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Proton Magnetic Resonance Study of Ligand Exchange on the Hexakis(*N*,*N*-diethylacetamide)scandium(III) Ion and Its *N*-Methylacetamide Analogue. General Considerations of the Lability of Scandium(III)

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^{1}H NMR studies show that the rate of ligand exchange on $[\mathrm{ScL_6}]^{3+}$ when L = *N*-methylacetamide, *N*,*N*-dimethylacetamide, *N*,*N*-diethylacetamide (dea), or *N*-phenylacetamide is within the NMR time scale at 90 MHz. Typically for $[\mathrm{Sc(dea)_6}]^{3+}$ the exchange rate constant for a single ligand is $k_{\mathrm{ex}} = k_1 + k_2[\mathrm{dea}]_{\mathrm{free}}$ where $k_1(300\ \mathrm{K}) = 12.5 \pm 0.4\ \mathrm{s^{-1}}$, $\Delta H_1^* = 43.9 \pm 1.0\ \mathrm{kJ\ mol^{-1}}$, $\Delta S_1^* = -78 \pm 3\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $k_2(300\ \mathrm{K}) = 18.1 \pm 0.7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $\Delta H_2^* = 23.5 \pm 0.9\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S_2^* = -142 \pm 3\ \mathrm{J\ K^{-1}\ mol^{-1}}$ in $\mathrm{CD_3CN}$ solution. In contrast when L = *N*-methylformamide, *N*,*N*-dimethylformamide, *N*,*N*,-diethylformamide, and *N*,*N*-di-*n*-butylformamide, ligand exchange occurs at a rate in the fast-exchange limit of the NMR time scale. These kinetic differences between the acetamide and formamide ligands are attributed largely to the differing steric effects of the acetyl methyl group and the formyl proton, and in addition the kinetic differences within the acetamide systems are attributed to the steric effects arising from the groups bonded to the amide nitrogen. It is shown that a linear relationship between ΔH^* and ΔS^* exists for ligand substitution on scandium(III) whose lability is also compared with that of other metal ions.

Introduction

Our studies[1-5] of ligand exchange on scandium(III) were prompted by the reported[6-8] unexpectedly high lability toward ligand substitution of the aqua–scandium(III) ion for which the estimated water-exchange rate constant, $k_{\mathrm{H_2O}}(298\ \mathrm{K})$, is $\sim 5 \times 10^7\ \mathrm{s^{-1}}$. This high lability has been taken as an indication that >6 aqua ligands are coordinated to scandium(III) and that at least one of them is particularly labile as a consequence of the coordination geometry. So far, however, it has not been possible to demonstrate the presence of >6 ligands coordinated to scandium(III) in solution[9] or to directly determine the rate of water exchange on scandium(III). Nonaqueous systems have proved more amenable to study, and it has been shown with use of NMR spectroscopy that the exchange of oxygen donor ligands on $[\mathrm{ScL_6}]^{3+}$ species where L = trimethyl phosphate (tmp),[1-3] dimethyl methylphosphonate (dmmp),[4] 1,1,3,3-tetramethylurea (tmu), and *N*,*N*-dimethylacetamide (dma)[5] is characterized by one- or two-term rate laws, which have been interpreted variously in terms of dissociative (D) and associative (A) mechanisms[10] depending upon the identity of L. However when L is dimethyl sulfoxide (dmso) or *N*,*N*-dimethylformamide (dmf), the rate of ligand exchange in solutions of the crystalline complex $[\mathrm{ScL_6}](\mathrm{ClO_4})_3$ and the free ligand is in the fast-exchange limit of the NMR time scale over the accessible temperature range.[5] These two ligands are the smallest of those examined, and it appears in consequence that steric effects may be of considerable importance in determining the lability of scandium(III) towards ligand exchange. Accordingly, a systematic study of steric effects upon ligand lability is now reported for the ligand series *N*-methylformamide (nmf), *N*-methylacetamide (nma), dmf, dma, *N*,*N*-diethylformamide (def), *N*,*N*-diethylacetamide (dea), *N*,*N*-di-*n*-butylformamide (dbf), *N*-phenylacetamide (npa), dmso, and 4,4′-ditolyl sulfoxide (tso).

