Relative Labilities of Five-co-ordinate Mono(acetonitrile)(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)-nickel(II) and -cobalt(II) Ions towards Associative Solvent Exchange

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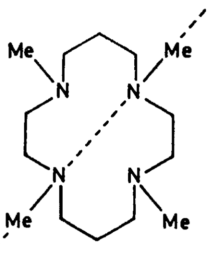
A comparison of the rates of solvent exchange and anation of the paramagnetic five-co-ordinate complex ions [ML(S)]$^{2+}$ (M = Co^{II} or Ni^{II}; L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, S = NCMe or OH$_2$) shows that the nickel(II) complexes are significantly more labile than the cobalt(II) analogues. For acetonitrile solvent exchange, $\Delta S^{\ddagger}$ values are large and negative and $\Delta H^{\ddagger}$ values are low for both the nickel(II) and cobalt(II) complexes, in line with an associative interchange (I_a) mechanism. Previous ^{13}C n.m.r. line-broadening results obtained for the [NiL(NCMe)]$^{2+}$ ion are confirmed by ^{15}N n.m.r., and an analogous ^{13}C and ^{15}N line-broadening study of the high-spin [CoL(NCMe)]$^{2+}$ ion gives (at 298.2 K): $10^{-5}\,k_{ex.}$ = 5.65 ± 0.50 s^{-1}, $\Delta H^{\ddagger}$ = 19.5 ± 0.8 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −69.5 ± 3.5 J K^{-1} mol^{-1}. Comparison with the parent hexasolvated metal ions shows that the quadridentate macrocyclic ligand (L) significantly lowers $\Delta H^{\ddagger}$ for acetonitrile exchange by 44 and 30 kJ mol^{-1} for nickel(II) and cobalt(II) ions respectively, but whereas this results in a marked rate increase (>10^3) for Ni^{II}, for Co^{II} the rate increases by less than a factor of two because of the more negative $\Delta S^{\ddagger}$ value. The results are compared with previous studies of the effects of amine ligands on the rates of acetonitrile and water exchange on cobalt(II) and nickel(II) ions.

THE macrocyclic quadridentate ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) reacts with solvated metal ions (*e.g.* M = Co^{II}, Ni^{II}, or Zn^{II}) to give five-co-ordinate complexes [ML(X)]$^{n+}$ [X = unidentate anion (n = 1) or solvent (n = 2)].[1,2] A ^{13}C n.m.r. study of the [ZnL(X)]$^{+}$ ions[3] and an ^{1}H n.m.r. study of the paramagnetic [NiL(Cl)]$^{+}$ ion[4] in nitromethane solution are consistent with these complexes having a trigonal-bipyramidal geometry at low temperatures [Figure 1(*a*)], the macrocycle having folded about the dashed line in the diagram, and with two pairs of N-methyl groups (axial and equatorial) on the same side of the macrocycle (*i.e.* with *R,S,R,S* nitrogen configurations). Such species are fluxional in solution as shown by their variable-temperature n.m.r. spectra; for example, the two pairs of N-methyl groups give rise to two resonances at low temperatures but only one resonance at, or above, room temperature.[3,4] The transition state or intermediate involved in this low-energy dynamic process ($\Delta G^{\ddagger}$ = 53.8 ± 3.0 kJ mol^{-1})[3] most likely has the square-pyramidal geometry found in the crystal structures of [NiL(N$_3$)]$^{+}$ and [ZnL(Cl)]$^{+}$ ions [Figure 1(*b*)].[3,5] The [ML(NCMe)]$^{2+}$ ions (M = Ni^{II} or Co^{II}) studied here are believed to behave in the same way, having the trigonal-bipyramidal geometry 1(*a*) at low temperatures, but a 'time-averaged' square-pyramidal geometry 1(*b*) at, or above, room temperature.



