Rates of Formation of Nickel(II) Chelate Complexes with Bidentate Substituted-pyridine Ligands in Dimethyl Sulphoxide Solution

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Rate data and activation parameters are reported for formation of mono-complexes of nickel(II) with the bidentate ligands 2-(aminomethyl)-, 2-(2-aminoethyl)-, 2-(aminomethyl)-6-methyl-, and 2-[(methylamino)methyl]-pyridine in anhydrous dimethyl sulphoxide (dmso) solution. At 298 K, all the rate constants are close to the value reported for solvent exchange between the $[Ni(dmso)_6]^{2+}$ ion and bulk dmso, but because of the wide variation in the activation parameters ($\Delta H^\ddagger$ in the range 8·8 to 14·5 kcal mol^{-1}, $\Delta S^\ddagger$ between −14 and +7 cal K^{-1} mol^{-1}) the agreement at elevated temperatures is not so good. The rate constants at 298 K ($10^{-3}k_f$ between 2·1 and 5·4 l mol^{-1} s^{-1}) confirm previous studies which indicate that the rates of reaction of the ion $[Ni(dmso)_6]^{2+}$ with 2,2′-bipyridine (bipy) and 2,2′;6′,2″-terpyridine (terpy) in dmso are unusually slow ($10^{-3}k_f$ 0·069 and 0·026 l mol^{-1} s^{-1} respectively). Steric factors are postulated to account for this rate difference. A plot of $\Delta H^\ddagger$ against ΔS is linear for the four ligands investigated, and, although values obtained previously for 4-phenylpyridine and for the solvent-exchange process agree with this correlation, values for bipy and terpy are not in agreement. The isokinetic temperature (at which the reactions would theoretically have the same rate) is 275 ± 10 K. ^{13}C N.m.r. spectra of the ligands are also given.

ALTHOUGH equation (1) can be used to predict rates of metal-complex formation in aqueous solution,[1] previous studies have shown that substitution reactions of nickel(II) in non-aqueous solvents are not always in good agreement with values calculated in this way.[2-4] Values of

$$k_f = k_{ex}K_0 \qquad (1)$$

the formation rate constant (k_f) sometimes fall well outside the range expected from the product of the overall solvent-exchange rate constant (k_{ex}) and the ion-pair or ion–dipole constant (K_0). This is particularly noticeable for multidentate ligands such as 2,2′-bipyridine (bipy) and 2,2′;6′,2″-terpyridine (terpy) where in dimethyl sulphoxide (dmso) solution observed values [2] of k_f are significantly smaller than values calculated from equation (1). Since the value of k_f obtained for the reaction of a unidentate ligand such as 4-phenylpyridine [4] or pyridine [3] with the $[Ni(dmso)_6]^{2+}$ ion is much closer to the value of k_{ex}, it was postulated that steric factors might be important in slowing rates of formation of the bipy and terpy complexes in dmso.[4] This could arise either during formation of the first metal–ligand bond, or during subsequent chelate-ring closures (the so-called sterically controlled substitution or S.C.S. mechanism [5]). Some evidence in favour of the latter conclusion was presented [4] on the basis of studies of H^+- and Hg^{2+}-induced dissociations of the $[Ni(bipy)]^{2+}$ ion, and this belief was supported for terpy complexes when a very slow ring-closure mechanism was observed during formation of $[Mn(terpy)]^{2+}$ in dmso.[6]

In the present study we have tried to substantiate our previous findings [4] for substitution reactions of nickel(II) in dmso, and to probe for steric factors associated with the ligands by investigating rates of formation of the mono-complexes with the bidentate ligands (L) 2-(aminomethyl)-, 2-(2-aminoethyl)-, 2-(aminomethyl)-6-methyl-, and 2-[(methylamino)methyl]-pyridine. The first two ligands were chosen to compare rates of formation of five- and six-membered chelate rings and to test for a possible S.C.S. mechanism, whereas the latter two were chosen to test the steric effect of substitution near to the sites of co-ordination. The reactions of these basic ligands in dmso are also of interest in relation to the internal conjugate base (i.c.b.) mechanism,[7] which is postulated for basic amines in aqueous media but which cannot operate in aprotic solvents.

