Rates of Formation and Dissociation, and the Stability of some Manganese(II) and Zinc(II) Complexes with Bipyridyl-type Ligands in Dimethyl Sulphoxide Solution

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The rates of formation and dissociation of 1 : 1 complexes of manganese(II) and zinc(II) ions with bipyridyl-type ligands have been examined in dimethyl sulphoxide (dmso) solution by the stopped-flow method at temperatures just above the freezing point of dmso. In some cases the reactions are too fast to measure {*e.g.* the reaction between the $[Mn(dmso)_6]^{2+}$ ion and 2,2′-bipyridine (bipy)}. Rate data are reported for the formation and the mercury(II)-ion induced dissociations of $[Mn(phen)(dmso)_4]^{2+}$ (phen = 1,10-phenanthroline) and $[Zn(bipy)(dmso)_4]^{2+}$ ions, and the kinetically determined first stability constants in dmso (I = 0·20 mol dm^{-3}, Na[ClO$_4$]) are $\log(K_1/\text{dm}^3\ \text{mol}^{-1})$ = 2·63 and 3·36 respectively. The rate constants for dmso solvent exchange (k_{ex}) are calculated to be $\log(k_{ex}/\text{s}^{-1})$ = 4·89 (291·7 K) and 5·94(292·2K) for Mn^{2+} and Zn^{2+} respectively. The reaction between a large excess of $[Mn(dmso)_6]^{2+}$ ion and 2,2′:6′,2″-terpyridine (terpy) is complicated; an initial very rapid reaction is followed by a much slower process which has been examined by repetitive-scan spectrophotometry. Rate data are reported for the two steps, and a mechanism is proposed in which the initial rapid reaction involves the formation of a binuclear intermediate and the slow step is associated with final chelate-ring closure.

ALTHOUGH the rates of substitution reactions of the very labile manganese(II) and zinc(II) ions in aqueous solution are often too large to investigate by the stopped-flow method,[1,2] we have shown previously that it is possible to study Mn^{2+} in this way in methanol solution and at low temperatures.[3] A comparison of the relative rates of

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[1] C. H. Langford and V. S. Sastri, *MTP Intern. Rev. Sci.*, Inorg. Chem. Ser., 1972, vol. 9, ch. 6.

[2] D. N. Hague, 'Inorganic Reaction Mechanisms,' Specialist Periodical Reports, The Chemical Society, 1972—1974, vols. 2 and 3, Part II, ch. 4.

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

formation of nickel(II) complexes in dimethyl sulphoxide (dmso) solution and in methanol,[4-6] together with rate constants obtained for Mn^{2+} in methanol [3] by extrapolation of our previous results at low temperatures, indicated that it might be possible to examine the rates of formation of manganese(II) and zinc(II) complexes in dmso by the stopped-flow method at room temperature (dmso freezes at 291.5 K). This possibility is partly confirmed by the present results.

To avoid the formation of bis complexes or higher species, studies of the formation 1 : 1 complexes are usually made in the presence of an excess of metal ion, and the pseudo-first-order rate constant (k) under these conditions is given by equation (1). The rate constants

$$k = k_f[M^{2+}] + k_d \qquad (1)$$

k_f and k_d are associated with the formation and dissociation of the 1 : 1 complex respectively, for which the equilibrium formation constant is $K_1 = k_f/k_d$. One of the problems encountered with studies of Mn^{2+} is a direct consequence of the very small values of K_1. Manganese(II) often has a high-spin $t_{2g}{}^3e_g{}^{*2}$ electronic configuration and, therefore, the majority of its complexes are not stabilised by ligand-field effects; the Irving–Williams stability sequence is $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. Since values of K_1 are usually small for Mn^{2+}, the corresponding values of k_d are large and this can be the dominant term in equation (1). This is the case observed in the present study for the reaction between Mn^{2+} and 2,2'-bipyridine (bipy) in dmso, the value of k_d being too large to permit an estimate of k_f by the stopped-flow method. Studies of this metal ion were restricted, therefore, to the reactions with ligands which form more stable complexes than bipy. It was possible to examine the reactions with 1,10-phenanthroline (phen), quinolin-8-ol (Hquin), and 2,2':6',2''-terpyridine (terpy). The latter reaction was more complicated than expected due to the formation of binuclear species. A summary of our evidence for a binuclear complex was the subject of a preliminary communication.[7] A previous study of the reaction between Mn^{2+} and terpy in aqueous solution [8] or in methanol [3] gave no evidence for the formation of binuclear species, and so the unusual behaviour in dmso was examined in some detail.

