Evidence for a Rate-determining Chelate-ring-closure Mechanism During the Formation of the (2,2′-Bipyridine)nickel(II) Ion in Dimethyl Sulphoxide Solution †

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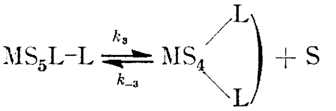
In dimethyl sulphoxide (dmso) as solvent, the rate constant at 298·1 K for formation of the mono-complex of Ni^{II} ion with the unidentate ligand 4-phenylpyridine ($k_f = 1{\cdot}64 \times 10^3$ l mol^{-1} s^{-1}) † is *ca.* 24 and 63 times as large as corresponding values for the polydentate ligands 2,2′-bipyridine (bipy) and 2,2′,2″-terpyridine (terpy) respectively, and nearer to the solvent-exchange rate ($k_{ex} = 7{\cdot}4 \times 10^3$ s^{-1}). These results are in marked contrast to values reported in aqueous solution where the rates of formation are about the same for py, bipy, and terpy, and a rate-determining chelate-ring-closure mechanism is postulated for the polydentate ligands in dmso. This postulate is supported by kinetic studies of the Hg^{II} and H^+ induced dissociations of the (2,2′-bipyridine)nickel(II) ion in dmso solution which indicate that, for 2,2′-bipyridine at 298·1 K, the rate of chelate-ring closure (rate constant k_{rc}) is *ca.* 60 times slower in dmso (k_{rc} *ca.* 47 s^{-1}) † than in water (k_{rc} *ca.* 3×10^3 s^{-1}).

USUALLY the rate of formation of a metal chelate complex in aqueous solution is controlled by the formation of the first metal–ligand bond, and subsequent chelate-ring closure(s) are very rapid.[1-3] If L–L represents the donor atoms of a bidentate ligand and MS_6 a solvated metal ion, the mechanism given in equations (1)—(4)

$$MS_6 + L\text{–}L \overset{\text{Rapid, }K_0}{\rightleftharpoons} MS_6,L\text{–}L \text{ (outer-sphere association)} \quad (1)$$

$$MS_6,L\text{–}L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MS_5,L\text{–}L + S \quad (2)$$

$$MS_5,L\text{–}L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MS_5L\text{–}L \text{ (unidentate complex)} \quad (3)$$



$$MS_5L\text{–}L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MS_4\left(\begin{matrix} L \\ L \end{matrix}\right) + S \quad (4)$$

applies.[1-3] In most cases, the solvent-exchange step (rate constant k_1) is rate determining and $k_3 \gg k_{-2}$. This is the behaviour usually found in aqueous solution and is supported by a considerable weight of experimental evidence.[1-3] It is somewhat surprising, therefore, to find that metal chelate-complex formations in non-aqueous solvents do not fit this pattern at all well.[4-6,‡] For Ni^{II} and Co^{II} ions it has been suggested[4] that the effect of the ligand on solvent structure is an important additional consideration in non-aqueous media, whereas with the more-labile Mn^{II} ion in methanol it was suggested that the rate of dissociation of the unidentate complex (rate constant k_{-2}) might compete with the rate of chelate-ring closure (rate constant k_3).[5] We now present evidence which indicates that the latter mechanism may be more widespread in non-aqueous media, since it appears that a rate-determining chelate-ring-closure mechanism is operative for the less-labile Ni^{II} ion in dimethyl sulphoxide solution.

TABLE 1

Pseudo-first-order rate constants (k) for the reaction of nickel(II) ion with 4-phenylpyridine (10^{-4} mol l^{-1}) in dimethyl sulphoxide solution [wavelength 285 nm, $I = 0{\cdot}21$ mol l^{-1} ($NaClO_4$)]

At 291·7 K

No. experiments	2	4	3
$10^2[Ni^{II}]$/mol l^{-1}	6·8	2·0	0·2
Average k/s^{-1}	105·1 ± 2·2 *	49·4 ± 2·5	32·6 ± 0·4

