Kinetics of Ternary Complex Formation between Manganese(II) Species and 2,2′-Bipyridine

By **David N. Hague*** and **Stephen R. Martin,** University Chemical Laboratory, Canterbury

The temperature-jump relaxation method has been used to measure rate constants and activation parameters for formation and dissociation of a 1 : 1 complex between manganese(II) and 2,2′-bipyridine (bipy) and of ternary complexes between bipy and ten substituted manganese species. The results are discussed in terms of the normal dissociative model and the possibility is considered that ring closure is contributing to the rate-determining step. The results confirm the previous indication that the first ligand generally has comparatively little influence on the kinetics of the reaction between manganese(II) and the second ligand.

THE formation of 1 : 1 complexes of labile metals in water is usually discussed[1] in terms of a dissociative mechanism involving formation of an outer-sphere intermediate in which the metal ion and the incoming ligand are separated by the inner hydration sphere of the metal ion. The rate-determining step is generally thought to involve replacement of a water molecule in the inner hydration sphere by the incoming ligand, even when the ligand contains a second or further binding group. This usually means that k_f, the rate constant for formation of the complex, is given by $K_{os}k_{ex}$, where K_{os} is the formation constant of the outer-sphere complex and k_{ex} is the (first-order) rate constant for water exchange. Confirmation of this model requires the comparison of k_f and k_{ex}. An important source of water-exchange data is n.m.r. spectroscopy, but the method is only appropriate for certain metal ions and so far nickel(II) has received more attention than any other species. Although the co-ordination number of Ni^{2+} in aqueous solution is generally six, the fact that this ion forms many stable complexes of lower co-ordination number is a potential complication; in addition, ligand-field effects are particularly significant for Ni^{2+}. It is therefore important to extend the studies to other labile metal ions for which these factors are unimportant but for which k_{ex} can still be measured directly. Manganese(II), with its high-spin d^5 configuration, is such a species.

An additional interest in the behaviour of manganese(II) arises through its importance in enzymatic reactions. Many enzyme systems which exhibit an absolute requirement for Mg^{2+} *in vivo* will also function *in vitro* with Mn^{2+} and there has been much recent work[2] in which the role of the metal has been studied by making use of the favourable magnetic properties of Mn^{2+}. In view of this and the importance of metal-bridged ternary complexes in many enzymatic and other metal-catalysed processes, it is important to discover the effects of partial substitution of the inner hydration sphere of the metal ion on the lability of the remaining water molecules. The purpose of the present study is to obtain an indication of this by investigating the effect of replacing varying numbers of inner-sphere water molecules by nitrogen- and oxygen-binding ligands on the kinetics of formation of the complex between manganese(II) and a neutral bidentate ligand. The substituent ligands L have been chosen to include branched- and open-chain polydentates and the charge on the complex [MnL] varies from +2 to −3. Rate constants and activation parameters, as measured by the temperature-jump method, are reported for formation (and dissociation) in aqueous solution of the complex between 2,2′-bipyridine (bipy) and hydrated manganese(II), and complexes of manganese(II) with polytriphosphate (tp), adenosine-5′-triphosphate (atp), *N*-methyliminodiacetate (mida), nitrilotriacetate (nta), uramil-*NN*-diacetate (uda), ethylenediamine-*NN*′-diacetate (edda), diethylenetriamine (dien), triethylenetetramine (trien), 2,2′,2″-triaminotriethylamine (tren), and 3,7-diazanonane-1,9-diamine (dnd or 2,3,2-tet). The results are compared with those of a similar study[3] involving the reaction of a more limited range of [MnL] species with 8-hydroxyquinoline (oxine, Hox). They are also compared with the available water-exchange data.[4,5]

EXPERIMENTAL

Solutions were prepared from manganese(II) perchlorate (Fluka, purum) and standardized against the disodium salt of EDTA. The following chemicals were used without further purification: nitrilotriacetic acid, uramil-*NN*-diacetic acid monohydrate, diethylenetriamine (dien), triethylenetetramine (trien) (Fluka, puriss. grade); 2,2′-bipyridine (bipy) (B.D.H.); *N*-methyliminodiacetic acid (Emanuel); ethylenediamine-*NN*′-diacetic acid (K. and K.); 3,7-diazanonane-1,9-diamine (dnd or 2,3,2-tet) (Eastman); disodium adenosine-5′-triphosphate (Boehringer). 2,2′,2″-Triaminotriethylamine (tren) was separated from technical grade trien as its hydrochloride,[6] and trien as its hydroperchlorate.[7] $Na_5P_3O_{10},6H_2O$ (Albright and Wilson) was twice recrystallized from aqueous ethanol.

