

Probing ligand substitution reactions in non-aqueous solvents by NMR methods: stopped-flow and high-pressure flow-Fourier-transform NMR and natural abundance ^{17}O NMR line broadening

Peter Moore

Chemistry Department, University of Warwick, Coventry CV4 7AL, U.K.

Abstract - Greater insight into the mechanisms of ligand substitution reactions at metal ions is being gained through the use of modern n.m.r. methods. Flow-Fourier-transform n.m.r. can be used to study some reactions which are difficult or impossible to examine by conventional methods, and to investigate reactions over a wider temperature range thereby improving the accuracy in ΔS^\ddagger values. High-pressure methods allow the determination of ΔV^\ddagger and ΔV_0^\ddagger values, and these parameters are proving to be especially useful for defining the mechanisms of such processes. High field n.m.r. is enabling access to low sensitivity nuclei, such as natural abundance ^{17}O , and in the presence of some paramagnetic metal ions the chemical shifts of the donor atoms of *O* or *N*-donor solvents can be so large that very fast rates become accessible.

INTRODUCTION

Attempts to establish the mechanism of ligand substitution reactions at metal ions in solution have been actively pursued for more than thirty years. Great progress was made possible by the development of rapid reaction techniques, notably flow-methods and pulsed or periodic relaxation techniques such as temperature-jump or ultrasonic sound absorption (Ref. 1). Nuclear magnetic resonance line-broadening methods have played an important part in the development of the subject, starting with continuous-wave spectrometers in the early days, and progressing rapidly since the introduction of commercial Fourier-transform spectrometers more than ten years ago. Whilst it was necessary to use highly enriched H_2^{17}O to study water exchange rates with continuous-wave spectrometers (the pioneering studies by T. J. Swift and R. E. Connick are especially noteworthy - Ref. 2), today we are fortunate in having access to high-field superconducting magnet spectrometers with much greater sensitivity, which reduces or often avoids the need for isotopic enrichment. This makes it possible to study *O*-donor non-aqueous solvents which are difficult or expensive to isotopically enrich. The growth in n.m.r. studies of ligand exchange kinetics has been very rapid (Ref. 3-8). Here we shall examine briefly some of the results from three very different types of n.m.r. experiments which have been made possible with modern Fourier-transform spectrometers.

Flow-n.m.r. is useful for obtaining complete spectra on a moderately rapid timescale (with our F.t.n.m.r. every 0.5s or so) following the rapid mixing of two reagents (Ref. 9-10). It is useful for extending studies of reactions over a wider temperature range (Ref. 11-14), and for giving structural information about intermediates involved in a reaction (Ref. 15-17). It has been possible to study some reactions by flow-n.m.r. which are difficult or impossible to investigate by line-broadening methods. For example, exchange of dimethyl sulphoxide (dmsO) with $[\text{V}(\text{dmsO})_6]^{3+}$ can be studied by flow-n.m.r. at low temperatures (Ref. 18), but not by n.m.r. line-broadening due to decomposition at elevated temperatures (Ref. 19). When flow-n.m.r. results at low temperatures are combined with data from line-broadening data at higher temperatures, improved accuracy in activation parameters especially ΔS^\ddagger , can be achieved. The Forsen-Hoffman spin saturation transfer method is also useful for obtaining data at intermediate temperatures (Ref. 20-21). There are considerable discrepancies in ΔS^\ddagger values reported from early n.m.r. experiments over narrow temperature ranges, and where sensitivity was low and computer fitting of data was not always possible. The diverse activation parameters reported for dmsO exchange with $[\text{Ni}(\text{dmsO})_6]^{2+}$ ion are typical of the difficulties encountered by early workers in this area (Ref. 7). The errors in ΔS^\ddagger values arise partly because ΔS^\ddagger is strongly correlated with ΔH^\ddagger , but also because ΔS^\ddagger is calculated from the intercept of a long extrapolation of an assumed linear Eyring plot.

$$\ln(k/T) = \ln(k_B T/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT \quad (1)$$

As can be seen from eqn. (1), ΔH^\ddagger values come from the slope of such a plot, and hence are usually more reliable than ΔS^\ddagger . By combining flow-n.m.r. data at lower temperatures with line-broadening results at higher temperatures, rate constants can be measured over more than a 100° temperature range in some cases (Ref. 12-14), and the values of ΔS^\ddagger then have more

mechanistic significance.