Experimental Section

The complexes $[\mathrm{Sc(nma)_6}](\mathrm{ClO_4})_3$ and $[\mathrm{Sc(dea)_6}](\mathrm{ClO_4})_3$ were prepared by heating a stirred solution of hydrated scandium perchlorate (G. Frederick Smith) (*x* mol) in triethyl orthoformate[11,12] (20*x* mol) at 330 K in a dry atmosphere for 1 h after which the distilled and dried ligand (6.5*x* mol) was added at ambient temperature. The white crystalline product was filtered off required ether in a dry nitrogen atmosphere prior to being pumped down on a vacuum line. The following modifications to the procedure were required to obtain the other five complexes in crystalline form. $[\mathrm{Sc(def)_6}](\mathrm{ClO_4})_3$ and $[\mathrm{Sc(dbf)_6}](\mathrm{ClO_4})_3$: After the addition of the ligand the volume of the reaction solution was reduced by ca. 60% on a vacuum line whereupon the complexes precipitated. $[\mathrm{Sc(npa)_6}](\mathrm{ClO_4})_3$: An oil formed after addition of the ligand, and dichloromethane was added to the reaction solution to induce crystallization. This product was recrystallized from a mixture of npa, acetonitrile, and ether and was then dried on a vacuum line. $[\mathrm{Sc(nmf)_6}](\mathrm{ClO_4})_3$: An oil formed after addition of the ligand. This oil was separated and washed with ether, benzene, and then ether prior to pumping down on a vacuum line, which resulted in crystallization. $[\mathrm{Sc(tso)_6}](\mathrm{ClO_4})_3$: The ligand was added as a solution in dry ethanol after which dry ether was added to precipitate the complex. Yields varied from 70 to 95%.

Analytical results appear in Table I. Analysis for scandium(III) as a trivalent ion was performed with use of an ion-exchange method,[13] and all other analyses were performed by the Australian Microanalytical Service, Melbourne. The infrared spectra of the complexes (recorded as Nujol mulls between sodium chloride plates) were consistent with the absence of water and coordinated perchlorate.

The ligands nmf, nma, dea, def, and dbf were dried by agitation over Linde 4A molecular sieves prior to fractional distillation under a reduced dry nitrogen atmosphere. The solvents $\mathrm{CD_2Cl_2}$, $\mathrm{CD_3CN}$, and $\mathrm{CD_3NO_2}$ were purified by distillation. All liquid reagents were stored over molecular sieves in a nitrogen-flushed glovebox. The solid ligands npa and tso were dried in vacuo over phosphorus pentoxide. Solutions of the complex and the free ligand in $\mathrm{CD_2Cl_2}$, $\mathrm{CD_3CN}$, or $\mathrm{CD_3NO_2}$ for NMR study were prepared by weight in 2-cm^3 volumetric flasks under a dry nitrogen atmosphere. Portions of each solution

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Table I. Analytical Data for Scandium(III) Complexes

	% Sc		% C		% H		% N	
	calcd	found	calcd	found	calcd	found	calcd	found
$[Sc(nma)_6](ClO_4)_3$	5.75	5.31	27.65	27.49	5.41	5.40	10.75	10.64
$[Sc(nmf)_6](ClO_4)_3$	6.44	6.36						
$[Sc(dea)_6](ClO_4)_3$	4.35	4.37	41.80	42.03	7.60	7.15	8.13	8.03
$[Sc(def)_6](ClO_4)_3$	4.73	4.80	37.92	37.75	7.00	6.83	8.84	8.80
$[Sc(npa)_6](ClO_4)_3$	3.90	3.90	49.95	49.67	4.72	4.80	7.28	7.20
$[Sc(dbf)_6](ClO_4)_3$	3.49	3.53	50.40	50.31	8.93	8.56	6.53	6.40
$[Sc(tso)_6](ClO_4)_3$	2.61	2.64	58.49	58.06	4.91	4.91		

Table II. Solution Composition and Kinetic Parameters for Ligand Exchange on Scandium(III)

