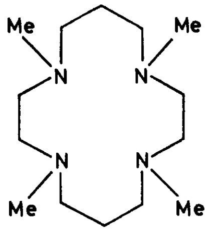
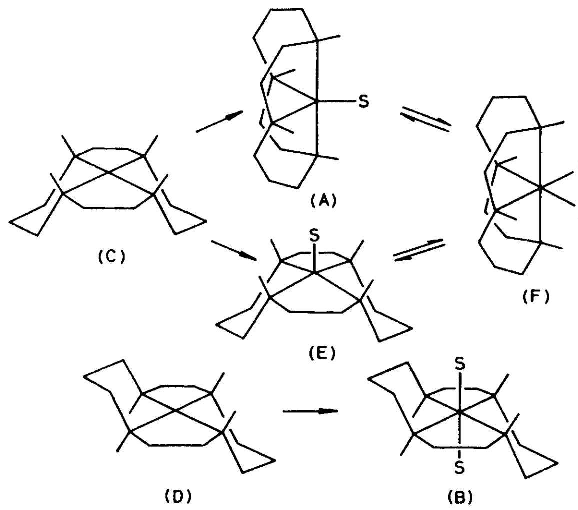
Rates and Activation Parameters for Acetonitrile Exchange with Five- and Six-co-ordinate Mono- and Bis-(acetonitrile)(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Perchlorate by Carbon-13 Paramagnetic Nuclear Magnetic Resonance Line Broadening

By **Norman Herron** and **Peter Moore,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Two isomers of $[NiL][ClO_4]_2$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) have been investigated in acetonitrile solution. One isomer has all four *N*-methyl groups on the same side of the macrocyclic ligand plane and forms a paramagnetic five-co-ordinate complex ion, $[NiL(NCMe)]^{2+}$ (A), in which the nickel is probably trigonal bipyramidal in solution. The second isomer has adjacent pairs of *N*-methyl groups on opposite sides of the macrocyclic plane and forms an octahedral complex ion, $[NiL(NCMe)_2]^{2+}$ (B). The rates of acetonitrile exchange with (A) and (B) have been determined by ^{13}C n.m.r. line broadening, and although at 298.2 K the rate constants are very similar [$10^{-6}k_{ex}$ = 5.2 and 14.7 s^{-1} for the exchange of a single solvent molecule from (A) and (B) respectively] the activation parameters differ markedly: (A), $\Delta H^‡$ = 19.8 ± 0.6 kJ mol^{-1} and $\Delta S^‡$ = −50 ± 3 J K^{-1} mol^{-1}; (B), $\Delta H^‡$ = 41.5 ± 1.1 kJ mol^{-1} and $\Delta S^‡$ = 32 ± 5 J K^{-1} mol^{-1}. This difference is interpreted in terms of an associative mechanism for the five-co-ordinate complex and a dissociative mechanism for the six-co-ordinate complex.



(L)



SCHEME Possible structures for two isomers of $[NiL][ClO_4]_2$ in acetonitrile (S) solution

NICKEL(II) complexes of the macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) were first prepared by Barefield and his co-workers [1-3] who established that the square-planar complexes could exist as two distinct isomers which do not interconvert. The complex prepared by adding hydrated nickel(II) perchlorate to 1 equivalent of L was shown to have the stereochemistry (C), where all four methyl groups lie on the same side of the macrocyclic plane.[2] This kinetically determined structure has no available route whereby it can undergo inversion of two of its nitrogen atoms to produce the thermodynamically more favourable [3] geometry (D). Complex (D) may only be produced by direct methylation of the nickel(II) complex of the parent macrocyclic ligand, cyclam (1,4,8,11-tetra-azacyclotetradecane).[3] Complexes with the stereochemistry (C) show a marked propensity towards five-co-ordination,[1,2,4] a fifth unidentate ligand (*e.g.* solvent or halide ion) co-ordinating on the same side of the macrocycle as the four *N*-methyl groups, thereby pulling the metal atom out of the macrocyclic plane and forcing the complex to adopt either a square-pyramidal (E) or trigonal-bipyramidal geometry (A).[5] The sixth co-ordination site in such complexes is hindered by the folded alkyl backbone of the macrocyclic ring and octahedral complexes are rare. Structure (D), however, frequently ligates on axis to produce an octahedral complex, (B), although five-co-ordinate species are also known with strong ligands such as cyanide or hydroxide ions.[3]

