A Proton Magnetic Resonance Study of Ligand Exchange on the Hexakis-(1,1,3,3-tetramethylurea)scandium(III) Ion and its *NN*-Dimethylacetamide Analogue

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Proton n.m.r. spectroscopic studies show that the rate law for tetramethylurea (tmu) exchange on the hexakis-(tetramethylurea)scandium(III) ion is: rate = $6k_1[\mathrm{Sc(tmu)_6}^{3+}]$ where, typically, k_1 (300 K) = 0.26 ± 0.03 s^{-1}, $\Delta H^{\ddagger}_1$ = 91.2 ± 2.3 kJ mol^{-1}, and $\Delta S^{\ddagger}_1$ = 47.8 ± 6.7 J K^{-1} mol^{-1} in CD_3NO_2 diluent, while k_1 (300 K) = 1.08 ± 0.05 s^{-1}, $\Delta H^{\ddagger}_1$ = 68.6 ± 1.3 kJ mol^{-1}, and $\Delta S^{\ddagger}_1$ = −15.7 ± 3.8 J K^{-1} mol^{-1} in CD_3CN diluent. In contrast, the rate law for ligand exchange on the hexakis(*NN*-dimethylacetamide)scandium(III) ion is: rate = $6(k_1 + k_2[\mathrm{dma}])[\mathrm{Sc(dma)_6}^{3+}]$ in CD_3NO_2 and CD_3CN diluents. For the nitromethane system, k_1 (300 K) = 4.6 ± 0.3 s^{-1}, $\Delta H^{\ddagger}_1$ = 30.3 ± 2.0 kJ mol^{-1}, and $\Delta S^{\ddagger}_1$ = −132 ± 6 J K^{-1} mol^{-1} and k_2 (300 K) = 112 ± 3 dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger}_2$ = 26.0 ± 0.6 kJ mol^{-1}, and $\Delta S^{\ddagger}_2$ = −119 ± 2 J K^{-1} mol^{-1}. Similar parameters characterize the acetonitrile solutions. Ligand exchange in solutions of either $[\mathrm{Sc(dmf)_6}][\mathrm{ClO_4}]_3$ or $[\mathrm{Sc(dmso)_6}][\mathrm{ClO_4}]_3$ lies in the fast-exchange limit of the n.m.r. time scale. The mechanistic implications of these data are discussed and comparisons are made with other tripositively charged metal complex systems.

RECENT studies[1-3] indicate that the $[\mathrm{ScL_6}]^{3+}$ species exhibits a greater degree of flexibility in the mode of ligand exchange than appears to be the case for other $[\mathrm{ML_6}]^{3+}$ ions. Thus for $[\mathrm{ScL_6}]^{3+}$, where L = trimethyl phosphate[2] (tmp), the dominant exchange path is dissociative[4] (*D*) in CD_3CN diluent, but associative[4] (*A*) in CD_3NO_2 diluent. When L = dimethyl methylphosphonate[3] (dmmp) the *A* mechanism is also dominant in CD_3NO_2 diluent but in CD_3CN both *A* and *D* mechanisms are operative. In general there is a paucity of data concerning both the mechanism of ligand exchange on scandium(III) species and the effects upon the mechanism of variation in the environment external to the first co-ordination sphere.

In this paper, ligand-exchange studies are extended to $[\mathrm{ScL_6}]^{3+}$ where L is either tetramethylurea (tmu) or *NN*-dimethylacetamide (dma) in CD_3CN and CD_3NO_2 diluents. The former species is demonstrated to undergo ligand exchange through a *D* mechanism in both diluents whereas for the latter species both *A* and *D* mechanisms appear to operate simultaneously in both diluents. In addition, ligand exchange on scandium(III) in solutions of $[\mathrm{ScL_6}][\mathrm{ClO_4}]_3$ where L is either *NN*-dimethylformamide (dmf) or dimethyl sulphoxide (dmso) is shown to be in the fast-exchange limit of the n.m.r. time scale.