soln	$[Sc(dea)_6{}^{3+}]$,[a] mol dm^{-3}	$[dea]_{free}$, mol dm^{-3}	$[CD_3CN]$, mol dm^{-3}	cn[b]	k_1(300 K),[c] s^{-1}	k_2(300 K),[c] dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$,[c] kJ mol^{-1}	$\Delta S^\ddagger$,[c] J K^{-1} mol^{-1}
1	0.219	1.471	10.6	5.9 ± 0.2				
2	0.181	1.095	13.6	6.0 ± 0.2	12.5 ± 0.4	...	43.9 ± 1.0	−78 ± 3
3	0.105	0.636	14.8	6.0 ± 0.2				
4	0.084	0.600	15.5	6.0 ± 0.2	...	18.1 ± 0.7	23.5 ± 0.9	−142 ± 3
5	0.048	0.289	17.0	6.0 ± 0.2				
6	0.018	0.126	17.3	6.0 ± 0.2				
soln	$[Sc(dea)_6{}^{3+}]$, mol dm^{-3}	$[dea]_{free}$, mol dm^{-3}	$[CD_3NO_2]$, mol dm^{-3}	cn	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}
7	0.193	1.489	11.2	5.8 ± 0.2				
8	0.158	0.876	14.1	5.9 ± 0.2	0.13 ± 0.02[d]	...	82 ± 3	10 ± 7
9	0.0901	0.504	15.9	5.9 ± 0.2				
10	0.0407	0.314	17.0	6.0 ± 0.2	...	14.9 ± 0.3	28.1 ± 0.6	−129 ± 2
11	0.0173	0.0965	17.5	6.0 ± 0.2				
12	0.0064	0.0495	17.6	5.8 ± 0.2				
soln	$[Sc(nma)_6{}^{3+}]$, mol dm^{-3}	$[nma]_{free}$, mol dm^{-3}	$[CD_3CN]$, mol dm^{-3}	cn	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}
13	0.0634	0.403	17.6	5.8 ± 0.2				
14	0.0882	0.391	17.3	5.9 ± 0.2	87 ± 6	...	27.3 ± 0.9	−117 ± 4
15	0.0403	0.207	17.9	5.9 ± 0.2				
16	0.0134	0.0883	18.1	5.9 ± 0.2	...	419 ± 38	26.1 ± 1.2	−108 ± 5
17	0.0039	0.0260	18.3	5.8 ± 0.2				
	$[Sc(dma)_6{}^{3+}]$,[e] mol dm^{-3}	$[dma]_{free}$, mol dm^{-3}	$[CD_3CN]$, mol dm^{-3}	cn	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}
	...	...	...	6	13.3 ± 1.6	...	32.2 ± 3.5	−116 ± 12
	...	...	...	...	...	167 ± 9	27.2 ± 1.2	−112 ± 4
	$[Sc(dma)_6{}^{3+}]$, mol dm^{-3}	$[dma]_{free}$, mol dm^{-3}	$[CD_3NO_2]$, mol dm^{-3}	cn	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}
	...	...	...	6	4.1 ± 0.4	...	30.8 ± 2.0	−131 ± 6
	...	...	...	...	...	114 ± 3	26.0 ± 0.6	−119 ± 2

[a] The chemical shift between the coordinated and free dea acetyl resonances varied systematically from 22.5 Hz in solution 1 to 16.8 Hz in solution 6 at 250 K. The analogous chemical shift of 33.6 Hz was virtually independent of concentration in solutions 7–12 at 250 K. The chemical shift between the acetyl resonances of coordinated and free *trans*-nma of 18.1 Hz was also almost concentration independent in solutions 13–17 at 225 K. The chemical shift between the *N*-methyl resonances of coordinated and free *trans*-nma varied systematically from 6.8 Hz for solution 13 to 6.2 Hz for solution 17 at 225 K. [b] cn = number of coordinated ligand molecules per scandium(III) ion, as determined from a comparison of the areas of the resonances arising from the coordinated and free ligand in the slow-exchange region. [c] In the determination of these kinetic parameters, data in the temperature ranges 262.1–341.9, 280.6–374.9, and 231.6–306.1 K were used for solutions 1–6, 7–12, and 13–17, respectively. For $[Sc(dma)_6]^{3+}$ the temperature ranges were 239.5–312.5 and 292.6–340.0 K for the CD_3CN and CD_3NO_2 solutions, respectively. The quoted errors represent one standard deviation. [d] At 300 K k_1 is small by comparison to k_2, but at 350 K the k_1 value of 14 s^{-1} is considerably more important relative to the k_2 value of 85 dm^3 mol^{-1} s^{-1}. [e] The concentrations of the solutions studied are given in ref 5, and the k_1, k_2, and appropriate activation parameters have been recalculated with use of DATAFIT but do not differ greatly from those quoted in ref 5.

were degassed and sealed under vacuum in 5-mm o.d. NMR tubes.

Proton NMR spectra were run at 90 MHz in the pft mode on a Bruker HX90E spectrometer locked on the solvent deuterium frequency. The spectra were stored as 1024 datum point blocks on a magnetic disk prior to line shape analysis using the BNC-12 minicomputer of the spectrometer. Temperature control, which was calibrated with a copper–constantan thermocouple, was better than ±0.3 K.

