

Kinetic and mechanistic studies on the oxidation of hydroxylamine by a tri-bridged manganese(IV,IV) dimer in weakly acidic media

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The complex ion, $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+}$ ($\mathbf{1}^{3+}$) (bipy = 2,2'-bipyridine) and its aqua derivatives $[\text{Mn}_2^{\text{IV}}(\mu\text{-O})_2(\text{bipy})_2(\text{H}_2\text{O})_4]^{4+}$ ($\mathbf{2}^{4+}$) and $[\text{Mn}_2^{\text{IV}}(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bipy})(\text{H}_2\text{O})_4]^{3+}$ ($\mathbf{3}^{3+}$) coexists in rapid equilibria in aqueous buffer in the presence of excess of bipy and MeCO_2^- in the range pH 4.00–5.30. The solutions are reasonably stable up to pH 5.50 and react quantitatively with hydroxylamine to produce manganese(II) and N_2O . The reactions follow simple first-order kinetics in the presence of excess hydroxylamine. There is UV-vis spectral evidence for the intermediate $\text{Mn}^{\text{III,IV}}$ complex, $[(\text{bipy})_2\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$, in the presence of excess bipy and deficit hydroxylamine which supports that $\mathbf{1}^{3+}$ and its hydrolytic derivatives are reduced by one-electron steps. Increased extent of aquation at the manganese(IV) centre leads to increased kinetic activity in the order: $\mathbf{1}^{3+} < \mathbf{2}^{4+} < \mathbf{3}^{3+}$. The rate of reduction increased with an increase in the concentration of hydroxylamine but decreased with increase in c_{bipy} and c_{OAc} . The mild oxidising character of the complex ion along with major structural changes associated with one-electron oxidation of hydroxylamine disfavours an outer-sphere pathway. The overall first-order rate constants decrease linearly with increased mol% of D_2O suggesting proton-coupled electron transfer pathways.

Introduction

Oxo- and ethanoate-bridged manganese dimers containing N-donor ligands are considered as “molecular bricks” for the oxygen evolving complex (OEC) in the photosystem II (PS II).^{1–4} Their reactivity and kinetic studies,⁵ though limited in numbers, provided interesting results. The dimanganese(IV,IV) complex, $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bipy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ ($\text{MeCO}_2 = \text{ethanoate}$, bipy = 2,2'-bipyridine) (Fig. 1), the

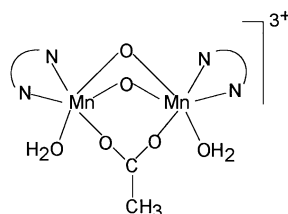


Fig. 1 Graphical structure for $\mathbf{1}^{3+}$ drawn on the basis of its crystal structure.

oxidant chosen for our study, includes simultaneously a bridging ethanoate ligand, two oxo-bridges and two water molecules, each coordinated to $\text{Mn}(\text{IV})$ ion⁶ and is quite attractive as a biological model of PS II and as a novel oxidant.⁴ Three of its structural features appear noteworthy: (a) a bending of the $\text{Mn}^{\text{IV}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}$ unit in the presence of an ethanoate bridge, (b) elongation of the equatorial Mn–N bonds due to *trans*-influence of the bridging oxygen atoms, and (c) presence of unprotonated water molecules in the coordination sphere of each $\text{Mn}(\text{IV})$. Features (a) and (b) significantly affect the solution chemistry of the cationic complex $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+}$, designated as $\mathbf{1}^{3+}$. For example, the bridging ethanoate and one of the bipy ligands are labile and in aqueous solution $\mathbf{1}^{3+}$ coexists with its aqua derivatives. Spectrophotometric studies indicated rapid solution equilibrium but no deprotonation of the coordinated water molecules at least up to pH 5.50.^{5d} The mechanism for oxidation of the manganese cluster (OEC) in PS II is now established^{4f} to occur by proton

coupled electron transfer steps mediated by O–H bond of a tyrosine residue forming a tyrosyl radical.