It is apparent, therefore, that the two nickel(II) complexes (C) and (D) afford an opportunity to compare the ligand-substitution kinetics of five- and six-co-ordinate species, a topic which has been the subject of interest in recent years,[6,7] and to compare the enthalpies of activation with the changes in the metal-ion co-ordination geometries. A recent ^{17}O n.m.r. study of the five-co-ordinate cobalt(II) complex ion $[CoL(OH_2)]^{2+}$ with ligand stereochemistry as in (C) has shown that the rate of water exchange is unusually slow, being some two orders of magnitude less than that observed for the $[Co(OH_2)_6]^{2+}$ ion.[8] These observations prompted us to measure the rates of acetonitrile exchange with the two nickel(II) complexes (A) and (B), to examine the effect of changing the conformation of the macrocyclic ligand on the rates and mechanisms of solvent exchange.

Acetonitrile was chosen as the solvent for study since it is ideal for n.m.r. line-broadening experiments, and because we found that solutions of (C) and (D) are completely converted into the respective five- and six-co-ordinate complexes in this solvent; u.v.–visible studies showed the absence of any residual four-co-ordinate species in acetonitrile. Carbon-13 n.m.r. spectroscopy proved to be the best technique for these studies since the nitrile resonance is broadened by the paramagnetic nickel(II) complexes much more than the ^1H and the ^{13}C resonances of the acetonitrile methyl group, the co-ordinated nitrile group being much closer to the nickel ion and, therefore, undergoing a greater contact shift. Linewidths are quite large for the nitrile resonance (between 5 and 140 Hz with $[Ni^{II}] = 0.019\,8$ mol kg^{-1}), and so the extent of the paramagnetic line broadening could be estimated with considerably greater accuracy.

RESULTS AND DISCUSSION

The visible spectra of isomers (C) and (D) in acetonitrile are given in Table 1. The absorption coefficients of isomer (D) are typical of octahedral co-ordination for Ni^{II}, consistent with the microanalysis data for the solid complex, and axial solvation to produce structure (B) is the most logical interpretation.[3] Isomer (C) has absorption coefficients consistent with high-spin five-co-ordinate Ni^{II},[1] although the visible spectrum does not allow distinction between square-pyramidal (E) and trigonal-bipyramidal (A) geometries. Alternative ^1H n.m.r. evidence for this complex and the analogous complex $[Ni(L)Cl][ClO_4]$ (unpublished) indicates structure (A) to be more likely, and this hypothesis is supported by other work in these laboratories.[5] The spectra of both isomers indicate no residual square-planar species in acetonitrile implying complete conversion into the high-spin species (A) and (B) in this solvent.

TABLE 1

Visible spectra of $[NiL][ClO_4]_2$ complexes in nitromethane and acetonitrile solutions

Complex geometry	Colour	Solvent		λ/nm (ε/dm³ mol⁻¹ cm⁻¹)
(A) or (E)	Blue	MeCN	Observed	1 480 (9), 981 (5), 790 (sh) (9), 610 (39.6), 386 (128)
			Reported *	1 480 (9), 981 (3), 790 (7), 610 (34), 390 (118)
(B)	Lilac	MeCN	Observed	950 (sh) (2.7), 830 (3.8), 540 (5.9), 340 (14.0)
(C)	Purple	$MeNO_2$	Observed	519 (185)
			Reported *	519 (184)
(D)	Red	$MeNO_2$	Observed	492 (83)

* Data from ref. 3.

