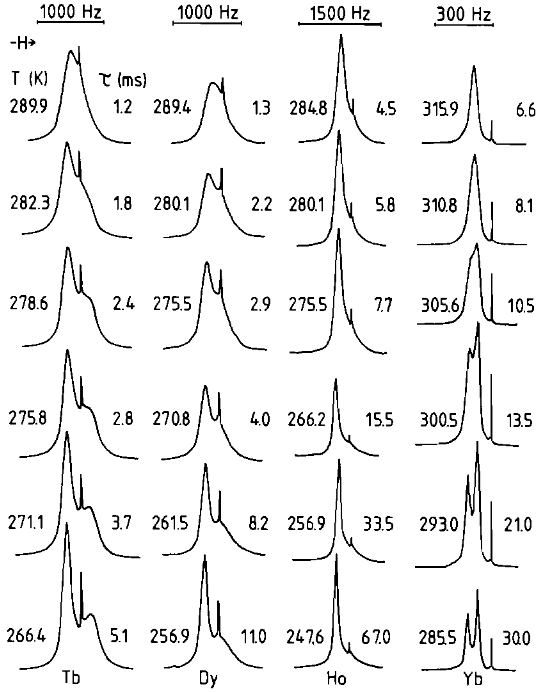

Fig. 2. The experimental temperature dependent ^{1}H (300.13 MHz) NMR spectra of solutions of $[Ln(tmu)_6]^{3+}$ and tmu in CD_3CN whose concentrations are 0.03331, 0.2228, and 17.63 mol dm^{-3}, respectively, for Ln = Tb; 0.03069, 0.1533, and 17.60 mol dm^{-3} for Ln = Dy; 0.1170, 0.6951, and 15.59 mol dm^{-3} for Ln = Ho; and 0.09352, 0.5514, and 15.89 mol dm^{-3} for Ln = Yb. The experimental temperature and the τ derived from lineshape analysis appear to the left and right, respectively, of each spectrum. When Ln = Tb, Dy, and Ho, the upfield resonance arises from $[Ln(tmu)_6]^{3+}$, whereas this resonance appears downfield when Ln = Yb. The narrow minor resonance arises from the proton impurity of CD_3CN.

$$1/\tau = k_{ex} = \text{exchange rate}/6[Tm(tmu)_6^{3+}] = k_BT/h\ \exp(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R) \qquad (1)$$

TABLE 2. Solution compositions and kinetic parameters[a] for ligand exchange on hexakis(1,1,3,3-tetramethylurea)erbium(III)

Solution[b]	$[Er(tmu)_6^{3+}]$ (mol dm^{-3})	$[tmu]_{free}$ (mol dm^{-3})	n[c]	k (298.2 K) (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
i	0.1012	0.6681	6.0 ± 0.1	220.5 ± 0.4	33.8 ± 0.4	−86.6 ± 1.2
ii	0.0484	0.3553	6.0 ± 0.1	216.5 ± 1.5	35.4 ± 0.5	−81.4 ± 1.5
iii	0.0254	0.1677	5.9 ± 0.1	203.5 ± 1.5	37.4 ± 0.4	−75.4 ± 1.5
i–iv				213.6 ± 1.7	35.5 ± 0.5	−81.3 ± 1.7

[a] Errors represent one standard deviation obtained from a linear regression fit of the experimental τ data to eqn. (1). [b] The concentrations of CD_3CN in solutions i, ii, and iii, are 16.22, 17.15, and 17.36 mol dm^{-3}, respectively. [c] n = coordination number determined from the ratio of the integrated areas of the resonances of free and coordinated tmu.

This first order process may arise from the operation of a dissociative (D) mechanism for tmu exchange in which the rate determining step is the formation of the reactive five-coordinated intermediate, $[\mathrm{Er(tmu)_5}]^{3+}$, as shown in eqn. (2).

$$[\mathrm{Er(tmu)_6}]^{3+} \xrightarrow{k} [\mathrm{Er(tmu)_5}]^{3+} + \mathrm{tmu}$$

$$[\mathrm{Er(tmu)_5}]^{3+} + {}^*\mathrm{tmu} \xrightarrow{\text{fast}} [\mathrm{Er(tmu)_5({}^*tmu)}]^{3+} \qquad (2)$$

Alternatively, the first order process may arise from the operation of an interchange (I) mechanism (eqn. (3)) in the limit where all of the $[\mathrm{Er(tmu)_6}]^{3+}$ exists in the encounter complex form, $[\mathrm{Er(tmu)_6}]^{3+}$...tmu, in which one tmu resides in the second coordination sphere, such that $k = k_i$.