One of the reasons why high pressure studies have gained popularity in recent years has been the accuracy with which the mechanistically important ΔV^\ddagger values can be obtained. This is partly because like ΔH^\ddagger , ΔV^\ddagger is calculated from a slope and not an intercept, this time from a plot of $\ln(k)$ versus pressure (P).

$$\ln(k) = \ln(k_0) - (\Delta V^\ddagger/RT)P + (\Delta\beta^\ddagger/2RT)P^2 \quad (2)$$

Accuracy in ΔV^\ddagger values also comes from the use of a wide pressure range (typically 0.1-200 MPa). The compressibility coefficient of activation, $\Delta\beta^\ddagger$ is often so small that the third term in eqn.(2) becomes negligible. In aqueous solution it is estimated that $\Delta\beta^\ddagger$ should be non-zero for a D -mechanism, but near to zero for an I_d mechanism (Ref. 22). In non-aqueous systems the situation is less clear, and the uncertainties in the values determined for this parameter make it unreliable for mechanistic assignments at the present time. However, there have been notable successes in the use of ΔV^\ddagger values for establishing mechanisms, often with greater reliability than the conclusions reached from variable temperature studies. The combination of high pressure techniques with most of the key rapid reaction methods such as n.m.r. (Ref. 23-26), stopped-flow (Ref. 27-30) and temperature-jump (Ref. 31-33) has been achieved in a very short space of time.

High-field n.m.r. can make accessible some very rapid ligand exchange rates especially when paramagnetic metal ions such as Ni^{2+} are present. By studying the ligand nucleus which coordinates directly to the metal ion (e.g. ^{17}O or ^{14}N), the very large contact chemical shifts which are produced have allowed us to access non-aqueous solvent exchange rates as high as $3 \times 10^8 \text{s}^{-1}$ (e.g. Ni^{2+} which is coordinated to a non-exchanging tetra-azamacrocyclic ligand (Ref. 34)). The effect of macrocycle (L) conformation on the rates and mechanism of non-aqueous solvent (S) exchange in complexes of the type $[\text{M}(\text{L})\text{S}_n]^{2+}$ ($\text{M} = \text{Ni}, \text{Co}, n = 1 \text{ or } 2$) have been examined (Ref. 34-35).

FLOW-F.T.N.M.R. STUDIES

When $[\text{Ga}(\text{dmsO})_6]^{3+}$ ion is mixed with an excess of $[\text{D}^2\text{H}]_6$ -dmsO in deuterionitromethane solution and successive ^1H n.m.r. spectra are rapidly recorded at low temperatures (253-273 K), the coordinated dmsO resonance (δ 3.0 p.p.m.) is observed to decay and a new resonance emerges at the shift of uncoordinated dmsO (δ 2.5 p.p.m.). Direct studies of solvent exchange made in this way can be combined with results from more conventional line-broadening experiments at higher temperatures (305-368 K) as illustrated in Fig. 1, (Ref. 12).

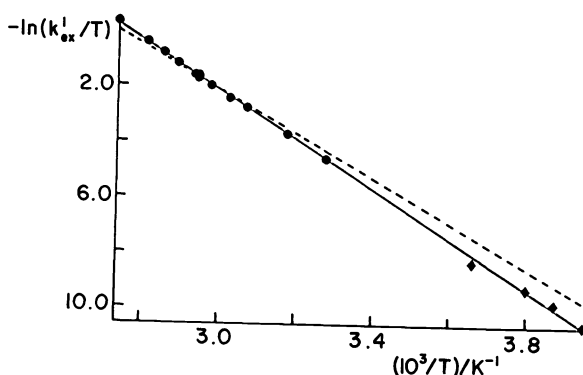


Fig. 1 Eyring plot for dimethyl sulphoxide (dmsO) exchange with $[\text{Ga}(\text{dmsO})_6]^{3+}$ ion; data are from line-broadening experiments (circles) and flow-n.m.r. (diamonds).