N.M.R. Line-broadening Studies.—The solvent n.m.r. line broadening caused by a paramagnetic ion may be expressed as in (1) where $\Delta\nu_{obs.}$ and $\Delta\nu_{ref.}$ are the full

$$1/T_{2P}P_M = \pi(\Delta\nu_{obs.} - \Delta\nu_{ref.})/P_M \qquad (1)$$

linewidths at half maximum height of the solvent and reference resonances in the presence of the paramagnetic ion, and P_M is the mol ratio of bound to free solvent. The function $(T_{2P}P_M^{-1})$ is dependent on the solvent-exchange lifetime (τ_M), the transverse relaxation time of the co-ordinated solvent nucleus (T_{2M}), and the difference in chemical shift between the free nucleus and that co-ordinated to the paramagnetic centre ($\Delta\omega_M$). These quantities are related by a set of well defined equations[9] which may be simplified in several limiting regions. Of these regions, that most useful for the determination of kinetic-exchange data is where the rate of solvent exchange is not too great (specifically either $\Delta\omega_M^2 \gg 1/T_{2M}^2$, $1/\tau_M^2$ or $1/T_{2M}^2 \gg \Delta\omega_M^2$, $1/\tau_M^2$) so that relation (2) holds. Under these conditions the

$$1/T_{2P} = P_M/\tau_M \qquad (2)$$

temperature dependence of the quantity $T_{2P}P_M^{-1}$ should be that of a reaction rate constant, since τ_M^{-1} is the solvent first-order exchange rate.

$$\frac{1}{\tau_M} = \frac{kT}{h}\exp(\Delta S^\ddagger/R - \Delta H^\ddagger/RT) \qquad (3)$$

The results of the linewidth measurements for (A) and (B) are shown in Figure 1. The quantity log $(T_{2P}P_M)^{-1}$ is plotted against 1/(absolute temperature) since this linearises all regions having an Arrhenius temperature dependence [equations (2) and (3)]. The various linear portions of the plot are adequately explained elsewhere,[10] but the region of most kinetic importance is that where the linewidth increases rapidly as the temperature increases (region I) and equation (2) is found to hold. From equation (2) it is clear that this region represents a direct Arrhenius plot of the exchange-rate data and as such least-squares fitting of this region produces the activation parameters shown in Table 2.

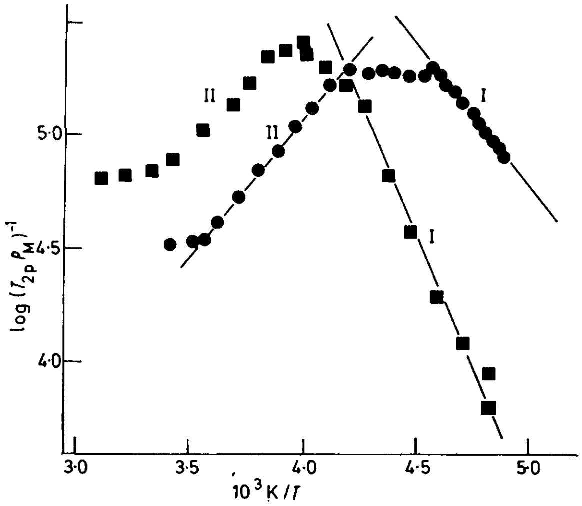


FIGURE 1 Linewidth data for acetonitrile exchange on (A) (●) and (B) (■)