EXPERIMENTAL

The four perchlorate complexes whose analytical data are presented in Table 1 were prepared by previously described[2,5] methods and with the exception of $[\mathrm{Sc(tmu)_6}][\mathrm{ClO_4}]_3$ have been characterized in the literature.[6] All preparative and handling procedures were carried out in a dry-nitrogen-flushed glove-box. It is interesting to note that complexes (3) and (4) are quite hygroscopic, (2) absorbs atmospheric moisture over a period of days, while (1) is air stable. The ligands tmu, dma, dmf, and dmso were purified by previously reported methods,[7] CD_3NO_2, CD_3CN, and CD_2Cl_2 by distillation, and all liquid reagents were dried over Linde 4A molecular sieves. Solutions consisting of complex, ligand, and diluent were prepared by weight in 2 or 5 cm volumetric flasks and portions of each solution degassed and sealed under vacuum in n.m.r. tubes (outside diameter 5 mm).

TABLE 1

Elemental analyses (%)

Complex		Sc	C	H	N or S
(1) $[\mathrm{Sc(tmu)_6}][\mathrm{ClO_4}]_3$	requires:	4.30	34.65	7.00	16.15
	found:	4.35	34.25	6.50	15.8
(2) $[\mathrm{Sc(dma)_6}][\mathrm{ClO_4}]_3$	requires:	5.20	33.3	6.30	9.70
	found:	5.20	32.95	5.95	9.65
(3) $[\mathrm{Sc(dmf)_6}][\mathrm{ClO_4}]_3$	requires:	5.75	27.65	5.40	10.75
	found:	5.75	27.6	5.45	10.35
(4) $[\mathrm{Sc(dmso)_6}][\mathrm{ClO_4}]_3$	requires:	5.55	17.75	4.45	23.7
	found:	5.60	17.6	4.55	23.9

Proton n.m.r. spectra were run at 90 MHz on a Bruker HX-90-E spectrometer operating in the pulsed free-precession (p.f.p.) mode using an internal ^{2}H lock. Computer-averaged spectra were stored as 1K data blocks (1 024 points per spectrum) on a magnetic disk and subsequently subjected to a complete lineshape analysis[8] using the BNC-12 minicomputer of the spectrometer. The spectrometer temperature-control unit (B-ST 100/700), which was calibrated with a copper–constantan thermocouple, provided a temperature control of better than ±0.3 K.

RESULTS AND DISCUSSION

Solutions of $[\mathrm{Sc(dma)_6}][\mathrm{ClO_4}]_3$ and $[\mathrm{Sc(tmu)_6}][\mathrm{ClO_4}]_3$ and their respective free ligands in CD_3NO_2 and CD_3CN exhibit co-ordinated ligand resonances downfield from those of the free ligands under conditions of slow exchange. A comparison of the integrated areas of the resonances arising from the co-ordinated and free ligands in the 18 solutions whose compositions are given in

Table 2 shows that [Sc(dma)$_6$]$^{3+}$ and [Sc(tmu)$_6$]$^{3+}$ are the predominant scandium(III) species in the relevant solutions. In the tmu systems singlet resonances were observed for both co-ordinated and free tmu [the separation varies somewhat with concentration and temperature; for example, 17.1 (250)—17.9 Hz (290 K) in solution (ii) and 5.9 (250)—7.9 Hz (310 K) in solution (vii)] in the region of the freezing point of the solutions and this observation is consistent with rotation about the C–N bonds in tmu being in the fast-exchange limit of the n.m.r. time scale at these temperatures (225 K for CD$_3$CN, 245 K for CD$_3$NO$_2$). The barrier to internal rotation in free tmu[9] has been estimated to be 25.5 kJ mol^{-1} with an approximate coalescence temperature (100 MHz) of 123 K. An increase in barrier height upon co-ordination to UO$_2^{2+}$ has been observed[10] but measurements in that study were made at temperatures well below those achievable for the [Sc(tmu)$_6$]$^{3+}$ solutions investigated in this study. In the [Sc(dma)$_6$]$^{3+}$ solutions (x)—(xiv) quantitative determinations of the species in solution were based upon the acetyl ^{1}H resonances of co-ordinated and free dma [separated typically by 30 Hz, a shift which exhibits a negligible temperature dependence, in solution (xi)]. In CD$_3$CN solutions the residual resonances due to proton impurity arising from the diluent are in the vicinity of the ^{1}H acetyl resonances, thus precluding determinations based upon the latter resonances in all but the most concentrated solution (xv). Measurements were then based on the N-methyl resonances for solutions (xvi)—(xviii), these being void of effects due to rotation about the C–N bond[11] below 340 K. It is seen in Figure 1 that the high- and low-field components of the N-methyl doublets of co-ordinated and free dma respectively are almost coincident. This pattern was observed consistently for solutions (xv)—(xviii).