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[1] R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

[2] H. P. Bennetto and E. F. Caldin, *Chem. Comm.*, 1969, 599; *J. Chem. Soc.* (*A*), 1971, 2191, 2198.

[3] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113.

[4] P. Moore and D. M. W. Buck, *J.C.S. Dalton*, 1973, 1602.

[5] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.

[6] D. M. W. Buck and P. Moore, *J.C.S. Chem. Comm.*, 1974, 60.

[7] D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891.

RESULTS

The reactions were studied by the stopped-flow method under pseudo-first-order conditions with $[\mathrm{Ni^{II}}](5 \times 10^{-3}$—$4 \times 10^{-2}$ mol $\mathrm{l^{-1}}$) in large excess over [L](5×10^{-4}—10^{-3} mol $\mathrm{l^{-1}}$). A constant ionic strength of 0·20 mol $\mathrm{l^{-1}}$ was maintained with anhydrous sodium perchlorate. The reactions were established as first order in $[\mathrm{Ni^{II}}]$ by varying the metal-ion concentration as widely as possible at a constant temperature (292·0 K). Concentrations were limited by the rapidity of the reactions. The pseudo-first-order rate constants (k) obtained at 292·0 K are presented in Table 1, and second-order rate constants (k_f), obtained by least-squares analysis from gradients of linear plots of k against $[\mathrm{Ni^{II}}]$, are shown in Table 2. At other temperatures, values of k_f were obtained from the relation $k_f = k/[\mathrm{Ni^{II}}]$. In Table 3 are collected rate constants and activation parameters at 298·1 K for formation of nickel(II) complexes with uncharged ligands in dmso, together with diverse data reported by various groups for the dmso solvent-exchange process.

TABLE 1

Pseudo-first-order rate constants (k) for formation of mono-complexes of nickel(II) with bidentate ligands (5×10^{-4} mol $\mathrm{l^{-1}}$) at 292·0 K [I = 0·20 mol $\mathrm{l^{-1}}$ ($\mathrm{NaClO_4}$)]

2-(Aminomethyl)pyridine				
$10^2[\mathrm{Ni^{II}}]$/mol $\mathrm{l^{-1}}$	0·48	0·98	1·98	
$k/\mathrm{s^{-1}}$	14·7 ± 0·3	26·9 ± 0·5	45·9 ± 1·8	
2-(2-Aminoethyl)pyridine				
$10^2[\mathrm{Ni^{II}}]$/mol $\mathrm{l^{-1}}$	0·95	1·95	2·95	
$k/\mathrm{s^{-1}}$	27·9 ± 0·5	55·5 ± 0·1	84·8 ± 0·7	
2-(Aminomethyl)-6-methylpyridine				
$10^2[\mathrm{Ni^{II}}]$/mol $\mathrm{l^{-1}}$	0·48	0·98	1·95	2·95
$k/\mathrm{s^{-1}}$	22·2 ± 0·1	35·4 ± 3·8	81·0 ± 3·0	111·2 ± 3·2
2-[(Methylamino)methyl]pyridine				
$10^2[\mathrm{Ni^{II}}]$/mol $\mathrm{l^{-1}}$	0·48	0·98	1·98	2·98
$k/\mathrm{s^{-1}}$	8·7 ± 0·1	13·6 ± 0·6	27·3 ± 1·2	43·8 ± 0·7

TABLE 2

Second-order rate constants (k_f) for formation of mono-complexes of nickel(II) with the bidentate ligands in dmso [I = 0·20 mol $\mathrm{l^{-1}}$ ($\mathrm{NaClO_4}$)]