The dashed line in Fig. 1 shows how data obtained from line-broadening results alone can sometimes lead to erroneous activation parameters and large errors in ΔS^\ddagger . The dashed line was the Eyring plot obtained from line-broadening results without taking into account the variation in the chemical shift separation with temperature, but when this variation was taken into account excellent agreement with the rate constants obtained by flow-n.m.r. was observed as shown in Fig. 1 (Ref. 12). Without the flow-n.m.r. it is quite likely that this discrepancy would have gone unnoticed.

Flow-n.m.r. can also be used to study solvent exchange with paramagnetic $[\text{M}(\text{dmsO})_6]^{3+}$ ions (e.g. $\text{M} = \text{Fe}, \text{V}$; Ref. 14 and 18), and in these cases the spectra are simpler because the protons of the coordinated dmsO molecules have very short T_2 values and their resonance is

too broad to be observed. Therefore, upon mixing $[M(\text{dmsO})_6]^{3+}$ ($M = \text{Fe}, \text{V}$) with excess $[^2\text{H}]_6$ -dmsO in $[^2\text{H}]_3$ -nitromethane solution at *ca* 245 K, a single resonance emerges as the proteo-dmsO molecules become detached from the metal ion. In the case of Fe^{3+} , the flow-n.m.r. data can be combined with ^{13}C n.m.r. line-broadening results at elevated temperatures to give the activation parameters. Line-broadening results cannot be obtained for $[\text{V}(\text{dmsO})_6]^{3+}$ due to decomposition at high temperatures, and so the activation parameters are unknown in this case. A summary of available data for $[\text{MS}_6]^{3+}$ ions ($S = \text{dmsO}, \text{dmf}$) is given in Table 1.

TABLE 1. Rates and activation parameters for non-aqueous solvent exchange with $[\text{MS}_6]^{3+}$ ions ($S = \text{dmsO}, \text{dmf}$) at 298.2 K (data from Ref. 14 and 36).

M	S	k_{ex}/s^{-1}	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1}\text{mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3\text{mol}^{-1}$
Al	dmsO	0.30	82.6	+22.3	+15.6
Ga	dmsO	1.87	72.5	+ 3.5	+13.1
Cr	dmsO	1.91×10^{-7}	96.7	-49.5	-11.3
V	dmsO	0.055^a			
Fe	dmsO ^b	0.26	52.1	-43	- 3.1
Al	dmf	0.05	99.3	+28.4	+13.7
Ga	dmf	1.72	85.1	+45.1	+ 7.9
Cr	dmf	3.3×10^{-7}	97.1	-58.4	- 6.3

^a at 244.7 K; the rate is very similar to that for Fe^{3+} at this temperature,
^b in nitromethane; in dmsO $k = 0.09 \text{ s}^{-1}$, $\Delta H^\ddagger = 62.5 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -17 \text{ JK}^{-1}\text{mol}^{-1}$, $\Delta V^\ddagger = -3.1 \text{ cm}^3\text{mol}^{-1}$ (Ref. 37).

In the case of $[\text{InS}_6]^{3+}$ and $[\text{ScS}_6]^{3+}$ the rates are too fast to measure for good nucleophilic solvents (e.g. $S = \text{dmsO}, \text{dmf}$), but have been measured for poorer nucleophiles such as trimethyl phosphate (Ref. 38-39). An I_a mechanism would be reasonable for these larger six coordinate ions, which can easily expand their coordination sphere, and would account for the fast rates observed for good nucleophilic solvents. However, $[\text{Sc}(\text{tmp})_6]^{3+}$ can undergo either dissociative or associative solvent exchange depending on the diluent (Ref. 39). The lanthanide ions, $[\text{Ln}(\text{dmf})_8]^{3+}$ have been investigated recently, and in nitromethane solution a D-mechanism was observed for Tm and Yb, and an interchange (I) mechanism for Tb to Er, with a mechanistic crossover at Er (Ref. 40).