At 295·3 K

No. experiments	2	3	3
$10^2[Ni^{II}]$/mol l^{-1}	6·8	2·0	1·0
Average k/s^{-1}	138·4 ± 3·0	68·2 ± 4·7	55·0 ± 1·1

At 299·7 K

No. experiments	4	3	3	4	3
$10^2[Ni^{II}]$/mol l^{-1}	6·8	4·0	2·0	1·0	0·2
Average k/s^{-1}	173·1 ±3·8	131·8 ±0·8	95·7 ±4·8	77·7 ±2·7	65·7 ±2·4

At 307·6 K

No. experiments	2	3	3
$10^2[Ni^{II}]$/mol l^{-1}	4·0	1·0	0·2
Average k/s^{-1}	286 ± 26	174 ± 26	136 ± 34

* Errors are quoted as ± one standard deviation for observed rate constants. Rate constants between 100 and 300 s^{-1} (which are near to the limits of our stopped-flow method) will have an error between 10 and 30%.

RESULTS AND DISCUSSION

Formation Studies.—The reaction of an excess of Ni^{II} ion (2×10^{-3}—$6{\cdot}8 \times 10^{-2}$ mol l^{-1}) with the uni-

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† P. K. Chattopadhyay and J. F. Coetzee (*Inorg. Chem.*, 1973, **12**, 113) have since reported similar results. For pyridine in dmso solution $k_f = ca.\ 2 \times 10^3$ l mol^{-1} s^{-1} at 298·1 K, and for 1,10-phenanthroline in dmso it is estimated that k_{rc} *ca.* 40 s^{-1} at **303** K.

‡ The results reported for thiocyanate ion in ref. 6 have been contested by F. Dickert and H. Hoffmann (*Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 1320). The latter pressure-jump study has been confirmed by a more recent stopped-flow study (J. F. Coetzee and E. Hsu, unpublished work) reported by P. K. Chattopadhyay and J. F. Coetzee (*Inorg. Chem.*, 1973, **12**, 113).

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[2] D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

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

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

[5] D. J. Benton and P. Moore, *J.C.S. Chem. Comm.*, 1972, 717; *J.C.S. Dalton*, 1973, 399.

[6] C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, 1970, **9**, 2346.

dentate ligand 4-phenylpyridine (10^{-4} mol l^{-1}) was examined in dimethyl sulphoxide (dmso) solution (Table 1) for comparison with results published for 2,2′-bipyridine (bipy) and 2,2′,2″-terpyridine (terpy) in the same solvent.[4] 4-Phenylpyridine (pK_a 5·5)[7] was chosen primarily because it resembles 2,2′-bipyridine more than pyridine alone (and should, therefore, have a similar effect on the solvent structure[4]), and also because it gave a better signal than unsubstituted pyridine. (We obtained similar results with isoquinoline.) The reactions were followed at 285 nm by the stopped-flow method[5] at four temperatures between 291·7 and 307·6 K. (This narrow temperature range was limited at the lower end by the freezing point of the solvent and at the upper end by the rapidity of the reactions.) Values of the formation (k_f) and dissociation rate constants (k_d) (Table 2) were obtained from the relation[6] $k = k_d + k_f[Ni^{II}]$, where k is the observed pseudo-first-order rate constant. Values of k_d were checked by following the back reaction directly using Hg^{II} ion to drive the reaction, and good agreement was observed (Table 2). Because of the narrow temperature range of these studies, only approximate activation parameters were obtained (Table 2). However, it is perhaps significant that $\Delta H_f^‡$ (9 ± 2 kcal mol^{-1}) is lower than the values for bipy ($\Delta H_f^‡ = 12·6$ kcal mol^{-1})[4] and terpy ($\Delta H_f^‡ = 11·9$ kcal mol^{-1}),[4,8] and closer to the value for solvent exchange ($\Delta H^‡ = 6·2 \pm 0·7$ kcal mol^{-1}).[8]

TABLE 2

Values of k_f [a] and k_d [a] from the relation $k = k_d + k_f[Ni^{II}]$ estimated by a weighted linear least-squares analysis of the data in Table 1