TABLE 2

Solution compositions and kinetic parameters for [ScL$_6$]$^{3+}$ systems

Solution	[ScL$_6^{3+}$] [a] (mol dm^{-3})		[L] [b] (mol dm^{-3})	[diluent] (mol dm^{-3})		N [c]	k_{ex} (350 K) [d] / s^{-1}	$\Delta H^{\ddagger}$ [e] / kJ mol^{-1}	$\Delta S^{\ddagger}$ [e] / J K^{-1} mol^{-1}
			[tmu]						
(i)	0.124	L = tmu	0.682	14.9	CD$_3$NO$_2$	5.9 ± 0.1	34.2 ± 1.5	99.1 ± 1.0	66.2 ± 2.8
(ii)	0.072 4		0.535	15.7		6.0 ± 0.2	33.5 ± 1.6	101 ± 1	70.7 ± 3.1
(iii)	0.053 4		0.294	15.8		5.9 ± 0.1	35.6 ± 1.5	92.7 ± 1.0	48.4 ± 2.8
(iv)	0.012 3		0.090 7	17.6		6.0 ± 0.1	45.5 ± 2.8	105 ± 2	84.7 ± 4.7
(v)	0.002 49		0.018 4	17.6		6.1 ± 0.1	57.4 ± 3.1	94.0 ± 1.4	56.1 ± 4.1
(vi)	0.001 45		0.010 8	17.7		5.8 ± 0.2	55.9 ± 5.7	91.2 ± 2.3	47.8 ± 6.7
(vii)	0.038 5		0.266	17.3	CD$_3$CN	5.9 ± 0.2	53.1 ± 1.2	80.5 ± 0.7	16.7 ± 2.2
(viii)	0.013 8		0.073 2	17.4		5.8 ± 0.2	63.1 ± 3.6	70.7 ± 1.6	−9.8 ± 4.8
(ix)	0.007 42		0.051 3	17.4		5.8 ± 0.2	64.1 ± 3.0	68.6 ± 1.3	−15.7 ± 3.8
(x)	0.039 5	L = dma	0.357	17.0	CD$_3$NO$_2$	6.0 ± 0.1			
(xi)	0.041 5		0.256	17.1		6.1 ± 0.1			
(xii)	0.019 8		0.109	17.5		5.9 ± 0.2			
(xiii)	0.010 3		0.0635	17.5		5.9 ± 0.2			
(xiv)	0.007 1		0.0390	18.0		6.0 ± 0.2			
(xv)	0.156 7		0.789 6	15.0	CD$_3$CN	6.0 ± 0.2			
(xvi)	0.050 5		0.255	16.2		5.9 ± 0.1			
(xvii)	0.032 4		0.163	17.9		5.8 ± 0.2			
(xviii)	0.019 5		0.098 1	18.0		5.9 ± 0.1			

[a] Added as [ScL$_6$][ClO$_4$]$_3$. [b] Added as L. [c] The mean number of ligands per scandium(III) ion as determined from a comparison of the integrated areas of the resonances of the co-ordinated and free ligands. [d] Taken from the linear regression of the plot of experimental ln($\tau_c T$) against $1/T$. The quoted errors represent one standard deviation. [e] Obtained from a linear regression of ln($\tau_c T$) against $1/T$. The quoted errors represent one standard deviation.