Even when some systems are studied over a wide temperature range ($> 100^\circ$) it is not always possible to assign a mechanism from the variable temperature results alone, despite the greater accuracy of the ΔS^\ddagger and ΔH^\ddagger values. For example, this is the case for $[\text{Ga}(\text{dmsO})_6]^{3+}$, although the significantly positive ΔV^\ddagger value leaves us in no doubt that solvent exchange proceeds with a dissociative mechanism. In contrast the negative ΔV^\ddagger and ΔS^\ddagger values for Cr^{3+} and Fe^{3+} are consistent with associative mechanisms. Since Ga^{3+} and Cr^{3+} have almost identical ionic radii (62 pm) the different mechanisms must be ascribed to the $3d^{10}$ and $3d^3$ electronic configurations respectively. Ga^{3+} does not have a vacant low-lying orbital capable of accepting a pair of electrons from the incoming nucleophile, whereas in Cr^{3+} one of the partially filled t_{2g} orbitals, which are essentially non-bonding, can readily act as the acceptor orbital in a seven-coordinate transition-state.

Most substitutions at 16-electron square-planar platinum(II) complexes are known to proceed with associative mechanisms. However, recently using flow-n.m.r. we have found evidence for dissociative substitution in *cis*- $[\text{Ph}_2\text{Pt}(\text{dmsO})_2]$ (Ref. 41). In these systems the dmsO molecules are *S*-bonded, and the *trans*-labilising influence of the phenyl groups enhances the dissociative activation mode, with a possible assistance from coordination to the oxygen atom of the remaining dmsO molecule in the transition-state (Fig. 2).

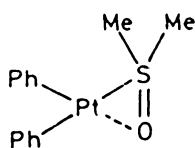


Fig. 2

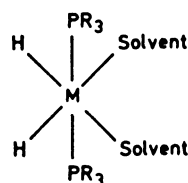


Fig. 3

Substitution of the dmsO molecules by 2,2'-bipyridine, 1,10-phenanthroline, and 1,2-bis(diphenylphosphino)ethane (dppe) also proceeds with a dissociative mechanism, but with a small associative pathway observed for dppe.

Flow-n.m.r. is especially useful for detecting intermediates during ligand substitution reactions. For example, in early work with $[Al(dmsO)_6]^{3+}$ we found good evidence for rate-determining chelate ring-closure mechanisms during the reactions with 2,2'-bipyridine (bipy) and 2,2':6',2''-terpyridine (terpy), but not with the more rigid 1,10-phenanthroline (phen) (Ref. 11). These reactions were followed by monitoring the ejection of the coordinated solvent molecules, which makes it easy to detect the end of each stage of a multistep chelation reaction. In recent studies of $[M(PR_3)_2(solvent)_2H_2]^+$ ions ($M = Rh, Ir$; $R = \text{phenyl or cyclohexyl}$; solvent = Me_2CO or $MeCN$; Fig. 3) reacting with dienes (norbornadiene, nbd, and cycloocta-1,3-diene, cod), we were able to monitor diene binding prior to any hydrogenation, and to detect two intermediates before H-transfer occurs (Ref. 13). Also we were able to show that binding of the more flexible cod involves a slow chelate-ring-closure, whereas for nbd chelate-ring-closure is rapid.

Detection of intermediates is often only possible by flow-n.m.r., for example in reactions involving nucleophilic (Ref. 17) and electrophilic (Ref. 15 and 16) attack at coordinated ligands.

HIGH PRESSURE WORK

Two of the most dramatic examples of the use of high-pressure n.m.r. to establish reaction mechanisms are illustrated in Figs. 4 and 5.

