Kinetics of the Acid and Mercury(II)-ion Induced Dissociations of some Nickel(II) Chelate Complexes of Substituted Pyridine Ligands in Dimethyl Sulphoxide Solution

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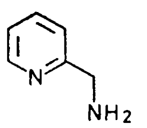
Rate data are reported for the H^+- and Hg^{II}-ion induced dissociations of mono complexes of nickel(II) ion with the bidentate ligands 2-(aminomethyl)pyridine, (I), 2-(2-aminoethyl)pyridine, (II), 2-(aminomethyl)-6-methylpyridine, (III), and 2-[(methylamino)methyl]pyridine, (IV), in dimethyl sulphoxide solution. Limiting ' neutral '-dissociation rate constants (k_d) at zero [Hg^{II}] and 292·0 K have been estimated by extrapolation to be $10^3 k_d$ = 1·12 ± 0·02, 4·46 ± 0·07, 10·7 ± 0·3, and 2·58 ± 0·01 s^{-1} for (I)—(IV) respectively. These results, together with data reported previously for the formation rate constants (k_f), give kinetically determined first stability constants K_1 (= k_f/k_d) in dmso at 292 K as log K_1 = 6·43, 5·80, 5·54, and 6·74 for (I)—(IV) respectively. In acidic solution the pseudo-first-order rate constants (k) vary with [H^+]. Limiting rate constants at high [H^+] (k_a) have been estimated and values of k_a/k_d are 54 ± 5, 365 ± 28, 1 565 ± 81, and 102 ± 26 for (I)—(IV) respectively. These results indicate that the formation reactions are ' normal ' [*i.e.* a chelate-ring-closure (S.C.S.) mechanism does not apply] and a previous suggestion that an S.C.S. mechanism occurs during formation of the mono(2,2'-bipyridine)nickel(II) ion in dmso is reviewed in the light of the marked acid dependence of the reactions studied here. The rate of the Hg^{II}-ion induced dissociation of the mono(1,10-phenanthroline)nickel(II) ion in dmso (at 321·3 K, k_d = 2·4 × 10^{-4} s^{-1}) indicates that a previous indirect estimate (at 318·1 K, k_d = 1·0 s^{-1}) is far too large.

A PREVIOUS study[1] of nickel(II) complex-formation reactions in dimethyl sulphoxide (dmso) solution indicates that for the flexible bidentate ligands (I)—(IV) steric effects are largely unimportant, whereas for 2,2'-bipyridine (bipy) and 2,2':6',2''-terpyridine (terpy) the reactions are slowed by steric hindrance.[2] This steric control for bipy and terpy could arise either during formation of the first metal–ligand bond, or during the subsequent chelate-ring closure(s).[2] The present study of the H^+- and Hg^{II}-ion induced dissociations of the mono complexes of Ni^{II} ion with the ligands (I)—(IV) was undertaken to try and resolve this problem, and to give an indication of how small variations in the ligands might affect the rates of chelate-ring closure in dmso; (I) and (II) were chosen to compare the relative rates of ring closure of five- and six-membered chelate rings, and (III) and (IV) to test the effect of substitution near to the sites of co-ordination. The estimated values of the limiting neutral-dissociation rate constants (k_d) also allow the first stability constants (K_1) to be calculated from the relation $K_1 = k_f/k_d$ (using the previously reported values of the formation rate constants k_f).[1] Stability data of this type in non-aqueous media are very limited and the present results allow a comparison with equilibrium studies in aqueous solution.[3]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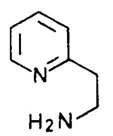
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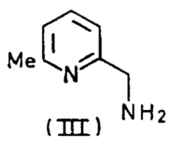
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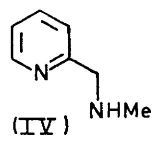
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RESULTS AND DISCUSSION

In the absence of electrophiles a likely scheme for the dissociation of these complexes is shown below (S = a solvent molecule, dmso; R = H or Me; n = 1 or 2, and charges are omitted for convenience). Addition of an electrophile (E), such as H^+ or Hg^{II}, drives the reaction from (A) to (D) either by the electrophile scavenging the released ligand (D) or by it complexing with the unco-ordinated donor atom in the unidentate intermediates (B) and (C). These additional paths are as in equations (1) and (2).