Complete lineshape analysis[8] of the ^{1}H spectra at selected temperatures yielded the mean site lifetimes of a single co-ordinated ligand, τ_c. Typical experimental spectra and best-fit calculated lineshapes for the [Sc(dma)$_6$]$^{3+}$–dma–CD$_3$CN system are depicted in Figure 1 along with corresponding τ_c values. The observed first-order rate constant is related to τ_c through equation (1) where x_C and x_F are the mol fractions of co-ordinated and free ligand (L) respectively and τ_F is the mean lifetime of a single ligand in the free state.

Two different types of kinetic behaviour for ligand exchange at the scandium(III) centre were observed in

$$k_{ex} = \tau_c^{-1} = x_F/\tau_F x_C = \text{exchange rate}/6[\text{ScL}_6^{3+}] \quad (1)$$

this study. The first type which characterizes the [Sc(tmu)$_6$]$^{3+}$ species is now described. The k_{ex} data for ligand exchange on [Sc(tmu)$_6$]$^{3+}$ in CD$_3$NO$_2$ [solutions (i)—(vi) in Table 2] show only a small variation with [tmu] consistent with the rate of the dominant ligand-exchange process being independent of free-ligand concentration, [tmu]. This is characteristic of a dissociative (D)[4] exchange mechanism in which the rate-determining step is the formation of the reactive intermediate [Sc(tmu)$_5$]$^{3+}$. This mechanism is typified by a rate equation identical to that in (1) and $k_{ex} = k_1$, the rate constant for the unimolecular rate-determining step. {A close inspection of the data for solutions (i)—(vi) reveals that k_{ex} exhibits a systematic 1.8-fold increase over a 63-fold decrease in [tmu]. It has been previously shown[2,3] that major changes in the environment of $[ScL_6]^{3+}$ can produce large variations in the ligand-exchange kinetics and it therefore seems probable that the variation in k_{ex} observed for $[Sc(tmu)_6]^{3+}$ reflects to some extent the relatively minor changes which occur in this environment as the concentration of the exchanging species is altered. These effects are discussed in more detail later.} If the postulated intermediate $[Sc(tmu)_5]^{3+}$ was insufficiently stable for a short, but independent, existence the observed exchange kinetics could be alternatively explained by the dissociative interchange mechanism $(I_D)^4$ in which the exchange process occurs through an ' encounter complex ' {in such a complex a tmu molecule resides in the second co-ordination sphere of $[Sc(tmu)_6]^{3+}$}. Ligand exchange then occurs through a process for which the major energetic component is the weakening of one scandium(III)–tetramethylurea bond to form the incipient $[Sc(tmu)_5]^{3+}$ moiety. At this point the leaving ligand and the entering ligand (already in the second co-ordination sphere) ' interchange ' positions, such that $[Sc(tmu)_5]^{3+}$ has no independent existence, and this is followed by relaxation back to the ground state, $[Sc(tmu)_6]^{3+}$. To reproduce the observed kinetics it is necessary that practically all of the $[Sc(tmu)_6]^{3+}$ units exist in the ' encounter complex ' form in solutions (i)—(vi) implying a high degree of preferential occupation of the second co-ordination sphere by tmu, for which there is no experimental evidence. On balance, therefore, it seems probable that a D mechanism is operating.

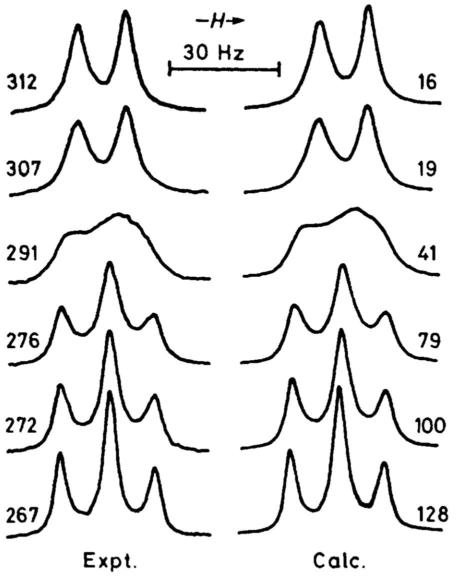

FIGURE 1 Proton n.m.r. (90-MHz) spectra characterizing ligand exchange on $[Sc(dma)_6]^{3+}$ in a solution in which $[Sc(dma)_6{}^{3+}]$, [dma], and $[CD_3CN]$ were respectively 0.0324, 0.163, and 17.9 mol dm^{-3}. The experimental spectra and the corresponding temperatures (K) appear to the left of the figure and the best-fit calculated lineshapes and the corresponding τ_c(ms) values appear to the right. The NMe_2 doublet of co-ordinated NN-dimethylacetamide is at low field