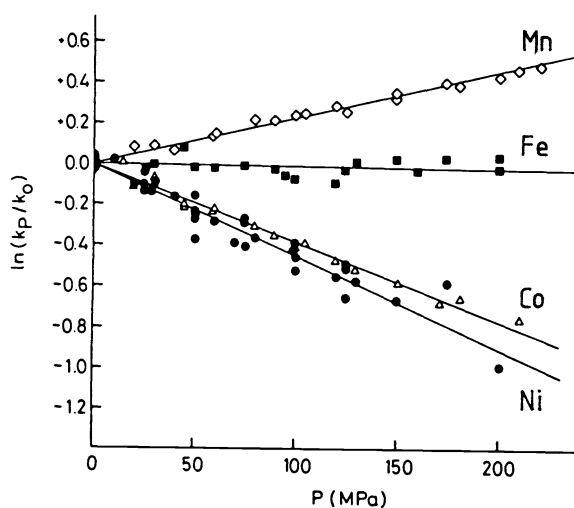


Fig. 4

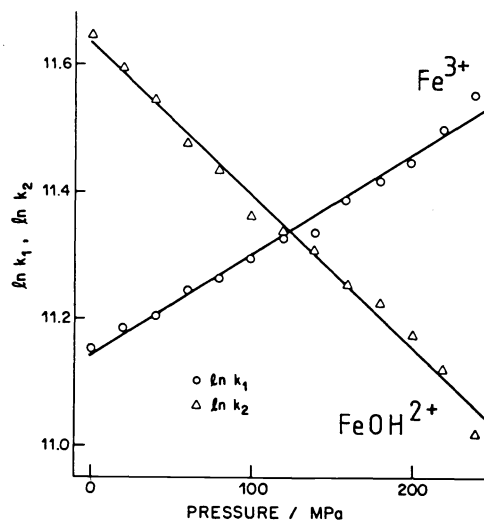


Fig. 5

From equation (2) it can be seen that when $\ln(k)$ is plotted *versus* P , a negative slope is observed if ΔV^\ddagger is positive. Hence from Fig. 4 it can be seen that there is a gradual change from positive ΔV^\ddagger values for solvent exchange with Ni^{2+} and Co^{2+} , to negative values for Mn^{2+} (and V^{2+}). It is concluded that in aqueous solution and in methanol, there is a gradual change from an I_d to an I_a mechanism in going from Ni^{2+} towards the left-hand side of the first row transition elements (Ref. 42). The incomplete occupancy of the t_{2g} set is again partly responsible for this trend.

Replacing a water molecule by OH^- ion in the inner-sphere of $[Fe(H_2O)_6]^{3+}$ has a remarkable effect on both the rate and mechanism of water exchange. The data in Fig. 5 leave us in no doubt that a change in mechanism has occurred from I_a (with $[Fe(H_2O)_6]^{3+}$ to I_d (with $[Fe(H_2O)_5OH]^{2+}$) (Ref. 43).

Neglecting outer-sphere effects, the magnitude of ΔV^\ddagger for dissociative loss of a solvent (S) from a hexakis(solvate), $[\text{MS}_6]^{n+}$, by a D-mechanism (eqn. 3) is given by eqn. 4.



$$\Delta V^\ddagger = V_{\text{MS}_5}^\circ + V_{\text{S}}^\circ - V_{\text{MS}_6}^\circ \quad (4)$$

In general the molar volume of the five-coordinate intermediate ($[\text{MS}_5]^{n+}$) is less than that of $[\text{MS}_6]^{n+}$, even for small solvent molecules such as water, and in general $\Delta V^\ddagger < V_{\text{S}}^\circ$ (the molar volume of the released solvent molecule). In aqueous solution ($V_{\text{S}}^\circ = 18 \text{ cm}^3 \text{ mol}^{-1}$) it is estimated that the maximum value of ΔV^\ddagger will be ca 9–11 $\text{cm}^3 \text{ mol}^{-1}$ for a D-mechanism (Ref. 5). The situation in non-aqueous solvents is not well established, but some clue as to the maximum values of ΔV^\ddagger to be expected comes from recent studies of ligand (L) exchange with *trans*- $[\text{CH}_3\text{Co}(\text{dmg})_2\text{L}]$. The activation parameters are summarised in Table 2.