Results

Solutions of $[Sc(dea)_6](ClO_4)_3$ and $[Sc(nma)_6](ClO_4)_3$ and their respective free ligands in CD_3NO_2 and CD_3CN exhibit coordinated ligand resonances downfield from those of the free ligand under slow-exchange conditions (Table II). A comparison of the integrated areas of these resonances observed for the 17 solutions studied shows that either $[Sc(dea)_6]^{3+}$ or $[Sc(nma)_6]^{3+}$ is the predominant scandium(III) species in solution (Table II). In CD_3CN free nma exists ~97% as the isomer in which the methyl groups bear a trans relationship across the C–N bond and 3% as the cis isomer at 300 K. In $[Sc(nma)_6]^{3+}$ the cis isomer proportion varies from ~7% at 250 K to ~9.5% at 350 K (Figure 1) and consequently the mole fraction of $[Sc(\textit{trans}\text{-nma})_5(\textit{cis}\text{-nma})]^{3+}$ approaches ≈0.5 at 350 K. At 90 MHz (Figure 1) the spectrum of this species is not resolved from that of $[Sc(\textit{trans}\text{-nma})_6]^{3+}$, and hence the derived ligand-exchange parameters discussed below are composite values characterizing both species. The probability

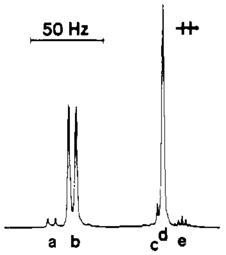


Figure 1. ^{1}H NMR (90-MHz) spectrum of $[\mathrm{Sc(nma)_6}]^{3+}$ in CD_3CN solution at 302 K. The N–CH_3 resonances of *cis*- and *trans*-nma are labeled a and b, the acetyl resonances are labeled c and d, and the solvent proton impurity resonance is labeled e, respectively. For *trans*- and *cis*-nma $J(\mathrm{NC}H_3\text{–N}H)$ = 4.9 and 5.3 Hz and $J(\mathrm{NC}H_3\text{–C}H_3)$ = 0.7 and <0.4 Hz, respectively.

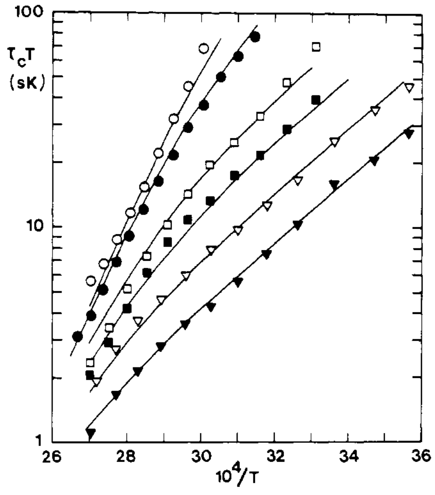
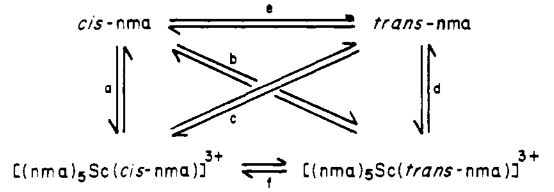


Figure 2. Semilog plot of τ_cT against $10^4/T$ for dea exchange on $[\mathrm{Sc(dea)_6}]^{3+}$ in CD_3NO_2 solution. The data sets correspond to solutions 7–12 (Table II), respectively, in ascending order of magnitude of τ_cT. The solid curves are those derived from a simultaneous fit of all of the data to eq 2.

of direct intermolecular exchange between *cis*-nma isomers in the coordinated and free states (path a) is relatively low by comparison to the cis–trans (paths b and c) and trans–trans (path d) intermolecular nma-exchange probabilities. Coalescence of the *cis*-nma resonances occurs as a consequence of exchange via paths a, b, and c, but because of the superimposition of these coalescing resonances upon those of the *trans*-nma resonances (which are much greater in amplitude), it was not practicable to obtain accurate kinetic parameters for the *cis*-nma exchange process. Thus the superimposed cis coalescence line shape was simply subtracted from the trans coalescence line shape, and kinetic parameters were derived through complete line shape analyses[14] of the coalescence of the *N*-methyl and acetyl resonances arising from coordinated and free *trans*-nma. These parameters, which appear in Table II, and which characterize a two-term exchange rate law similar to that described in eq 1, refer predominantly to the direct exchange of *trans*-nma. Rotation about the C–N bond in both coordinated and free nma and dea is in the slow-exchange limit over the temperature range encompassed by this study, and thus the intramolecular cis–trans isomerizations (paths e and f) produce no line shape modifications affecting the derivation of the nma-exchange parameters through the line shape analyses.