$$[\mathrm{Er(tmu)_6}]^{3+} + {}^*\mathrm{tmu} \underset{\text{fast}}{\overset{K_0}{\rightleftharpoons}} [\mathrm{Er(tmu)_6}]^{3+}\ldots{}^*\mathrm{tmu} \qquad (3)$$

$$[\mathrm{Er(tmu)_6}]^{3+}\ldots{}^*\mathrm{tmu} \xrightarrow{k_i} [\mathrm{Er(tmu)_5({}^*tmu)}]^{3+}\ldots\mathrm{tmu}$$

However, to be in this limit of an I mechanism an encounter complex stability constant, K_0, of *c.* 100 $\mathrm{dm^3\ mol^{-1}}$ is necessary. This is *c.* 200 times greater than that determined for the formation of the $[\mathrm{Tb(dmf)_8}]^{3+}$...dmf encounter complex and its $\mathrm{Tm^{3+}}$ analogue in $\mathrm{CD_3NO_2}$ solution [4], and also that calculated through the Fuoss equation [18]. (The concentration of $\mathrm{CD_3CN}$ ranges from 16.22–17.36 $\mathrm{mol^{-1}\ dm^3}$ in solutions i–iii in Table 2, so that on a statistical basis the expectation of finding one tmu in the second coordination sphere of $[\mathrm{Er(tmu)_6}]^{3+}$ ranges from 80–20% for solutions i–iii assuming 15–20 solvent molecules in the second coordination sphere.) Thus it appears unlikely, both by comparison with known K_0 values and statistical probabilities, that $[\mathrm{Er(tmu)_6}]^{3+}$ exists predominantly as an encounter complex under the conditions of this study. Therefore it seems more probable that the D mechanism is operative. However, the large negative $\Delta S^{\neq}$ characterising $[\mathrm{Er(tmu)_6}]^{3+}$ is unexpected for a d activated exchange process, and further consideration is given to the mechanistic implications of this later.

Solutions in which $[\mathrm{Yb(tmu)_6}^{3+}]$ and [tmu] range from 0.1216 and 0.6866 mol $\mathrm{dm^{-3}}$, respectively, and 0.0150 and 0.0919 mol $\mathrm{dm^{-3}}$, respectively, yield a coordination number of 6.0 ± 0.1, consistent with $[\mathrm{Yb(tmu)_6}^{3+}]$ being the greatly predominant $\mathrm{Yb^{3+}}$ species in solution. Also there is little variation of $k_{\mathrm{ex}} = k$ over this concentration range, and the combined data from the four solutions studied yield the kinetic parameters in Table 3, which are subject to the same mechanistic interpretation as proposed for $[\mathrm{Er(tmu)_6}]^{3+}$. Similar observations have been made for $[\mathrm{Ln(tmu)_6}]^{3+}$ where Ln = Tm [8], Lu [7], and also for $[\mathrm{Y(tmu)_6}]^{3+}$ [13] and $[\mathrm{Sc(tmu)_6}]^{3+}$ [19].

For $[\mathrm{Ln(tmu)_6}]^{3+}$, when Ln = Tb, Dy, and Ho in particular (Fig. 2), a substantial overlapping of the free and coordinated tmu resonances occurs through a combination of a broad resonance for coordinated tmu and an insufficiently great chemical shift difference. Nevertheless, fitting of the low temperature spectra to two overlapping Lorentzian lineshapes yields coordination numbers of 6.0 ± 0.2, but this overlapping makes the derivation of kinetic parameters for tmu exchange (Table 3) less reliable than for $[\mathrm{Er(tmu)_6}]^{3+}$ and $[\mathrm{Yb(tmu)_6}]^{3+}$. Accordingly only one solution each has been studied for Ln = Tb, Dy and Ho, and the overall exchange rate laws have not been determined. It is seen that for the $[\mathrm{Ho(tmu)_6}]^{3+}$ system the resolution of the resonances of free and coordinated tmu is particularly poor (Fig. 2). This precludes a direct determination of the temperature variation of the chemical shifts and linewidths of free and coordinated tmu resonances in the absence of tmu exchange which are required for the determination of τ through lineshape analysis. The approach adopted assumes similar temperature dependences of the chemical shifts and linewidths of the free and coordinated tmu resonances for the Ho system as observed in the Er and Yb systems, and applies them to the free and coordinated tmu resonances derived through Lorentzian analysis of the low temperature spectra.

