Reductions of Hexakis(urea)- and Hexakis(dimethyl sulfoxide)-manganese(III) by Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) in Acetonitrile†

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The kinetics of outer-sphere electron transfer between $[MnL_6]^{3+}$ [L = urea or dimethyl sulfoxide (dmso)] and $[Fe(tmphen)_3]^{2+}$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) has been studied at 25 °C in acetonitrile with the salts added as the perchlorates. Contrary to the literature, the manganese complexes are substitutionally labile as recognised by the considerable decrease in redox rates when extra L is added. Slight ligand displacement on $[Mn(dmso)_6]^{3+}$ in CD_3CN could also be detected by ^1H NMR spectroscopy. To accommodate the variations in rate constant, three rapid solvation equilibria, $[MnL_6]^{3+} \rightleftharpoons [MnL_3]^{3+} + 3L$ (co-ordinated MeCN is omitted), have to be invoked with all solvate species available reacting. Further, the strong acceleration with salt is well described by ion pairing and ion tripling of the trivalent ions, reducing the Coulombic repulsion in forming the precursor complexes. Perchlorate association with $[Mn(dmso)_6]^{3+}$ is somewhat stronger than with $[Mn\{OC(NH_2)_2\}_6]^{3+}$ despite the presence of acidic hydrogens in the latter. This unexpected result is in keeping with conductance data analysed by the Lee–Wheaton equation.

In sharp contrast to the eagerness in studying outer-sphere (non-co-ordinating) solvent effects on electron-transfer rates of metal complexes, little attention has been paid to the influence of co-ordinated solvent molecules on the electron-transfer rates of metal solvates. However, this topic must eventually be approached because many practical redox agents are solvated metal ions and after all the most important role of a solvent is first-sphere ion solvation. We are particularly interested in learning about the effect of ligated solvent molecules on redox reactivity in terms of empirical solvent basicity parameters such as the donor number. So we decided to enlarge the scope by the inclusion of substitutionally labile metal complex reactants, exchanging ligands with solvent molecules.[1–4]

Amongst others, we used solutions of $[Fe(dmf)_6]^{3+}$ (dmf = dimethylformamide) in acetonitrile as an oxidising agent.[2] Initially, we did not expect notable competition between MeCN and dmf for co-ordination to iron(III), in the framework of hard–soft considerations. In the end, however, the concurrent existence of four $[Fe(dmf)_n]^{3+}$ species (n = 3–6) had to be invoked for adequate fitting of NMR and kinetics data.

In the light of these results we were puzzled by a recent report[5] on the kinetics of reduction of hexakis(urea)-manganese(III) perchlorate in MeCN with the manganese reductant treated as an inert species. Since, however, urea and dmf are of similar donor strength[6–8] and additionally because of a dynamic Jahn–Teller effect in this complex,[9] solvation equilibria between urea and MeCN similar to those with iron(III) are to be envisaged. We, therefore, decided to reinvestigate this reaction, subjecting it to the same analysis as before.[2] We also tried to investigate other manganese solvate complexes, but in addition to $[Mn\{OC(NH_2)_2\}_6]^{3+}$ only the dimethyl sulfoxide solvate, $[Mn(dmso)_6]^{3+}$, proved to yield reasonably stable solutions in MeCN. As the reducing agent, and simultaneously as the redox indicator, tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II), $[Fe(tmphen)_3]^{2+}$, was chosen. All salts were used as the perchlorates.

Experimental

Hexakis(urea)manganese(III) perchlorate was prepared by a published procedure,[9,10] and purified by recrystallisation from methanol by slowly adding benzene under a nitrogen atmosphere (Found: C, 10.50; H, 3.15; N, 22.70. Calc. for $C_6H_{24}Cl_3MnN_{12}O_{18}$: C, 10.10; H, 3.40; N, 23.55%). Purification is essential since otherwise no reproducible kinetics was obtained. Further, rates were markedly lower with the purified product. Hexakis(dimethyl sulfoxide)manganese(III) perchlorate was prepared in the same manner (Found: C, 17.85; H, 4.00; Cl, 12.80. Calc. for $C_{12}H_{36}Cl_3MnO_{18}S_6$: C, 17.55; H, 4.40; Cl, 12.95%). 3,4,7,8-Tetramethyl-1,10-phenanthroline was obtained from Loba. The complex $[Fe(tmphen)_3][ClO_4]_2$ was synthesised as described.[11] The solvents MeCN and dmso were dried and purified by standard methods.[12,13] Urea (E. Merck) was used as obtained. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium hydroxide (Riedel-de Haen) and perchloric acid (Fluka) and recrystallised from ethanol.[13]

CAUTION: Owing to the hazardous nature of metal perchlorates containing organic ligands, the drying temperature was kept below 50 °C. Only small amounts were prepared at a time and handled with extreme care.