Studies of substitution reactions of the smaller Zn^{2+} in dmso are somewhat easier because of the larger formation constants, and the resulting smaller values of k_d [equation (1)]. The reaction with bipy was examined in the present study, but it was impossible to examine the reaction with phen, probably because of the larger value of k_f.

To ascertain values of the equilibrium constants (K_1) in dmso, the kinetics of the mercury(II)-ion induced dissociations of $[Mn(phen)]^{2+}$ and $[Zn(bipy)]^{2+}$ ions were measured under the same conditions as the formation reactions. The procedure was essentially the same as that adopted in our previous studies.[3,6] Representing the complex as $[ML]^{2+}$ and omitting co-ordinated solvent molecules, the mechanism of these reactions is simply as in equations (2) and (3). Although in principle it is possible to obtain values of k_d from the formation studies

$$[ML]^{2+} \xrightarrow{k_d} M^{2+} + L \qquad (2)$$

$$L + Hg^{2+} \xrightarrow{\text{rapid}} [HgL]^{2+} \qquad (3)$$

{*i.e.* from intercepts of plots of k against $[M^{2+}]$ [equation (1)]}, the results obtained in this way can be very unreliable,[3,6] and this procedure is impossible if $k_f[M^{2+}] \gg k_d$ (*i.e.* for very stable complexes). In the present study good agreement was obtained between values of k_d measured directly [reactions (2) and (3)] and from equation (1) for the $[Mn(phen)]^{2+}$ ion, but for the $[Zn(bipy)]^{2+}$ ion the agreement was poor. It is recommended, therefore, that values of k_d are obtained directly as described here since this leads to more reliable results. An example of the widely different values of k_d obtained by the two methods was reported previously for the $[Ni(phen)(dmso)_4]^{2+}$ ion.[6] The reason for this discrepancy is still uncertain.

RESULTS AND DISCUSSION

Formation Studies.—Data obtained for the formation of the 1 : 1 complexes are collected in Table 1. The ionic strength was adjusted to 0.20 mol dm^{-3} with anhydrous sodium perchlorate as in previous studies.[3,6] Reactions were followed under pseudo-first-order conditions with the metal ions in large excess. The formation rate constants (k_f) were obtained from gradients of linear plots of the pseudo-first-order rate constants (k) against $[M^{2+}]$ by linear least-squares analysis (Table 2). The formation reactions were too fast to measure by stopped-flow at elevated temperatures, and so the activation parameters could not be obtained.

The data shown in Table 2 are the only values reported so far for the formation of manganese(II) and zinc(II) complexes in dimethyl sulphoxide solution. Previous studies of these two metal ions in non-aqueous media are also strictly limited, a few results having appeared for reactions of Mn^{2+} in methanol.[3] The rates of formation and dissociation of mono- and di-chloro-complexes of Zn^{2+} in methanol were also reported recently.[9] Rate data for the solvent-exchange processes are not available for Mn^{2+} and Zn^{2+} in dmso solution {a lower limit of 1.86×10^3 s^{-1} at 298.1 K was reported for the $[Mn(dmso)_6]^{2+}$ ion},[10] and so it is not possible to test whether or not the

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[4] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2191 2198; H. P. Bennetto and Z. S. Imani, *J.C.S. Faraday I*, 1975, 1143.