For complex (B) region I covers a sufficiently wide temperature range (30 K) to allow a reasonable degree of confidence in the parameters obtained, whereas for complex (A) this region is limited to a range of only 12 K due to the solvent freezing as the temperature is reduced. In order to increase the range of the Arrhenius plot for complex (A) we extended our study of this system into region II, making use of an approximate form of the linewidth equation appropriate to this region. It is

$$1/(T_{2P}P_M) = \tau_M\Delta\omega_M^2 + 1/T_{2M}, \quad \text{where } \Delta\omega_M \simeq \Delta\omega_{obs.}/P_M \qquad (4)$$

clear that if the condition $\Delta\omega_M^2 \gg 1/T_{2M}\tau_M$ holds then the term in $1/T_{2M}$ can be neglected and a combination of shift and linewidth data allows an estimate of τ_M to be made in this region. Such an approximation allows the temperature range studied for complex (A) to be extended to 70 K and the data sets for both regions give values of $\Delta H^\ddagger$ in good agreement (Table 2), although $\Delta S^\ddagger$ is found to become more negative for data taken from region II. This discrepancy in $\Delta S^\ddagger$ may be due to the nature of the approximations inherent in equation (4) which would be expected to lead to larger systematic errors in the absolute values of τ_M^{-1} ($\propto\Delta S^\ddagger$) but not so large in their relative values ($\propto\Delta H^\ddagger$). It must also be noted that $\Delta H^\ddagger$ values quoted in Table 2 contain no correction for any contribution of second and further removed spheres of the complex ion to the exchange activation energy. This is because sufficiently low temperatures to make this correction feasible were prohibited by solvent freezing in both cases. (The contribution from 'outer-sphere' effects is found to be of the order of 6 kJ mol^{-1} for Ni^{II}.[11]) The shift data for both isomers are illustrated in Figure 2 and follow the behaviour predicted by theory.[9]

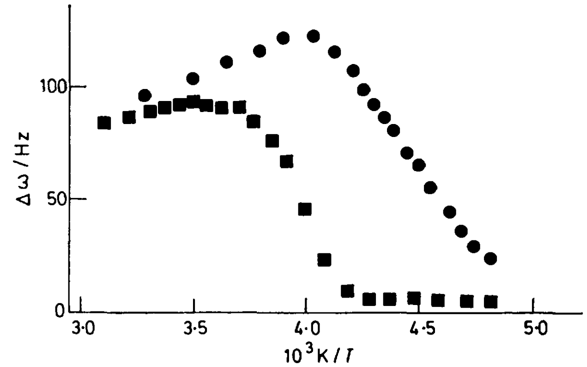


FIGURE 2 Temperature dependence of the chemical shift, Δω (referenced to dioxan), for (A) (●) and (B) (■) in acetonitrile solution

TABLE 2

Rate data at 298.2 K for acetonitrile exchange with the complexes studied, referring to the exchange of a single solvent molecule

	Complex	Temperature range/K	Fitted region	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$10^{-3}\,k_{ex}$/s^{-1}
(A)	$[NiL(NCMe)][ClO_4]_2$	206—218	I	23.2 ± 0.8	−35 ± 4	8 400
		240—280	II	24.2 ± 1.5	−51 ± 8	770
(B)	$[NiL(NCMe)_2][ClO_4]_2$	207—239	I	41.0 ± 1.8	+22 ± 8	6 200
	$[Ni(NCMe)_6][ClO_4]_2$ [a]		Complete fit	63.4 ± 3.0	+45 ± 4	10.7
	[b]		I	68.4 ± 2.0	+50 ± 8	2
(A) [c]		206—280	Complete fit	19.8 ± 0.6	−50 ± 3	5 190 ± 400
(B) [c]		207—322	Complete fit	41.5 ± 1.1	+32 ± 5	14 720 ± 2 150