The kinetic measurements were done at 25 °C on a Durrum D-110 stopped-flow spectrophotometer using a 2 cm cell as before[2] by following the consumption of $[Fe(tmphen)_3]^{2+}$ (λ_{max} = 501 nm, ε = 16 000 dm^3 mol^{-1} cm^{-1}). Pseudo-first-order conditions were maintained by taking an excess of $[Mn\{OC(NH_2)_2\}_6]^{3+}$ or $[Mn(dmso)_6]^{3+}$ ($\approx 10^{-4}$ mol dm^{-3}) over the reductant concentration ($\approx 10^{-5}$ mol dm^{-3}). Absorbance data were processed as before.[4]

Proton NMR measurements were carried out on a Brucker AC 250 instrument operating at 250.13 MHz, equipped with a Eurotherm AC TBL temperature controller calibrated to 80% ethylene glycol in $[^2H_6]$dmso with an accuracy of ± 1 °C. The cyclic voltammetric measurements were done as before.[2] Conductance measurements were made with a WTW-LF535 microprocessor conductivity meter fitted with a WTW-LTA1 electrode.

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† *Non-SI unit employed:* Å = 100 pm.

Results

Speciation of Mn^{3+}.—Proton NMR spectra of $[Mn(dmso)_6][ClO_4]_3$ dissolved in CD_3CN (8 mmol dm^{-3}, stock solution) were recorded at 20, 50 and 67 °C, respectively. Chemical shifts are given relative to the residual protons of CD_3CN (δ 1.93 *vs.* $SiMe_4$). Separate resonances of co-ordinated and bulk dmso could be detected at all temperatures studied. At 20 °C co-ordinated dmso showed a single broad peak at δ 15.27 ($W_{\frac{1}{2}}$ = 164 Hz). The signal of free dmso was found at δ 2.89. Upon addition of extra dmso this peak increased in intensity without affecting the signal of co-ordinated dmso implying a slow ligand exchange on the NMR time-scale. An average co-ordination number of dmso co-ordinated to Mn^{3+}, $n_{\text{co-ord}}$, of 5.96 ± 0.2 was calculated from the areas of the broad peaks between δ 3 and 24, and from the peak area at δ 2.89. With increasing temperature the signal of co-ordinated dmso broadened and shifted upfield to δ 12.3 and 8.3, respectively. The chemical shift and linewidth of the signal of free dmso did not show any temperature dependence; however, it gained intensity owing to the formation of more free ligand. Average co-ordination numbers, $n_{\text{co-ord}}$, of 5.88 ± 0.2 and 5.70 ± 0.2, respectively, were determined at 50 and 67 °C. Unfortunately, because of the low solubility of the dmso salt, no concentration dependence of the NMR spectrum was available.

The ^1H NMR spectrum of $[Mn\{OC(NH_2)_2\}_6][ClO_4]_3$ (10 mmol dm^{-3}, in CD_3CN) did not reveal any evidence for the presence of free ligand though it cannot be conclusively ruled out. It is complicated by broadening of the resonances of the amide protons due to the quadrupole moment of the adjacent ^{15}N nucleus. In the present situation these resonances are expected to be additionally broadened due to the paramagnetism of Mn^{3+} (high spin, d^5), thus making them difficult to detect.