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Recently we measured the rates of acetonitrile exchange with the five-co-ordinate [NiL(NCMe)]$^{2+}$ and six-co-ordinate [NiL(NCMe)$_2$]$^{2+}$ ions using paramagnetic ^{13}C n.m.r. line broadening.[6] In the six-co-ordinate complex the macrocycle has a different conformation with an *R,S,S,R* set of N-donor configurations as shown in Figure 1(*c*). The five-co-ordinate complex was found to react with an associative solvent-interchange (I_a) mechanism ($\Delta S^{\ddagger}$ = −50 J K^{-1} mol^{-1}) whereas the six-co-ordinate complex exchanges with the more usual dissociative interchange (I_d) mechanism ($\Delta S^{\ddagger}$ = 32 J

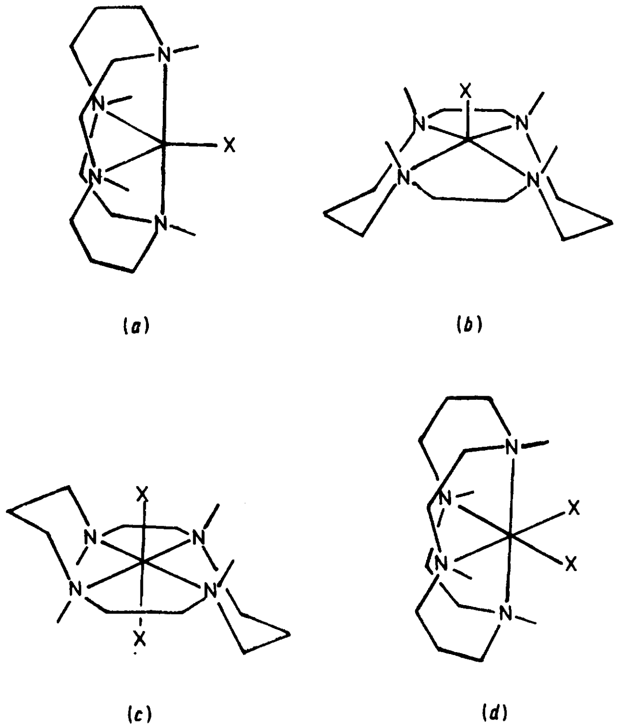

FIGURE 1 Various structures for metal complexes of (L)

K^{-1} mol^{-1}). Both complexes are significantly more labile than the $[Ni(NCMe)_6]^{2+}$ ion, in line with previous findings of an accelerating effect of N-donor ligands upon the rates of solvent exchange on nickel(II) and cobalt(II) ions.[7,8]

In this study we have measured the rate of acetonitrile exchange with the high-spin five-co-ordinate $[CoL(NCMe)]^{2+}$ ion. This work was prompted by the report of an unusually slow rate of water exchange for the high-spin $[CoL(OH_2)]^{2+}$ ion (10^{-4} $k_{ex.} = 4.2$ s^{-1}) where, in contrast to the behaviour found for nickel(II), L appears to have a marked decelerating effect upon the rate of solvent exchange.[9] An associative interchange mechanism is again favoured for the $[CoL(OH_2)]^{2+}$ ion ($\Delta S^{\ddagger} = -34$ J K^{-1} mol^{-1}), and so the present study enables a direct comparison to be made between closely related five-co-ordinate nickel(II) and cobalt(II) complexes, all of which are expected to react with the same (I_a) mechanism. There have been very few studies of the reactivities of five-co-ordinate nickel(II) and cobalt(II) complexes, and their relative labilities are not well established.

Previous work showed that natural-abundance ^{13}C n.m.r. is a far more useful probe than ^1H n.m.r. for measuring the rates of acetonitrile exchange with paramagnetic nickel(II) complexes because of the greater contact shift of the nitrile carbon resonance.[6] In fitting paramagnetic line-broadening data to the equations of Swift and Connick,[10] more reliable activation parameters are obtained if data are available over as wide a temperature range as possible for that linear region of the curve where line broadening is controlled primarily by the rate of ligand exchange. The greater the chemical shift of the bound-ligand resonance, the easier it is to access this important linear region of the curve as shown, for example, by previous studies of acetonitrile exchange using ^{14}N rather than ^1H n.m.r.[11] Since the quadrupolar ^{14}N nucleus gives rise to very broad resonances even in the absence of a paramagnetic metal ion or exchange broadening, we have examined in this work how useful natural-abundance ^{15}N n.m.r. might be as a probe for measuring ligand-exchange rates for N-donor ligands (the ^{15}N nucleus has spin $\frac{1}{2}$, and unbroadened linewidths <2 Hz). Despite the very low natural abundance of the ^{15}N nucleus and the very low sensitivity of ^{15}N n.m.r., for neat solvents it is relatively easy to obtain ^{15}N n.m.r. spectra with signal accumulation using a high-field Fourier-transform spectrometer, even when the resonances are paramagnetically broadened. A comparison of the relative advantages of ^{13}C and ^{15}N n.m.r. is illustrated here by the results obtained for acetonitrile exchange with both the $[NiL(NCMe)]^{2+}$ and $[CoL(NCMe)]^{2+}$ ions. An approximate value for the rate of water exchange with the $[NiL(OH_2)]^{2+}$ ion was also estimated.