Hydroxylamine, the presently chosen reductant, is useful for probing reaction mechanisms of inorganic complexes, and the mechanistic versatility noted in its reactions is attractive in the way that it acts both as an oxidant or a reductant⁷ and can coordinate through either the N- or the O-end.⁸ Furthermore, the estimated dissociation energy for the N–H bond of hydroxylamine (92 kcal mol^{-1})⁹ and that of O–H bond of tyrosine ($86.5 \text{ kcal mol}^{-1}$)¹⁰ are similar and it is interesting to examine whether hydroxylamine may take part in a proton coupled electron transfer, as tyrosine does in PS II.

Experimental

Materials

The title complex, $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bipy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, was prepared following a known procedure^{6a} involving oxidation of Mn^{2+} by Ce^{4+} in the presence of ethanoate and bipyridine. The crystals obtained are sufficiently pure and gave satisfactory analyses (Found: C, 30.3; H, 3.1; N, 6.4. $\text{C}_{22}\text{H}_{25}\text{Cl}_3\text{Mn}_2\text{N}_4\text{O}_{19}$ requires C, 30.5; H, 2.9; N, 6.5%). Its equivalent weight found by iodometry (214) was in good agreement with the calculated value (216.5). Hydroxylamine nitrate was prepared in solution by double decomposition of hydroxylamine sulfate (G.R., E. Merck) with barium nitrate (G.R., E. Merck) and standardised by oxidation¹¹ with KBrO_3 in presence of dilute H_2SO_4 . We found this solution to be stable for at least six months when kept at $\sim 10^\circ\text{C}$. Aqueous solutions of NaNO_3 and MeCO_2Na (both are G.R., E. Merck) were prepared in freshly boiled double distilled water and standardised by passing through a Dowex 50W X-8 strong cation exchange resin in the H^+ form and titrating the liberated acid with standard NaOH to a phenolphthalein end-point. 2,2'-Bipyridine (G.R., E. Merck) was used as received. All other chemicals were of reagent grade. Double distilled, freshly boiled water was used throughout.

Physical measurements and kinetics

All absorbances and electronic spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cells. The kinetics was monitored *in situ* in the 'kinetic mode' of the instrument at 420 nm in the electrically controlled thermostated (25.0 ± 0.1 °C) cell-housing (CPS-240A). In this mode the change in absorbance is automatically and continuously recorded. Hydroxylamine solution (adjusted to the desired pH) was directly injected into the spectrophotometer cell containing other components of the reaction mixture kept at the same pH. The desired concentration of complex and reducing agent was achieved after mixing. The ionic strength (I) was maintained at 1.0 mol dm^{-3} (NaNO_3). Excess of 2,2'-bipyridine was added to the reaction mixture. The total 2,2'-bipyridine concentration, $c_{\text{bipy}} (= [\text{Hbipy}^+] + [\text{bipy}])$, and ethanoate concentration, $c_{\text{OAc}} (= [\text{MeCO}_2\text{H}] + [\text{MeCO}_2^-])$ ($\text{HOAc} = \text{HO}_2\text{CMe}$) were in the ranges 5–35 and 4–150 mmol dm^{-3} respectively. Limited solubility of 2,2'-bipyridine in the experimental condition prohibited the use of a wider range for c_{bipy} . Solution pH values (4.00–5.30) were measured with an Orion pH-meter (model 710A) electrode before and after the reaction. The linearity of the electrode was established using pH 4, 7 and 9 buffers as described earlier.¹² For reactions in D_2O , pD was calculated¹³ as $\text{pD} = (\text{pH})_{\text{measured}} + 0.40$. Excess reducing agent, $c_{\text{R}} (= [\text{NH}_3\text{OH}^+] + [\text{NH}_2\text{OH}])$, 1–5 mmol dm^{-3} over the complex (0.1 mmol dm^{-3}) was maintained in all the kinetic runs. The observed rate constants (first-order) were measured from the least-squares slope of $\ln A$, versus time data.