The solutions were made up with triply distilled water, an ionic strength of 0·30M being maintained with $NaClO_4$. Pseudo-first-order conditions were achieved by using concentrations of Mn^{2+} or [LMn] at least 30 times greater

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[1] See, for example, M. Eigen and R. G. Wilkins, ' Mechanisms of Inorganic Reactions,' ed. R. F. Gould, *Adv. Chem. Series*, No. 49, Amer. Chem. Soc., Washington, D.C., 1965, p. 55; D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

[2] See, for example, M. Cohn and J. Reuben, *Accounts Chem. Res.*, 1971, **4**, 214.

[3] D. N. Hague and M. S. Zetter, *Trans. Faraday Soc.*, 1970, **66**, 1176; D. N. Hague, S. R. Martin, and M. S. Zetter, *J.C.S. Faraday I*, 1972, **68**, 37.

[4] M. S. Zetter, M. W. Grant, E. J. Wood, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1972, **11**, 2701.

[5] M. S. Zetter, H. W. Dodgen, and J. P. Hunt, *Biochemistry*, 1973, **12**, 778.

[6] L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, 1968, **90**, 6041.

[7] G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 974.

than that of total 2,2′-bipyridine. The total concentration of L was chosen so as to maximize the fraction of manganese present as [MnL]; an L : Mn ratio of 1·05 : 1 was used in all cases except $[Mn(tp)]^{3-}$, $[Mn(atp)]^{2-}$, and $[Mn(trien)]^{2+}$, where it was 2·0, 1·3, and 1·3 : 1, respectively. In all cases it was possible to eliminate relaxation effects associated with free Mn^{2+} and $[MnL_2]$. The system Mn^{2+}–dien was found to be air-sensitive but oxidation of the metal could be avoided by using an atmosphere of nitrogen.

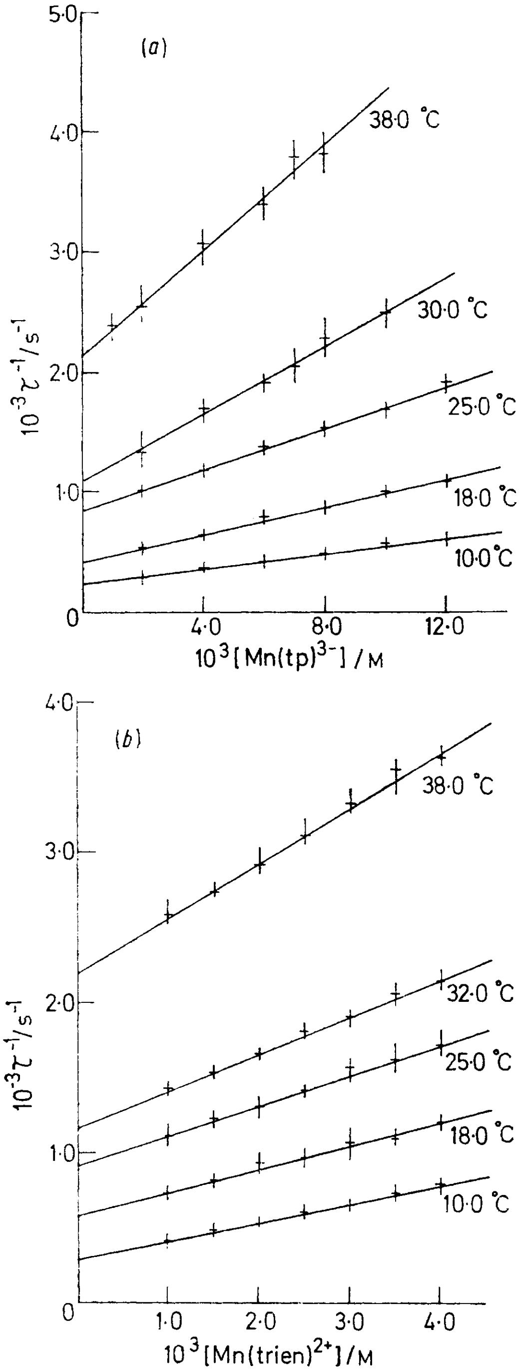

FIGURE 1 Typical plots showing the variation of τ^{-1} with concentration for reaction of (*a*) $[Mn(tp)]^{3-}$ and (*b*) $[Mn(trien)]^{2+}$ with bipy at different temperatures. The vertical lines on each point indicate experimental scatter (representing, on average, five experiments)