The constancy of the coordination number of 6 observed for the $[\mathrm{Ln(tmu)_6}]^{3+}$ and Y and Sc analogues in $\mathrm{CD_3CN}$ solution indicates that $\mathrm{CD_3CN}$ does not detectably compete with tmu for coordination sites.

Variation of Lability with Ionic Radius and Coordination Number

The increase in coordination number in the sequence $[\mathrm{Ln(tmu)_6}]^{3+}$, $[\mathrm{Ln(dmf)_8}]^{3+}$ and $[\mathrm{Ln(H_2O)_9}]^{3+}$ for the lanthanides in Table 3 is attributable to the decreasing size of the ligands (and to the commensurate increase in ionic radius [20] with increase in coordination number). There appears to be little relationship between coordination number and the electron donating abilities of the ligands as expressed through their Gutmann donor numbers D_{N} [21], which are: tmu (29.6), dmf (26.6) and $\mathrm{H_2O}$ (18.0 or 33 [22]).

Inspection of Table 3 reveals that k characterising $[\mathrm{Ln(tmu)_6}]^{3+}$ tends to decrease as ionic radius decreases, consistent with the consequent increase in $\mathrm{Ln^{3+}}$–ligand dipole attraction decreasing lability. (Both $[\mathrm{Y(tmu)_6}]^{3+}$ and $[\mathrm{Sc(tmu)_6}]^{3+}$, which also exhibit k values independent of concentration, fit into this trend.) Similarly, k characterising $[\mathrm{Ln(H_2O)_9}]^{3+}$ also decrease with ionic radius, but the lability of $[\mathrm{Ln(H_2O)_9}]^{3+}$ is *c.* 10^5–10^6 greater than

TABLE 3. Parameters[a] for ligand and solvent exchange on trivalent lanthanide and pseudo lanthanide ions

M^{3+}	r [b] (pm)	k (298.2 K) (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})
$[Ln(tmu)_6]^{3+}$ [c]					
Tb^{3+}	92.3	1380 ± 20	38.2 ± 0.5	−56.7 ± 1.8	
Dy^{3+}	91.2	1290 ± 30	38.6 ± 0.7	−56.0 ± 2.4	
Ho^{3+}	90.1	510 ± 20	40.9 ± 0.9	−55.9 ± 3.1	
Y^{3+} [d]	90.0	253 ± 10	27.1 ± 0.5	−108 ± 2	
Er^{3+}	89.0	214 ± 2	35.5 ± 0.5	−81.3 ± 1.7	
Tm^{3+} [e]	88.0	145 ± 1	29.3 ± 0.3	−105 ± 1	
Yb^{3+}	86.8	65.5 ± 0.9	38.3 ± 1.0	−81.8 ± 3.1	
Lu^{3+} [f]	86.1	41.9 ± 2.7	41.7 ± 0.6	−74 ± 2	
Sc^{3+} [g]	74.5	0.90 ± 0.5	68.6 ± 1.3	−15.7 ± 3.8	
$[Ln(dmf)_8]^{3+}$ [h]					
Tb^{3+}	104.0	1.9×10^7	14.09	−58.25	5.2
Dy^{3+}	102.7	6.3×10^6	13.76	−68.54	6.1
Ho^{3+}	101.5	3.6×10^6	15.31	−68.13	5.2
Er^{3+}	100.4	1.3×10^7	23.64	−29.57	5.4
Tm^{3+}	99.4	3.1×10^7	33.18	9.85	7.4
Yb^{3+}	98.5	9.9×10^7	39.30	39.95	11.8
$[Ln(H_2O)_9]^{3+}$ [i]					
Gd^{3+}	110.7	1.06×10^9	12.0	−31.9	
Tb^{3+}	109.5	4.96×10^8	12.08	−37.9	
Dy^{3+}	108.3	3.86×10^8	16.57	−25.0	
Ho^{3+}	107.2	1.91×10^8	16.36	−31.5	
Er^{3+}	106.2	1.18×10^8	18.37	−28.8	
Tm^{3+}	105.2	8.1×10^7	22.68	−17.4	
Yb^{3+}	104.2	4.1×10^7	23.29	−21.0	

[a] The errors quoted represent one standard deviation for the fit of the temperature variation of the experimental k to eqn. (2). [b] Six-, eight- and nine-coordinate radii from ref. 20. [c] This work (CD_3CN solution). [d] Ref. 13. [e] Ref. 8. [f] Ref. 7. [g] Ref. 19. [h] Ref. 4. [i] Ref. 6.