2-(Aminomethyl)pyridine					
T/K	292·0	296·0	301·2	306·1	
$10^{-3}k_f{}^a$/l $\mathrm{mol^{-1}\,s^{-1}}$	3·06 ± 0·06	4·09 ± 0·07	5·24 ± 0·31	6·72 ± 0·09	
2-(2-Aminoethyl)pyridine					
T/K	292·0	300·1	308·7	314·1	
$10^{-4}k_f$/l $\mathrm{mol^{-1}\,s^{-1}}$	2·85 ± 0·05	5·12 ± 0·23	9·76 ± 0·04	13·7 ± 0·02	
2-(Aminomethyl)-6-methylpyridine					
T/K	292·0	300·5	307·3	312·8	
$10^{-3}k_f$/l $\mathrm{mol^{-1}\,s^{-1}}$	3·74 ± 0·26	6·80 ± 0·05	12·2 ± 0·10	22·4 ± 0·67	
2-[(Methylamino)methyl]pyridine					
T/K	292·0	292·2	300·2	310·3	314·9
$10^{-3}k_f$/l $\mathrm{mol^{-1}\,s^{-1}}$	1·41 ± 0·08	1·54 ± 0·07	2·63 ± 0·07	3·76 ± 0·15	4·84 ± 0·15

[a] Values refer to data obtained at $[\mathrm{Ni^{II}}] = 4{\cdot}8 \times 10^{-3}$ mol $\mathrm{l^{-1}}$. The value at 292 K obtained from Table 1 is $10^{-3}k_f = 2{\cdot}70 \pm 0{\cdot}33$ l $\mathrm{mol^{-1}\,s^{-1}}$, and using this rate constant slightly different activation parameters were obtained: $\Delta H^‡$ = 8·6 ± 0·9 kcal $\mathrm{mol^{-1}}$; $\Delta S^‡$ = −13·1 ± 2·8 cal $\mathrm{K^{-1}\,mol^{-1}}$.

TABLE 3

Rate constants (k_f) and activation parameters for formation of mono-complexes of nickel(II) with uncharged ligands in dimethyl sulphoxide solution at 298·1 K (values in parentheses refer to aqueous solution)

Ligand	Ionic strength (I/mol $\mathrm{l^{-1}}$)	k_f/l $\mathrm{mol^{-1}\,s^{-1}}$	$\Delta G^‡$/kcal $\mathrm{mol^{-1}}$	$\Delta H^‡$/kcal $\mathrm{mol^{-1}}$	$\Delta S^‡$/cal $\mathrm{K^{-1}\,mol^{-1}}$
2-(Aminomethyl)pyridine	0·2	4 360	12·5 ± 1·0	9·12 ± 0·56	−11·3 ± 1·9
		(8 600) [a]			
2-(2-Aminoethyl)pyridine	0·2	4 490	12·4 ± 0·3	12·3 ± 0·2	−0·4 ± 0·5
		(9 500) [b]			
2-(Aminomethyl)-6-methylpyridine	0·2	5 370	12·3 ± 2·2	14·5 ± 1·1	7·1 ± 3·6
2-[(Methylamino)methyl]pyridine	0·2	2 140	12·9 ± 1·4	8·77 ± 0·70	−13·9 ± 2·3
Pyridine	*c*	*ca.* 2 000 [d]			
		(*ca.* 4 000) [e]		(*ca.* 11·5) [f]	
4-Phenylpyridine [e]	0·2	1 640		9·0 ± 2·0	−13·5 ± 6·7
1,10-Phenanthroline	*c*	350 [d]	14	8·3 ± 0·3	−19
		(3 900) [f]		(13·1) [f]	(+2) [f]
2,2′-Bipyridine [g]	*c*	60	14·9	12·6 ± 0·1	−7·7
		(1 500) [f]		(13·2) [f]	(0) [f]
2,2′;6′,2″-terpyridine	*c*	26 [g]	15·5 ± 0·4	11·6 ± 0·2	−13·1 ± 0·5
		25 [d]	15·6	15·0 ± 0·7	−2
		33 [h]	15·4	11·9 ± 0·2	−11·6 ± 0·5
		(1 400)	(13·2)	(14·1)	(+3)
Dimethyl sulphoxide [i]	*j*	3 200 [k]	12·6	13·0	1·4
	j	4 200 [l]	12·5 ± 0·4	12·1 ± 0·3	−1·3 ± 0·5
	j	5 570 [m]	12·2	8·05	−14·0
	j	11 000 [n]	11·7 ± 0·8	12·1 ± 0·5	1·2 ± 1
	j	7 400 [h]	12·2 ± 1·3	6·2 ± 0·7	−20 ± 2
	j	10 200 [o]	12·0 ± 1·1	8·7 ± 0·5	−11 ± 2