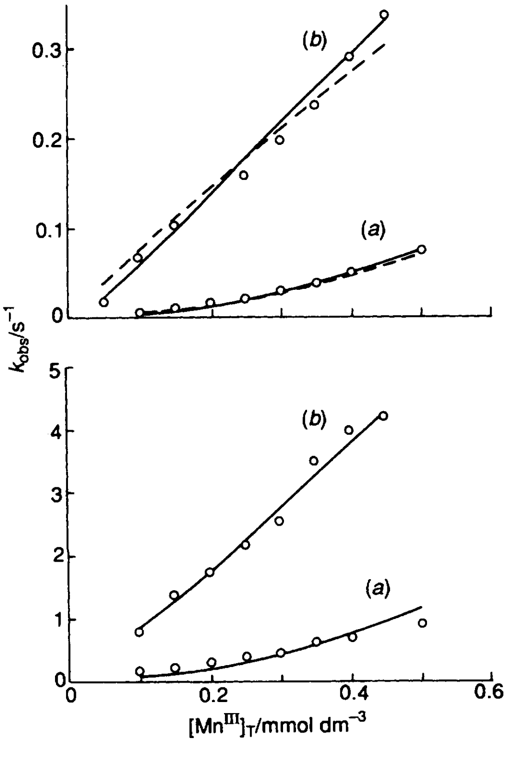


Fig. 1 Dependence of the observed rate constant k_{obs} for the oxidation of $[Fe(tmphen)_3]^{2+}$ on the total concentration of manganese(III) under different conditions. Curves: (*a*) without adding NBu_4ClO_4; (*b*) at constant perchlorate concentration. L = urea (upper), $[Fe(tmphen)_3{}^{2+}]_T$ = 0.020 mmol dm^{-3}, dmso (lower), $[Fe(tmphen)_3{}^{2+}]_T$ = 0.024 mmol dm^{-3}. Points are experimental, solid lines are calculated with equation (8) and parameters given in Table 2. For urea the broken lines are calculated on the basis of one solvation equilibrium (see text)

Kinetics.—Since both complexes behave quite similarly, they are described together, termed as Mn^{III}. Throughout, the manganese(III) oxidant was taken in at least five-fold excess, giving pseudo-first-order constants, k_{obs}. In addition, quantitative conversions were ascertained from the absorbance changes.

Values of k_{obs} were measured under a variety of conditions. They were found to increase non-linearly with $[Mn^{III}]$ when no electrolyte was added and to increase almost linearly when the variation in perchlorate concentration was compensated for by the addition of NBu_4ClO_4 (Fig. 1). The variation in rate constant with NBu_4ClO_4 at fixed $[Mn^{III}]$ is shown in Fig. 2. Finally, the rate constants decreased notably when extra L was added (Fig. 3), independently of whether L was admixed to the Mn^{III} or the $[Fe(tmphen)_3]^{2+}$ reactant solutions before the reaction.

Electrochemical Data.—Redox potentials are available only for the unmixed complexes and are summarised in Table 1. These values are in good agreement with those from the literature[14] measured *vs.* the normal hydrogen electrode NHE. Thus, a strong shift of $E°$ is expected upon the addition of L to a MeCN solution of $[Mn(MeCN)_6]^{2+}$. This is in fact found but a detailed study is not worthwhile because of the occurrence of an electrochemical-chemical-electrochemical-chemical mechanism[15] (*cf.* ref. 1) with too many unknowns involved (solvation equilibria at both Mn^{3+} and Mn^{2+}).

Conductance Data.—The molar conductivities (S $mmol^{-1}$) measured in MeCN at 25 °C for concentrations (mmol dm^{-3}) in parentheses are as follows: $[Mn\{OC(NH_2)_2\}_6][ClO_4]_3$, 0.0464 (0.551), 0.0428 (1.047), 0.0401 (1.547), 0.0383 (2.083), 0.0363 (2.890), 0.0340 (4.133), 0.0319 (5.500), 0.0301 (6.881) and 0.0281 (9.072); $[Mn(dmso)_6][ClO_4]_3$, 0.0384 (1.203), 0.0350 (2.016),