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

[6] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1974, 2082; 1975, 409.

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

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

[9] H. Hoffmann, G. Platz, and M. Franke, *Proc. 16th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, abstract 3.35.

[10] G. S. Vigee and P. Ng, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2477.

Eigen–Wilkins mechanism [11] is valid in the present cases. If we assume that a dissociative interchange (I_d) mechanism is applicable to these reactions, then a value for the rate of solvent exchange can be estimated from the values of k_f in Table 2 using the approximate equations [3] (4) and (5). In equation (4), n_C is the co-ordination number

$$k_f = n_c k_{ex}{}^I K_O f \qquad (4)$$

$$\text{or } k_f \approx (\text{constant}) k_{ex}{}^I \qquad (5)$$

of the solvated metal ions (probably $n_C = 6$ for Mn^{2+}, but for Zn^{2+} a smaller value is possible)[12] and $k_{ex}{}^I$ is the normally quoted first-order rate constant for the loss of one solvent molecule; f is a discrimination factor which takes into account the fact that solvent exchange may not lead to complex formation,[3] and K_O is the outer-sphere ion–dipole or ion-pair formation constant. For metal ions of similar ionic radius and the same charge reacting with the same ligand, it is expected that n_c, K_O, and f are very similar, in which case the approximate equation (5) applies. Thus, for phen reacting with the $[Ni(dmso)_6]^{2+}$ ion,[5] $k_f = 3.5 \times 10^2$ dm^3 mol^{-1} s^{-1} and $k_{ex}{}^I = 3.2 \times 10^3$ s^{-1}; hence for phen the constant in equation (5) is estimated to have a value of 0.11 dm^3 mol^{-1}. Since $k_f = 7.7 \times 10^3$ dm^3 mol^{-1} s^{-1} for the formation of the $[Mn(phen)(dmso)_4]^{2+}$ ion (Table 2), we calculate in this way that $k_{ex}{}^I = 7.7 \times 10^4$ s^{-1} for the $[Mn(dmso)_6]^{2+}$ ion at 291.7 K. The value of k_f obtained for the first stage of the reaction between the $[Mn(dmso)_6]^{2+}$ ion and terpy is believed to relate to the formation of a bipy complex,[7] and this mechanism is consistent with equation (5). Thus $k_f = 69$ dm^3 mol^{-1} s^{-1} for the formation of the $[Ni(bipy)(dmso)_4]^{2+}$ ion and, therefore, for the reaction of similar metal ions with bipy in dmso the constant in equation (5) can be estimated to have a value of *ca.* 2.2×10^{-2} dm^3 mol^{-1}. Using the value of $k_f = 1.64 \times 10^3$ dm^3 mol^{-1} s^{-1} obtained for the first stage of the reaction between the $[Mn(dmso)_6]^{2+}$ ion and terpy, together with the constant of 2.2×10^{-2} dm^3 mol^{-1}, a second estimate of $k_{ex}{}^I = 7.6 \times 10^4$ s^{-1} can be made for the $[Mn(dmso)_6]^{2+}$ ion at 292.1 K in excellent agreement with the value estimated from the phen results. A similar calculation is more dubious for Zn^{2+} in dmso since the co-ordination number (n_c) is uncertain in this solvent. In methanol the solvation number of Zn^{2+} is reported to vary from six at low dilution to four at higher concentrations.[13] Since a low-co-ordinate species might well react by a bimolecular mechanism thereby making equations (4) and (5) invalid, any attempt to calculate a value of $k_{ex}{}^I$ in this way is liable to error. Nevertheless, assuming equation (5) is applicable and using the results obtained for the reaction between Zn^{2+} and bipy, we estimate $k_{ex}{}^I = 8.7 \times 10^5$ s^{-1} at 292.2 K for Zn^{2+} in dmso, and this value compares favourably with the approximate value of $k_{ex}{}^I = 5 \times 10^5$ s^{-1} in methanol {calculated at 298.1 K from the average activation parameters reported for solvent exchange of the $[Zn(HOMe)_6]^{2+}$ ion}.[13] At 298.1 K, values of $\log(k_{ex}{}^I/s^{-1})$ are 5.5 and 4.3 for Co^{2+} and 3.5 and 3.0 for Ni^{2+} in dmso and MeOH respectively, in agreement with the trend in the predicted values for Zn^{2+}. It seems likely, therefore, that an I_d mechanism is applicable to the formation of 1 : 1 complexes of Zn^{2+} in dmso. A similar conclusion was reached recently from measurements of volumes of activation for the reaction between Zn^{2+} and glycinate ions in aqueous solution.[14]

