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A Nuclear Magnetic Resonance Study of Ligand Exchange on the Hexakis(dimethylmethylphosphonate)scandium(III) Ion

DINO L. PISANIELLO and STEPHEN F. LINCOLN*

Department of Physical and Inorganic Chemistry, University of Adelaide, S. A., 5001, Australia

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^{1}H NMR spectroscopy has been used to investigate the exchange of DMMP (dimethylmethylphosphonate) on $[\mathrm{Sc(DMMP)_6}]^{3+}$ *in* $\mathrm{CD_3CN}$ *and* $\mathrm{CD_3NO_2}$ *diluents. The observed rate of ligand exchange for a given set of reactant concentrations* $= 6k_{ex}[\mathrm{Sc(DMMP)_6}]^{3+}$*. In* $\mathrm{CD_3CN}$ *diluent* $k_{ex} = k_1 + k_2[\mathrm{DMMP}]$ *where* $k_1(300\ K) = 3.2 \pm 0.2\ s^{-1}$, $\Delta H_1^\ddagger = 43.5 \pm 1.8\ kJ\ mol^{-1}$ *and* $\Delta S_1^\ddagger = -90.3 \pm 5.4\ J\ K^{-1}\ mol^{-1}$*; and* $k_2(300\ K) = 14.8 \pm 0.4\ mol^{-1}\ dm^3\ s^{-1}$, $\Delta H_2^\ddagger = 24.4 \pm 1.1\ kJ\ mol^{-1}$ *and* $\Delta S_2^\ddagger = -141 \pm 4\ JK^{-1}\ mol^{-1}$*. In* $\mathrm{CD_3NO_2}$ *diluent* $k_{ex} = k_2[\mathrm{DMMP}]$ *where* $k_2(300\ K) = 13.7 \pm 0.5\ mol^{-1}\ dm^3\ s^{-1}$, $\Delta H_2^\ddagger = 29.7 \pm 1.1\ kJ\ mol^{-1}$ *and* $\Delta S_2^\ddagger = -124 \pm 4\ J\ K^{-1}\ mol^{-1}$*. The mechanistic implications of these rate laws are discussed.*

Introduction

The factors determining both the rate and mechanism of ligand substitution on scandium(III) are not well understood. The rate of ligand substitution in the aqua-scandium(III) system is unexpectedly rapid for a trivalent metal ion occurring early in the periodic table [1, 2], whereas in the first completely characterized ligand exchange study concerning scandium(III), the rate of trimethylphosphate (TMP) exchange on $[\mathrm{Sc(TMP)_6}]^{3+}$ was found to be moderately rapid but much as expected for a hexa-coordinated metal ion of the surface charge density of scandium(III) [3, 4]. It was also observed, however, that the rate law for TMP exchange was sensitive to the reaction medium [4]. Thus, in $\mathrm{CD_3CN}$ diluent the TMP exchange rate was independent of the free TMP concentration, [TMP], whereas in $\mathrm{CD_3NO_2}$ a first order dependence upon [TMP] was observed. Accordingly, we now report a study of dimethylmethylphosphonate (DMMP) exchange on $[\mathrm{Sc(DMMP)_6}]^{3+}$ which provides further insight into the dynamics of ligand exchange on scandium(III).

Experimental

The preparation and handling of the white crystalline $[\mathrm{Sc(DMMP)_6}](\mathrm{ClO_4})_3$ complex was similar to that reported for the TMP analogue [4]. The complex is air stable (Found: Sc, 4.14; C, 19.6; H, 4.96; P, 16.8. $[\mathrm{Sc(DMMP)_6}](\mathrm{ClO_4})_3$ requires: Sc, 4.13; C, 19.87; H, 5.0; P, 17.08). Solutions of $[\mathrm{Sc(DMMP)_6}](\mathrm{ClO_4})_3$ and DMMP in distilled and dried (Linde 4A molecular sieves) $\mathrm{CD_3CN}$ and $\mathrm{CD_3NO_2}$ were prepared in 2 cm^3 volumetric flasks immediately prior to the NMR experiments. Portions of each solution were degassed and sealed under vacuum in 5 mm o.d. NMR tubes.

The NMR spectra, ^{1}H (90 MHz) and ^{31}P (36.43 MHz with ^{1}H broad band decoupling), were run on a Bruker HX90E spectrometer in PFP and PFT modes respectively using the deuterium resonance of $\mathrm{CD_3CN}$ and $\mathrm{CD_3NO_2}$ as the locking signals. Computer averaged PFP and PFT spectra for each temperature were stored on a magnetic disk, and the ^{1}H spectra subsequently subjected to a complete lineshape analysis using the BNC-12 mini-computer of the spectrometer. The spectrometer temperature control was better than ±0.3 K.