RESULTS AND DISCUSSION

For the $[NiL(NCMe)]^{2+}$ ion the contact shift of the bound acetonitrile resonances vary as expected in the order $^{15}N > {}^{13}CN \gg {}^1H$. A comparison of the relative advantages of ^{15}N and ^{13}C n.m.r. paramagnetic line broadening is illustrated for Ni^{II} by the variation of the linewidths with temperature shown in Figure 2. Nitrogen-15 n.m.r. significantly extends the low-temperature linear region of the Swift–Connick curve, and a much lower complex concentration could be used (mol ratio of bound to free solvent, $P_M = 2.12 \times 10^{-4}$) than that used in the ^{13}C studies ($P_M = 1.8 \times 10^{-3}$). The necessity to use much higher concentrations of metal ion in some ^1H n.m.r. line-broadening studies {*e.g.* for $[Ni(NCMe)_6]^{2+}$ ion, concentrations of 0.1—0.2 mol dm^{-3} are commonly used, corresponding to P_M values of *ca.* 0.02—0.03},[12] is a disadvantage especially as the solvent-exchange rate data are commonly compared with complex-formation rates which are often obtained at high dilution (*e.g.* in tests of the Eigen–Wilkins equation $k_f \simeq k_{ex.}K_0$).[13]

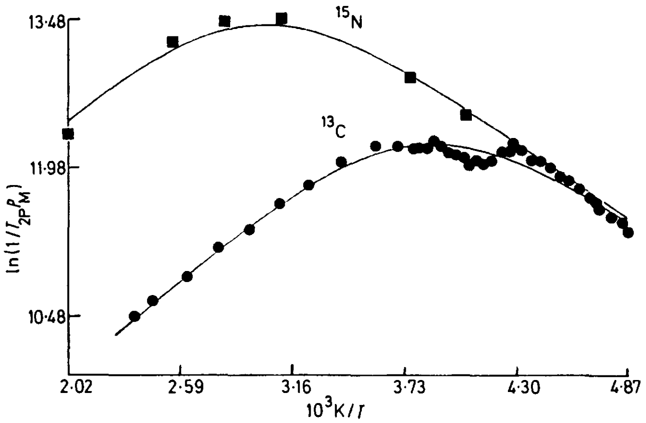

FIGURE 2 Plot of $\ln(1/T_{2P}P_M)$ against $1/T$ for the $[NiL(NCMe)]^{2+}$ ion: (●), ^{13}C data; (■), ^{15}N data

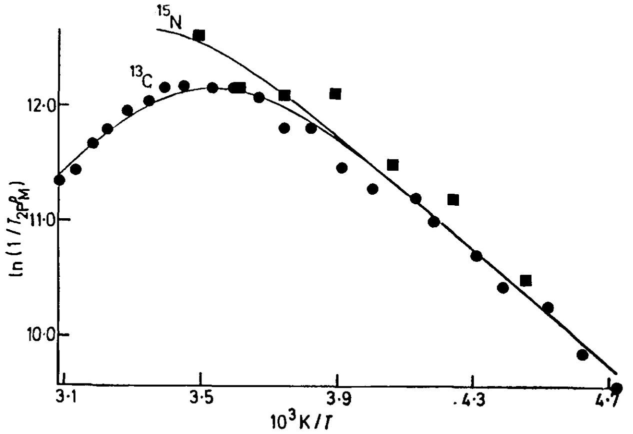

FIGURE 3 Plot of $\ln(1/T_{2P}P_M)$ against $1/T$ for the $[CoL(NCMe)]^{2+}$ ion: (●), ^{13}C data; (■), ^{15}N data

A fit of the ^{15}N n.m.r. data in Figure 2 to the Swift–Connick equations gives activation parameters in good agreement with the ^{13}C n.m.r. results (Table), and a combination of the ^{13}C and ^{15}N data gives the slightly improved activation parameters shown in the Table. The solid lines in Figure 2 are computer-calculated curves using the final estimated activation parameters. A non-linear least-squares regression analysis was used in these calculations.