[a] Data from R. E. Richards, *Mol. Phys.*, 1971, **30**, 933. [b] Data from S. F. Lincoln and R. J. West, *Austral. J. Chem.*, 1973, **26**, 255. [c] Complete fits of the linewidth data for (A) and (B) to the full Swift–Connick equations have since been completed and are included above. The four parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$ (or k_{ex}), $\Delta\omega_M T$ and T_{2M} were taken as unknown parameters in the fit [$T_{2M} = 0$ for (A) and $T_{2M} = (\text{constant})\exp(4\,000/RT)$ for (B)]. Simultaneous fits to the linewidth and shift data were also attempted and although the fits to the linewidth data were not so good, the rate data obtained are not very different: (A) $\Delta H^\ddagger = 18.6 \pm 0.8$ kJ mol^{-1}; $\Delta S^\ddagger = -51 \pm 4$ J K^{-1} mol^{-1}; (B) $\Delta H^\ddagger = 40.0 \pm 0.8$ kJ mol^{-1}; $\Delta S^\ddagger = 24 \pm 4$ J K^{-1} mol^{-1}.

It is worthy of mention that the nitrile carbon nucleus was chosen for this study not only because of the possible choices (^{1}H or ^{13}C) (this nucleus being closest to the paramagnetic nickel centre is most sensitive to the contact broadening produced by this ion) but also because it is the only one which shows the complete linewidth profile expected in such cases (Figures 1 and 2) for the temperature range accessible in this solvent system. This latter criterion is essential in order to establish the various regions to which the approximate equations (3) and (4) apply.[9]

Comparison of the activation parameters for (A) and (B) (Table 2) shows (A) to have a negative value of $\Delta S^\ddagger$ while $\Delta S^\ddagger$ is positive for (B). A negative value of $\Delta S^\ddagger$ is indicative of a greater ordering in the transition state and would therefore imply an associative-exchange mechanism for (A), while (B) shows a positive $\Delta S^\ddagger$ consistent with the expected dissociative mechanism for an octahedral complex. A consideration of the structural properties of complexes of geometry (C) and their five-co-ordinate analogues [(A) and (E)] shows that there is considerable evidence for a folding of the macrocycle away from planarity (E) towards a trigonal-bipyramidal geometry (A) {*e.g.* in $[Zn(L)Cl][ClO_4]$[5]} as the fifth ligand becomes co-ordinated in solution. It has also been found that with a 'rod-like' donor molecule, such as thiocyanate ion, this folding can be taken to its extreme, allowing co-ordination of two thiocyanate anions as in *cis*-$[NiL(NCS)_2]$ [1] (F). This evidence would suggest that the implied associative acetonitrile-exchange mechanism for isomer (A) may well proceed through a transition state with two solvent molecules co-ordinated in a *cis* geometry similar to structure (F). It seems, therefore, that the values of $\Delta S^\ddagger$ are consistent with an associative mechanism for solvent exchange on (A) and a dissociative mechanism for (B). This proposed associative path has been observed recently for another high-spin five-co-ordinate nickel(II) complex.[7]