TABLE 2. Rate constants (at 298.2 K) and activation parameters for the exchange of ligand L with *trans*- $[\text{CH}_3\text{Co}(\text{dmg})_2\text{L}]$ (dmg = dimethylglyoximate ion)

L	k/s^{-1}	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1}$	$V_{\text{S}}^\circ/\text{cm}^3 \text{ mol}^{-1}$
MeOH	1140	64.9	+31	+6.8	40.5
Me ₂ NCHO	270	67.2	+27	+7.9	77.5
(PhCH ₂) ₃ Sb	12	80.6	+46	+12.9	solid
Me ₂ NCHS	0.45	88.9	+47	+13.6	85.0
Me ₂ S	0.68	92.8	+63	+15.6	73.5
(MeO) ₃ P	0.0069	92.6	+24	+16.8	112.5

These systems are known to react with a D-mechanism, and the values of ΔV^\ddagger are very much less than V_{S}° as expected. There is an interesting, but as yet unexplained correlation of ΔV^\ddagger with ΔH^\ddagger . The expected (Ref. 44) correlation of ΔV^\ddagger with ΔS^\ddagger was not observed.

Studies of *mer*- $[\text{VCl}_3(\text{MeCN})_3]$ by ¹H n.m.r. have revealed two well-resolved solvent exchange rates, the solvent molecule in a *trans*-position to chloride being much more labile than the two mutually *trans* solvent molecules. The preliminary values of ΔV^\ddagger (Table 3) indicate that the two reactions have a dissociative mechanism, although the magnitude and sign of the ΔS^\ddagger values is surprisingly different for the two reactions.

TABLE 3. Rate constants (at 298.2 K) and activation parameters for two acetonitrile exchange rates observed for *mer*- $[\text{VCl}_3(\text{MeCN})_3]$ in $[\text{D}_2\text{H}]_3$ -nitromethane solution.

	Mutually <i>trans</i> -MeCN ^a	MeCN in <i>trans</i> -position to Cl ^{-b}
k/s^{-1}	1.6×10^3	3.6×10^5
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	30.3	48.9
$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	-82	+26
$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1}$	+6.1	+15.5

^a in acetonitrile solution, ¹⁴N n.m.r. gives $k = 0.79 \times 10^3 \text{ s}^{-1}$
^b in acetonitrile solution, ¹⁴N n.m.r. gives $k = 8.2 \times 10^5 \text{ s}^{-1}$, $\Delta H^\ddagger = 51.5 \text{ kJ mol}^{-1}$,
 $\Delta S^\ddagger = +41.2 \text{ JK}^{-1} \text{ mol}^{-1}$

For ionic reactions involving charge separation or contraction in the transition-state, solvent electrostriction tends to produce the dominant contribution to the values of ΔV^\ddagger , and the volumes of activation can be quite large. For example, from recent high-pressure stopped-flow studies of the base hydrolysis of the dichromate ion, values of ΔV^\ddagger were in the range -18 to -27 $\text{cm}^3 \text{ mol}^{-1}$ for reactions with OH⁻, NH₃, H₂O and 2,6-lutidine (Ref. 45). The volume profile for the reaction with OH⁻ ion is shown in Fig. 6.