Line-broadening results obtained by ^{13}C and ^{15}N n.m.r. for the $[CoL(NCMe)]^{2+}$ ion are shown in Figure 3. For the cobalt(II) ion the paramagnetic shifts are not so large as for nickel(II), and the advantage of ^{15}N n.m.r. over ^{13}C is reduced. It was found necessary to use comparable complex concentrations in both ^{13}C and ^{15}N studies ($P_M = 1.68 \times 10^{-2}$), and so most results were obtained by the more accessible ^{13}C technique. The activation parameters are compared with those for the analogous nickel(II) complex in the Table. The available data for acetonitrile exchange with other related cobalt(II) and nickel(II) complexes, together with analogous data for water exchange with $[ML(OH_2)]^{2+}$ and $[M(OH_2)_6]^{2+}$ ions (M = Ni^{II} or Co^{II}), are also collected in the Table. An approximate value for the rate of water exchange with the $[NiL(OH_2)]^{2+}$ ion was obtained from the broadening of the macrocyclic ligand ^1H resonances observed at low temperatures, and taking into account the equilibrium between diamagnetic (four-co-ordinate) and paramagnetic (five-co-ordinate) species reported previously.[4] The estimated value is in reasonable agreement with the acetonitrile-exchange rate.

Comparison of the effects of nitrogen-donor ligands on the rates and activation parameters for acetonitrile and water exchange with nickel(II) and cobalt(II) complexes (at 298.2 K unless specified)

Complex [a]	$10^{-4}k/s^{-1}$	$\Delta H^‡/kJ\ mol^{-1}$	$\Delta S^‡/J\ K^{-1}\ mol^{-1}$	$\Delta G^‡/kJ\ mol^{-1}$	Comments
$[Ni(NCMe)_6]^{2+}$	0.284 ± 0.005	64.3 ± 0.9	37 ± 3	53.3	*b*
$[NiL(NCMe)]^{2+}$	556 ± 39	20.3 ± 0.5	−47.8 ± 2.2	34.6	*c, h*
$[NiL(NCMe)_2]^{2+}$	1 472 ± 215	41.5 ± 1.1	31.6 ± 4.7	32.1	*d*
$[Ni(tren)(NCMe)_2]^{2+}$	16.5 ± 3.5	45.2 ± 6.3	5.8 ± 20.9	43.5	*e, f*
$[Ni(triam)(NCMe)_3]^{2+}$	55.5 ± 6.0	38.9 ± 4.2	−3.8 ± 14.6	40.0	*f*
$[Ni(Me_6tren)(NCMe)]^{2+}$	<0.01 (353 K)				*f*
$[Ni(OH_2)_6]^{2+}$	3.37 ± 0.09	52.3 ± 0.6	17.2 ± 2.1	47.2	*g*
$[NiL(OH_2)]^{2+}$	*ca.* 200 (300 K)				*h*
$[Ni(tren)(OH_2)_2]^{2+}$	82 and *ca.* 900	33.5			*i*
$[Ni(trien)(OH_2)_2]^{2+}$	57 ± 16	34.3 ± 3.8	−19 ± 15	40.0	*i*
$[Ni(tetren)(OH_2)]^{2+}$	1 120 ± 220	36.0 ± 2.9	10.5 ± 10.5	32.9	*i*
$Co(NCMe)_6]^{2+}$	33.8 ± 0.4	49.5 ± 0.7	27 ± 2	41.4	*j*, $\mu_{eff.}$ = 5.2 B.M.
$CoL(NCMe)]^{2+}$	56.5 ± 5.0	19.5 ± 0.8	−69.5 ± 3.5	40.2	*h, k*, $\mu_{eff.}$ = 4.81 B.M.
$[Co(cyclam)(NCMe)]^{2+}$	>80 (266 K)				*f*, $\mu_{eff.}$ = 2.45 B.M.
$[Co(tren)(NCMe)]^{2+}$	>200 (233 K)				*f*, $\mu_{eff.}$ = 4.7 B.M.
$[Co(Me_6tren)(NCMe)]^{2+}$	<0.01 (353 K)				*f*
$[Co(OH_2)_6]^{2+}$	318 ± 17	46.9 ± 1.2	37.2 ± 2	35.8	*l*
$[CoL(OH_2)]^{2+}$	4.2	36.5 ± 1.4	−34 ± 4	46.6	*m*, $\mu_{eff.}$ = 4.45 B.M.