Kinetic and equilibrium measurements were made by standard methods [8] and the data reported here refer to relaxation effects observed in the 50 μs—5 ms region. The kinetics were generally followed at 300—312 nm, the actual wavelength depending on the relaxation amplitude of the particular solution. Temperatures were accurate to ±0·2 °C.

RESULTS

In the temperature-jump relaxation technique, the position of a chemical equilibrium is altered by means of a rapid temperature rise. The new equilibrium concentrations are approached exponentially and the relaxation time τ is related to these concentrations and the appropriate rate constants. In the case of reaction (1), from

$$\text{Mn(or [MnL])} + \text{bipy} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{[Mn(bipy)] \{or [LMn(bipy)]\}} \qquad (1)$$

which charges have been omitted, this relation is, neglecting activity coefficients, $\tau^{-1} = k_f(\bar{c}_m + \bar{c}_{bipy}) + k_d$, where $\bar{c}_m$ is the (new) equilibrium concentration of the free metal ion or metal–L species and $\bar{c}_{bipy}$ is the (new) equilibrium concentration of free bipy. Since the latter was negligible compared with the former, a plot of τ^{-1} against total

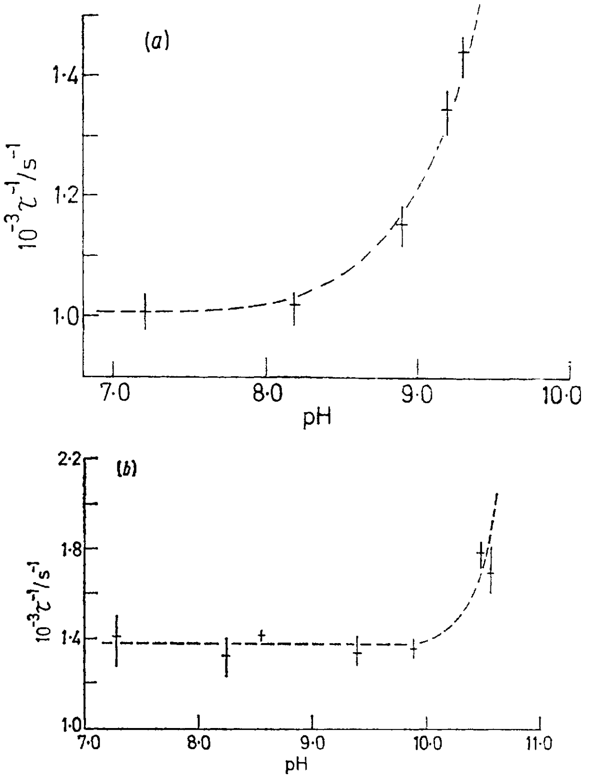

FIGURE 2 Variation of τ^{-1} with pH for reaction of manganese(II) species with bipy at 25·0 °C and ionic strength 0·30M ($NaClO_4$) (vertical lines on each point indicate experimental scatter): (*a*) Mn^{2+} ($1·00 \times 10^{-3}$M); (*b*) $[Mn(tp)]^{3-}$ ($6·00 \times 10^{-3}$M)

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[8] G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, **1971**, **67**, 786.

manganese(II) (or [MnL]) concentration was a straight line with gradient k_f and intercept k_d. The results are shown in Figure 1 and Table 1. The relaxation times were shown to be independent of total bipy concentration and pH in the ranges indicated in Table 2. For Mn^{2+} and $[Mn(tp)]^{3-}$ the relaxation times were pH-dependent above pH 8·0 and 9·9, respectively; typical pH profiles are shown in Figure 2. The results quoted in Table 1 for these species apply to the pH-independent ranges.