Stoichiometry

The stoichiometry was measured by estimating unchanged hydroxylamine spectrophotometrically. Excess hydroxylamine was mixed with the complex in the presence of bipyridyl and acetate buffer in the range pH 4.00–5.30. Soon the reaction mixtures turned colourless indicating complete reduction of Mn^{IV}_2 to Mn^{II} . Excess $\text{Fe}_2(\text{SO}_4)_3$ (kept at 0.5 mol dm^{-3} HNO_3) was then added into the reaction mixtures and the pH of the solutions were adjusted to ~4.0 using additional acetate buffer. The red coloration produced due to the formation of $[\text{Fe}(\text{bipy})_3]^{2+}$, generated by the quantitative reduction of Fe^{III} by excess hydroxylamine, was measured at 522 nm ($\epsilon = 8710 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).¹⁴

Since the formation and decay of HNO_2 was observed^{15,16} in some oxidation reactions of NH_2OH , we tested for the presence of whether any HNO_2 or NO_2^- was formed. A 25 ml mixture of $0.10 \text{ mmol dm}^{-3}$ complex, $c_{\text{R}} = 1.0 \text{ mmol dm}^{-3}$, $c_{\text{bipy}} = 0.035 \text{ mol dm}^{-3}$, $c_{\text{OAc}} = 0.10 \text{ mol dm}^{-3}$ at pH 4.50 was taken. The product solution after complete reaction was eluted through a Dowex 50W X-8 cation exchanger in the Na^+ form, made up to 100 ml and subjected to the Griess–Ilsovey reaction¹⁷ for nitrous acid by reaction with sulfanilic acid followed by a coupling reaction with 1-naphthylamine to give an azo dye ($\lambda_{\text{max}} = 520 \text{ nm}$, $\epsilon = 40000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).¹⁸ A 1% sulfanilic acid solution was prepared by dissolution of the powder in 25% acetic acid. A 0.6% solution of 1-naphthylamine was also prepared in 25% acetic acid.

Results and discussion

Stoichiometry and reaction products

Results of the stoichiometric experiments yielded $\Delta[\text{Mn}^{\text{IV}}_2]/\Delta[\text{NH}_2\text{OH}] = 0.507 \pm 0.019$ (Table 1) which suggests quantitative oxidation to N_2O .

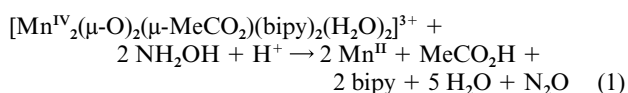


Table 1 Stoichiometry of reduction of the Mn^{IV}_2 complex by hydroxylamine nitrate (R)^a

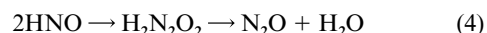
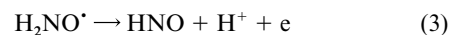
$[\text{Mn}^{\text{IV}}_2]$	pH	[R]	$\Delta[\text{Mn}^{\text{IV}}_2]/\Delta[\text{R}]$
0.20	4.00	1.00	0.51
0.40	4.30	2.40	0.52
0.60	4.50	4.20	0.49
0.80	4.80	5.60	0.48
1.00	5.10	8.00	0.51
1.20	5.30	12.0	0.53

Average = 0.507 ± 0.019

^a $c_{\text{bipy}} = 100$, $c_{\text{OAc}} = 35$; all concentrations are in mmol dm^{-3} , $T = 25$ °C.

Under the experimental conditions no indication of formation of N^{III} was detected by the Griess–Ilsovey reaction and the spectra of the product solutions were practically superimposed on that of a mixture of $\text{Mn}(\text{NO}_3)_2$ and 2,2'-bipyridine under the reaction conditions of concentration and pH.