The marked acid dependence observed in the present studies (Table 1) contrasts with the lack of acid catalysis observed during the H^+-promoted dissociation of

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[1] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1974, 2082.

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

[3] D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, 1959, **63**, 1246.

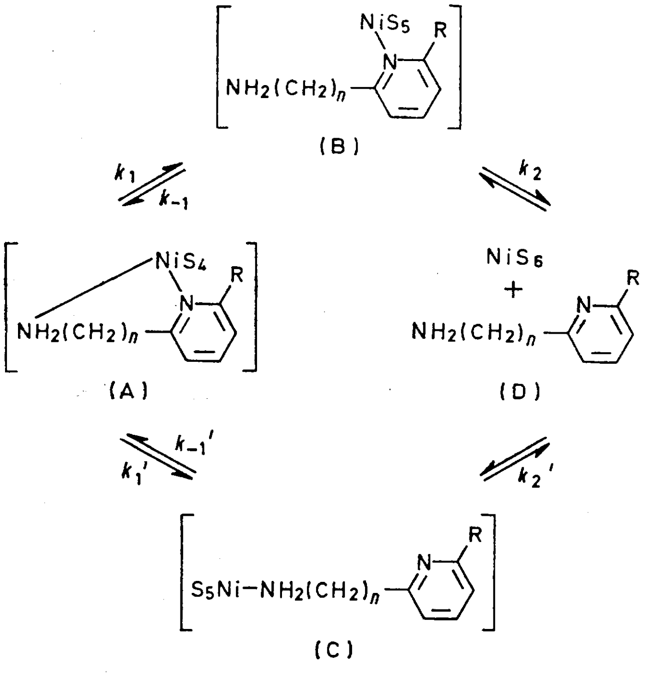
$[Ni(bipy)]^{2+}$ in dmso (bipy = 2,2′-bipyridine).[2] The most likely reason for this difference lies in the greater basicity of ligands (I)—(IV) compared with that of bipy. Similarly, we expect the relative magnitudes of K_E and K_E' to be different when (E) = H^+. The tertiary nitrogen atom in (C) will be much less basic than the primary nitrogen atom in (B); also it is known that the pK_a of pyridine is reduced from 5·2 in H_2O to 3·4 in dmso.[4] Since the presence of the nickel(II) ion is expected to further reduce the pK_a values of the uncoordinated donor atoms in (B) and (C) (probably by *ca.* 2 pK_a units [5]), it seems likely that K_E' will be very small when (E) = H^+, and in any case $K_E' \ll K_E$. Therefore, it is probable that the acid-catalysed path for the dissociation of these complexes will be *via* (1) rather than (2), and the limiting rate at high acidity [5] will be equal to k_1. At intermediate pH the observed pseudo-first-order rate constant (k) for path (1) is given by equation (3) ([E] = [H^+]). If $k_E K_E[E] \gg (k_{-1} + k_2)$,

$$k = k_1(k_2 + k_E K_E[E])/(k_{-1} + k_2 + k_E K_E[E]) \quad (3)$$

it can be seen from (3) that $k = k_1$. In the acidity range investigated ([H^+] = 0·02—0·20 mol l^{-1}) this limiting rate is not reached, but, assuming $k_E K_E[E] \gg k_2$, rearrangement of (3) gives the approximate equation (4). Plots of $1/k$ against $1/[H^+]$ were linear as shown in Figure 1, and from these plots approximate values of k_1 can be estimated by extrapolation to $1/[H^+] = 0$. The gradient of these plots can also be used to give estimates

$$1/k = 1/k_1 + (k_{-1} + k_2)/(k_1 k_E K_E[E]) \quad (4)$$

of $(k_{-1} + k_2)/k_1 k_E K_E$. The results are collected in Table 2.