TABLE 1

Rate constants for reaction of manganese(II) species with bipy ($0{\cdot}4$—$2{\cdot}4 \times 10^{-4}$M) at various temperatures

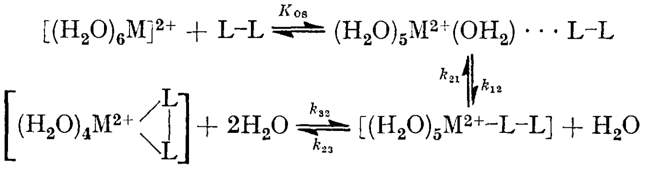
System	t/°C	10^3 Concn. range/M	$10^{-5}k_f$/ l mol^{-1} s^{-1}	$10^{-3}k_d$/ s^{-1}
Mn^{2+}	10·0	0·5—4·0	1·18 (0·16)	0·22 (0·04)
	15·0	0·5—4·5	1·57 (0·25)	0·35 (0·06)
	20·0	0·5—4·5	2·1 (0·2)	0·50 (0·07)
	25·0	0·5—4·5	2·8 (0·2)	0·75 (0·06)
	30·0	0·5—4·0	3·7 (0·2)	0·99 (0·06)
	35·0	0·5—4·5	4·9 (0·3)	1·44 (0·08)
	38·0	0·5—4·5	5·4 (0·3)	1·86 (0·08)
$[Mn(tp)]^{3-}$	10·0	2·0—12·0	0·31 (0·05)	0·24 (0·04)
	18·0	2·0—12·0	0·57 (0·05)	0·42 (0·04)
	25·0	2·0—12·0	0·85 (0·09)	0·85 (0·06)
	30·0	2·0—10·0	1·41 (0·26)	1·08 (0·16)
	38·0	1·0—8·0	2·2 (0·3)	2·1 (0·1)
$[Mn(atp)]^{2-}$	10·0	1·0—5·0	1·04 (0·2)	0·19 (0·05)
	18·0	1·0—5·0	1·77 (0·2)	0·36 (0·06)
	25·0	1·0—5·0	2·9 (0·4)	0·68 (0·10)
	30·0	1·0—5·0	3·4 (0·2)	0·91 (0·07)
	38·0	1·0—4·0	5·5 (0·6)	1·32 (0·17)
[Mn(mida)]	10·0	0·5—3·5	2·9 (0·2)	0·3 (0·04)
	18·0	0·5—3·6	4·1 (0·4)	0·45 (0·09)
	25·0	0·5—3·5	5·7 (0·5)	1·03 (0·10)
	30·0	0·5—3·6	9·1 (0·7)	1·34 (0·10)
	35·0	0·5—3·5	11·7 (1·0)	2·2 (0·2)
$[Mn(nta)]^-$	10·0	1·0—7·0	7·3 (0·6)	2·1 (0·2)
	18·0	1·0—7·0	11·1 (0·9)	2·8 (0·3)
	25·0	1·0—8·0	13·0 (1·0)	5·4 (0·2)
	30·0	2·0—6·0	16·1 (1·9)	6·9 (0·7)
	32·0	2·0—8·0	18·3 (0·9)	7·5 (0·5)
$[Mn(uda)]^-$	10·0	1·0—6·0	11·1 (1·1)	5·9 (0·5)
	18·0	1·0—6·0	14·0 (1·4)	9·6 (0·5)
	25·0	1·0—6·0	17·2 (1·6)	16·7 (0·5)
	30·0	1·0—6·0	21·0 (2·0)	23·0 (1·0)
	38·0	1·0—6·0	29·0 (2·0)	38·0 (1·0)
[Mn(edda)]	10·0	0·8—4·8	1·2 (0·1)	0·17 (0·02)
	18·0	0·8—4·8	1·9 (0·2)	0·37 (0·04)
	25·0	0·8—4·0	2·6 (0·2)	0·62 (0·05)
	30·0	1·6—4·8	3·3 (0·3)	0·95 (0·10)
	38·0	0·8—4·8	4·9 (0·4)	1·55 (0·10)
$[Mn(dien)]^{2+}$	10·0	1·0—4·0	2·6 (0·4)	0·32 (0·10)
	18·0	1·0—4·0	3·5 (0·5)	0·55 (0·12)
	25·0	1·0—4·0	5·7 (0·6)	1·12 (0·20)
	30·0	1·0—4·0	6·2 (0·7)	1·74 (0·21)
	35·0	1·0—4·0	8·8 (0·8)	2·1 (0·3)
$[Mn(trien)]^{2+}$	10·0	1·0—4·0	1·26 (0·20)	0·29 (0·05)
	18·0	1·0—4·0	1·56 (0·20)	0·58 (0·04)
	25·0	1·0—4·0	2·1 (0·4)	0·91 (0·09)
	32·0	1·0—4·0	2·5 (0·2)	1·17 (0·05)
	38·0	1·0—4·0	3·7 (0·4)	2·2 (0·09)
$[Mn(tren)]^{2+}$	10·0	1·0—4·0	1·12 (0·10)	0·26 (0·03)
	18·0	1·0—4·0	1·49 (0·15)	0·48 (0·03)
	25·0	1·0—4·0	2·2 (0·2)	0·71 (0·06)
	30·0	1·0—4·0	2·7 (0·3)	1·07 (0·07)
	32·0	1·0—4·0	2·7 (0·3)	1·18 (0·05)
$[Mn(dnd)]^{2+}$	10·0	1·0—8·0	1·0 (0·10)	0·28 (0·04)
	18·0	1·0—8·0	1·32 (0·10)	0·47 (0·03)
	25·0	1·0—8·0	1·98 (0·15)	0·89 (0·05)
	30·0	1·0—8·0	2·3 (0·2)	1·23 (0·06)
	38·0	1·0—8·0	3·1 (0·2)	2·1 (0·1)