[a] J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1968, **90**, 6045. [b] C. D. Hubbard and W. Palaitis, *Inorg. Chem.*, 1973, **12**, 480. [c] Unknown or not adjusted, usually <0·05. [d] Ref. 3. [e] See ref. 4 and references therein. [f] Ref. 1. [g] Ref. 2. [h] P. A. Cock, C. E. Cottrell, and R. K. Boyd, *Canad. J. Chem.*, 1972, **50**, 402. [i] Refers to solvent exchange. [j] Not adjusted but usually quite large (*ca.* 0·1). [k] Ref. 12. [l] Ref. 14. [m] G. S. Vigee and P. Ng, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2477. [n] C. Boubel and J. J. Delpuech, *J. Chim. phys.*, 1973, **70**, 578. [o] S. Blackstaffe and R. A. Dwek, *Mol. Phys.*, 1968, **15**, 279.

DISCUSSION

There are two features which are striking about the present results when compared with those of previous studies. First, the rate constants obtained for all the present ligands were much larger than those for the less-flexible bipy and terpy, and nearer to the value of k_f for an uncharged unidentate ligand such as pyridine[3] or 4-phenylpyridine.[4] At room temperature the rates were also close to the solvent-exchange rate [k_{ex}, equation (1)]. These results confirm our belief that the reactions of Ni^{II} with bipy and terpy are unusually slow in dmso. Steric hindrance is the most likely cause, and this could arise either during formation of the first metal–ligand bond or during the subsequent chelate-ring closure(s). In aqueous solution, steric effects for bipy and terpy appear to be of no importance,[1] but steric effects are reported for *N*-substituted alkyl derivatives of alkylamines and of 1,2-diaminoethane.[8] In dmso the *O*-co-ordinated tetrahedral solvent molecules are much bulkier and steric hindrance is much more likely.

The ligands bipy and terpy are unusual in having their donor sites flanked by a large aromatic ring. Since bipy and terpy exist in solution in a *trans*- or *trans–trans*-configuration respectively,[9] approach of the first donor atom towards the metal ion will resemble the approach of a hindered ligand such as 2-phenylpyridine. The co-ordinating ability of ligands like 2-phenylpyridine is known to be very weak,[10] and therefore it is not surprising that bipy is reluctant to bond, especially in the presence of bulkier co-ordinated solvent molecules where the vacant site following solvent dissociation will be less accessible. Chelate-ring closure could also be hindered for the same reason.[4] However, steric effects have recently been ruled out for $[Ni(bipy)]^{2+}$ formation in ethanol,[11] since in this solvent the value of k_f and the associated activation parameters are much closer to values obtained for the solvent-exchange process. It appears, therefore, that $[Ni(bipy)]^{2+}$ formation in ethanol is ‘normal’ and resembles the behaviour in aqueous solution, whereas in dmso steric effects are more important for bipy and terpy and to a lesser extent for phen.

The second feature of the present results which is noteworthy is the considerable variation in the activation parameters. A plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ is shown in Figure 1, and with the exception of bipy and terpy there is a reasonable linear correlation. Analysis of data for the present ligands, together with those for 4-phenylpyridine[4] and the best estimate for the solvent-exchange process,[12] gives relation (2).* The isokinetic temperature at which these reactions have the same rate is, therefore, 275 ± 10 K. It is dangerous to draw too many conclusions from such relations,[2,3] but one observation is perhaps worthwhile. The results obtained for bipy and terpy lie well outside the range of equation (2) (Figure 1). This is taken as further evidence that the reactions of these ligands are sterically hindered as described above. Values of $\Delta G^\ddagger$ are also significantly larger for these two ligands and for phen (Table 3). We also note that the variation in the activation parameters is much greater than observed for substitution reactions of nickel(II) in aqueous solution.[5] One consequence of this is that, whereas equation (1) could be used to predict the value of k_f for the present ligands with reasonable accuracy at room temperature, at higher temperatures the estimate will be inaccurate.