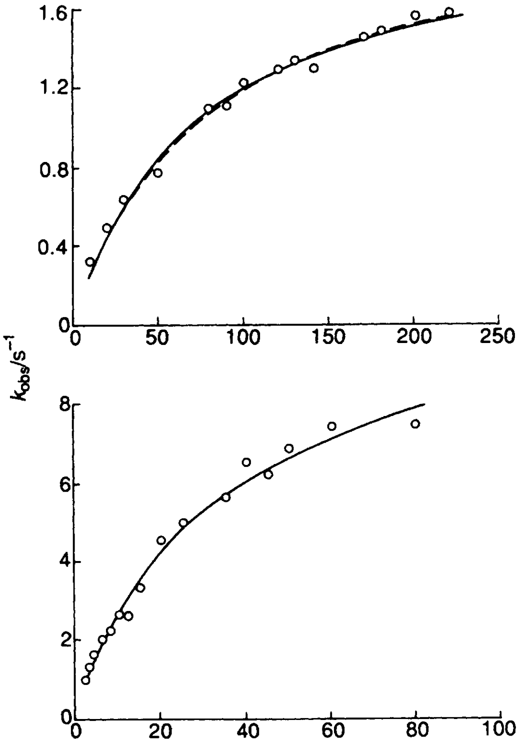


Fig. 2 Dependence of the observed rate constant k_{obs} for the oxidation of $[Fe(tmphen)_3]^{2+}$ with manganese(III) on the total concentration of perchlorate. Upper: $[Mn\{OC(NH_2)_2\}_6{}^{3+}]_T$ = 0.25 mmol dm^{-3}, $[Fe(tmphen)_3{}^{2+}]_T$ = 0.020 mmol dm^{-3}. Lower: $[Mn(dmso)_6{}^{3+}]_T$ = 0.25 mmol dm^{-3}, $[Fe(tmphen)_3{}^{2+}]_T$ = 0.024 mmol dm^{-3}. Other details as in Fig. 1

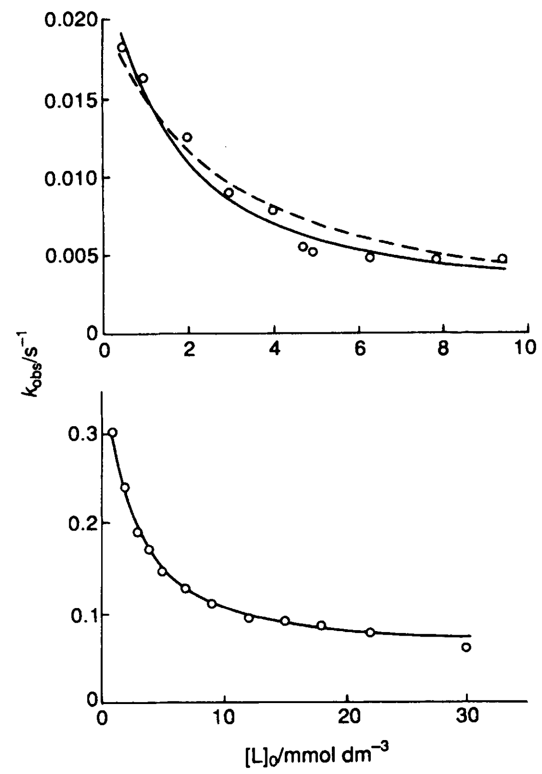


Fig. 3 Dependence of the observed rate constant k_{obs} for the oxidation of $[Fe(tmphen)_3]^{2+}$ with manganese(III) on the concentration of extra added ligand. Upper: $[Mn\{OC(NH_2)_2\}_6{}^{3+}]_T$ = 0.25 mmol dm^{-3}, $[Fe(tmphen)_3{}^{2+}]_T$ = 0.020 mmol dm^{-3}. Lower: $[Mn(dmso)_6{}^{3+}]_T$ = 0.25 mmol dm^{-3}, $[Fe(tmphen)_3{}^{2+}]_T$ = 0.024 mmol dm^{-3}. Other details as in Fig. 1

Table 1 Redox potentials[a] in acetonitrile at 25 °C

Complex	$E_{\frac{1}{2}}{}^{b}$/V (this work)	E^{c}/V (ref. 14)
$[Fe(tmphen)_3]^{3+/2+}$	1.57_5	
$[Mn\{OC(NH_2)_2\}_6]^{3+/2+}$	1.66_8	1.68
$[Mn(dmso)_6]^{3+/2+}$	$1.96_3{}^{d}$	1.76
$[Mn(MeCN)_6]^{3+/2+}$	2.98_1	3.11

[a] The potentials are referenced to $[Cr(Ph\text{-}Ph)_2]^{0/+}$ (−1.118 V *vs.* ferrocene–ferrocenium). [b] Potentials represent the mean of the cathodic and the anodic peak potentials from cyclic voltammograms (scan rate 0.1 V s^{-1}, electrolyte was 0.1 mol dm^{-3} NBu_4ClO_4, reactant concentration ≈ 1 mmol dm^{-3}). [c] Cathodic peak potentials for L = urea or dmso and anodic peak potential for L = MeCN. Measured *vs.* NHE and converted by adding +0.565 V. [d] Measured in dmso.