The complicated redox chemistry of hydroxylamine in solution has been studied extensively.⁷ It was observed that hydroxylamine is most commonly oxidised to N_2O .^{19–21} Oxidation to N_2 , NO_2^- , NO_3^- and NO are relatively rare.^{8,19–21} EPR spectroscopy has established the formation of the $\text{H}_2\text{NO}^\bullet$ radical in the oxidation of NH_2OH with one-electron oxidants.²² The ultimate oxidation product varies depending on the mode of decay (eqns. (2)–(4)) of the $\text{H}_2\text{NO}^\bullet$ radical under different conditions.⁷ Thus $\text{H}_2\text{NO}^\bullet$ may decay to N_2 (eqn. (2)) or may be further oxidised (eqn. (3)) to HNO , which dimerises to *cis*- and *trans*-hyponitrous acid.²³ The *trans* form is more stable than the *cis* form and decomposes into N_2O .²⁴ With strong oxidants such as $\text{Mn}^{3+}(\text{aq})$ or $\text{Ag}^{2+}(\text{aq})$, present in excess, the free radical is further oxidised to NO_3^- .²⁵



The thermodynamic oxidising strength of the title complex $\mathbf{1}^{3+}$ under investigation is moderate. Hence NO_3^- is not an expected oxidation product.

The reduction of Mn^{IV}_2 to 2Mn^{II} involves a net 4e-change and must be a multistep process. It is likely that all steps in eqn. (1) are 1e-changes and all manganese species except manganese(II) are binuclear in line with the evidences (a)–(c). (a) Electrochemical reduction of $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2(\mu\text{-HPO}_4)(\text{bipy})_2(\text{H}_2\text{PO}_4)_2]$ yields $[(\text{bipy})_2\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$. Electrochemical^{26,27} and chemical^{5a–c} reduction of this and several other $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ complexes with a $\{\text{Mn}_2\text{O}_2\}^{3+}$ core in turn, produce Mn^{III}_2 dimer and then a mixture of Mn^{III} and Mn^{II} species. (b) Different oxidation levels of the binuclear catalase enzyme models²⁸ preserve nuclearity. (c) The various oxidation levels (S-states)^{2a} of the manganese cluster in PS II²⁹ also apparently retain bond connectivity. (d) Manganese has a high tendency³⁰ for the generation and retention of the di(μ -oxo) bridged unit $\{\text{Mn}_2\text{O}_2\}^{n+}$.

In an attempt to detect any intermediate manganese complex, we mixed $\mathbf{1}^{3+}$ with less than stoichiometric amounts of hydroxylamine and recorded the spectra. Typically, with complex : hydroxylamine = 2 : 1; pH 4.50; $c_{\text{bipy}} = 0.035 \text{ mol dm}^{-3}$; $c_{\text{OAc}} = 0.1 \text{ mol dm}^{-3}$, we observed the growth of a narrower band at 684 nm with a shoulder near at 555 nm (Fig. 2). Both bands are fingerprints^{27c} for $[(\text{bipy})_2\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$, a complex which formed by chemical, 1e-reduction^{5d} of $\mathbf{1}^{3+}$ by $\text{S}_2\text{O}_3^{2-}$ and by the electrochemical reduction²⁶ of $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2(\mu\text{-HPO}_4)(\text{bipy})_2(\text{H}_2\text{PO}_4)_2]$. It appears very much likely that hydroxylamine also reduces complex $\mathbf{1}^{3+}$ by one-electron steps and that all the intermediates are binuclear.