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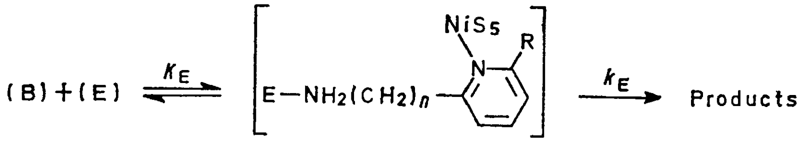
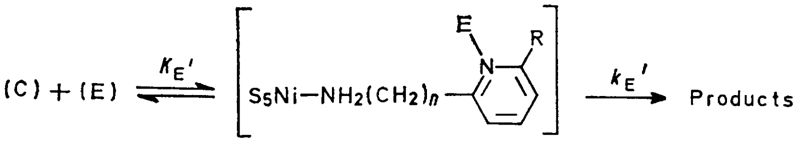


(1)



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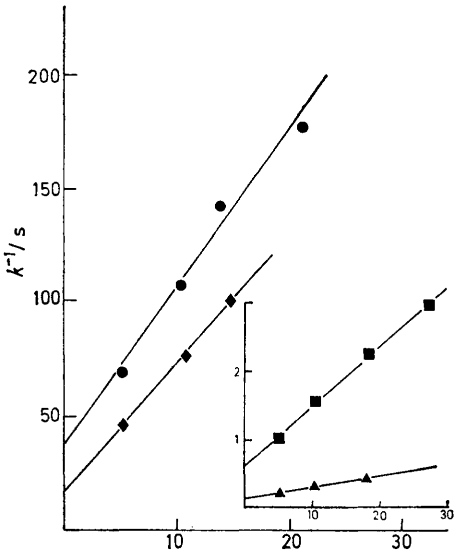

FIGURE 1 Plot of $1/k$ against $1/[H^+]$ for the acid dissociation of mono complexes of Ni^{II} ion with the ligands (I) (♦), (II) (■), (III) (▲), and (IV) (●)

When (E) = Hg^{II} values of K_E and K_E' are expected to be much smaller than when (E) = H^+. Indeed in aqueous solution [6] or in methanol [7] a dependence on [Hg^{II}] is usually not observed and then dissociation only occurs by the Hg^{II} ion scavenging the totally released ligand (D). Since a dependence on [Hg^{II}] was

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[4] I. M. Kolthoff, *Pure Appl. Chem.*, 1971, **25**, 305.

[5] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1959, 3700.

[6] R. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1965, **4**, 929; 1966, **5**, 622.

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

TABLE 1

Pseudo-first-order rate constants (k) for the dissociation of mono complexes of nickel(II) ion (0·025 mol l^{-1}) with bidentate ligands (0·015 mol l^{-1}) (I = 0·27 mol l^{-1} $NaClO_4$, unless specified otherwise)