T/K	291·7	295·3	299·7	307·6
k_f/l mol^{-1} s^{-1}	1090 ± 38	1437 ± 14	1716 ± 56	3891 ± 1539
k_d/s^{-1}	30·4 ± 0·5	40·6 ± 0·4 [b]	62·6 ± 2·1	131·0 ± 17·2

[a] At 298·1 K, activation parameters associated with the values of k_f are $\Delta H_f^‡ = 9·0 \pm 2·0$ kcal mol^{-1} and $\Delta S_f^‡ = -13·5 \pm 6·7$ cal K^{-1} mol^{-1}, and with the values of k_d are $\Delta H_d^‡ = 14·6 \pm 1·1$ kcal mol^{-1} and $\Delta S_f^‡ = -1·9 \pm 3·6$ cal K^{-1} mol^{-1}. [b] This value is in good agreement with that obtained directly by dissociating (4-phenylpyridine)nickel(II) ion (10^{-3} mol l^{-1} Ni^{II} + 4×10^{-4} mol l^{-1} 4-phenylpyridine) with mercury(II) perchlorate (2×10^{-3} mol l^{-1}) in dmso, *i.e.* $k_d = 39·4 \pm 2·9$ s^{-1} at 295·3 K ($\lambda = 305$ nm).

TABLE 3

Comparison of rate data for the formation and dissociation reactions of mono-complexes of Ni^{II} ion in aqueous solution and in dimethyl sulphoxide solution

	In aqueous solution					In dimethyl sulphoxide				
Ligand	T/K	I [a]	10^{-3} k_f [b]	10^4k_d (acid) [c]	10^4k_d (neutral) [d]	T/K	I [a]	$10^{-1}k_f$ [b]	10^4k_d (acid) [c]	10^4k_d (neutral)
Pyridine	298·1	*ca.* 0	*ca.* 4 [e]	380 000 [f]		298·1		*ca.* 200 [g]		*ca.* 700 000 [g,h]
4-Phenylpyridine						298·1	0·21	164		524 000 [i]
2,2′-Bipyridine	298·1	*ca.* 0	1·5	34	0·5 [j]	298·1	*ca.* 0	6·9 [k]		
						314·4	0·5		27 [l]	15 [i]
2,2′,2″-Terpyridine	298·1	*ca.* 0	1·4				*ca.* 0	2·6 [k]		

[a] Ionic strength (adjusted with $NaClO_4$)/mol l^{-1}. [b] Formation rate constant l mol^{-1} s^{-1}. [c] Dissociation rate constant/s^{-1} in an excess of acid (0·1—0·5 mol l^{-1} H^+). [d] Dissociation rate constant/s^{-1} under neutral conditions. [e] Ref. 9. [f] Acid independent. [g] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113. [h] At 293·1 K. [i] Using Hg^{II}. [j] $^{63}Ni^{2+}$ Exchange rate; this method was compared with that used here (Table 4) by using copper(II) perchlorate to study the reaction in aqueous solution. At 308 K, good agreement was obtained ($10^4k = 2·03 \pm 0·02$ s^{-1}) compared with the value ($10^4k = 2·05 \pm 0·02$ s^{-1}) reported by P. Ellis, R. Hogg, and R. G. Wilkins, *J. Chem. Soc.*, 1959, 3308. [k] Ref. 4. [l] Average value between 0·11 and 0·48 mol l^{-1} HBF_4 (Table 4).

A comparison of the values of k_f for pyridine (or 4-phenylpyridine), bipy, and terpy in water and in dmso solution (Table 3) shows an unexpected pattern. Whereas in aqueous solution rate constants for unidentate and polydentate ligands are very similar,[9] in dmso solution the rate constants vary by a factor of 63 and values for the bipy and terpy complexes are unusually small. This behaviour is explicable if either k_2 or k_3 is much smaller in dmso solution than in water, and therefore an attempt was made to measure k_3 indirectly by the method of Wilkins and his co-workers.[9]