0.0313 (3.611), 0.0306 (3.908), 0.0286 (5.790), 0.0272 (7.228) and 0.0259 (8.671). These results were analysed by the exact Lee–Wheaton equation[16] because no fit was obtained unless both the higher terms were included. In the analysis various parameters were fixed before fitting. (*i*) The second-stage association constant, $K_2{}^0$, was linked to the fitted value of $K_1{}^0$ [equations (3)–(5)] by the Fuoss equation (6). This equation includes the distance parameter r and so the ratio $K_1{}^0:K_2{}^0$ varies with each value of r. It was not possible to get a fit by setting $K_2{}^0 = 0$. Moreover, we could see no point in adding $K_2{}^0$ as a separate variable or introducing tris(perchlorate) ion pairs. (*ii*) The molar conductance of perchlorate was taken as 103.8 S cm^2 mol^{-1}.[17] (*iii*) The ratio of the conductance of the ion to that of the ion pair $Mn(ClO_4)^{2+}:Mn^{3+}$ and $Mn(ClO_4)_2{}^{+}$: $Mn(ClO_4)^{2+}$ was set at 0.8 : 1 from past experience.[18]

Owing to the high experimental concentrations chosen, values of both $K_1{}^0$ and $\lambda_0(MnL_6{}^{3+})$ depend dramatically on r. With the latter set at 8 Å, the results were, for $[Mn\{OC(NH_2)_2\}_6][ClO_4]_3$, $K_1{}^0$ = 1370 dm^3 mol^{-1}, $\lambda_0[\frac{1}{3}Mn\{OC(NH_2)_2\}_6{}^{3+}]$ = 111.2 S cm^2 mol^{-1} and for $[Mn(dmso)_6][ClO_4]_3$, $K_1{}^0$ = 1600 dm^3 mol^{-1}, $\lambda_0[\frac{1}{3}Mn(dmso)_6{}^{3+}]$ = 100.9 S cm^2 mol^{-1}. The Fuoss link $K_1{}^0:K_2{}^0$ = 6.48 : 1. Thus, the main result, for our purposes, is that the degree of association of the two salts is similar but the dmso one is slightly more associated.

Discussion

In accordance with previous reports[2–4] on labile Fe^{3+}, the decrease in rate when extra L is added, shown in Fig. 3, is indicative of solvation equilibria between L and MeCN coordinated at Mn^{3+}, with ions of higher L content being less reactive. The large effect of small additions of L would further suggest, in accordance with the NMR results, that not much ligand is lost from either complex. Moreover, since the effect of L is independent of the mode of addition (*i.e.* either to the reductant or the oxidant solutions), these equilibria (1) and (2)

$$[MnL_6]^{3+} \xrightleftharpoons{\beta_1} [MnL_5]^{3+} + L \qquad (1)$$

$$[MnL_6]^{3+} \xrightleftharpoons{\beta_2} [MnL_4]^{3+} + 2L \qquad (2)$$

are rapid compared to the redox processes (in the following, coordinated MeCN is omitted). The various solvate species available should have highly different reactivities as is evident from Table 1, as a consequence of the vastly different behaviour of MeCN which is soft (or better, a strong π base), stabilising the divalent, and L which is hard, stabilising the trivalent state. Thus, the reduction potential difference is expected to be of the order of 0.2 V for the replacement of one L by MeCN.

In addition to the solvate speciation also different ionic species are to be considered due to the high-charge type of reaction of +3/+2, in the solvent MeCN of moderate relative permittivity. We are thus left with the problem of deconvoluting simultaneously two kinds of speciation, the solvate and ionic speciations. The multiplicity of variables that must be invoked renders a rigorous analysis impossible, but upon the following approximations from previous work[2,3] the amount of parametrisation is diminished.