TABLE 1

Pseudo-first-order rate constants (k) [a] for the formation of 1 : 1 complexes of manganese(II) and zinc(II) in dimethyl sulphoxide solution ($I = 0.20$ mol dm^{-3} $Na[ClO_4]$)

(*a*) Reaction between Mn^{2+} and 1,10-phenanthroline (5×10^{-5} mol dm^{-3}) at 291.7 K and 293 nm

$10^3[Mn^{2+}]$/mol dm^{-3}	0.5	1.0	2.5	5.0
k/s^{-1}	35.8 ± 4.4	42.1 ± 1.8	55.1 ± 0.6	71.4 ± 2.0

(*b*) First stage of the reaction between Mn^{2+} and 2,2′:6′,2″-terpyridine (10^{-4} mol dm^{-3}) at 292.1 K and 330 nm

$10^3[Mn^{2+}]$/mol dm^{-3}	4.94	5.15	10.3	14.8	20.6
k/s^{-1}	54.7 ± 0.3	54.1 ± 2.3	62.6 ± 1.7	71.3 ± 0.3	79.4 ± 5.1

(*c*) Reaction between Mn^{2+} and quinolin-8-ol (5×10^{-5} mol dm^{-3}) at 292.1 K and 270 nm

$10^2[Mn^{2+}]$/mol dm^{-3}	1.0 [b]	2.0	3.0	4.0
k/s^{-1}	4.81 ± 0.12 [b]	6.73 ± 0.11	8.75 ± 0.19	11.0 ± 0.2

(*d*) Reaction between Zn^{2+} and 2,2′-bipyridine (10^{-5} mol dm^{-3}) at 292.2 K and 310 nm

$10^4[Zn^{2+}]$/mol dm^{-3}	1.95	4.95	9.95	24.95
k/s^{-1}	34.5 ± 2.2	42.2 ± 1.2	54.4 ± 1.0	78.4 ± 6.0

[a] Average values from at least three separate determinations. [b] $k = 32.7 \pm 0.7$ s^{-1} in the presence of 10^{-2} mol dm^{-3} 2,6-dimethylpyridine buffer. The rate constants reported here relate to the reaction with the unionised ligand.

TABLE 2

Gradients (k_f/dm^3 mol^{-1} s^{-1}) and intercepts (s^{-1}) from linear plots of k against $[M^{2+}]$ from the data in Table 1

System	10^{-3} Gradient/dm^3 mol^{-1} s^{-1}	Intercept/s^{-1}
Mn^{2+} + phen	7.7 ± 0.6	33.7 ± 1.7
Mn^{2+} + terpy (first stage)	1.64 + 0.06	46.1 ± 0.6
Mn^{2+} + Hquin	0.20 ± 0.01	2.71 ± 0.12
Zn^{2+} + bipy	18.7 ± 1.5	32.9 ± 2.0

Slow Stage in the Reaction between Excess of Mn^{2+} *and* terpy.—Following the initial rapid reaction between