Studies of the tmu exchange process in CD_3CN diluent were confined to a relatively small concentration range [solutions (vii)—(ix)] as a consequence of the limited solubility of $[Sc(tmu)_6][ClO_4]_3$ in CD_3CN and the appearance of small extraneous ^1H resonances in the region of interest at low concentrations and temperature due, perhaps, to scandium(III) species of different co-ordination number or co-ordination of acetonitrile to scandium(III). {In solution (ix) the extraneous signal area was less than 2% of the main signal of $[Sc(tmu)_6]^{3+}$.} Nevertheless, the dominant path for ligand exchange upon $[Sc(tmu)_6]^{3+}$ appears to be independent of [tmu] which is consistent with a D mechanism. The variation of k_{ex} is attributed largely to the environmental effects mentioned above. A comparison of $\Delta H^‡$ and $\Delta S^‡$ values for solutions (i)—(ix) suggests that a major environmental modification has occurred on going from CD_3NO_2 as diluent to CD_3CN whilst still maintaining a dissociative mechanism over the concentration ranges reported. For the purposes of comparison with other systems later it is considered that the $\Delta H^‡$ and $\Delta S^‡$ values obtained from the more dilute solutions in each series are most characteristic of the ligand-exchange process in each diluent. Accordingly, the data for solutions (vi) and (ix) are quoted in Table 3.

The second type of kinetic behaviour is that characterizing exchange on $[Sc(dma)_6]^{3+}$ in CD_3NO_2 and CD_3CN for which k_{ex} is given by equation (2). The k_{ex} data

$$k_{ex} = k_1 + k_2[\text{dma}] \quad (2)$$

plotted in Figure 2 were interpolated from linear-regression analyses of ln τ_c *versus* $1/T$ for solutions (x)—(xiv) of Table 2. These k_{ex} data were then subjected to a further linear-regression analysis according to equation (2) to obtain the k_1 and k_2 values from which the corresponding $\Delta H^‡$ and $\Delta S^‡$ values were derived. The data obtained in CD_3CN diluent were similarly treated. {If the small environmental effects upon k_{ex} observed for the $[Sc(tmu)_6]^{3+}$ systems are also present in the $[Sc(dma)_6]^{3+}$ systems, it is unlikely that the derived k_1 values will be significantly affected as they are essentially derived by

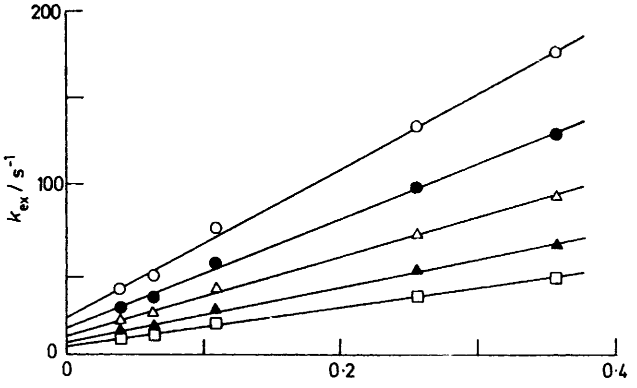

FIGURE 2 Plots of interpolated k_{ex} values for ligand exchange on $[Sc(dma)_6]^{3+}$ in CD_3NO_2 diluent. T = 340 (○), 330 (●), 320 (△), 310 (▲), and 300 K (□). The solid lines represent the linear-regression lines (*i.e.* for $k_{ex} = k_1 + k_2$[dma])