Table 2 First-order rate constants^b at $T = 25\text{ }^\circ\text{C}$, $I = 1.0\text{ mol dm}^{-3}$ (NaNO_3), $\lambda = 420\text{ nm}$

pH	$c_{\text{OAc}}/\text{mmol dm}^{-3}$	$c_{\text{bipy}}/\text{mmol dm}^{-3}$	$c_{\text{R}}/\text{mmol dm}^{-3}$	$10^3 k_0/\text{s}^{-1}$
4.00	100	35.0	1.0	6.40 (6.45)
4.22				5.12 (5.10)
4.36				4.42 (4.39)
4.54				3.61 (3.65)
4.75				2.99 (3.01)
4.86				2.75 (2.74)
5.12				2.25 (2.26)
5.30				2.01 (1.99)
4.75	100	5.00		6.50 (6.50)
		10.0		4.63 (4.62)
		15.0		3.85 (3.90)
		20.0		3.50 (3.52)
		25.0		3.30 (3.28)
		30.0		3.10 (3.12)
	4.00	35.0		10.5 (10.4)
	20.0			6.62 (6.67)
	50.0			4.33 (4.30)
	80.0			3.40 (3.37)
	150			2.50 (2.48)
	100		2.0	6.02 (6.01)
			2.5	7.48 (7.51)
			3.0	9.04 (9.02)
			3.5	10.5 (10.5)
			4.0	12.0 (12.0)
			4.5	13.5 (13.5)
			5.0	15.0 (15.0)

^b Concentration of complex used 0.10 mol dm^{-3} . Individual rate constants are averages from 2 or 3 experiments and k_0 values are reproducible within 3%. Calculated k_0 values are given in parentheses.

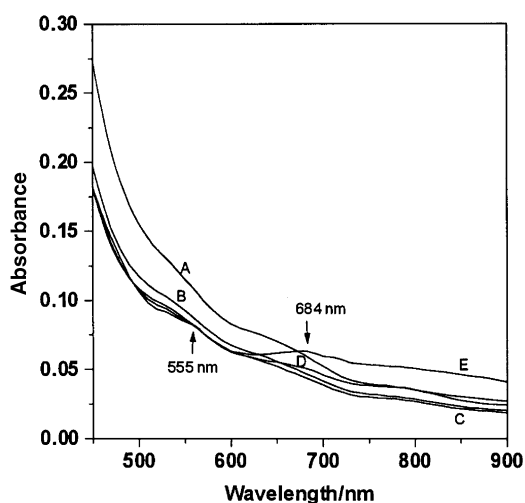


Fig. 2 (A): Spectra of $0.15\text{ mol dm}^{-3}\text{ I}^{3+}$. Spectra of a mixture of (A) with hydroxylamine (2 : 1) immediately after mixing (B), after 10 min (C), after 25 min (D) and after 80 min (E) of mixing; $c_{\text{bipy}} = 0.035\text{ mol dm}^{-3}$, $c_{\text{OAc}} = 0.1\text{ mol dm}^{-3}$, $I = 1.0\text{ mol dm}^{-3}$, $T = 25\text{ }^\circ\text{C}$.

Kinetics

At a fixed pH, c_{bipy} and c_{OAc} , the observed first-order rate constants, k_0 (Table 2) increase linearly with increase in total hydroxylamine concentration. k_0 also increases with a decrease in pH (Fig. 3), c_{bipy} or c_{OAc} . These observations along with previous equilibrium studies^{5d} indicate rapid ligand dissociation equilibria (5) and (6) and increased kinetic activities for the aquated derivatives 2^{4+} and 3^{3+} .