[a] tren = $N(CH_2CH_2NH_2)_3$; triam = $CH_3C(CH_2NH_2)_3$; Me_6tren = $N(CH_2CH_2NMe_2)_3$; cyclam = 1,4,8,11-tetra-azacyclotetra. decane; trien = $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$; tetren = $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ [b] K. E. Newman, F. K. Meyer, and A. E. Merbach, *J. Amer. Chem. Soc.*, 1979, **101**, 1470; $\Delta V^‡ = 9.6 \pm 0.4\ cm^3\ mol^{-1}$. [c] Obtained from the combined ^{13}C and ^{15}N results in Figure 2. Previous ^{13}C results alone gave $10^{-4}\ k = 519 \pm 70\ s^{-1}$, $\Delta H^‡ = 19.8 \pm 0.9$ kJ mol^{-1}, and $\Delta S^‡ = -50.1 \pm 0.4\ J\ K^{-1}\ mol^{-1}$ (ref. 6). [d] Structure 1(*c*); ref. 6. [e] Data refer to exchange of MeCN in *trans* position to the tertiary N atom. For MeCN in *trans* position to an NH_2 group, $10^{-4}k > 200\ s^{-1}$ at 233 K. [f] Ref. 8. [g] Y. Ducommun, W. L. Earl, and A. E. Merbach, personal communication. [h] This work. [i] Ref. 7. [j] K. E. Newman, F. K. Meyer, and A. E. Merbach, personal communication. [k] Obtained from the combined ^{13}C and ^{15}N results in Figure 3. The ^{13}C and ^{15}N results separately gave $\Delta H^‡ = 19.6 \pm 0.1$ kJ mol^{-1}, $\Delta S^‡ = -69.6 \pm 0.5\ J\ K^{-1}\ mol^{-1}$, and $\Delta H^‡ = 19 \pm 4$ kJ mol^{-1}, $\Delta S^‡ = -71 \pm 17$ J $K^{-1}\ mol^{-1}$ respectively. [l] Y. Ducommun, K. E. Newman, and A. E. Merbach, personal communication. [m] Ref. 9; $\mu_{eff.}$ at pH 8.4.

It can be seen from the results in the Table that the macrocycle (L) significantly lowers the activation enthalpies for acetonitrile exchange on both nickel(II) and cobalt(II) ions, but whereas this results in a marked rate increase for Ni^{II}, for the Co^{II} the rate increase is only marginal because of the much more negative $\Delta S^‡$ value. The large negative $\Delta S^‡$ values and low values of $\Delta H^‡$ for the $[ML(NCMe)]^{2+}$ ions (M = Co^{II} or Ni^{II}) is strong evidence for an associative interchange (I_a) mechanism in both cases, with a transition state having a *cis*-octahedral geometry as shown in Figure 1(*d*). Precedence for such a geometry has been found in the complexes *cis*-$[NiL(NCS)_2]$ [1] and *cis*-$[Pb(cyclam)(ONO_2)_2]$ [14] (cyclam = L with Me replaced by H), and its formation can be readily envisaged from structure 1(*a*), requiring only addition of a second solvent molecule (X) with a minimal movement of the macrocycle framework. Steric hindrance is no doubt important in this process since the vacant site is flanked by the four N-methyl groups of L and approach of the solvent molecule will also be hindered by the macrocycle carbon framework. In terms of the collision theory expression $k = PZe^{-E/RT}$, a low probability factor (P) can be expected, and this will contribute to the large negative $\Delta S^‡$ values observed. The importance of steric hindrance in studies of acetonitrile exchange with the trigonal-bipyramidal $[M(Me_6tren)(NCMe)]^{2+}$ ions [M = Co^{II} or Ni^{II}; Me_6tren = $N(CH_2CH_2NMe_2)_3$] has been reported previously.[8] Here the co-ordinated acetonitrile molecule occupies an axial position and is flanked by all six N-methyl groups which results in a very slow solvent-exchange rate (Table).