$$\Delta H^\ddagger = (275{\cdot}0 \pm 9{\cdot}7)\Delta S^\ddagger + (12{\cdot}52 \pm 0{\cdot}09) \times 10^3 \text{ cal} \qquad (2)$$

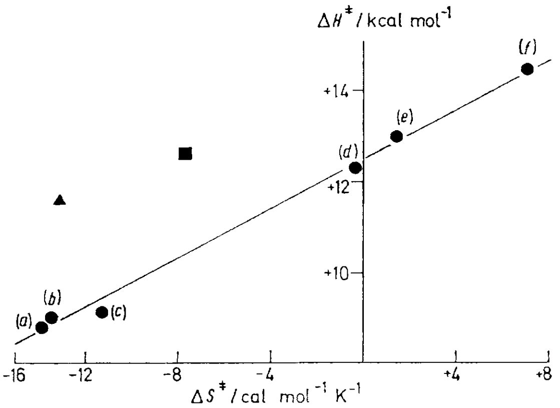

FIGURE 1 Plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ for formation of nickel(II) complexes in dmso: (*a*), 2-[(methylamino)methyl]pyridine; (*b*), 4-phenylpyridine; (*c*), 2-(aminomethyl)pyridine; (*d*), 2-(2-aminoethyl)pyridine; (*e*), dmso solvent exchange; (*f*), 2-(aminomethyl)-6-methylpyridine; (▲), terpy; and (■), bipy

The cause of the variation in the activation parameters is not immediately obvious since several factors could contribute to the overall effect. Some of these factors have been discussed previously including the effect of the ligands on solvent structure[2] and steric effects.[3,4] Nevertheless, the variation is larger than one might have expected, especially for the present four closely related ligands. In recent studies evidence has been presented in favour of an associative (I_a) rather than a dissociative (I_d or D) mechanism in substitution reactions of several inert metal ions (notably Cr^{III}, possibly Rh^{III}, but not Co^{III}).[13] One is tempted, therefore, to postulate that an I_a mechanism may be operative for the reactions studied here. Alternatively, since nickel(II) is well known for its ability to distort tetragonally, a

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* 1 cal = 4·184 J.

[8] D. B. Rorabacher and C. A. Melendez-Cepeda, *J. Amer. Chem. Soc.*, 1971, **93**, 6071; T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, 1972, **11**, 288.

[9] W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.

[10] K. Kahmann, H. Sigel, and H. Erlenmeyer, *Helv. Chim. Acta*, 1964, **47**, 1754.

[11] M. L. Sanduja and W. MacF. Smith, *Canad. J. Chem.*, 1973, **51**, 3975.

[12] L. S. Frankel, *Inorg. Chem.*, 1971, **10**, 814; although this study was in a mixed solvent (dmso–nitromethane), the nitromethane is believed to have a small rate effect, and the wider temperature range accessible in this way is believed to result in more reliable results (R. B. Jordan, personal communication).

[13] T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357; G. Guastalla and T. W. Swaddle, *Canad. J. Chem.*, 1973, **51**, 821.

low concentration for a four- or five-co-ordinate species may be present in non-aqueous media. The following mechanism (S = solvent, L = ligand) would allow for some ligand specificity because of the associative nature of reaction (4). A tetrahedral species has been

$$[NiS_6]^{2+} \rightleftharpoons [NiS_{6-n}]^{2+} + nS \quad (n = 1 \text{ or } 2) \qquad (3)$$

$$[NiS_{6-n}]^{2+} + L \xrightarrow{s} [NiS_5L]^{2+} \qquad (4)$$

observed for Co^{II} in trimethyl phosphate,[14] but there is no spectral evidence for other than an octahedral geometry for nickel(II) ions in dmso.[15] However, this does not exclude the presence of such a species in low concentration, and since octahedral–square planar equilibria are known to be rapid for nickel(II) ion,[16-18] only a small concentration of a more-reactive species of lower co-ordination number would be necessary. The observation that the values of $\Delta V^{\ddagger}$ are large and positive for substitution reactions of nickel(II) in aqueous solution [19] gives a good indication of a dissociative mechanism in that medium. Perhaps a similar high-pressure study in dipolar aprotic solvents would be a better indicator of mechanism in the present case.