2-(Aminomethyl)pyridine, (I), at 292·0 K						
(a) Dissociation by Hg^{II}						
10^2[Hg^{II}]/mol l^{-1}	2·25	4·25	5·90			
10^3k/s^{-1}	1·73 ± 0·06	2·31 ± 0·12	2·73 ± 0·03			
(b) Dissociation by CF_3SO_3H						
10^2[CF_3SO_3H]/mol l^{-1}	6·75	9·25	19·25			
10^3k/s^{-1}	9·88 ± 0·04	13·1 ± 0·6	21·6 ± 0·7			
2-(2-Aminoethyl)pyridine, (II), at 292·0 K						
(a) Dissociation by Hg^{II}						
10^2[Hg^{II}]/mol^{-1}	0·285 [a,b]	2·25 [a,b]	2·75 [c,d]	4·75 [a,b]	7·80 [b,e]	8·75 [f,g]
10^3k/s^{-1}	4·8 ± 0·1	6·6 ± 0·3	8·7 ± 0·1	9·9 ± 0·2	13·0 ± 0·5	14·3 ± 0·2
(b) Dissociation by HBF_4						
10^2[HBF_4]/mol l^{-1}	3·75	5·75	9·75	19·75		
10 k/s^{-1}	3·41 ± 0·02	4·59 ± 0·05	6·49 ± 0·14	9·77 ± 0·20		
2-(Aminomethyl)-6-methylpyridine, (III), at 292·0 K						
(a) Dissociation by Hg^{II}						
10^2[Hg^{II}]/mol l^{-1}	0·175	0·350	1·00	2·25	4·75	
10^2k/s^{-1} [a]	1·48 ± 0·04	1·88 ± 0·06	3·34 ± 0·10	6·17 ± 0·14	12·6 ± 0·6	
(b) Dissociation by HBF_4						
10^2[HBF_4]/mol l^{-1}	5·75	9·75	19·45			
k/s^{-1}	2·37 ± 0·05	3·63 ± 0·04	6·01 ± 0·29			
(c) Dissociation by CF_3SO_3H						
10^2[CF_3SO_3H]/mol l^{-1}	4·75	7·25	9·75	19·75		
k/s^{-1}	2·71 ± 0·12	3·58 ± 0·06	4·41 ± 0·02	7·24 ± 0·20		
2-[(Methylamino)methyl]pyridine, (IV), at 292·0 K						
(a) Dissociation by Hg^{II}						
10^2[Hg^{II}]/mol l^{-1}	1·1	2·1	4·1			
10^4k/s^{-1} [c,h]	2·70 ± 0·01	2·79 ± 0·01	3·01 ± 0·01			
(b) Dissociation by CF_3SO_3H						
10^2[CF_3SO_3H]/mol l^{-1}	4·75	7·25	9·75	19·75		
10^3k/s^{-1}	5·64 ± 0·02	7·01 ± 0·05	9·30 ± 0·10	14·5 ± 0·9		
2-(Aminoethyl)pyridine at 312·6 K						
(a) Dissociation by Hg^{II}						
10^2[Hg^{II}]/mol l^{-1}	2·25	4·25	5·90			
10^2k/s^{-1}	1·11 ± 0·08	1·48 ± 0·04	1·82 ± 0·12			
(b) Dissociation by CF_3SO_3H						
10^2[CF_3SO_3H]/mol l^{-1}	4·30	6·85	9·40	19·55		
10^2k/s^{-1}	7·39 ± 0·07	11·8 ± 0·5	13·0 ± 0·2	23·9 ± 0·4		
2-(Aminomethyl)pyridine at 312·6 K						
(a) Dissociation by Hg^{II}						
10^2[Hg^{II}]/mol l^{-1}	2·25	4·25	5·90			
10^2k/s^{-1}	9·02 ± 0·02	10·3 ± 0·2	11·3 ± 0·2			
(b) Dissociation by CF_3SO_3H						
10^2[CF_3SO_3H]/mol l^{-1}	4·30	6·85	9·40	19·55		
k/s^{-1}	4·97 ± 0·26	6·97 ± 0·08	8·75 ± 0·10	12·7 ± 0·5		
1,10-Phenanthroline						
Dissociation by Hg^{II} (5 × 10^{-2} mol l^{-1}) [i]						
T/K	313·1 [j]	321·3	331·1			
10^5k/s^{-1}	9·14 ± 0·02	24·1 ± 0·5	56·8 ± 0·3			

$\Delta H^{\ddagger} = 20·3 \pm 0·5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -12·3 \pm 1·1$ cal K^{-1} mol^{-1} (1 cal = 4·184 J).

[a] I = 0·20 mol l^{-1}. [b] [Ni^{II}] = 6 × 10^{-3}, [Ligand] = 5 × 10^{-3} mol l^{-1}. [c] I = 0·30 mol l^{-1}. [d] [Ni^{II}] = 5 × 10^{-2}, [Ligand] = 2·5 × 10^{-2} mol l^{-1}. [e] I = 0·34 mol l^{-1}. [f] I = 0·40 mol l^{-1}. [g] [Ni^{II}] = 3·4 × 10^{-2}, [Ligand] = 2·5 × 10^{-2} mol l^{-1}. [h] [Ni^{II}] = 2·5 × 10^{-2}, [Ligand] = 1·8 × 10^{-2} mol l^{-1}. [i] Rate independent of [Hg^{II}]; [Ni^{II}] = 2 × 10^{-5}, [Ligand] = 10^{-3}, and I = 0·15 mol l^{-1}. [j] At I = 0·30 mol l^{-1}, 10^5k = 7·18 ± 0·01 s^{-1}; at I = 0·30 and [Hg^{II}] = 0·10 mol l^{-1}, 10^5k = 7·60 ± 0·01 s^{-1}.