Results and Discussion

Under conditions of slow ligand exchange the broad band ^{1}H decoupled ^{31}P octuplet resonance arising from co-ordinated DMMP ($J\,^{45}\mathrm{Sc}$–$^{31}\mathrm{P} \approx 35$ Hz, $I = 7/2$ for ^{45}Sc) was observed downfield from the singlet resonance of free DMMP (Fig. 1) in both $\mathrm{CD_3CN}$ and $\mathrm{CD_3NO_2}$ diluents, but partial superimposition of the two resonances prevented a reliable estimate of the number of DMMP ligands co-ordinated to scandium(III) by integration. The ^{1}H doublet resonance from the -O-Me groups* of co-

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*Author to whom correspondence should be addressed.

*The doublets arising from the P-Me groups of co-ordinated and free DMMP appear upfield of the O-Me doublets but superimposition of the proton impurity resonance of $\mathrm{CD_3CN}$ on the former doublets renders quantitative study impossible and consequently this study is confined to the O-Me doublets.

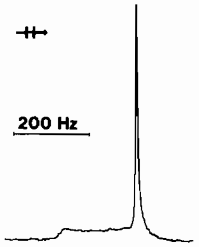

Fig. 1. A ^1H decoupled ^{31}P (36.43 MHz) FT NMR spectrum of a solution of $[Sc(DMMP)_6](ClO_4)_3$ (0.0657 mol dm^{-3}) and DMMP (0.3607 mol dm^{-3}) in CD_3CN diluent at 250 K. The broad octuplet arises from co-ordinated DMMP and the singlet from free DMMP.

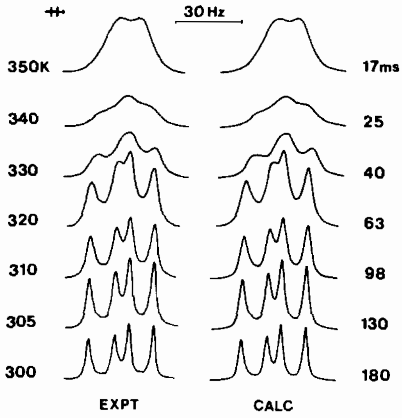

Fig. 2. ^1H (90 MHz) spectra from a solution of $[Sc(DMMP)_6](ClO_4)_3$ (0.0308 mol dm^{-3}) and DMMP (0.203 mol dm^{-3}) in CD_3CN diluent. The experimental temperatures (K) appear to the left of the figure and the best fit site life times of co-ordinated DMMP, τ_c (ms), appear to the right of the figure as do the best fit computer calculated spectra. The doublet arising from co-ordinated DMMP appears downfield.

ordinated DMMP was observed downfield from the analogous doublet for free DMMP in solutions (i) to (xi) (Table I) under conditions of slow ligand exchange, and a comparison of the integrated areas of these two doublets (Fig. 2) showed $[Sc(DMMP)_6]^{3+}$ to be the dominant scandium(III) species. In both CD_3CN and CD_3NO_2 diluents the slow exchange condition was observed at increasingly greater temperatures as the free DMMP concentration, [DMMP], was decreased. Thus in CD_3CN slow exchange conditions applied at and below 280 K and 300 K respectively for solutions (i) and (vi) which represent the extremes of the concentration range, and the analogous temperatures were 275 K and 305 K respectively for the CD_3NO_2 solutions (vii) and (xi). Above these temperatures a coalescence of the doublet signals was observed consistent with the occurrence of ligand exchange on $[Sc(DMMP)_6]^{3+}$ (Fig. 2).

The best fit mean lifetime, τ_c, of DMMP co-ordinated to scandium(III) at each temperature was determined by a complete lineshape analysis of the experimental spectrum using a computer programme based upon the exchange modified Bloch equations [5]. This programme requires as input the chemical shifts between the doublets and the linewidths of each resonance in the absence of exchange and also the site populations. Input parameters were extrapolated from the slow exchange region. For fixed values of $[Sc(DMMP)_6^{3+}]$ and [DMMP] the exchange rate is given by eqn. (1)

$$\begin{aligned} k_{ex} &= \text{exchange rate } (6\ [Sc(DMMP)]_6^{3+})^{-1} \\ &= (k_bT/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R) \end{aligned} \qquad (1)$$

where $k_{ex}\chi_c = \chi_c/\tau_c = \chi_F/\tau_F$ and τ_c and τ_F are the mean site lifetimes of co-ordinated and free DMMP,

TABLE I. Solution Compositions for the $[Sc(DMMP)_6]^{3+}$ Studies.