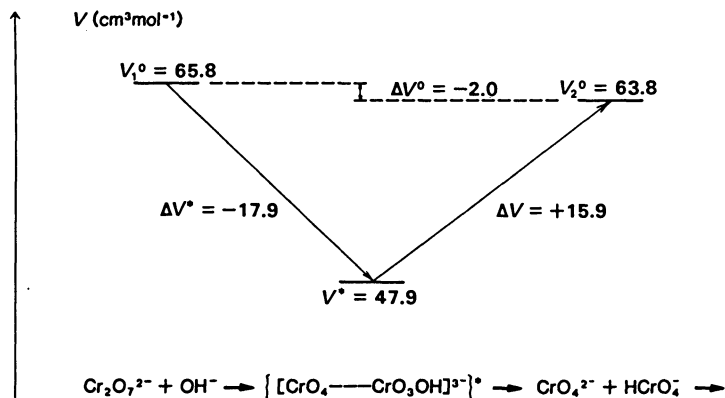


Fig. 6 Volume profile for the OH^- -hydrolysis of $[\text{CrO}_7]^{2-}$ at 298.2 K. Partial molar volumes V° are referred to $V_{\text{H}^+}^\circ = 0$. $V_1^\circ = V_{\text{Cr}_2\text{O}_7^{2-}}^\circ + V_{\text{OH}^-}^\circ$; $V_2^\circ = V_{\text{HCrO}_4^-}^\circ + V_{\text{CrO}_4^{2-}}^\circ$, $V_{\text{Cr}_2\text{O}_7^{2-}}^\circ = 69.8 \text{ cm}^3 \text{ mol}^{-1}$ [6], $V_{\text{OH}^-}^\circ = -4.0 \text{ cm}^3 \text{ mol}^{-1}$ [7], $V_{\text{CrO}_4^{2-}}^\circ = +19.7 \text{ cm}^3 \text{ mol}^{-1}$ [7], $V_{\text{HCrO}_4^-}^\circ = +44.1 \text{ cm}^3 \text{ mol}^{-1}$ [6].

There is a good linear correlation of ΔV^\ddagger and ΔS^\ddagger values in this case (Table 4).

TABLE 4. Rate constants and activation parameters at 298.2 K for the base hydrolysis of the dichromate ion (data from Ref. 45).

Base	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1}$
OH^-	20.5	-126.4	-17.9
NH_3	7.9	-161.1	-19.2
H_2O	36.8	-184.9	-24.9
2,6-lutidine	α 3.3	-239	-26.9

NATURAL ABUNDANCE ^{17}O N.M.R. LINE-BROADENING

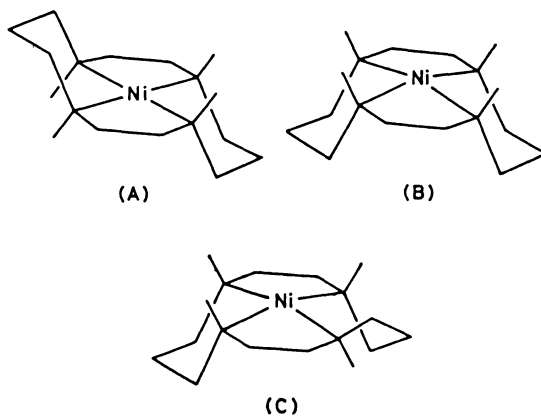


Fig. 7

Two isomers are known for nickel(II) complexes with the tetra-aza-macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) as shown in Fig. 7. The *trans*-III or *R, S, S, R* - isomer (A) forms six-coordinate complexes of the type $[\text{Ni}(\text{L})(\text{S})_2]^{2+}$

(S = solvent) by coordination symmetrically above and below the macrocycle plane, whereas the *trans*-I or *R, S, R, S* - form (B) forms five-coordinate $[\text{Ni}(\text{L})(\text{S})]^{2+}$ ions by axial ligation by S on the same side of the macrocyclic ligand plane as the four Me-N-groups. Small amounts of the *R, S, R, R* - isomer (C) have also been detected and the interconversion of (A) and (B) observed (ref. 46). The four-coordinate square-planar species $[\text{Ni}(\text{L})]^{2+}$ co-exist with the five- or six-coordinate solvates in the presence of solvents such as H_2O , dmsO and dmf.



Thermodynamic data for equilibria (5) can be obtained by ^1H n.m.r. (Ref. 47), visible spectrophotometry or ^{17}O n.m.r. (Ref. 34). The results are summarised in Table 5.

TABLE 5. Thermodynamic data at 298.2 K for equilibrium (5)

Isomer	Solvent	$-\Delta\text{H}^\circ /$ kJ mol^{-1}	$-\Delta\text{S}^\circ \text{ }^{\text{a}} /$ $\text{J K}^{-1} \text{ mol}^{-1}$	$-\Delta\text{S}^\circ \text{ }^{\text{b}} /$ $\text{J K}^{-1} \text{ mol}^{-1}$	Method
<i>trans</i> -(I), (A)	D_2O	19.9	46.0	75.5	^1H n.m.r.
	dmf	19.6	40.9	62.2	Spectral
	MeCN	16.8	32.0	56.6	Spectral
<i>trans</i> -(III), (B)	D_2O	37.6	112	171	^1H n.m.r.
	D_2O	37.9	115	174	^{17}O n.m.r.
	dmf	27.7	84	126	Spectral
	dmf	29.3	89	132	^{17}O n.m.r.