The variation of the mean lifetime of a single dea ligand in $[\mathrm{Sc(dea)_6}]^{3+}$, τ_c, with temperature and free dea concentration, determined from the coalescence of the acetyl resonances, is shown in Figure 2 from which it is seen that there is a distinctive curvature of the semilog plot of τ_cT against $1/T$. These data are symptomatic of a two-term rate law for the ligand-exchange process of the form of eq 1 where k_{ex} $(=1/\tau_c)$

$$\text{exchange rate} = 6k_{ex}[\mathrm{Sc(dea)_6}^{3+}] = 6(k_1 + k_2[\mathrm{dea}]_{\mathrm{free}})[\mathrm{Sc(dea)_6}^{3+}] \tag{1}$$

is the observed first-order rate constant, and k_1 and k_2 typify first-order and second-order ligand-exchange processes, which are characterized by significantly different ΔH^* values. Accordingly these data were simultaneously best fitted to the two-term Eyring equation (2) through an iterative procedure using the program DATAFIT.[15,16]

$$k_{ex} = \frac{k_BT}{h}\left[\exp\left(\frac{-\Delta H_1^*}{RT} + \frac{\Delta S_1^*}{R}\right) + [\mathrm{dea}]_{\mathrm{free}}\exp\left(\frac{-\Delta H_2^*}{RT} + \frac{\Delta S_2^*}{R}\right)\right] \tag{2}$$

The resultant kinetic parameters for this and for the other systems, which were also derived with use of this method, appear in Table II. At 300 K the k_1 term typifying the $[\mathrm{Sc(dea)_6}]^{3+}$ system in CD_3NO_2 appears inconsequential by comparison to the k_2 term, but it should be noted that at 350 K, which is close to the midpoint of the experimental temperature range (Table II), $k_1 = 14\ \mathrm{s^{-1}}$ and $k_2 = 85\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. The coordinated and free ligand resonances of the nma system in CD_3NO_2 were just coalesced at 250 K and entered the fast-exchange limit at higher temperatures. The low solubility of $[\mathrm{Sc(npa)_6}](\mathrm{ClO_4})_3$ precluded a study in CD_3NO_2, but in CD_3CN N–H resonances arising from coordinated and free npa consistent with the stoichiometry $[\mathrm{Sc(npa)_6}]^{3+}$ were observed at 230 K. However quantitative studies of the kinetics of the ligand-exchange process were precluded by the superimposition of the CD_3CN proton impurity resonances on the acetyl resonances and also by the width (16 Hz at 260 K for free npa) of the N–H resonances and their considerable increase in width with increase in temperature as a consequence of the ^{14}N quadrupolar interaction. The nmf, def, and dbf systems were in the fast-exchange limit over the liquid temperature range of CD_3CN (230–350 K) and also of CD_2Cl_2 (180–315 K) in the latter two cases, as was the tso system. Detailed examination of the proton impurity resonances of CD_3CN and CD_3NO_2 over the temperature and concentration ranges studied revealed no resonances attributable to coordination of these solvents. This and the constancy of the coordination number (Table II) over the concentration ranges suggest that neither of these solvents compete effectively for

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(15) To be submitted for publication.

(16) This procedure was adopted as τ_c was not determined at the same temperature over the entire range of $[\mathrm{dea}]_{\mathrm{free}}$, and consequently derivation of k_1 and k_2 through eq 1 prior to the derivation of the activation parameters required the interpolation of τ_c values for each desired temperature with a possible introduction of error as a consequence of the curvature evident in Figure 2. When this procedure was adopted, the values obtained (e.g., for $[\mathrm{Sc(dea)_6}]^{3+}/\mathrm{CD_3NO_2}$: $k_1(300\ \mathrm{K}) = 0.18 \pm 0.05\ \mathrm{s^{-1}}$, $\Delta H_1^* = 77 \pm 4\ \mathrm{kJ\ mol^{-1}}$, $\Delta S_1^* = -1 \pm 10\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $k_2(300\ \mathrm{K}) = 19.5 \pm 0.3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $\Delta H_2^* = 22.6 \pm 0.9\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S_2^* = -145 \pm 2\ \mathrm{J\ mol^{-1}\ K^{-1}}$) were found to differ somewhat from those obtained directly through eq 2, but this does not affect the general mechanistic interpretation.

sites in the first coordination sphere of scandium(III).