extrapolation to infinite dilution. The derived k_2 values may incorporate small environmental effects but, as a consequence of the strong dependence of k_{ex} upon [dma], the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values in Table 3 should refer predominantly to the second-order process characterized by k_2.} The observation of two ligand-exchange paths suggests similar energies for the intermediates $[Sc(dma)_5]^{3+}$ and $[Sc(dma)_7]^{3+}$ arising from *D* and *A* mechanisms respectively. It could be argued that the k_2 term in equation (2) arises from an I_D mechanism under the limiting condition in which [encounter complex] $\ll$ $[Sc(dma)_6{}^{3+}]$ such that $k_2 = k'K$, where k' is the rate constant for the interchange process and K is the equilibrium constant for the formation of the encounter complex. An inspection of Table 3 and Figure 2 indicates that if an I_D mechanism were operative it would be necessary for $k' > 10k_1$ which seems implausible since the primary energetic step in both the *D* and I_D mechanisms is fission of the metal–ligand bond.* As six-,[12] seven-,[13] eight-,[14] and nine-co-ordinate [15] scandium(III) species are well documented and demonstrate the ability of scandium(III) to increase its co-ordination number above six, it seems more plausible to assign the k_2 term to an *A* mechanism.†

TABLE 3

Parameters for exchange of unidentate oxygen-donor ligands on $[ML_6]^{3+}$ species

Ion	Diluent	Assigned exchange mechanism	k_1(300 K) / s^{-1}	k_2(300 K) / $dm^3\ mol^{-1}\ s^{-1}$	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}	Ref.
$[Sc(tmu)_6]^{3+}$	CD_3NO_2	*D*	0.26 ± 0.03		91.2 ± 2.3	47.8 ± 6.7	*a*
	CD_3CN	*D*	1.08 ± 0.05		68.6 ± 1.3	−15.7 ± 3.8	*a*
$[Sc(dma)_6]^{3+}$	CD_3NO_2	*D*	4.6 ± 0.3		30.3 ± 2.0	−132 ± 6	*a*
	CD_3NO_2	*A*		112 ± 3	26.0 ± 0.6	−119 ± 2	*a*
	CD_3CN	*D*	6.7 ± 4.2		28.3 ± 5.5	−135 ± 26	*a*
	CD_3CN	*A*		199 ± 19	29.0 ± 1.0	−104 ± 4	*a*
$[Sc(tmp)_6]^{3+}$	CD_3NO_2	*A*		51.3 ± 1.8	26.0 ± 0.9	−126 ± 3	2
	CD_3CN	*D*	65.7 ± 2.5		29.8 ± 0.4	−111 ± 2	2
$[Sc(dmmp)_6]^{3+}$	CD_3NO_2	*A*		13.7 ± 0.5	29.7 ± 1.1	−124 ± 3	3
	CD_3CN	*D*	3.2 ± 0.2		43.5 ± 1.8	−90.3 ± 5.4	3
	CD_3CN	*A*		14.8 ± 0.4	24.4 ± 1.1	−141 ± 3	3
$[Al(tmp)_6]^{3+}$	CD_3NO_2	*D*	0.45		98.3	76.1	24, 25
$[Al(dmmp)_6]^{3+}$	CD_3NO_2	*D*	5.1		79.5	33.0	24, 25
$[Al(OH_2)_6]^{3+}$		*D*	0.18		113	117	28
$[Ga(tmp)_6]^{3+}$	CD_3NO_2	*D*	6.3		87.9	63.2	24, 25
$[Ga(OH_2)_6]^{3+}$		*A*	2 500	(45.5) [b]	26.4	−92 (−125) [b]	28
$[In(tmp)_6]^{3+}$	CD_3NO_2	*A*		7.9	35.6	−109.2	24,25

[a] This work. [b] Calculated from the data in ref. 28 after assuming $[H_2O] = 55$ mol dm^{-3}.