^a Based on $K = [\text{NiLS}_n] / [\text{NiL}] \alpha_{\text{S}}^n$ where $\alpha_{\text{D}_2\text{O}} = 0.80$ and $\alpha_{\text{dmf}} = 0.90$, assuming unit activity coefficients.

^b Based on $K = [\text{NiLS}_n] [\text{NiL}][\text{S}]^n$ where $[\text{D}_2\text{O}] = 27.8 \text{ mol dm}^{-3}$ and $[\text{dmf}] = 11.6 \text{ mol dm}^{-3}$.

Notice that values of ΔS° are large and negative as expected. A study of the kinetics of equilibrium (6) requires a knowledge of the thermodynamic data, and the use of high-field ^{17}O n.m.r. to access the very large rate constants involved. The results of a 54.24 MHz ^{17}O n.m.r. study are summarised in Table 6 (Ref. 34).

 TABLE 6. Rate constants and activation parameters at 298.2 K for the loss of a single solvent (S) molecule from $[\text{Ni}(\text{L})\text{S}_n]^{2+}$ (eqn. 5) compared with $[\text{NiS}_6]^{2+}$ ions.

Complex	k/s^{-1}	$\Delta\text{H}^\ddagger/\text{kJ mol}^{-1}$	$\Delta\text{S}^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$
<i>trans</i> -(I)- $[\text{NiL}(\text{D}_2\text{O})]^{2+}$	1.6×10^7	24.7	-24
<i>trans</i> -(I)- $[\text{NiL}(\text{dmf})]^{2+}$	1.5×10^7	30.1	-6.4
<i>trans</i> -(I)- $[\text{NiL}(\text{MeCN})]^{2+}$	0.56×10^7	20.3	-48
<i>trans</i> -(II)- $[\text{NiL}(\text{D}_2\text{O})_2]^{2+}$	1.6×10^8	37.4	+38
<i>trans</i> -(III)- $[\text{NiL}(\text{dmf})_2]^{2+}$	3.3×10^8	38.3	+47
<i>trans</i> -(III)- $[\text{NiL}(\text{MeCN})_2]^{2+}$	0.15×10^8	41.5	+32
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	0.87×10^4	56.9	+32
$[\text{Ni}(\text{dmf})_6]^{2+}$	0.87×10^4	64.4	+46
$[\text{Ni}(\text{MeCN})_6]^{2+}$	0.28×10^4	64.3	+37

The remarkable accelerating effect of tetra-azamacrocyclic ligands on the rates of solvent exchange is evident from the data in Table 6, values of k_{ex} increasing by factors of 10^3 - 10^4 . The rate acceleration arises primarily from a reduction in the ΔH^\ddagger values by 15-26 kJ mol^{-1} for the six-coordinate complexes and by 28-44 kJ mol^{-1} for the five-coordinate species. Significantly the values of ΔH^\ddagger are lowest for the five-coordinate complexes, and the values

of ΔS^\ddagger are negative for these complexes. The six-coordinate complexes all react with positive ΔS^\ddagger values. The conclusion is that the five-coordinate complexes undergo associative solvent exchange, and the six-coordinate species dissociative exchange. However, a recent measurement of ΔV^\ddagger for acetonitrile exchange with the five-coordinate $[\text{Ni}(\text{L})(\text{MeCN})]^{2+}$ ion gave $\Delta V^\ddagger = +2.3 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$, and the authors argue for a dissociative D-mechanism. (Ref. 35). This conclusion is not consistent with the variable temperature kinetic and thermodynamic data, and further work is needed to resolve this dichotomy (Ref. 34).

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