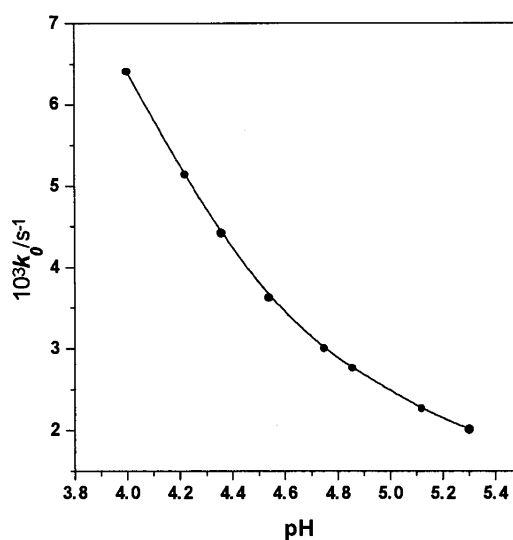
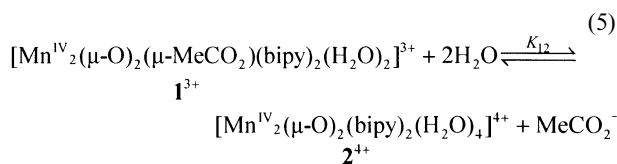
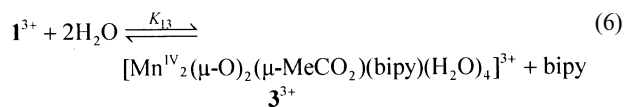


Fig. 3 The rate (k_0)–pH profile at $[\text{complex}] = 0.1\text{ mol dm}^{-3}$, $c_{\text{bipy}} = 0.035\text{ mol dm}^{-3}$, $c_{\text{OAc}} = 0.1\text{ mol dm}^{-3}$, $I = 1.0\text{ mol dm}^{-3}$, $c_{\text{R}} = 1.0\text{ mol dm}^{-3}$, $T = 25\text{ }^\circ\text{C}$.



It is unlikely that the observed increase in k_0 at lower pH is due to greater kinetic activity of NH_3OH^+ over NH_2OH . First, it is very unusual for a conjugate acid to be a better reducing agent than the parent base. Secondly, under the present experimental conditions the reducing agent is almost exclusively present as NH_3OH^+ ($\text{p}K_{\text{a}} = 6.0$)³¹ and the very modest variation in its concentration in equilibrium with NH_2OH at different pH can not create such a substantial change in k_0 as observed here. The rate–pH profile therefore augments the anticipation of higher kinetic activity of the hydrolytic species of 1^{3+} .

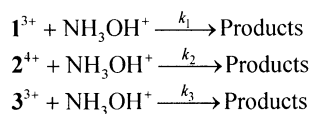
Solution equilibria

As evident from its crystal structure, the complex salt $\mathbf{1}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ contains an ethanoate bridge, and two oxo-bridges. There is also one bipy and one water molecule directly coordinated to each Mn(IV) ion.^{6a} The ethanoate bridge and a bipy ligand are labile and dissociates in aqueous solutions according to equilibria (5) and (6).^{5d} The solution is otherwise stable under the present experimental conditions.

A labile ethanoate bridge is found also in the dinuclear Mn(III,IV) complex $[\text{Mn}^{\text{III,IV}}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{fac-bpea})_2]^{2+}$ [bpea is *N,N*-bis(2-pyridylmethyl)ethylamine] and in its diferric analogue, $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-MeCO}_2)_2(\text{L})_2]^{2+}$ (L is substituted bpea).^{32–34} The chelating ligands in the complexes $[\text{L}'_2\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}\text{L}'_2]^{3+}$ (L' = 2,2'-bipyridine or 1,10-phenanthroline) are also labile.^{5b,c,e,27e,35,36} The binding sites in the S_3 -states [the S-state notation^{2a} identifies the number of oxidising equivalents stored in the manganese cluster in the water oxidation complex of PS II] are labile and exchange ^{18}O -labeled water in <1 s.³⁷ However, the bridging oxo-ligands are kinetically inert.^{38,39} Interestingly, equilibrium as well as kinetic studies^{5d,40} suggest that coordinated water molecules in $\mathbf{1}^{3+}$ and its aqua derivatives do not deprotonate, at least up to pH 5.50. The weak acidity of coordinated water is known also for $[\text{Mn}^{\text{IV}}_3(\mu\text{-O})_4(\text{bipy})_4(\text{H}_2\text{O})_2]^{4+}$ (ref. 41) and $[\text{Mn}(\text{pd})_2(\text{H}_2\text{O})_2]^+$ (pd is petane-2,4-dione). The latter complex has a $\text{p}K_{\text{a}}$ value of 7.3.^{42–44} The weak acidity observed is consistent with recent findings that the strength of O–H bond in water coordinated to higher valent manganese is comparable to that for phenolic O–H bond strength in tyrosine.¹⁰