The ionic strength ($NaClO_4$) was 0·3M. The estimated maximum error (in parentheses) represents, on average, five experiments at each of seven concentrations in the stated range.

The ratio $k_f : k_d$ is equal to K, the stability constant of the complex and in three cases this was checked spectrophotometrically [8] (K_{spec}). The agreement between K_{spec} and the kinetically determined values (Table 2) is satisfactory.

DISCUSSION

The formation of a complex between a hydrated metal ion $[M(OH_2)_6]^{2+}$ and a bidentate ligand L–L is shown in the Scheme. Provided that the concentrations of the intermediates (*i.e.* the outer-sphere complex and the complex in which there is only one M–L bond) are small, the observed rate constant for formation of the chelate complex is given by $k_f = K_{os}k_{12}k_{23}/(k_{21} + k_{23})$ and that for its dissociation by $k_d = k_{21}k_{32}/(k_{21} + k_{23})$. If the first metal–ligand bond is strong (*i.e.* $k_{23} \gg k_{21}$) these expressions become $k_f = K_{os}k_{12}$ and $k_d = k_{21}k_{32}/k_{23}$, and the kinetics of chelate-complex formation are identical to those observed with a unidentate ligand. If, however, the first metal–ligand bond is weak or if ring closure is inhibited for some reason (*e.g.*, through steric interference) the simplifying inequality does not apply and chelate-complex formation is slower than the corresponding reaction with a unidentate ligand. Substitution of some of the water molecules in the inner hydration sphere of the metal by a multidentate ligand L could affect k_f by altering K_{os} (reducing the net positive charge on the metal ion if L is anionic) or k_{12}, which would be reflected by a change in the water-exchange rate constant k_{ex}. [An additional reduction in k_f arises from the reduction in the number of replaceable water molecules. It is usual to allow for this by multiplying the measured k_f value by an appropriate statistical factor, in the present case $6/(6 - n)$, where n is the number of co-ordination positions occupied by L, to give $k_f{}^s$. Similarly, K is multiplied by $6/(6 - n)$ to give K^s.] Substitution may also affect k_{21} and it is possible that, whereas for the aquo-ion $k_{23} \gg k_{21}$ and so $k_f = K_{os}k_{12}$, for [ML] this condition does not hold and ring closure now contributes to the rate-determining step.