The relative labilities of these five-co-ordinate $[ML(NCMe)]^{2+}$ ions ($Co^{II} < Ni^{II}$), is, of course, the opposite behaviour to that found in most octahedral complexes of Co^{II} and Ni^{II} and can be seen to arise primarily from the more negative $\Delta S^‡$ value for Co^{II} ($\Delta H^‡$ values are very similar). This would suggest that there is greater steric hindrance to the approach of the incoming acetonitrile molecule for the cobalt(II) complex, and this is understandable if the cobalt(II) ion is less accessible than Ni^{II} in forming the transition-state structure (*d*). In terms of the 'time-averaged' ground-state structure

1(*b*), greater steric hindrance from the four N-methyl groups would be expected if the metal ion were closer to the plane of the four nitrogen atoms, since as the metal ion is forced out of this plane the four N-methyl groups move further apart giving greater access to the incoming solvent molecule. In the solid state, co-ordination of the fifth ligand on the square-pyramidal C_4 axis is known to pluck the metal ion out of the N_4 plane,[3,5] and the stronger the co-ordination of this fifth ligand the further this out-of-plane movement of the metal ion is likely to be. Therefore, since Ni^{II}–ligand bonds are usually more stable than those found in related cobalt(II) complexes (the Irving–Williams stability sequence is $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II}$) it is possible that the nickel(II) ion may be further from the N_4 plane than is the case for Co^{II}. This in turn would give more access to the Ni^{II} and result in an increased rate of solvent exchange. The possibility that the cobalt(II) and nickel(II) complexes might have different ground-state geometries at low temperatures (square pyramidal and trigonal bipyramidal respectively) is unlikely since the cobalt(II) complex is high-spin ($\mu_{eff.} = 4.81$ B.M.).* Low-spin cobalt(II) complexes {*e.g.* for $[Co(cyclam)(NCMe)]^{2+}$, $\mu_{eff.} = 2.45$ B.M.}[8] are subject to Jahn–Teller distortion and are invariably found with a square-pyramidal geometry.[15] The $[CoL(NCMe)]^{2+}$ ion is probably close to the point of a spin-crossover since other (tetra-aza-macrocycle)cobalt(II) complexes have been found which are low spin,[16] and the possibility cannot be ruled out that for the $[CoL(NCMe)]^{2+}$ ion a spin change occurs in forming the six-co-ordinate transition state. This would hinder solvent exchange still further since the cobalt(II) ion would be less accessible to solvent in a low-spin square-pyramidal geometry 1(*b*) compared with the more open trigonal-bipyramidal geometry 1(*a*). A spin-crossover was postulated recently to account for the relative rates of racemisation and dissociation of low-spin $[M(phen)_3]^{2+}$ ion (M = Cr, Fe, or Co; phen = 1,10-phenanthroline).[17]

An examination of the values of $\Delta H^‡$ in the Table shows that co-ordination of the macrocycle (L) lowers $\Delta H^‡$ for acetonitrile exchange by 44 kJ mol^{-1} for Ni^{II} and 30 kJ mol^{-1} for Co^{II} when compared with the parent hexakis(acetonitrile) complexes. This effect is less marked for six-co-ordinate complexes such as the $[NiL(NCMe)_2]^{2+}$, $[Ni(tren)(NCMe)_2]^{2+}$, and $[Ni(triam)(MeCN)_3]^2$ ions [triam = $CH_3C(CH_2NH_2)_3$], where co-ordination of quadri- and ter-dentate amine ligands lowers $\Delta H^‡$ by *ca.* 19—25 kJ mol^{-1}. The greater reduction of $\Delta H^‡$ in the five-co-ordinate $[ML(NCMe)]^{2+}$ ions is additional confirmation that solvent exchange occurs with an I_a mechanism, since bond making as well as breaking is important in the transition state, whereas the six-co-ordinate complexes react with an I_d mechanism where bond breaking is dominant. For an I_a mechanism the bond-making step is expected to lower $\Delta H^‡$ still further as observed. The overall reduction in $\Delta H^‡$ values produced by amine ligands has been reported previously, and is understandable in terms of their increased σ-donor strength which weakens the remaining metal–solvent bonds.[7,8] The effect has been quantified recently for macrocyclic ligands of different ring size by Busch and co-workers.[18] For unmethylated tetra-aza-macrocycles co-ordinated to Ni^{II} the greatest value of the in-plane ligand-field strength, as measured by D_q^{xy}, is achieved with the 14-membered symmetric ligand cyclam and this produces the weakest 'axial' ligand-field strength (D_q^z).