observed here (Table 1), one must postulate that either or both of the paths (1) and (2) occur. Now 2-substituted pyridines in general form very weak complexes in solution so we can again postulate $K_E \gg K_E'$ and also $k_E \gg k_E'$, when (E) = Hg^{II}. Hence path (1) will dominate over (2) and the observed pseudo-first-order rate constants in the presence of Hg^{II} will be given by equation (5). Since K_E will be small (often negligible) at low [Hg^{II}], $k_E K_E[E] \ll (k_{-1} + k_2)$ and equation (5)

$$k = \{k_1(k_2 + k_E K_E[E])/(k_{-1} + k_2 + k_E K_E[E])\} + k_1'k_2'/(k_{-1}' + k_2') \quad (5)$$

reduces to (6). The data in Table 1 conform with equation (6) as shown by plots of k against [Hg^{II}] in

$$k = k_1k_2/(k_{-1} + k_2) + k_1'k_2'/(k_{-1}' + k_2') + [k_1k_EK_E/(k_{-1} + k_2)][E] \quad (6)$$

Figure 2. Extrapolation to zero [Hg^{II}] then gives the limiting 'neutral' dissociation rate constants k_d [equation (7)], and the gradient of the lines in Figure 2 give estimates of $k_1k_EK_E/(k_{-1} + k_2)$ (Table 2).

$$k_d = k_1k_2/(k_{-1} + k_2) + k_1'k_2'/(k_{-1}' + k_2') \quad (7)$$

TABLE 2

Gradients and intercepts of the plots in Figures 1 and 2 and derived rate and equilibrium data in dimethyl sulphoxide solution (I = 0·27 mol l^{-1} NaClO$_4$)

(a) At 292·0 K	From Figure 1			From Figure 2			
Ligand	10^2 Gradient	10^2 Intercept	10$^2k_1$/s^{-1}	10^3 Gradient	10^3 Intercept [e]	k_1/k_d [a]	log K_1 [b]
2-(Aminomethyl)-pyridine, (I)	569 ± 11	1 660 ± 135	6·02 ± 0·49	27·3 ± 0·5	1·12 ± 0·03	53·8 ± 4·6	6·43 (7·23)
2-(2-Aminoethyl)-pyridine, (II)	8·80 ± 0·27	61·2 ± 4·5	163 ± 12	112 ± 2	4·46 ± 0·07	365 ± 28	5·80 (5·25)
2-(Aminomethyl)-6-methylpyridine, (III)	2·09 ± 0·02 [c]	5·97 ± 0·26 [c]	1 675 ± 73	2 290 ± 40	10·7 ± 0·3	1 565 ± 81	5·54
2-[(Methylamino)-methyl]pyridine, (IV)	685 ± 72	3 818 ± 997	2·62 ± 0·68	1·04 ± 0·05	0·258 ± 0·001	102 ± 26	6·74 (6·93)
(b) At 312·6 K							
(I)	52·0 ± 3·2	162 ± 34	61·7 ± 10·0	194 ± 6	6·67 ± 0·26	95·5 ± 15·4	6·15 [d] (6·9)
(II)	0·679 ± 0·009	4·34 ± 0·14	2 304 ± 72	625 ± 10	76·2 ± 0·4	302 ± 10	5·20 [d] (4·9)

[a] $k_1/k_d \approx k_{-1}/k_2$, except possibly when R = Me [ligand (III)] (see Discussion section). [b] $K_1 = k_f/k_d$ at 292 K and I = 0·2 mol l^{-1}; values in parentheses refer to aqueous solution at 293 K and I *ca.* 0·1 mol l^{-1}. [c] Similar results were obtained using CF$_3$SO$_3$H; 10^2 Intercept = 6·3 ± 0·8; 10^2 Gradient = 1·54 ± 0·08. [d] Values of k_f were calculated from the activation parameters (ref. 1) and so estimates of K_1 are less accurate at this temperature. [e] Intercept = k_d/s^{-1}.

Since the stabilities of complexes of 2-substituted pyridines are much smaller than those of unhindered and more basic alkylamines, we expect $k_2 \gg k_2'$; except when R = Me, it seems very likely that k_1 and k_1' will be comparable in magnitude and, therefore, to a good approximation we expect equation (7) to reduce to (8).