Solutions of $[Sc(dmf)_6][ClO_4]_3$ and dmf in CD_2Cl_2 exhibit environmentally averaged dmf resonances down to 180 K and solutions of $[Sc(dmso)_6][ClO_4]_3$ and dmso in CD_3NO_2 have only one dmso resonance at 245 K. The chemical shift between co-ordinated and free resonances should be >10 Hz in each case on the basis of shift measurements of complex and ligand in isolation. This requires k_{ex} to be greater than 40 s^{-1} at the lowest temperatures examined. As the slow-exchange limit was not reached it was not possible to assign a value of n in the species $[Sc(dmf)_n]^{3+}$ or its dimethyl sulphoxide analogue. It therefore appears that the increased lability of these species may arise as a consequence of either an increase in co-ordination number to seven in the ground state, as has been suggested for the aqueous system,[17-19] or a markedly greater value for k_2 than has been measured for scandium(III) species to date.

The kinetic parameters and mechanisms for ligand exchange on the $[ScL_6]^{3+}$ systems studied in detail so far (L = tmp, dmmp, tmu, or dma) are presented in Table 3. Molecular models suggest that steric crowding decreases in the sequence L = tmu > tmp > dmmp > dma. The dominance of the k_1 term and the *D* mechan-

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* If [encounter complex] $\ll$ $[Sc(dma)_6{}^{3+}]$ and K[dma]$\ll 1$ for all the solutions studied, then for a solution with [dma] = 0.5 mol dm^{-3}, $K \ll 2$ dm^3 mol^{-1}. At 300 K (Table 3), k_2/k_1 (= $k'K/k_1$) *ca.* 24 in CD_3NO_2 solutions and *ca.* 30 in CD_3CN solutions which means that $k'/k_1 > 10$.

† An alternative mechanism may be postulated in which the diluent, X, enters the first co-ordination sphere to produce the highly reactive species $[ScL_6X]^{3+}$ and $[ScL_5X]^{3+}$ (which are consequently present in low concentration) according to the scheme below in which k_x characterizes the rate-determining

$$[ScL_6]^{3+} + X \rightleftharpoons [ScL_6X]^{3+} \xrightleftharpoons{k_x} [ScL_5X]^{3+} + L$$

step for the exhange of L. Operation of this ligand-exchange path, in parallel with the k_2 path for which an *A* mechanism has previously been proposed, would produce the k_1 term of equation (2). Such a mechanism is analogous to that proposed for ligand substitution on square-planar platinum(II) species.[16] However such a mechanism seems unnecessarily complicated for the scandium(III) systems for which the k_1 term only is observed, and is not operative when the k_2 term is observed alone. Whereas in the platinum(II) systems the simultaneous operation of *D* and *A* mechanisms would require the generation of reactive intermediate species of co-ordination number three and five respectively, the analogous co-ordination numbers of five and seven required for the scandium(III) species represent a less drastic variation in co-ordination number. Whilst there appears to be no definite report of a five-co-ordinate ground-state scandium(III) species in solution, the observation of $[Sc(trop)_3]$ and $[Sc(trop)_4]^-$ (where trop is the anion of 2-hydroxycyclohepta-2,4,6-trien-1-one, $C_7H_5O_2{}^-$) species [12,14] in the solid state demonstrates the ability of scandium(III) to vary its co-ordination number by two in the presence of a given ligand as a consequence of environmental changes.