Solution	$[Sc(DMMP)_6]^{3+}$ mol dm^{-3}	[DMMP] mol dm^{-3}	$[CD_3CN]$ mol dm^{-3}	$[CD_3NO_2]$ mol dm^{-3}	C.N.[a]
(i)	0.134	0.8869	13.4	–	6.1 ± 0.1
(ii)	0.0657	0.3607	16.7	–	6.0 ± 0.1
(iii)	0.0308	0.203	17.6	–	6.0 ± 0.1
(iv)	0.0089	0.0487	18.2	–	5.9 ± 0.1
(v)	0.0060	0.0396	18.2	–	6.0 ± 0.2
(vi)	0.0014	0.0075	18.5	–	5.9 ± 0.1
(vii)	0.165	1.042	–	12.7	5.9 ± 0.2
(viii)	0.166	0.791	–	14.1	5.9 ± 0.1
(ix)	0.0783	0.373	–	16.3	5.8 ± 0.2
(x)	0.0377	0.238	–	16.7	6.0 ± 0.1
(xi)	0.0261	0.124	–	17.2	5.8 ± 0.2

[a] C.N. = number of co-ordinated DMMP molecules as determined from integration of the resonances of co-ordinated and free DMMP in the slow exchange temperature region.

TABLE II. Kinetic Parameters for Ligand Exchange.

System		k_1(300 K)	k_2(300 K)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Ion	Diluent	s^{-1}	$dm^3\ mol^{-1}\ s^{-1}$	$kJ\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$
$[Sc(DMMP)_6]^{3+}$	CD_3NO_2	–	13.7 ± 0.5	29.7 ± 1.1	−124 ± 4
$[Sc(DMMP)_6]^{3+}$	CD_3CN	3.2 ± 0.2	–	43.5 ± 1.8	−90.3 ± 5.4
$[Sc(DMMP)_6]^{3+}$	CD_3CN	–	14.8 ± 0.4	24.4 ± 1.1	−141 ± 4
$[Sc(TMP)_6]^{3+}$[a]	CD_3NO_2	–	51.3 ± 1.8	26.0 ± 0.9	−126 ± 4
$[Sc(TMP)_6]^{3+}$[a]	CD_3CN	65.7 ± 2.6	–	29.8 ± 0.4	−111 ± 2
$[Al(DMMP)_6]^{3+}$[b]	CH_3NO_2	5.1	–	79.5	33.0
$[Al(TMP)_6]^{3+}$[b]	CH_3NO_2	0.45	–	98.3	76.1
$[Al(TMP)_6]^{3+}$[c]	CD_3NO_2	0.36	–	87	35
$[Be(DMMP)_4]^{2+}$[d]	CH_3NO_2	–	0.99	60.2	−44.4
$[Be(TMP)_4]^{2+}$[d]	CH_3NO_2	–	1.7	56	−54
$[Be(TMP)_4]^{2+}$[e]	CH_2Cl_2	3.9	–	56.9	−43.9
$[Mg(TMP)_6]^{2+}$[f]	CD_2Cl_2	8.6×10^5	–	51.3	39.5
$[Mg(TMP)_6]^{2+}$[f]	$(CD_3)_2CO$	8.8×10^5	–	53.8	48.2

[a] From refs. 3 and 4. [b] From ref. 7. [c] From ref. 8. [d] From ref. 14. eFrom ref. 13. [f] From ref. 15.

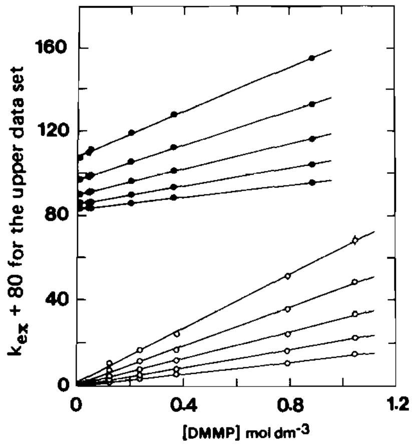

Fig. 3. Plots of interpolated $k_{ex}(s^{-1})$ values for ligand exchange on $[Sc(DMMP)_6]^{3+}$ against [DMMP]. The upper data set (●) was obtained in CD_3CN diluent while the lower set (○) refers to solutions in CD_3NO_2. The temperatures range in 10 K intervals from 340 K (upper line in each set) to 300 K (lower line). The lines represent linear regression lines.