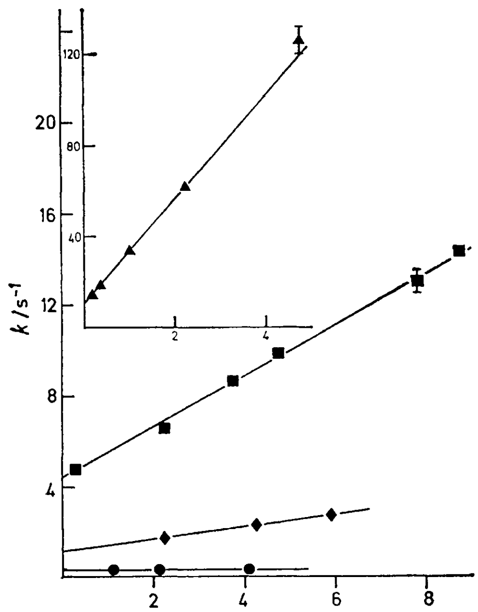

FIGURE 2 Plot of k against [Hg^{II}] for the Hg^{II}-ion induced dissociations of mono complexes of Ni^{II} ion with the ligands (I) (♦), (II) (■), (III) (▲), and (IV) (●)

$$k_d \approx k_1k_2/(k_{-1} + k_2) \quad (8)$$

However, when R = Me it seems very likely that because of steric acceleration $k_1' \gg k_1$ and so the second term in equation (7) will be more important, and (8) may well be invalid in this case. For the other three systems studied here a combination of equation (8) with the values of k_1 estimated from the acid-dissociation studies then allows values of $(k_{-1}/k_2) \approx k_1/k_d$ to be calculated and these results are shown in Table 2. The abnormally high value of k_1/k_d for ligand (III) may indicate that our approximations are invalid in this case, although steric crowding might be responsible for an unusually high value of k_{-1}. However, the values of k_1/k_d obtained for the other three ligands can reasonably be equated with k_{-1}/k_2. The generally large values obtained confirm our belief that the complex-formation reactions with these ligands are 'normal,' *i.e.* a rate-determining chelate-ring-closure mechanism (S.C.S. mechanism) is not operative. This conclusion was also reached from a study of the formation reactions,[1] and contrasts with earlier results for bipy and terpy where steric hindrance to complex formation was noted.[2]

However, the present results also demonstrate that our earlier conclusion concerning the mechanism of formation of bipy (and terpy) complexes of Ni^{II} in dmso (namely that an S.C.S. mechanism is operative) may well be invalid. This conclusion was reached partly on the basis of a small ratio of the limiting acid–neutral-dissociation rates (indicating a relatively small rate of chelate-ring closure) and partly because the values of the formation rate constants (k_f) for [Ni(dmso)$_6$]$^{2+}$ reacting with bipy and terpy in dmso are much smaller than for the reactions with pyridine or with the more flexible ligands (I)—(IV). There is no doubt that the values of k_f for bipy and terpy are much smaller than the values obtained with ligands (I)—(IV). However, the observation of a marked acid dependence for the dissociation reactions studied here (Figure 1) leads us to suggest an alternative reason for the lack of acid catalysis observed for the dissociation of $[Ni(bipy)]^{2+}$ in dmso. We now believe that in dmso a more plausible explanation is simply that the protonation constant [analogous to K_E' of equation (2)] is too small for significant protonation to occur at the unidentate intermediate formed during the dissociation of $[Ni(bipy)]^{2+}$. This difference in behaviour between aqueous solution and dmso parallels the significant reduction in the pK_a of pyridine between these two media noted previously.[4] In view of this alternative explanation of our earlier results, it now seems more likely that the small values of k_f observed for bipy and terpy reacting with the $[Ni(dmso)_6]^{2+}$ ion in dmso indicate steric hindrance to formation of the first metal–ligand bond rather than rate-determining chelate-ring closure. Bipy and terpy are atypical ligands in so far as formation of the first metal–ligand bond will be analogous to the reaction with a sterically hindered ligand such as 2-phenylpyridine.[1] Therefore, changes in the co-ordinated solvent molecules may be expected to have a significant effect on the rates of the bipy and terpy complex-formation reactions because of the variation in the size of the vacant site following dissociation of a solvent molecule from the hexasolvated metal ion. In dmso the co-ordinated solvent molecules are bulkier than water, and this may reduce the size of the available co-ordination position sufficiently to hinder the approach of bipy and terpy, but will have little effect on the reactions of the less-hindered ligands (I)—(IV). For this reason it seems very likely that first bond formation with ligands (I)—(IV) is *via* the primary or secondary aliphatic nitrogen-donor atom rather than the pyridine nitrogen. In support of this conclusion is the observation that the methyl group in 2-methylpyridine causes sufficient steric hindrance to prevent complex formation with nickel(II) ion in aqueous solution.[8]