that for $[Ln(tmu)_6]^{3+}$. This large difference in lability is consistent with an increase in coordination number coinciding with an increase in bond length and a weakening of the interaction between the ligand and Ln^{3+}, which results in an increase in lability. (In the solid state the Er–O distances in tricapped trigonal prismatic $[Er(H_2O)_9]^{3+}$ [23] are 252 and 237 pm for the capping and prismatic waters, respectively, which compare with Er–O distances of 225 and 218.5–219.8 pm in octahedral $[Er(H_2O)_6]^{3+}$ [24] and $[Er(tmu)_6]^{3+}$ [12], respectively.

The $\Delta H^{\neq}$ values characterising $[Ln(tmu)_6]^{3+}$ are greater than those for $[Ln(H_2O)_9]^{3+}$, which is consistent with a greater contribution to $\Delta H^{\neq}$ arising from the stronger electrostatic interaction between the ligand and Ln^{3+} in the former species. The $\Delta S^{\neq}$ characterising $[Ln(tmu)_6]^{3+}$ are more negative than those characterising $[Ln(H_2O)_9]^{3+}$, but the mechanistic interpretation of this observation is not clear. Nevertheless, the systematic trends in the magnitude of k for both species suggest that there is no significant mechanistic variation within either the $[Ln(tmu)_6]^{3+}$ or the $[Ln(H_2O)_9]^{3+}$ series.

The k values for $[Ln(dmf)_8]^{3+}$ are c. 10^4–10^6 greater than those for $[Ln(tmu)_6]^{3+}$, but vary from being much less than, to being greater than, that for $[Ln(H_2O)_9]^{3+}$ for the Tb and Yb species respectively (Table 3). It is further observed that k for $[Ln(dmf)_8]^{3+}$ does not show a systematic decrease with ionic radius, and that $\Delta S^{\neq}$ changes from positive to negative as ionic radius increases. These variations reflect a mechanistic change across the lanthanide contraction. The positive $\Delta V^{\neq}$ values and the rate laws for dmf exchange are consistent with the operation of I_d and D dmf exchange mechanisms for $[Tb(dmf)_8]^{3+}$ and $[Tm(dmf)_8]^{3+}$, respectively, with the negative $\Delta S^{\neq}$ for the former species being largely attributed to the involvement of a ninth dmf in the transition state [4].

Mechanistic Aspects of Ligand Exchange on $[Ln(tmu)_6]^{3+}$

As a consequence of their large numbers of extranuclear electrons the trivalent lanthanides are able to exhibit coordination numbers ranging from 6 to 10, which is not possible for lighter metal ions. Thus mechanistic possibilities may arise for ligand exchange on six-coordinated lanthanide complexes, such as $[\mathrm{Ln(tmu)}]^{3+}$, which are not feasible for six-coordinated complexes of lighter metal ions. It was noted earlier that the large negative $\Delta S^{\neq}$ values observed for $[\mathrm{Ln(tmu)_6}]^{3+}$ are unexpected for a d activated exchange mechanism. However, if a substantial contribution to $\Delta S^{\neq}$ arises from interactions outside the first coordination sphere, these negative $\Delta S^{\neq}$ may be explicable. If it is assumed that $[\mathrm{Ln(tmu)}]^{3+}$ retains a tendency to form a tri-capped trigonal prismatic structure in which the three capping ligands are up to 9% more distant from Ln than the six prismatic ligands, as in $[\mathrm{Ln(H_2O)_9}]^{3+}$ [1], it may be envisaged that, during the tmu exchange process, opposed trigonal faces of the $[\mathrm{Ln(tmu)_6}]^{3+}$ octahedron rotate to form a trigonal prism, with simultaneous lengthening of the Ln–tmu bonds and weak coordination of three CD_3CN on the square faces. If one of the Ln–tmu bonds dissociates during this process, a transition state will be formed through a highly concerted process which induces significant ordering into the second coordination sphere of the erstwhile octahedral species, and should produce a substantial negative contribution to $\Delta S^{\neq}$. This mechanism is similar to one proposed earlier [8], and is very speculative. However, it does illustrate a type of exchange mechanism, which may be available to six-coordinated lanthanide complexes, and perhaps six-coordinated yttrium(III) complexes, but is unlikely to be available to complexes of lighter metal ions.

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