Comparing the effects of the macrocycle (L) upon the rates of acetonitrile and water exchange on Co^{II}, it can be seen that at 298 K whereas the rate of water exchange is reduced by a factor of *ca.* 76, the rate of acetonitrile exchange is increased by a factor of *ca.* 1.7. The difference arises because $\Delta H^‡$ is reduced far more for the acetonitrile complex (by 30 kJ mol^{-1}) than for the aquo-complex (where $\Delta H^‡$ is reduced by only 10 kJ mol^{-1}), the effect being offset considerably by the more negative $\Delta S^‡$ value in the case of the acetonitrile solvate. Probably of major importance here is the fact that the 'rod-like' acetonitrile molecule is a far better ligand for these sterically hindered complexes than the V-shaped water molecules. For example, in aqueous solution only partial solvation of the square-planar $[ML]^{2+}$ ions occurs, whereas in acetonitrile solution there is complete conversion into the five-co-ordinate species.[4] It is not too surprising, therefore, that addition of a second solvent molecule (S) in forming the transition state or intermediate species $[ML(S)_2]^{2+}$ is energetically easier in acetonitrile than in aqueous solution.

It is interesting that for associative ligand exchange between tetrahedral $[M(PR_3)_2Br_2]$ and PR_3 (R = phenyl or *p*-tolyl) in $CDCl_3$ the lability order is again $Ni^{II} > Co^{II}$, but in these cases the greater reactivity of the nickel(II) complexes arises from the 12 kJ mol^{-1} lower $\Delta H^‡$ value compared with Co^{II}, offset somewhat by a more negative $\Delta S^‡$ value.[19]

EXPERIMENTAL

Natural-abundance ^{13}C and ^{15}N n.m.r. spectra were obtained in 10 mm diameter tubes at 22.63 MHz (Brüker WH 90) and 18.24 MHz (Brüker WH 180), with 10% 1,4-dioxan and 7% $Me^{15}NO_2$ (95 atom %) added as shift and line width markers, in the ^{13}C and ^{15}N experiments respectively. Paramagnetic line-broadening results (Figures 2 and 3) were fitted to the Swift–Connick equations[10] to obtain the rate data shown in the Table. A non-linear least-squares regression analysis was used, with $\Delta H^‡$, $\Delta S^‡$, and $\Delta\omega_m T$ fitted as the unknown parameters.[6] Outer-sphere line broadening was neglected in these calculations, and is not believed to be important in the accessible temperature range. Temperatures were measured with a calibrated Comark thermocouple.

The complex $[CoL(NCMe)][ClO_4]_2$ was prepared by mixing solutions of anhydrous cobalt(II) chloride (0.129 g) and L (0.256 g) in dry acetonitrile (10 cm^3). A solution of silver perchlorate (0.414 g) in acetonitrile was then added and the resulting precipitate filtered off. The filtrate was evaporated to dryness and the purple residue recrystallised

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

from dry acetonitrile {Found: C, 34.5; H, 6.10; N, 12.65. Calc. for $[CoL(NCMe)][ClO_4]_2$: C, 34.6; H, 6.30; N, 12.6%}.

The magnetic moment of a solution of the complex (2.97×10^{-2} mol dm^{-3}) in t-butyl alcohol–acetonitrile (1 : 9 v/v) was determined by the method of Evans[20] using a capillary of t-butyl alcohol–acetonitrile (1 : 1) as a shift marker. At 300 K, a shift of 0.60 p.p.m. was recorded corresponding to a magnetic moment, $\mu_{eff.} = 4.81$ B.M.

Acetonitrile was dried before use by refluxing over CaH_2 followed by distillation under dry nitrogen.

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