Because of the approximations involved in estimating values of k_{-1}/k_2 from the ratio k_1/k_d too much reliance should not be placed on the small variations observed (Table 2). Nevertheless, it is a little surprising to find that this ratio is larger for the six-membered chelate ring formed with ligand (II) than for the five-membered chelate rings formed with (I) and (IV). If this difference is significant, then, since we expect the value of k_2 to be about the same for all these three ligands, the implication is that in dmso the rate of chelate-ring closure is greater for the six-membered than for the five-membered rings. This behaviour is directly opposite to that found in aqueous solution where six-membered chelate rings usually form more slowly.[9] Increasing the temperature from 292·0 to 312·6 K does not reverse this trend, but the values of k_{-1}/k_2 for ligands (I) and (II) are closer at the higher temperature.

Stability Constants and Relative Labilities.—Values of k_1 and k_d for ligands (I)—(IV) vary in the sequence (III) > (II) > (I) > (IV). Consequently the stability constants (K_1) vary in the reverse order. This is the expected trend: opening of the more stable five-membered chelate rings formed by (I) and (IV) is slower than the six-membered ring formed by (II), whereas for (III) steric acceleration by the methyl group in the 6-position of the pyridine ring considerably increases the rate of dissociation and lowers the complex stability. The slower rate of ring opening and greater stability of the complex of ligand (IV) compared with (I) is also in line with the greater basicity of (IV), and supports our belief that first bond dissociation occurs primarily at the bond with the primary or secondary aliphatic nitrogen atom rather than at the bond with the pyridine nitrogen atom. The greater stability of the pyridine–metal bond indicates significant π-bonding which is not possible at the aliphatic nitrogen–metal bonds. This conclusion is also supported by the greater stability of complexes of bipy compared with those of 1,2-diaminoethane (en).

The stability constants in dmso are very similar to the values in aqueous solution (Table 2). Close agreement was also obtained previously for the complexes of Mn^{II} with bipy, terpy, and phen (1,10-phenanthroline) in methanol and in water.[7] We were a little surprised, therefore, to find a value of K_1 reported [10] for $[Ni(phen)]^{2+}$ in dmso (log K_1 *ca.* 3) which is unbelievably small compared with the value in aqueous solution (log K_1 8·8).[11] This discrepancy prompted us to measure the rate of the Hg^{II}-ion induced dissociation of $[Ni(phen)]^{2+}$ in dmso, and our results are collected in Table 1. Values of k_d were found to be very much smaller than the values obtained indirectly from a study of the formation reaction,[10] and using our direct estimate of k_d (by extrapolation, at 298·1 K, $k_d = 1{\cdot}84 \times 10^{-5}\ s^{-1}$) together with the value of k_f reported previously [10] (at 298·1 K, $k_f = 3{\cdot}5 \times 10^{2}\ l\ mol^{-1}\ s^{-1}$) a value of K_1 can be estimated for $[Ni(phen)]^{2+}$ in dmso (at 298·1 K, log K_1 7·28) which is much closer to the value reported in aqueous solution.

EXPERIMENTAL

Materials.—Most materials were prepared and analysed as described previously.[1,2] Trifluoromethanesulphonic acid (Emanuel) was vacuum distilled in a greaseless apparatus. The salt $[Hg(dmso)_6][ClO_4]_2$ was prepared as described.[12] Stock solutions of Hg^{II} were analysed by titration with a standard solution of chloride ion.[13]

Kinetic Studies.—Stopped-flow and Cary 14 spectrophotometers were used as in earlier studies.[1,2] Temperatures were controlled to ±0·1 K and the ionic strength adjusted in most cases to $I = 0{\cdot}27\ mol\ l^{-1}$ by the addition of anhydrous sodium perchlorate. Acid-dissociation studies were originally carried out using a solution of HBF_4 in dmso (prepared as described [2]), but in later work it was found more convenient to use trifluoromethanesulphonic

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acid as our source of anhydrous acid. The trifluoromethanesulphonate ion is recommended because of its low co-ordinating ability.[14] Very similar results were obtained using HBF_4 and CF_3SO_3H as shown by our data for 2-(aminomethyl)-6-methylpyridine. Reactions were generally followed between 600 and 645 nm.

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