Because of the variation in the activation parameters, it is difficult to make comparisons of the rate constants for the present ligands at any particular temperature. However, it is apparent that there is very little difference in the rates of formation of five- and six-membered chelate rings at room temperature, and at elevated temperatures the six-membered chelate ring [2-(2-aminoethyl)pyridine] is slower to form than that of the five-membered ring [2-(aminomethyl)pyridine]. This may indicate that chelate-ring closure becomes increasingly difficult for the six-membered chelate ring at higher temperatures, but an S.C.S. mechanism does not contribute to the rate-determining step at room temperature. This trend would also explain the high value of $\Delta H^{\ddagger}$ for 2-(aminomethyl)-6-methylpyridine where the 6-methyl group would hinder chelate-ring closure at elevated temperatures. Substitution by a methyl group at the other donor site in 2-[(methylamino)methyl]-pyridine does not have such a marked effect as expected.[8] Further evidence for a possible S.C.S. mechanism for ligand 2-(aminomethyl)-6-methylpyridine may come from a study of the reverse reactions under acidic and neutral conditions which is now under way.

Finally we note that 2-(aminomethyl)pyridine reacts with nickel(II) a little faster than 4-phenylpyridine at all temperatures (Table 3). The rate enhancement is about the same as that observed for basic amines in aqueous solution where an i.c.b. mechanism has been postulated to account for the variation.[7] Since it is difficult to picture a conjugate-base mechanism in dmso, either the i.c.b. mechanism is of questionable validity, or a dissociative interchange (I_d) mechanism is not operative for these reactions in dmso.

EXPERIMENTAL

Ligands were obtained from Emanuel. They were purified by vacuum distillation under N_2 from KOH pellets, and stored under N_2 in a refrigerator. We found that ^1H-decoupled ^{13}C n.m.r. spectra gave a useful check on ligand purity [*e.g.* the ligands tris(2-aminoethyl)amine (tren) and 3,6-diazaoctane-1,8-diamine (trien) can be readily identified in this way, whereas other spectroscopic evidence such as i.r. and ^1H n.m.r. does not give conclusive results].

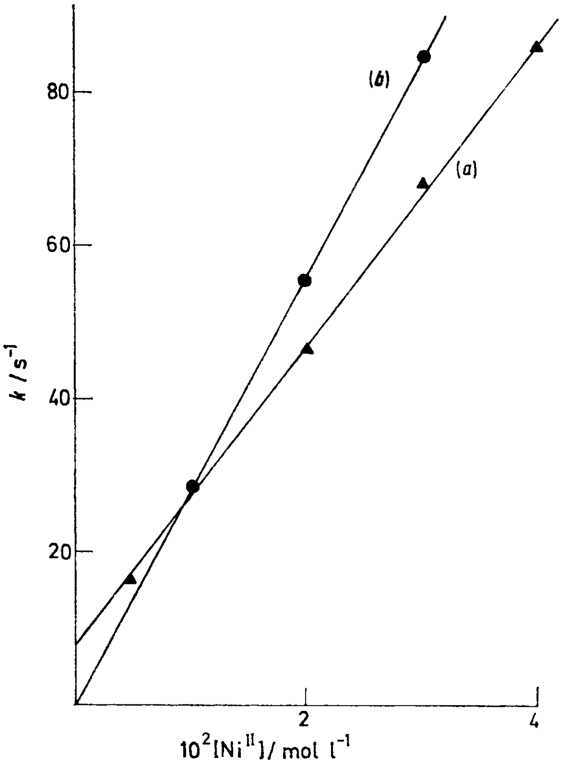

FIGURE 2 Variation of pseudo-first-order rate constants (k) for formation of [(2-aminoethyl)pyridine]nickel(II) in dmso: (*a*), obtained using dehydrated $Ni(ClO_4)_2$ as source of Ni^{II}; (*b*), using $[Ni(dmso)_6][ClO_4]_2$