(*i*) The two kinds of speciation do not affect each other, that is ion association is qualitatively and quantitatively the same for all solvate species and *vice versa* (in the following, $X^- = ClO_4{}^-$) [equations (3) and (4)].

$$[MnL_n]^{3+} + X^- \xrightleftharpoons{K_1} [MnL_nX]^{2+} \qquad (3)$$

$$[MnL_nX]^{2+} + X^- \xrightleftharpoons{K_2} [MnL_nX_2]^{+} \qquad (4)$$

(*ii*) The reaction of each solvate species is considered as varying with both ionic strength and counter ion concentration. Ionic strength effects are treated by Coulombic work terms with extrapolation to infinite ionic strength. Ion-pairing equilibrium constants are approximated as real constants within the experimental ionic strength range. (They cannot be scaled to infinite ionic strength since they approach zero according to theory. Apart from this fact, ionic strength effects on ion-pairing constants tend to be of minor importance in reaction kinetics because of these constants appearing in both the nominator and denominator of the rate equation.) Ion pairing lowers the electrostatic work needed to bring the reactants together, in other words it lowers the charge type of the reaction, and, relative to this effect, does not alter the electron-transfer reactivity. (Possible lowering of the latter is typically by about a factor of 2.[19,20] On the other hand, the Coulombic work expression predicts an about 15-fold retardation of a +2/+3 charge-type reaction relative to a reaction in which electrostatic work is not involved.[4])

Along these lines each solvate species is characterised by a single electrostatics-free rate constant, independent of the anions attached. Support for this procedure is at least five-fold from previous work.[2-4] (*i*) Experimental rate-constant dependences are very well reproduced. (*ii*) Values for β calculated from the kinetics are in accordance with those derived from NMR data. (*iii*) The order of magnitude of the ion-pairing constants calculated from the kinetic analyses numerically agrees with those derived from conductance measurements valid for unit activity and corrected to the experimental conditions by the use of equation (5) for MeCN (D_s = 37.5, T = 298 K, and r is the distance parameter in Å).[3,21]

$$K_1 = K_1^0 \cdot \exp\frac{7.12I^{\frac{1}{2}}}{1 + 0.48rI^{\frac{1}{2}}} \qquad (5)$$

(*iv*) For ion tripling, the ratio of fitted values of K_1 and K_2 is in the expected range on the basis of the Fuoss ratio[3,18,22] [equation (6)].

$$K_1/K_2 = \exp[560.75/(D_s r)] \qquad (6)$$

(*v*) Numerical values of electrostatics-free rate constants obtained from fitting procedures for the 3+/2+ charge type agree with those for a 3+/0 charge type, *i.e.* in the absence of Coulombic repulsion, under otherwise similar conditions.[4]

An additional point of our procedure should be mentioned. Instead of working at constant ionic strength, to eliminate ionic strength effects, we obtained several dependences of pseudo-first-order rate constants as shown in the Figures and fitted them simultaneously to a unique rate constant equation, varying the number of solvation equilibria until adequate fits were obtained by treating equilibrium constants for solvation and ion pairing and rate constants for the various solvate species as variables.

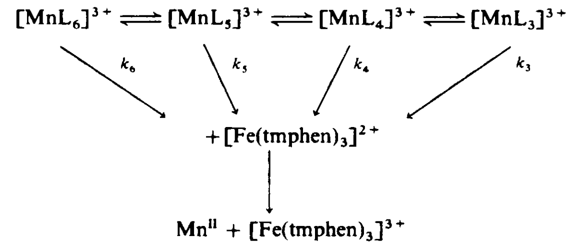
In addition to equations (3) and (4), slight ion pairing was also allowed for the ferroin reactant [equation (7)] with K_3

$$[Fe(tmphen)_3]^{2+} + X^- \overset{K_3}{\rightleftharpoons} [Fe(tmphen)_3X]^+ \qquad (7)$$

fixed at 3 dm^3 mol^{-1} as obtained before.[2] Therefore, six ionic paths were considered for each solvate species, represented in turn by the six terms in the numerator of equation (8b) where the charge type is accounted for by the exponential terms (*e.g.* the term e^{6A} stands for the free-ion path, *etc.*).