Discussion

The observation that ligand exchange is within the NMR time scale for $[ScL_6]^{3+}$ when L = nma, dma, dea, and npa but is in the fast-exchange limit of that time scale when L = nmf, dmf, def, and dbf emphasizes the importance of the acetyl methyl group and the formyl proton in determining ligand lability in these scandium(III) systems. A comparison of the Gutmann donor numbers[17,18] of dmf, dma, def, and dea, which are 26.6, 27.8, 30.9, and 32.2, respectively, suggests that electron donating ability is not the major factor determining the relative labilities of these ligands in $[ScL_6]^{3+}$, and the same is assumed to be the case for the other amides studied. Hence the steric interactions arising from R_1 in $O{=}C(R_1)NR_2R_3$ appear to be the predominant interactions determining ligand lability while the steric interactions arising from R_2 and R_3 are of lesser importance. When R_1 = H, an increase in coordination number in either the transition state, in which case an A mechanism will operate, or the ground state, in which case ligand labilization should result as a consequence of increased bond lengths as postulated for the aqua-scandium(III) species,[6,7] should occur more readily than when R_1 = Me. Alternatively it is possible that a greater decrease in scandium(III) ligand bond length for the nonleaving ligands may occur when R_1 = H during the formation of a D transition state with a consequently greater lability being conferred on $[ScL_6]^{3+}$ than is the case in the more sterically hindered cases where R_1 = Me. The absence of directly determined coordination numbers and ligand-exchange rate laws for the systems in which R_1 = H precludes further mechanistic discussion in contrast to the situation prevailing for those systems in which R_1 = Me. The k_1 and k_2 terms of the ligand-exchange rate law characterizing $[ScL_6]^{3+}$ where L = nma, dma, and dea may be assigned to D and A mechanisms, which proceed through five- and seven-coordinate reactive intermediates, respectively. There appears to be no report of a five-coordinate ground state species, but the observation of six- and eight-coordinate scandium(III)[21,22] in $[Sc(trop)_3]$ and $[Sc(trop)_4]^-$ (trop is the anion of 2-hydroxy-2,4,6-cycloheptatrien-1-one, $C_7H_5O_2^-$) illustrates the ability of scandium(III) to vary its coordination number by two in the presence of the same ligand, and consequently it is reasonable to expect a similar ability to be manifest in transition states and reactive intermediates. (A similar two-term rate law is observed for ligand exchange on $[Sc(dmmp)_6]^{3+}$ in CD_3CN.) At 300 K both k_1 and k_2 observed in CD_3CN solution are markedly greater for the $[Sc(nma)_6]^{3+}$ system in which the ligand has the least steric bulk as is seen below:

	$[Sc(nma)_6]^{3+}$	$[Sc(dma)_6]^{3+}$	$[Sc(dea)_6]^{3+}$
k_1, s^{-1}	87	13.3	12.5
k_2, $dm^3\ mol^{-1}\ s^{-1}$	419	167	18.1

This persists over the liquid temperature range (ca. 230–350 K) of the solutions studied and probably reflects the lesser steric crowding caused by R_2 and R_3 in $[Sc(nma)_6]^{3+}$ by comparison to that occurring in the other two systems. The activation parameters characterizing the ligand-exchange processes in CD_3CN (Table II) do not show a definite trend from which mechanistic conclusions may be drawn, but it is noticeable that when the solvent is changed to CD_3NO_2, the activation parameters characterizing $[Sc(dma)_6]^{3+}$ do not change significantly while those characterizing $[Sc(dea)_6]^{3+}$ change markedly. This latter effect of changing solvent has also been observed in other scandium(III)[2-5] systems as well as beryllium(II)[23,24] and dioxouranium(VI) systems[3] and indicates that interactions outside the first coordination sphere can make significant contributions toward observed activation parameters,[25,26] but it does not appear that additional mechanistic insight may be gained from this effect at this stage.