Turning now to the enthalpy data, these show (A) to undergo solvent exchange with a markedly lower activation energy than for (B). This may be explained in part in terms of the crystal-field activation energies (c.f.a.e.) of the two exchange mechanisms postulated above. Table 3 lists the crystal-field stabilisation energies (c.f.s.e.s) of the starting and assumed transition-state geometries for each isomer and the corresponding c.f.a.e. of the exchange mechanism.[12] These clearly indicate that the five-co-ordinate complex (A) has a negative c.f.a.e. for exchange whereas (B) has a positive value, and therefore these calculated values mirror the order of the observed activation enthalpies (A) $<$ (B). Also, since bond formation is more important for the reaction of (A) while bond breaking is more important for (B), the lower $\Delta H^{\ddagger}$ for (A) is reasonable.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both complexes conspire to produce rate constants at 298 K which are almost identical, and which are in the range expected for acetonitrile exchange on a nickel(II) complex with an N_4 set of donor atoms.[13,14] This latter result for (A) is inconsistent with data derived for the analogous cobalt(II) aqua-complex where the solvent-exchange rate was, unusually, found to be slower than for the corresponding hexa-aqua-complex,[8] although the result is in agreement with that found by Lincoln and West for a five-co-ordinate cobalt(II) complex. In this work [15] a comparison of the two five-co-ordinate complexes $[Co(tren)(NCMe)]^{2+}$ (a) and $[Co(Me_6tren)(NCMe)]^{2+}$ (b) shows a very marked difference in the rate of acetonitrile exchange. For (a), with the relatively ' unhindered ' ligand tren (2,2′,2″-triaminotriethylamine), the rate is of the expected order [13] ($k_{ex} > 2 \times 10^6$ s^{-1} at 233 K), the acetonitrile being labilised with respect to the $[Co(NCMe)_6]^{2+}$ ion. For (b), however, the increase of steric hindrance in going to hexamethylated tren as the ligand markedly reduces the solvent-exchange rate ($k_{ex} < 10^2$ s^{-1} at 353 K). The explanation given for these remarkable results is that the addition of the six methyl groups in (b) so hinders the remaining co-ordination site that solvent-assisted exchange is severely limited. These findings would suggest, therefore, that the cobalt(II) and nickel(II) complexes with L might differ significantly in their ability to allow any involvement of the bulk solvent in the exchange mechanism, and more precisely that the $[CoL(OH_2)]^{2+}$ ion may not be able to expand its co-ordination sphere in the exchange transition state whereas the $[NiL(NCMe)]^{2+}$ ion may. One possibility is that the cobalt(II) complex may be rigidly square pyramidal whereas the nickel(II) complex can fold to become trigonal bipyramidal and thence octahedral as suggested above.

TABLE 3

Crystal-field stabilisation energies (c.f.s.e.) and activation energies (c.f.a.e.) in Dq units for d^8 high-spin nickel(II) complexes. Data from ref. 12

Complex	Ground-state geometry	c.f.s.e.	Transition-state geometry	c.f.s.e.	c.f.a.e.
(A)	Trigonal bipyramidal	−6.67	Octahedral	−12	−5.33
(E)	Square pyramidal	−9.96	Octahedral	−12	−2.04
(B)	Octahedral	−12	Square pyramidal	−9.96	+2.04
(B)	Octahedral	−12	Trigonal bipyramidal	−6.67	+5.53

In the trigonal-bipyramidal complex ion $[Cu(tren)(OH_2)]^{2+}$ the water-exchange rate is unusually slow for Cu^{II}, but can be regarded as fairly normal for an ' equatorial ' water molecule on Cu^{II} since this is not subject to a Jahn–Teller weakening of the Cu–O bond.[16,17] Preliminary experiments we have carried out show that the water-exchange rate in $[NiL(OH_2)]^{2+}$ is very similar to the acetonitrile-exchange rate in $[NiL(NCMe)]^{2+}$, and it will be interesting to establish whether or not acetonitrile exchange is unusually slow in the $[CoL(NCMe)]^{2+}$ ion. This experiment is now underway.

EXPERIMENTAL

The two isomers of $[NiL][ClO_4]_2$, (C) and (D), were prepared by standard procedures,[1-3] recrystallised from nitromethane–methanol, and the solid complexes dried over P_4O_{10}. Purity was checked by nickel elemental analysis [Found: Ni, 11.45 for (C) and 11.2 for (D). Calc.: Ni, 11.4%], and by a comparison of reported and observed visible spectroscopic absorption coefficients, in dry nitromethane for (C) (Table 1). The acetonitrile complexes (A) and (B) were characterised, as crystalline solids, by elemental analysis {Found: C, 33.8; H, 6.0; N, 12.2; Ni, 10.35. Calc. for $[NiL(NCMe)][ClO_4]_2$, (A): C, 34.6; H, 6.30; N, 12.6; Ni, 10.6. Found: C, 35.3; H, 6.0; N, 14.1; Ni, 9.20. Calc. for $[NiL(NCMe)_2][ClO_4]_2$, (B): C, 36.3; H, 6.40; N, 14.1; Ni, 9.85%}. and in solution by means of their visible spectra (Table 1). Both sets of data are consistent with the proposed solution geometries (A) and (B). Visible spectra were recorded with a Cary 14 or a Pye-Unicam SP 800 spectrometer and metal analyses carried out with a Varian AA6 atomic-absorption spectrophotometer.