In adopting the reactive species, we tried to use a minimum of solvation equilibria, based on the NMR results. Clearly, all species available should also react including $[MnL_6]^{3+}$, in view of the more positive potential for both the hexakis-urea and the -dmso complex compared to $[Fe(tmphen)_3]^{3+/2+}$ (Table 1). In the case of the urea system, a quite good description (broken lines in the Figures) of all k_{obs} dependences was achieved upon admission of a single equilibrium involving two reactive species. A non-linear least-squares regression yielded β_1 = (2.32 ± 1.83) × 10^{-3} mol dm^{-3}, K_1 [equation (3)] = 153 ± 114 dm^3 mol^{-1}, K_2 [equation (4)] = 32.6 ± 16.6 dm^3 mol^{-1}, k_5 = (1.13 ± 0.08) × 10^4 dm^3 mol^{-1} s^{-1} and a quite poorly defined value for k_6 = 9.74 ± 4 dm^3 mol^{-1} s^{-1}. (Here and in the following, the subscripts on the rate constants denote the number of L ligands bound.)

From experience,[2-4] however, a β value of the order of 10^{-3} is sufficiently high that further solvation stages may not be neglected. In the dmso case a reasonable description of the data was not feasible unless three solvation equilibria were taken into account, as was also necessary in the previously reported Fe^{3+} system with dmf as the ligand.[2] For that iron case, only $[FeL_3]^{3+}$ and $[FeL_4]^{3+}$ are redox-active because both $[FeL_6]^{3+}$ and even $[FeL_5]^{3+}$ are too positive in potential. This difference from the present manganese reactions (all four species reacting) is nicely displayed in the variation of k_{obs} with [oxidant] measured at constant $[ClO_4^-]$ (to minimise charge effects): the linear increase with $[Mn^{III}]_T$ (Fig. 1) reflects the importance of the $[MnL_6]^{3+}$ path, while in case of iron the k_{obs} values go through a maximum as the concentration of $[FeL_3]^{3+}$ actually decreases when $[Fe^{III}]_T$ is increased.[2] Both manganese(III) systems were successfully analysed in terms of Scheme 1.



Scheme 1 L = dmso or urea

The expression (8a) is obtained for the rate constant with all assumptions made above included where Q is given by (8b) and A by (8c). In fitting the kinetic data by equation (8), both the

$$k_{obs} = Q\frac{k_3\beta_3 + k_4\beta_2[L] + k_5\beta_1[L]^2 + k_6[L]^3}{[L]^3 + \beta_1[L]^2 + \beta_2[L] + \beta_3}[Mn^{III}]_T \qquad (8a)$$

$$Q = \frac{e^{6A} + K_1[X^-]e^{4A} + K_3[X^-]e^{3A} + K_1K_2[X^-]^2e^{2A}}{(1 + K_3[X^-])(1 + K_1[X^-] + K_1K_2[X^-]^2)} + \frac{K_1K_3[X^-]^2e^{2A} + K_1K_2K_3[X^-]^3e^{A}}{(1 + K_3[X^-])(1 + K_1[X^-] + K_1K_2[X^-]^2)} \qquad (8b)$$

$$A = \frac{7.12I^{\frac{1}{2}}}{1 + 0.48rI^{\frac{1}{2}}} - \frac{15}{r} \qquad (8c)$$

free ligand and the free perchlorate concentrations were supplied from the roots of the respective material-balance equations through Newton's method as before.[2] On the basis of equation (8c), the rate constants in (8a) refer to infinite ionic strength.[1,21] The approach distance r was taken as 13.5 Å as the sum of the radii of $[Mn\{OC(NH_2)_2\}_6]^{3+}$ (5.5 Å)[5] and $[Fe(tmphen)_3]^{2+}$ (8 Å).[2] The quality of the fits of the data is seen by the solid lines in the Figures, with best-fit parameters listed in Table 2.

Owing to the amount of parametrisation, the parameters themselves must have inherently rather large error limits. In particular the error associated with the $[MnL_3]^{3+}$ path (β_3, k_3) is large. The mean co-ordination number of dmso calculated from the β values for 8 mmol dm^{-3} of the dmso salt is 5.70. This is in fair concordance with the value of 5.94 derived for 25 °C

Table 2 Summary of association constants, solvation equilibrium constants and electrostatics-free rate constants for the reactions of $[Fe(tmphen)_3]^{2+}$ in acetonitrile at 25 °C