Fourier-transform ^{13}C n.m.r. spectra (average of 2 000 fast scans for a 50% solution in $CDCl_3$) were recorded with a Bruker WH90 spectrometer, and indicated no sign of impurities (<0·5%) (Table 4). Assignments were made by comparison with published data.[20] Carbon atoms in position 2 [or 6 of 2-(aminomethyl)-6-methylpyridine] were identified by small intensities arising from the absence of a nuclear-Overhauser effect.

The salt $[Ni(dmso)_6][ClO_4]_2$ was prepared by a published method [21] from hydrated nickel(II) perchlorate {Found: Ni, 8·20. $[Ni(dmso)_6][ClO_4]_3$ requires Ni, 8·10%}. This solid

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[14] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 2579.

[15] W. L. Reynolds, *Progr. Inorg. Chem.*, 1970, **12**, 1.

[16] R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4326.

[17] K. J. Ivin, R. Jamison, and J. J. McGarvey, *J. Amer. Chem. Soc.*, 1972, **94**, 1763.

[18] C. Creutz and N. Sutin, *J. Amer. Chem. Soc.*, 1973, **95**, 7177.

[19] E. F. Caldin, M. W. Grant, and B. B. Hasinoff, *Chem. Comm.*, 1971, 1351; *J.C.S. Faraday I*, 1972, 2247; 1973, 1648.

[20] J. B. Stothers, 'Carbon-13 N.m.r. Spectroscopy,' Academic Press, New York, 1972.

[21] J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nuclear Chem.*, 1961, **16**, 219.

TABLE 4

^{1}H-Decoupled ^{13}C n.m.r. spectra of the ligands (δ/p.p.m. ± 0·1 p.p.m.) relative to external Me_4Si

Ligand	C(2)	C(3)	C(4)	C(5)	C(6)	CH_2	N-CH_3	C-CH_3
2-(Aminomethyl)pyridine	162·4	121·5	136·3	121·7	149·1	47·8		
2-(2-Aminoethyl)pyridine	160·5	123·3	136·1	121·1	149·4	42·3 42·1		
2-(Aminomethyl)-6-methylpyridine	161·7	118·0	136·7	121·1	157·8	48·0		24·4
2[(Methylamino)methyl]pyridine	160·4	122·1	136·2	121·7	149·3	57·4	36·2	

was used to prepare nickel(II) solutions since use of dehydrated $Ni(ClO_4)_2$ was observed to give spurious results. The problem is illustrated in Figure 2; (*a*) was obtained using solutions prepared from dehydrated $Ni(ClO_4)_2$ [dried by heating *in vacuo* (10^{-6} Torr) for 2 d over P_2O_5 at 363 ± 2 K].[3] The small intercept in Figure 2 (similar intercepts have been reported in previous studies [2,3,22]) was eliminated by using anhydrous $[Ni(dmso)_6][ClO_4]_2$ as our source of nickel(II) [(*b*)]. Intercepts obtained in our previous study [22] presumably arose from the same cause, and this problem can be attributed to the formation of hydroxy- or hydroxo-bridged species.[3] Fortunately the small intercepts do not affect the gradients significantly and our previous values of k_i for Mn^{II} are probably not in serious error. Nickel(II) solutions were analysed by titration with ethylenediaminetetra-acetic acid.

Kinetic studies were carried out by the stopped-flow method as described previously.[4] Wavelengths were chosen as follows: 310, 305, 290, and 305 nm for 2-(aminomethyl)-, 2-(2-aminoethyl)-, 2-(aminomethyl)-6-methyl-, and 2-[(methylamino)methyl]pyridine respectively.

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[22] D. J. Benton and P. Moore, *J.C.S. Dalton*, 1973, 399.