Solutions of (A) and (B) [(A), molality = 0.043 90 or 0.031 71 mol kg^{-1}, P_M = 0.0018 or 0.0013; (*B*), molality = 0.019 8 mol kg^{-1}, P_M = 0.001 6] were made up in freshly distilled (from CaH_2) acetonitrile under an atmosphere of dry nitrogen. An n.m.r. lock signal of 10% [$^2H_3$]nitromethane and a shift and natural linewidth reference of 1,4-dioxan (*ca.* 5%) were added to the solutions. All the ^{13}C n.m.r. spectra were recorded with a Bruker WH 90 spectrometer at 22.63 MHz. The sample temperature was measured using a calibrated Comark thermocouple and held constant ±0.5 K with a standard Bruker temperature-control unit. Linewidth measurements were carried out using an iterative line-fitting procedure, LSHAPE 3,[18] on a Nicolet 1080 computer. This program is an adaptation of our previously published Algol 60 program [19] suitable for use with this computer.

A comparison of the measured dioxan reference linewidth in the presence and absence of the paramagnetic nickel(II) complexes showed that no appreciable broadening of this reference occurred in the paramagnetic samples. This allowed direct internal measurements of the natural linewidth in all samples. All shift data were recorded referenced to dioxan and normalised to the shift of acetonitrile in a solution containing all the components except the paramagnetic ion. The apparent flatness in the linewidth profile between regions I and II for (A) (Figure 1) is a little unusual but is most probably due to experimental error in this region where the linewidths show a relatively small temperature dependence.

We thank the M.R.C. and S.R.C. for support (to P. M.), the S.R.C. for the award of a studentship (to N. H.), and Dr. D. A. Couch for translating our Algol 60 lineshape program for use with the Nicolet 1080 computer.

[8/494 *Received*, 17*th March*, 1978]

REFERENCES

[1] E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.

[2] M. J. D'Aniello, jun., M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Amer. Chem. Soc.*, 1975, **97**, 192.

[3] F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1976, **15**, 408.

[4] K. D. Hodges, R. G. Wollmann, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2746.

[5] N. W. Alcock, N. Herron, and P. Moore, *J.C.S. Dalton*, 1978, 1282.

[6] D. A. Sweigart and P. Heidtmann, *J.C.S. Dalton*, 1975, 1686.

[7] M. J. Hynes and P. F. Brannick, *J.C.S. Chem. Comm.*, 1977, 942.

[8] P. Meier, A. Merbach, S. Burki, and T. A. Kaden, *J.C.S. Chem. Comm.*, 1977, 36.

[9] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.

[10] T. R. Stengle and C. H. Langford, *Co-ordination Chem. Rev.*, 1967, **2**, 349.

[11] D. K. Ravage, T. R. Stengle, and C. H. Langford, *Inorg. Chem.*, 1967, **6**, 1252.

[12] J. J. Zuckermann, *J. Chem. Educ.*, 1965, **42**, 315; R. Krishnamurthy and W. B. Schaap, *ibid.*, 1969, **46**, 799.

[13] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

[14] S. F. Lincoln and R. J. West, *J. Amer. Chem. Soc.*, 1974, **96**, 400.

[15] S. F. Lincoln and R. J. West, *Inorg. Chem.*, 1973, **12**, 494.

[16] G. Cayley, D. Cross, and P. Knowles, *J.C.S. Chem. Comm.*, 1976, 837.

[17] D. P. Rablen, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1972, **94**, 1771.

[18] D. A. Couch, LSHAPE version 3, Nicolet Users Society.

[19] P. Moore, *J.C.S. Faraday I*, 1976, 826.