Complex	$[Mn\{OC(NH_2)_2\}_6]^{3+}$	$[Mn(dmso)_6]^{3+}$
K_1/dm^3 mol^{-1}	140 ± 15	503 (+100, −50)
K_2/dm^3 mol^{-1}	36.3 ± 18.5	78.6 ± 8.9
β_1/mol dm^{-3}	(1.90 ± 0.21) × 10^{-4}	(5.78 ± 0.28) × 10^{-4}
β_2/mol^2 dm^{-6}	(2.80 ± 0.53) × 10^{-7}	(5.40 ± 0.28) × 10^{-7}
β_3/mol^3 dm^{-9}	1.68 × 10^{-15}*	(5.10 ± 1.19) × 10^{-12}
k_6/dm^3 mol^{-1} s^{-1}	(9.44 ± 4) × 10^2	(1.19 ± 0.85) × 10^4
k_5/dm^3 mol^{-1} s^{-1}	(5.79 ± 0.53) × 10^4	(2.23 ± 0.07) × 10^5
k_4/dm^3 mol^{-1} s^{-1}	(3.07 ± 1.25) × 10^3	(9.78 ± 4) × 10^2
k_3/mol^{-1} s^{-1}	1.46 × 10^5*	(5.48 ± 1.16) × 10^5

* The error limits cannot be defined.

from the NMR data. For the urea salt of the same concentration the β values yield a somewhat higher value of 5.77. In view of such high co-ordination numbers, clearly, the fits of the kinetic data cannot be sensitive to β_3. In the urea case, error limits of the parameters are further increased because of the low solubility of this ligand limiting the concentration range available in the extra added-urea series (Fig. 3).

For the association constants, the stronger ion pairing found for the dmso salt seems to be at variance with expectation in terms of the acidic hydrogens of urea. However, the conductance data likewise point to the dmso salt being slightly more associated. Moreover, the individual values of the ion-pair equilibrium constants fit in the framework of equations (5) and (6), proceeding from the association constants for unit activity derived from the conductance measurements. The finding that the urea complex does not yield enhanced ion pairing may be comparable with the interactions of anions with liquid ammonia suggesting that this solvent should be classified with basic aprotic solvents rather than with protic solvents.[2,3]

The order in reactivities of the various solvate species is worth noting. Whereas in the case of Fe^{III} a smooth increase in reactivity is very probable[2–4] in going from $[FeL_6]^{3+}$ to $[FeL_3]^{3+}$, in the present manganese reactions the $[MnL_4]^{3+}$ species are both co-ordination-chemically and redox-kinetically stabilised relative to the adjacent species. This feature is apparently related to the Jahn–Teller distortion.

In the Fe^{3+} systems,[2–4] experimental rate constants could not satisfactorily be fitted by an equation similar to (8) unless the assumption was introduced that the various solvate species react *via* different ion-paired paths. This was explained[4] in terms of competition of driving force changing with inner-sphere composition and the Coulombic work changing with ion pairing. If the driving force is a linear function of solvate stoichiometry,[24,25] the change in it on replacement of one L by MeCN is comparable in magnitude to the reduction in Coulombic work in changing the charge type from $+2/+3$ to $+2/+$, that is when $[FeL_n]^{3+}$ reacts as such or as the triplet. In other words, the overall reactivity of *e.g.* $[FeL_3]^{3+}$ is comparable to that of $[FeL_4X_2]^{+}$. In the present manganese reactions, however, the fits even slightly deteriorated upon use of this procedure. This is not unexpected if the reactivities of the $[MnL_n]^{3+}$ species are not a linear function of the number of L molecules.

To sum up, the present reactions are rather complex, virtually reaching the limit of adequate analysis. It is notwithstanding a major message of this work that care is advised in premature classification of a metal complex as substitutionally inert. Aside from this, two further points may be made with reference to Macartney's work. First, our experimental constants are all lower than his values by about a factor of 2. This might be due to some impurities in Macartney's sample of $[Mn\{OC(NH_2)_2\}_6][ClO_4]_3$. In fact, our crude material, without recrystallisation, showed an increased reactivity towards reduction. Finally, the equilibrium constant of the $[Mn\{OC(NH_2)_2\}_6]^{3+}$–$[Fe(tmphen)_3]^{2+}$ reaction is $\ln K = 3.62$ instead of 12.8 given in ref. 5. This large difference originates from the reduction potential of the ferroin moiety which is about 0.2 V more negative in 1 mol dm^{-3} H_2SO_4 (Macartney's value is taken from this medium) than in MeCN.

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