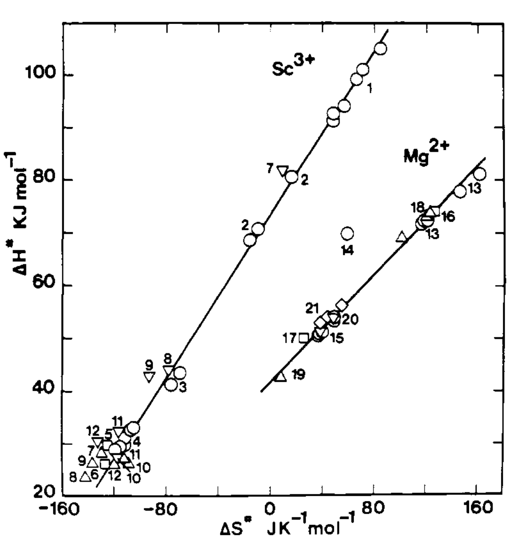

Figure 3. Plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ for ligand exchange on scandium(III) (upper data set) and magnesium(II) (lower data set). Individual systems are identified as follows: (identifying number) exchanging ligand, solvent, reference. The following solvent abbreviations are used: CD_3CN, an; CD_3NO_2, nm; CD_2Cl_2, cd; $C_2H_2Cl_4$, ch; $(CD_3)_2CO$, ac. For $[ScL_6]^{3+}$ circles denote systems in which exchange occurs through a D mechanism alone: (1) tmu, nm, 5; (2) tmu, an, 5; (3) tmp, ch, 2; (4) tmp, an, 2. Squares denote that exchanges occur through an A mechanism alone: (5) dmmp, nm, 4; (6) tmp, nm, 2. Inverted triangles and triangles, respectively, denote the D and A data from two-term rate laws: (7) dea, nm, this study; (8) dea, an, this study; (9) dmmp, an, 4; (10) nma, an, this study; (11) dma, an, 5; (12) dma, nm, 5. All of the $[MgL_6]^{2+}$ systems undergo ligand exchange through D mechanisms: (13) dmf, cd, 34; (14) methanol, methanol, 31; (15) tmp, cd, 35; (16) ethanol, ethanol, 32; (17) acetone, acetone, 33; (19) water, water, 30; (20) tmp, ac, 35; (21) dmf, ac, 34. Datum point 18 refers to ligand exchange on pentakis(triphenylphosphine oxide)magnesium(II) in cd.[36] The solid line through the scandium(III) data is the linear regression line for points 1–4 inclusive, and that through the magnesium(II) data is the linear regression line for points 13–21 excluding 14.

The recent accumulation of kinetic data for the exchange of a variety of unidentate oxygen donor ligands on six-coordinate scandium(III) facilitates a comparison of the lability of this ion with that of other metal ions toward ligand exchange. One method of comparison is through $\Delta G^{\ddagger}$ derived from $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ isokinetic relationships characterizing the exchange of a range of ligands on different metal ions[3] as shown for scandium(III) and magnesium(II) in Figure 3. The scandium(III) data for those systems considered to undergo ligand exchange through a D mechanism alone lie about the linear regression line $\Delta H^{\ddagger} = \Delta G^{\ddagger} + T(\Delta S^{\ddagger})$ for which $\Delta G^{\ddagger}$

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(18) The Gutmann donor number is equal to $-\Delta H_f$ (in kcal mol^{-1}) for the formation of a 1:1 adduct between $SbCl_5$ and the donor molecule concerned and consequently specifically refers to the Sb–donor interaction. Recently ^{23}Na NMR chemical shift measurements[19,20] have provided data substantially in agreement with these donor numbers. As these data appear to provide the most general guide to ligand donor power, it is assumed in this study that they at least provide an estimate of relative donor power toward scandium(III).

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= 73.3 ± 0.4 (one standard deviation) kJ mol^{-1} and T = 385.3 K (95% confidence interval 394.7-375.9 K). There is some randomness in the variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ characterizing the $[\mathrm{Sc(tmu)_6}]^{3+}$/tmu system in $\mathrm{CD_3NO_2}$ solution with change in the concentration of the exchanging species, but in $\mathrm{CD_3CN}$ solution both parameters decrease systematically with decrease in the concentrations of the exchanging species.[5] The $[\mathrm{Sc(tmp)_6}]^{3+}$/tmp system in $\mathrm{CD_3CN}$ is also characterized by a systematic variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with change in concentration.[2] It is possible that to some extent experimental error produces an internal $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation, which results in an apparent isokinetic relationship for the first system, but the systematic $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ variation of the latter two systems may reflect changes occurring in the environment outside the first coordination sphere as the concentrations of the exchanging species are varied.[27]

A statistical method of assessing the significance of the linearity of isokinetic plots has been proposed in the literature[28] according to which this linearity may be attributed to chemical origins with 95% certainly if the harmonic mean of the experimental temperatures, T_{hm}, lies outside the 95% confidence interval for T (the slope of the $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ plot) derived through linear regression. Since the lower 95% confidence limit of T is 375.9 K, which is greater than the highest temperature examined (370 K), it is clear that the position of a given system in the scandium(III) isokinetic plot may be attributed in part at least to chemical origins.