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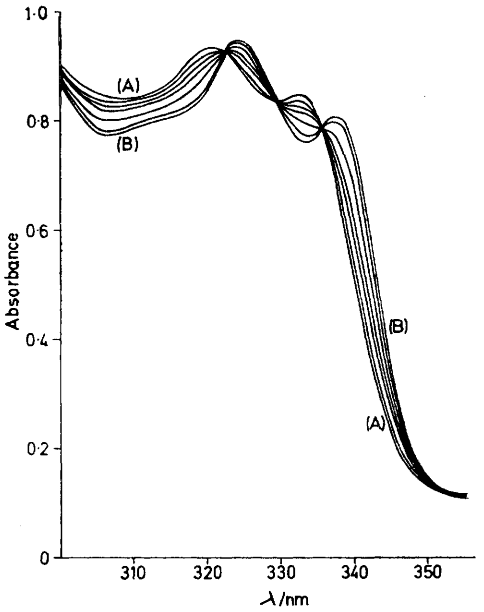
[11] R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes,' Allyn and Bacon Inc., Boston, 1974.

[12] S. F. Lincoln, *Co-ordination Chem. Rev.*, 1971, **6**, 309; A. Fratiello, *Progr. Inorg. Chem.*, 1972, **17**, 57; W. L. Reynolds, *ibid.*, 1970, **12**, 1.

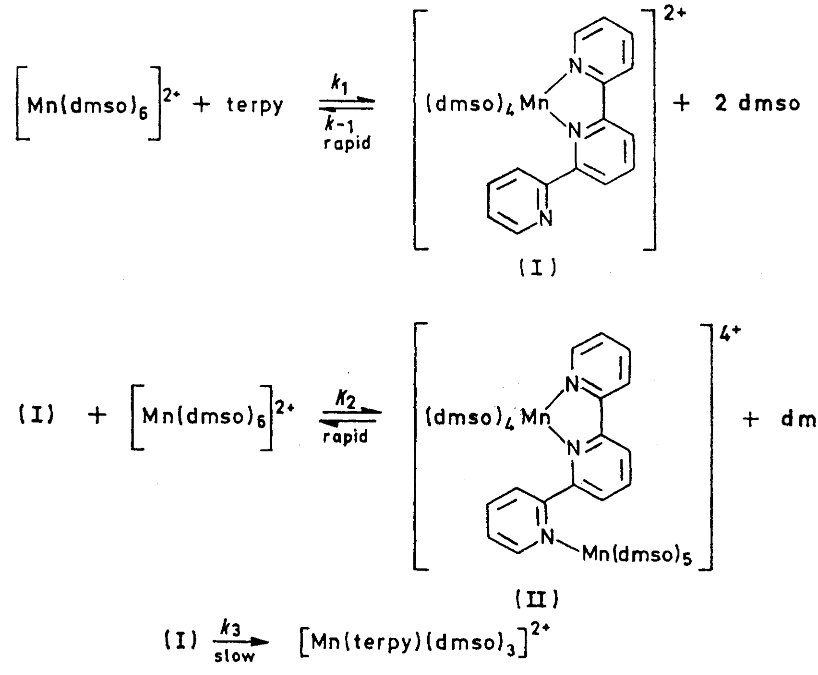
[13] S. A. Al-Baldawi and T. E. Gough, *Canad. J. Chem.*, 1969, **47**, 1417.

[14] M. W. Grant, *J.C.S. Faraday I*, 1973, 560.



U.v. spectra following the addition of terpy (2.5×10^{-5} mol dm^{-3}) to $[Mn(dmso)_6]^{2+}$ ion (0.45 mol dm^{-3}) at 314.3 K (2-cm cell). A to B: 1, 5, 11, 20, 30, 150, and ∞ min after mixing

excess of Mn^{2+} and terpy (Table 1) a much slower process was observed which could be examined by repetitive-scan spectrophotometry over quite a long period of time (Figure). Our interpretation of this behaviour was the subject of a preliminary communication,[7] and can be summarised by the mechanism depicted in the Scheme. The slow step involves final chelate-ring closure and is inhibited by increasing the concentration of Mn^{2+} as shown by the results in Table 4. A plot of $1/k$ against $[Mn^{2+}]$ is linear, and from this plot we estimate [7] $k_3 = (2.6 \pm 0.5) \times 10^{-3}$ s^{-1} and $K_2 = 17.4 \pm 1.4$ dm^3 mol^{-1}. Recently, further evidence has been found for terpy acting as bidentate ligand (with one pyridyl ring uncoordinated), a bis complex of Cu^+ having been reported to have a structure analogous to that postulated for the intermediate (I).[15]