Dissociation Studies.—The rates of the reverse (dissociation) reaction of the $[Ni(bipy)]^{2+}$ complex were measured in dmso solution under acidic [k_d(acidic)] and neutral [k_d(neutral)] conditions (Table 4). It has been shown[1,3,5] that the ratio of these rate constants k_d(acidic) : k_d(neutral) = $(k_{-2} + k_3) : k_{-2}$. In aqueous solution this ratio is *ca.* 70, and, if we equate k_{-2} to the

TABLE 4

Rate constants (average of two estimations) at 314·4 ± 0·1 K for the dissociation of (2,2′-bipyridine)nickel(II) ion in dimethyl sulphoxide solution [$I = 0·48$ mol l^{-1} ($NaClO_4$), wavelength 322 nm]

Decomposing ion / mol l^{-1}	10^4[bipy] / mol l^{-1}	$10^4[Ni^{II}]$ / mol l^{-1}	10^3k_d / s^{-1}
0·05 (Hg^{II})	5·0	5·0	1·48 ± 0·05
0·002 (Cu^{II})	2·0	20·0	1·29 ± 0·02
0·114 (H^+) [a]	2·0	2·0	3·07 ± 0·17
0·479 (H^+) [a]	2·0	2·0	2·40 ± 0·12

[a] HBF_4 in dry dmso [prepared by passing $NaBF_4$ in dmso through a dried column of cation-exchange resin (Zeocarb 225) in the H^+ form].

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[8] P. A. Cock, C. E. Cottrell, and R. K. Boyd, *Canad. J. Chem.*, 1972, **50**, 402.

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

rate of dissociation of the complex $[\mathrm{Ni(py)}]^{2+}$, then one can estimate[9] k_3 *ca.* 3×10^3 s^{-1}. Corresponding values *in dmso* solution are 1·9 and, equating k_{-2} to the value of k_d obtained for the (4-phenylpyridine)nickel(II) ion (52·4 s^{-1}), it appears that k_3 *ca.* 47 s^{-1} in dmso solution, or at least 60 times slower than the value in aqueous solution.

One can only speculate as to the reason for this considerable difference in the rate of chelate-ring closure in different solvents, but possibly it arises from the bulkiness of the co-ordinated dmso molecules (compared with the much smaller co-ordinated water molecules) which might affect values of both k_2 and k_3 by hindering the approach of the donor atoms on co-ordination. Work with other solvents (which is underway) may help to clarify the situation.

EXPERIMENTAL

4-Phenylpyridine (Aldrich) was recrystallised from ethanol until it had the reported melting point.[7] 2,2′-Bipyridine (AnalaR) was used without purification. Solutions of the complex $[\mathrm{Ni(dmso)_6}](\mathrm{ClO_4})_2$ were prepared by dissolving anhydrous nickel(II) perchlorate in dry dimethyl sulphoxide (dmso).[4] This method is unsuitable for mercury(II) perchlorate since the heat liberated causes decomposition, and so solutions of Hg$^{\mathrm{II}}$ in dmso were prepared from the solid complex[10] $[\mathrm{Hg(dmso)_6}](\mathrm{ClO_4})_2$. Solutions of the complex $[\mathrm{Cu(dmso)_6}](\mathrm{ClO_4})_2$ were prepared in the same way. Solutions of perchloric acid in dmso are hazardous[11] and so a solution of tetrafluoroboric acid was used. A *ca.* 0·5 mol l^{-1} solution of $\mathrm{HBF_4}$ was prepared by passing a solution of $\mathrm{NaBF_4}$ (50 cm^3, 1 mol l^{-1}) in dmso through a cation-exchange resin (100 g of Zeo-Karb 225 in the H$^+$ form, pre-dried by washing with dry methanol, then dry dmso until clean) and eluting with dmso (50 cm^3).

Stock solutions of Hg$^{\mathrm{II}}$, Cu$^{\mathrm{II}}$, Ni$^{\mathrm{II}}$, and $\mathrm{HBF_4}$ in dmso were analysed by published methods[12] after first diluting with distilled water. Stopped-flow and Cary 14 spectrophotometers were used as described previously.[13]

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