SCHEME

Unfortunately, the amount of data available on formation of Mn^{II} complexes is still very limited. The value of k_f for the reaction of Mn^{2+}(aq) with bipy (Table 2; $\log k_f{}^s = 5{\cdot}45$) is similar to those for reaction of Mn^{2+} with the other neutral ligands oxine, Hox (5·69 [3]), 2,2′,2″-terpyridine (5·0 [9]), and 1,10-phenanthroline (5·1 [10] at 11 °C). However, the first-order rate constant for water exchange (per water molecule) is [4] $2·3 \times 10^7$ s^{-1} and the value of K_{os} estimated from k_f^s/k_{ex} is 0·012 l mol^{-1}, which is lower than that usually assumed for a neutral ligand (*ca.* 0·15 l mol^{-1} [11]). There are small differences in the values of log k_f^s for bipy and Hox in the cases of $[Mn(tp)]^{3-}$ (Table 3) and $[Mn(atp)]^{2-}$ (the value of n for the latter is now taken as 3, *cf.* ref. 5), but the two quantities are identical for the complexes $[Mn(nta)]^-$ and $[Mn(uda)]^-$. No comparison is possible with the other [MnL] species. Water-exchange data are available only for the complexes $[Mn(atp)]^{2-}$ (ref. 5) and $[Mn(nta)]^-$ (ref. 4) and the values of K_{os} computed for bipy on the basis of the exchange rates (Table 3) are 0·0054 and 0·00093 l mol^{-1}, respectively, which are also low on the normal picture of rate-limiting water substitution. Activation enthalpies and entropies for reaction of a given [MnL] complex with Hox and bipy are similar except in the case of $[Mn(tp)]^{3-}$; for Mn^{2+}, $[Mn(atp)]^{2-}$, and $[Mn(nta)]^-$, $\Delta H_f^{\ddagger}$ is also close to the activation enthalpy for the exchange process (Table 3).

TABLE 2

Rate and equilibrium constants and activation parameters for reaction of manganese(II) species with bipy (estimated maximum errors in parentheses)

	Mn^{2+} ($n = 0$)	$[Mn(tp)]^{3-}$ ($n = 3$)	$[Mn(atp)]^{2-}$ ($n = 3$) [a]	[Mn(mida)] ($n = 3$)	$[Mn(nta)]^-$ ($n = 4$)	$[Mn(uda)]^-$ ($n = 4$)
k_f/l mol^{-1} s^{-1}	$2·8(0·3) \times 10^5$	$9·4(0·9) \times 10^4$	$2·7(0·4) \times 10^5$	$6·8(0·5) \times 10^5$	$1·4(0·1) \times 10^6$	$1·8(0·2) \times 10^6$
log k_f^s	5·45	5·28	5·73	6·13	6·62	6·74
$\Delta H_f^{\ddagger}$/kcal mol^{-1}	9·2(1·0)	12·1(1·8)	9·8(1·6)	9·9(1·5)	6·1(1·4)	5·1(0·9)
$\Delta S_f^{\ddagger(s)}$/cal K^{-1} mol^{-1}	−3(3)	+6(6)	+2(6)	+3(5)	−8(5)	−11(3)
k_d/s^{-1}	720(60)	780(60)	610(200)	980(60)	5 100(300)	16 000(1 000)
$\Delta H_d^{\ddagger}$/kcal mol^{-1}	12·0(1·3)	13·6(1·1)	12·4(2·1)	14·3(1·1)	10·2(1·5)	11·1(0·8)
$\Delta S_d^{\ddagger}$/cal K^{-1} mol^{-1}	−5(4)	0(4)	−5(7)	+3(4)	−8(5)	−2(3)
$\log_{10} K$						
(*a*) kinetic	2·59(0·08)	2·08(0·08)	2·65(0·23)	2·84(0·06)	2·44(0·06)	2·05(0·08)
(*b*) spectrophotometric	2·57(0·15)				2·63(0·15)	
$\log_{10} K^s$	2·58	2·38	2·95	3·14	3·01	2·53
pH-Independent in the range:	6·0—8·0	8·6—9·9	7·5—9·5	6·5—9·5	6·5—10·0	6·5—9·5