SCHEME

Dissociation Studies and Stability Constants.—The mercury(II)-ion induced dissociations of $[Mn(phen)]^{2+}$ and $[Zn(bipy)]^{2+}$ ions [reactions (2) and (3)] were measured in dmso ($I = 0.20$ mol dm^{-3} $Na[ClO_4]$) to enable the equilibrium formation constants, K_1, to be estimated from the relation $K_1 = k_f/k_d$. The reactions were sufficiently slow to enable a variable-temperature stopped-flow study, although only approximate activation parameters could be obtained for the $[Mn(phen)]^{2+}$ ion because of the rapidity of the reactions. Values of k_d are collected in Table 5, and in Table 3 the activation parameters are given and the stability constants (K_1) are compared with previous values for these complexes in other solvents. There are no remarkable differences between the stabilities of the complexes in methanol, water, and dmso, in line with our previous observations for complexes of Ni^{2+}.[6] The somewhat lower stabilities of the $[Mn(phen)]^{2+}$ and $[Zn(bipy)]^{2+}$ ions in dmso compared with values in an aqueous medium agree with the trend observed for the $[Ni(phen)]^{2+}$ ion (log K_1 7.3 and 8.8 in dmso and water respectively).[6] This difference in stability between the two solvents arises not from a difference in the dissociation rates but rather from a

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[15] A. L. Crumbliss and A. T. Poulos, *Inorg. Chem.*, 1975, **14**, 1529.

TABLE 3

Comparison of the rates of formation and dissociation and the stability of manganese(II) and zinc(II) complexes in various solvents

Ligand	$\frac{T}{\text{K}}$	$\frac{I}{\text{mol dm}^{-3}}$	Solvent	$\log(k_f/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	$\log(k_{ex}/\text{s}^{-1})$ [a]	$\log(k_d/\text{s}^{-1})$	$\log(K_1/\text{dm}^3\ \text{mol}^{-1})$
(*a*) Manganese(II)							
phen	298.1	*ca.* 0	H_2O	5.1 [b]	7.49 [c]	1.5 [b]	3.6 [b]
	298.1	0.2	MeOH	4.95 [d]	5.57 [e]	1.15 [d]	3.8 [d]
	291.7	0.2	dmso	3.89 [f]	>3.26 [g] 4.89 [h]	1.26 [f,i]	2.6 [f]
terpy	298.1	*ca.* 0	H_2O	5.0 [b]	7.49	0.6 [b]	4.4 [b]
	298.1	0.2	MeOH	3.72 [d]	5.57	−1.33 [d]	5.0 [d]
	292.1	0.2	dmso	3.21 [f,j]	>3.26 4.88 [h]		
Hquin	226.4	0.2	MeOH	2.92 [d]	5.57		
	292.1	0.2	dmso	2.30 [f]	>3.26		
quin	289.1	0.1	H_2O	8.0 [k]	7.49	2.1 [k]	5.9 [k]
(*b*) Zinc(II)							
bipy	298.1		H_2O	6.0 [b]	7.48 [l]	1.2	4.8
	292.2	0.2	dmso	4.27 [f]	5.94 [h]	0.916 [f,m]	3.4 [f]
Cl^-	233.1		MeOH	5.8 [n]	5.7 [o]	3.9 [n]	1.9 [n]