and χ_c and χ_F are the appropriate mole fractions. The derived ln ($T\tau_c$) values were plotted against $^1/T$ and a linear regression analysis was carried out for these data for each of the solutions (i)–(xi). The k_{ex} values taken from the linear regression lines at various temperatures were then plotted against [DMMP] as shown in Fig. 3. It is apparent from Fig. 3 that in CD_3CN $k_{ex} = k_1 + k_2$[DMMP] whereas in CD_3NO_2 $k_{ex} = k_2$[DMMP] (the apparent small positive intercepts at [DMMP] = 0 observed in CD_3NO_2 do not differ significantly from zero). The kinetic parameters characterising the $[Sc(DMMP)_6]^{3+}$ system in both diluents are given in Table II as also are those characterising the $[Sc(TMP)_6]^{3+}$ system for which $k_{ex}(= k_1)$ is independent of [TMP] in CD_3CN diluent whereas $k_{ex} = k_2$[TMP] in CD_3NO_2 diluent. It is readily apparent that the mechanism of ligand exchange on hexa-co-ordinated scandium(III) is sensitive to both the nature of the ligand and the diluent. The k_1 term observed for the $[Sc(TMP)_6]^{3+}$ and $[Sc(DMMP)_6]^{3+}$ systems in CD_3CN diluent may be attributed to a dissociative [6] ligand exchange process in which the formation of a reactive intermediate of reduced co-ordination number makes the major contribution to the transition state energetics. In the latter system, however, a second ligand exchange pathway, characterized by k_2, becomes competitive whereas no k_2 pathway is observed for the $[Sc(TMP)_6]^{3+}$ system in CD_3CN diluent. The slightly smaller size and anticipated greater electron donating power of DMMP relative to TMP might be expected to cause the formation of a dissociative transition state and a transition state involving the incoming ligand with $[Sc(DMMP)_6]^{3+}$ to be respectively less and more favoured than the analogous transition states arising from $[Sc(TMP)_6]^{3+}$. However it is clear that interactions outside the first co-ordination sphere are also important in determining mechanism as indicated by the dominance of the k_2 term in CD_3NO_2 diluent. This k_2 term may arise from either an associative mechanism or a dissociative interchange mechanism [6] in which the encounter complex (*i.e.* $[Sc(DMMP)_6 .....DMMP]^{3+}$ in which the seventh ligand resides in the second co-ordination sphere) concentration is small by comparison to the total scandium(III) concentration. In this latter mechanism the dissociation of a ligand from the first co-ordination sphere is the major factor in the rate determining step for ligand exchange but this exchange can only occur through the encounter complex. Thus the observed first order exchange rate constant k'_{ex} is given by eqn. (2)

$$k'_{ex} = kK[DMMP]/(1 + K[DMMP]) \qquad (2)$$

where $K = [Sc(DMMP)_6^{3+}....DMMP]/([Sc(DMMP)_6^{3+}]$-$[DMMP])$ and k is the specific first order rate constant for exchange occurring through the encounter complex. When $K[DMMP] \ll 1$, $k'_{ex} \approx kK[DMMP]$ and is the condition under which the mechanism could produce the $k_2(= k'_{ex})$ terms observed in this study.

Whilst, on the basis of the kinetic data, it is impossible to determine whether the associative or the dissociative interchange mechanism is the origin of the k_2 pathway, the fact that ligand exchange on $[Al(DMMP)_6]^{3+}$ and $[Al(TMP)_6]^{3+}$ in CH_3NO_2 diluent is characterized by a k_1 pathway alone [7, 8] (Table II) suggests that the greater ionic radius (Sc^{3+}, 0.68 Å; Al^{3+}, 0.45 Å) of scandium(III) facilitates the formation of a transition state of increased co-ordination number. The observation of six [9], seven [10], eight [11] and nine [12] co-ordinate scandium(III) in the solid state further indicates the plausibility of the postulation of a transition state of stoichiometry $[Sc(DMMP)_7]^{3+}$.

The variation in the relative importance of the k_1 and k_2 pathways with change in diluent indicates that the k_1 and k_2 transition states possess similar free energies and that a significant component of these free energies arises from interactions in the second co-ordination sphere. This effect is also observed [13, 14] in the $[Be(TMP)_4]^{2+}$ system where the rate of ligand exchange is respectively independent of, and proportional to, [TMP] in CH_2Cl_2 and CH_3NO_2. For the case of $[Mg(TMP)_6]^{2+}$ in CD_2Cl_2 and $(CD_3)_2CO$ diluents there is a rate independence [16] of [TMP].

At present the kinetic data is rather sparse but it appears that changes in the order of the ligand exchange rate law with changes in the nature of the diluent may give some indication of the relative stabilities of transition states of different co-ordination numbers. Thus for beryllium(II) co-ordination numbers three and five are of similar stability, for magnesium(II) and aluminium(III) five appears to be more stable whilst for scandium(III) five and seven are evidently of similar stability.

This study shows that neither $[Sc(DMMP)_6]^{3+}$ nor $[Sc(TMP)_6]^{3+}$ are especially labile by comparison to their aluminium(III), magnesium(II) or beryllium(II) analogues (Table II). Nevertheless, it should be noted that TMP and DMMP have similar ligating properties and the possibility remains that other ligands, particularly if the ground state co-ordination number of scandium(III) becomes greater than six, may exhibit markedly shorter life times in the first co-ordination sphere in accordance with the suggestion made in the case of the aqua-scandium(III) ion [1, 2].

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