Six-coordinate scandium(III) and magnesium(II) are characterized by effective ionic radii[29] of 0.745 and 0.72 Å, respectively, and thus a comparison of their ligand-exchange parameters should reflect the differing formal charges to a significant extent. Ligand-exchange data for magnesium(II),[30-36] which are thought to characterize D mechanisms, also exhibit a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Figure 3) for which $\Delta G^{\ddagger}$ = 41.9 ± 0.4 kJ mol^{-1}, T = 252.8 K (262.4, 243.2 K), and T_{hm} = 223.9 K. (The reason for the $[\mathrm{Mg(MeOH)_6}]^{2+}$ point lying considerably off the isokinetic line is not understood, and it has been excluded from the linear regression analysis.) The difference in $\Delta G^{\ddagger}$ for scandium(III) and magnesium(II) suggests that the magnitude of the surface charge density exerts a major influence on the magnitude of $\Delta G^{\ddagger}$ for D ligand-exchange processes. In agreement with this supposition $\Delta G^{\ddagger} \sim 69.5$ kJ mol^{-1} ($T \sim 410$ K), derived from a recent compilation[37] of data for ligand exchange on six-coordinate aluminum(III), is closer to the scandium(III) value than to the magnesium(II) value. However, these data also reflect the approximate nature of the relationship between $\Delta G^{\ddagger}$ and surface charge density; if this relationship was exact, the smaller aluminum(III) center (ionic radius = 0.53 Å),[29] should produce a significantly greater $\Delta G^{\ddagger}$ value than does scandium(III). While the three metal ions considered all possess electronic dispositions that are not readily polarized, it is nevertheless to be expected that differences in bonding will be superimposed upon the metal ion-ligand dipole interaction. The close proximity to the linear regression line of the data arising from ligand exchange on scandium(III) proceeding through an A mechanism (Figure 3) suggests that surface charge density is a significant determinant for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this mechanism also.

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Registry No. $[\mathrm{Sc(nma)_6}](\mathrm{ClO_4})_3$, 78199-04-9; $[\mathrm{Sc(nmf)_6}](\mathrm{ClO_4})_3$, 78199-06-1; $[\mathrm{Sc(dea)_6}](\mathrm{ClO_4})_3$, 78217-04-6; $[\mathrm{Sc(def)_6}](\mathrm{ClO_4})_3$, 78199-08-3; $[\mathrm{Sc(npa)_6}](\mathrm{ClO_4})_3$, 78199-10-7; $[\mathrm{Sc(dbf)_6}](\mathrm{ClO_4})_3$, 78199-12-9; $[\mathrm{Sc(tso)_6}](\mathrm{ClO_4})_3$, 78199-14-1.

Supplementary Material Available: Table III listing k_{ex} values and experimental temperatures used in the derivation of the kinetic parameters for the dea and nma systems given in Table II (3 pages). Ordering information is given on any current masthead page.

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(27) It should be noted that the variation in k_{ex} at the midpoint of the experimental temperature range and the free ligand concentration variation are respectively 1.7- and 63-fold for $[\mathrm{Sc(tmu)_6}]^{3+}$/tmu/$\mathrm{CD_3NO_2}$, 1.2- and 5-fold for $[\mathrm{Sc(tmu)_6}]^{3+}$/tmu/$\mathrm{CD_3CN}$, and 2- and 100-fold for $[\mathrm{Sc(tmp)_6}]^{3+}$/tmp/$\mathrm{CD_3CN}$, consistent with ligand exchange proceeding predominantly through a D mechanism. In contrast k_{ex} ($=1/\tau_{\mathrm{c}}$) increases greatly and systematically with increase in the free ligand concentration for those systems characterized by an A mechanism[2,4] or the simultaneous operation of D and A mechanisms[4,5] as seen in Figure 2. Thus if the k_{ex} variations observed in the three systems above are taken as a measure of environmental effects, the influence of these effects upon the kinetic parameters derived for those systems undergoing ligand exchange through A or simultaneous D and A mechanisms is likely to be small.

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Synthesis, Vibrational Spectroscopy, and Mössbauer-Effect Study of Tin(II) Complexes of 15-Crown-5

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Three new complexes of the polyether 15-crown-5 and stannous salts have been prepared and characterized by elemental analysis and infrared and ^{119}Sn Mössbauer-effect spectroscopy. With tin(II) chloride and thiocyanate, 2:3 complexes are formed that contain two different kinds of metal atoms in the ratio 2:1. One of the metal atoms interacts directly with the crown ether ligands while the other metal atoms are present as anionic counterions in the structure. With tin(II) perchlorate, the crown ether forms a 2:1 complex with a unique $\mathrm{Sn^{2+}}$ ion in the structure. The ^{119}Sn Mössbauer isomer shift due to this metal ion is among the most positive (at 78 K) so far reported and can be characterized as a "bare" stannous ion sandwiched between two ring polyether moieties. The lattice dynamics of these complexes (as probed by the tin Mössbauer resonance) and the infrared spectra of these new complexes are discussed.

In an earlier study,[1] we have reported the synthesis, vibrational spectroscopy, and ^{119}Sn Mössbauer-effect parameters for a number of the complexes formed between stannous salts and the macrocyclic ethers 18-crown-6 and dibenzo-18-