ism in both CD_3NO_2 and CD_3CN for $[Sc(tmu)_6]^{3+}$ is consistent with steric crowding stabilizing the $[Sc(tmu)_5]^{3+}$ intermediate over the $[Sc(tmu)_7]^{3+}$ intermediate. In contrast, in less sterically crowded $[Sc(dma)_6]^{3+}$ systems, $[Sc(dma)_7]^{3+}$ is evidently of similar stability to $[Sc(dma)_5]^{3+}$ and furthermore provides the dominant exchange path at high [dma] values. These trends may also be discerned in the data for the $[Sc(tmp)_6]^{3+}$ and $[Sc(dmmp)_6]^{3+}$ systems, but it is clear that the nature of the diluent is also important in determining the exchange mechanism. The constancy of the co-ordination number of scandium(III) over wide concentration ranges together with the non-appearance of resonances arising from co-ordinated diluent [2,3] {except possibly in the $[Sc(tmu)_6]^{3+}$–tmu–CD_3CN system at low [tmu]} indicate that it is improbable that the effect of either diluent upon the exchange mechanism is a consequence of diluent entering the first co-ordination sphere (unless the mechanism discussed in the footnote operates). As the dielectric constants of CH_3NO_2 and CH_3CN are very similar it appears unlikely that a bulk environmental effect is instrumental in favouring one exchange mechanism over another and consequently it would seem that specific interactions between the first and second co-ordination spheres are of importance. The maximum difference between the interactions of CD_3NO_2 and CD_3CN with the spherical array of methyl groups presented by the first co-ordination sphere of all four $[ScL_6]^{3+}$ species arises if the NO_2 and CN groups of these diluents are oriented towards the scandium(III) centre. The electrostriction of the first and second co-ordination spheres may well cause the stereochemistry of the NO_2 and CN groups to be critical in determining the orientation of the methyl groups at the surface of the first co-ordination sphere and therefore the relative energies of $[ScL_6]^{3+}$ and the $[ScL_5]^{3+}$ and $[ScL_7]^{3+}$ intermediate or transition-state species. When the degree of steric crowding in the primary co-ordination sphere is high or low the tendency for a change in mechanism should not depend critically on a change in the diluent but nevertheless some disparity may be expected in activation parameters. In intermediate cases of steric crowding, which $[Sc(tmp)_6]^{3+}$ and $[Sc(dmmp)_6]^{3+}$ evidently are, a change in diluent may cause a change from a *D* to an *A* mechanism. On the basis of the limited data available it appears that the CD_3NO_2 diluent favours the *A* mechanism to a greater extent than does CD_3CN. The possible contributions to the observed ligand-exchange activation parameters of modification of the environment external to the first co-ordination sphere have been discussed elsewhere.[20-22]

A comparison of the mechanistic characteristics of ligand exchange of $[ScL_6]^{3+}$ with those of some other $[ML_6]^{3+}$ species may be made through the data in Table **3**. Such a comparison also requires a reference to the appropriate ionic radii [23] (Å) which are: Sc^{3+}, 0.68 (0.81); Al^{3+}, 0.45 (0.50); Ga^{3+}, 0.60 (0.62); and In^{3+}, 0.81 (0.81) where the Goldschmidt and Pauling radii appear in that order. Ligand exchange in the $[AlL_6]^{3+}$ systems [24-26] in Table **3** (and also when L = dmf,[26] dmso,[27] or dimethyl hydrogenphosphite [24]) apparently proceeds through a *D* mechanism which may be attributed to the small ionic radius of Al^{3+} and the concomitant steric crowding in $[AlL_6]^{3+}$. [It should, however, be noted that ligand exchange on the tetrakis(hexamethylphosphoramide)aluminium(III) ion is characterized by an *A* mechanism.[24]] In the case of $[Ga(OH_2)_6]^{3+}$ an *A* mechanism appears to operate for water exchange,[28,29] whereas in the case of $[Ga(tmp)_6]^{3+}$ a *D* mechanism operates.[30] Evidently, the larger ionic radius of Ga^{3+} compared to Al^{3+} causes the relative sizes of ligands to become important in determining mechanism. A further increase in ionic radius results in ligand exchange upon $[In(tmp)_6]^{3+}$,[30] and probably upon $[In(OH_2)_6]^{3+}$ also,[29] proceeding *via* an *A* mechanism. It thus appears from the data in Table **3** that at least three factors control the mechanism of ligand exchange on these $[ML_6]^{3+}$ species: (*i*) ionic radius of M^{3+}, (*ii*) the size of L, and (*iii*) the environment external to the first co-ordination sphere. In view of the similarity in ionic radii of Sc^{3+}, Ga^{3+}, and In^{3+} and the apparent ability of Ga^{3+} to undergo mechanistic change with the nature of L, it would be of interest to investigate the mechanistic characteristics of $[GaL_6]^{3+}$ and $[InL_6]^{3+}$ as the nature of L and the diluent are varied.

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