[a] k_{ex} is the solvent-exchange rate constant at 298.1 K. [b] At 284.1 K, ref. 8. [c] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307. [d] Extrapolated from data at lower temperature, ref. 3. [e] F. W. Breivogel, *J. Chem. Phys.*, 1969, **51**, 445. [f] This work. [g] Ref. 10. [h] Calculated values (see text). [i] Calculated from the activation parameters $\Delta H_d^\ddagger = 21.3 \pm 1.5$ kcal mol⁻¹ and $\Delta S_d^\ddagger = 20 \pm 5$ cal K⁻¹ mol⁻¹ (1 cal = 4.184 J). [j] First stage of a two-stage reaction (see text). [k] At 289.1 K, $I = 0.1$ mol dm⁻³ ($K[NO_3]$). M. S. Zetter and D. N. Hague, *Trans. Faraday Soc.*, 1970, **66**, 1176. [l] F. Fittipaldi and S. Petrucci, *J. Phys. Chem.*, 1967, **71**, 3414. [m] $\Delta H_d^\ddagger = 14.4 \pm 0.1$ kcal mol⁻¹, $\Delta S_d^\ddagger = -4.96 \pm 0.27$ cal K⁻¹ mol⁻¹. [n] Ref. 9. [o] Ref. 13.

smaller rate of formation in dmso. We believe this trend can be attributed to steric effects as discussed previously.[6] It is interesting to note that even though these complexes are less stable in dmso, the rates of dissociation are slower than in water. This behaviour contrasts with that observed in aqueous solution where a more stable complex usually dissociates more slowly.[11]

TABLE 4

Pseudo-first-order rate constants (k) at 314.1K observed for the slow step in the reaction between excess of Mn^{2+} and terpy

$10^2[Mn^{2+}]$/mol dm⁻³	49	45	30	15	5	3.9
10^4k/s⁻¹	3.12 ± 0.09	3.33 ± 0.36	4.48 ± 0.11	9.71 ± 0.97	10.4 ± 0.4	17.3 ± 0.6

EXPERIMENTAL

Materials.—Anhydrous $[Hg(dmso)_6][ClO_4]_2$, $[Mn(dmso)_6][ClO_4]_2$, and $[Zn(dmso)_4(ClO_4)_2]$ were prepared from AnalaR grade materials as described.[16,17] Stock solutions were prepared in a dry-box using dry dmso[6] and analysed for metal-ion concentration (after dilution with water) by titration with ethylenediaminetetra-acetic acid.[18]

TABLE 5

First-order rate constants (k_d)[a] for the mercury(II)-ion induced dissociations of $[Mn(phen)]^{2+}$ and $[Zn(bipy)]^{2+}$ ions in dimethyl sulphoxide ($I = 0.20$ mol dm⁻³ $Na[ClO_4]$)

(*a*) Dissociation by Hg^{2+} (5×10^{-3} mol dm⁻³) of the 1 : 1 complex formed between Zn^{2+} (2×10^{-3} mol dm⁻³) and bipy (5×10^{-5} mol dm⁻³) studied at 321 nm

T/K	292.2	299.4	305.3	311.6
k_d/s⁻¹	8.25 ± 0.07 [b]	15.3 ± 0.4	25.0 ± 0.3	38.5 ± 2.4

(*b*) Dissociation by Hg^{2+} (5×10^{-3} mol dm⁻³) of the 1 : 1 complex formed between Mn^{2+} (2.5×10^{-3} mol) and phen (2×10^{-4} mol dm⁻³) studied at 318 nm

T/K	297.9	302.3	305.9
k_d/s⁻¹	40.1 ± 0.2	66.5 ± 2.1	113.6 ± 4.4

[a] Average values from three separate determinations. [b] At $[Hg^{2+}] = 10^{-2}$ mol dm⁻³ and 292.2 K, $k_d = 8.1 \pm 0.1$ s⁻¹.

Kinetic Studies.—Stopped-flow and Cary 14 spectrophotometers were used as before.[6]

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[18] A. I. Vogel, ' A Textbook of Quantitative Inorganic Analysis,' Longman, 3rd edn., 1961.