	[Mn(edda)] ($n = 4$)	$[Mn(dien)]^{2+}$ ($n = 3$)	$[Mn(trien)]^{2+}$ ($n = 4$)	$[Mn(tren)]^{2+}$ ($n = 4$)	$[Mn(dnd)]^{2+}$ ($n = 4$)
k_f	$2·6(0·2) \times 10^5$	$5·3(0·4) \times 10^5$	$2·2(0·4) \times 10^5$	$2·1(0·2) \times 10^5$	$1·9(0·2) \times 10^5$
log k_f^s	5·89	6·03	5·81	5·80	5·75
$\Delta H_f^{\ddagger}$	8·0(1·1)	7·9(1·1)	6·0(1·1)	6·8(1·6)	6·7(1·0)
$\Delta S_f^{\ddagger(s)}$	−5(4)	−5(4)	−12(4)	−9(5)	−10(4)
k_d	650(50)	1 100(200)	900(10)	750(60)	850(60)
$\Delta H_d^{\ddagger}$	13·1(0·9)	13·4(2·2)	12·1(1·1)	11·1(1·3)	12·5(1·1)
$\Delta S_d^{\ddagger}$	−2(3)	0(8)	−4(4)	−8(5)	−3(4)
$\log_{10} K$					
(*a*) kinetic	2·60(0·07)	2·68(0·12)	2·39(0·08)	2·45(0·07)	2·35(0·08)
(*b*) spectrophotometric				2·46(0·15)	
$\log_{10} K^s$	3·08	2·98	3·08	2·93	2·83
pH-Independent in the range:	7·5—9·5	8·8—9·5	7·3—8·8	7·3—8·8	7·3—8·8

Rate constants refer to 25 °C and ionic strength 0·3M ($NaClO_4$); n is the number of co-ordination positions of Mn^{2+} assumed to be occupied by the ligand L. A superscript s indicates that a statistical correction has been applied (see text).

[a] n Was taken as 4 in ref. 3 (see text).

TABLE 3

Rate constants and activation parameters for formation of complexes of manganese(II) species with Hox and bipy and for water exchange

		Mn^{2+}	$[Mn(tp)]^{3-}$	$[Mn(atp)]^{2-}$	$[Mn(nta)]^-$	$[Mn(nda)]^-$
log k_f^s	bipy	5·45	5·28	5·73	6·62	6·74
	Hox	5·69	5·90	6·27	6·71	6·62
log k_{ex}		7·36		7·70	9·18	
$\Delta H_f^{\ddagger}$/kcal mol^{-1}	bipy	9·2	12·1	9·8	6·1	5·1
	Hox	9·1	6·4	8·3	5·5	4·5
$\Delta H_{ex}^{\ddagger}$/kcal mol^{-1}		7·8		9·6	6·6	
$\Delta S_f^{\ddagger(s)}$/cal K^{-1} mol^{-1}	bipy	−3	+6	+2	−8	−11
	Hox	−2	−10	+1	−9	−13

k_f^s Is a statistically corrected second-order rate constant (see text) and k_{ex} is the first-order rate constant (per water molecule) for water exchange.

Sources of data: bipy, this work; Hox, ref. 3; water exchange, refs. 4 and 5.

The value of log k_f^s for Hox + $[Mn(atp)]^{2-}$ was evaluated on the assumption that $n = 3$ (see ref. 5).

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

[10] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1965, **4**, 929.

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

The activation enthalpies and entropies are necessarily less accurate than the rate constants but there are indications in Table 2 of a compensation between $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger(s)}$ and between $\Delta H_d^{\ddagger}$ and $\Delta S_d^{\ddagger}$. Thus, although it is not possible to decide definitely at this stage whether ring closure contributes to the rate-determining step (as is thought[12] to be the case for reaction of Mn^{2+} with bipy in methanol), the mechanism is probably the same for Hox and bipy, and also for all the manganese(II) species studied here.

Dissociation rate constants k_d for the [MnL(bipy)] complexes on the whole reflect the formation rate constants k_f^s, so there is less variation in K^s than in k_f^s or k_d. Although this is by no means always true for labile metal ternary complexes, a similar result has been obtained[13] for the reaction of substituted cobalt(II) with the neutral bidentate ligand pyridine-2-azo-*p*-dimethylaniline. In this case also it was found that nta produces a significant increase in the reactivity of the metal ion and that this increased reactivity is not due solely to the charge on the bound ligand.

The results of this study therefore support the previous conclusion[3] that substitution of part of the inner hydration sphere of manganese(II) generally has little effect on the reactivity of the metal ion towards further substitution.

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

[13] M. A. Cobb and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 3069.