Kinetics and reaction scheme

The trend in the dependence of k_0 on c_{R} , c_{bipy} , c_{OAc} and pH may be reconciled with the following rate scheme, where the analytical concentrations of the manganese species can be derived from equilibria (5) and (6).



which leads to the rate-law

$$k_0 = \{(k_1A + k_2B + k_3C)/(A + B + C)\}[\text{H}^+]c_{\text{R}}/(K_{\text{a}} + [\text{H}^+]) \quad (7)$$

where, $A = K_{\text{HOAc}}K_{\text{Hbipy}}c_{\text{OAc}}c_{\text{bipy}}$, $B = K_{12}K_{\text{Hbipy}}c_{\text{bipy}}(K_{\text{HOAc}} + [\text{H}^+])$ and $C = K_{13}K_{\text{HOAc}}c_{\text{OAc}}(K_{\text{Hbipy}} + [\text{H}^+])$, which may be rearranged to eqn. (8).

$$k_0/c_{\text{R}} \{K_{\text{HOAc}}K_{\text{Hbipy}}c_{\text{OAc}}c_{\text{bipy}} + K_{12}K_{\text{Hbipy}}c_{\text{bipy}}(K_{\text{HOAc}} + [\text{H}^+]) + K_{13}K_{\text{HOAc}}c_{\text{OAc}}(K_{\text{Hbipy}} + [\text{H}^+])\} = \{k_1K_{\text{HOAc}}K_{\text{Hbipy}}c_{\text{OAc}}c_{\text{bipy}} + k_2K_{12}K_{\text{Hbipy}}c_{\text{bipy}}(K_{\text{HOAc}} + [\text{H}^+]) + k_3K_{13}K_{\text{HOAc}}c_{\text{OAc}}(K_{\text{Hbipy}} + [\text{H}^+])\}[\text{H}^+]/(K_{\text{a}} + [\text{H}^+]) \quad (8)$$

where $K_{12} = [(1.0 \pm 0.1) \times 10^{-2}] \text{ mol dm}^{-3}$ (ref. 5d), $K_{13} = [(1.0 \pm 0.1) \times 10^{-3}] \text{ mol dm}^{-3}$ (ref. 5d), $K_{\text{HOAc}} = [\text{H}^+][\text{OAc}^-]/[\text{HOAc}] = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ (ref. 45), $K_{\text{Hbipy}} = [\text{H}^+][\text{bipy}]/[\text{Hbipy}] = 3.8 \times 10^{-5} \text{ mol dm}^{-3}$ (ref. 46) and $K_{\text{a}} = [\text{H}^+][\text{NH}_2\text{OH}]/[\text{NH}_3\text{OH}^+] = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$ (ref. 31).

The rate equation can be transformed into a set of simultaneous equations $a_i = k_1x_i + k_2y_i + k_3z_i$, where a = left-hand side of eqn. (8) and x , y , z are the known functions containing known values of the parameters K_{HOAc} , c_{OAc} , K_{Hbipy} , c_{bipy} and $[\text{H}^+]$. The rate constants k_1 , k_2 and k_3 (Table 3) were evaluated by solving the series of simultaneous equations using Gauss's method.⁴⁷ These values reproduce k_0 values within a maximum

of 3%. This supports the reaction scheme with the NH_3OH^+ as the only active reductant towards the tetravalent metal centres. We anticipate that the hard donor oxygen prefers hard Mn^{IV} centres in the title complex.

As discussed earlier, the spectral detection of the Mn(III,IV) species likely indicates that $\mathbf{1}^{3+}$ and its hydrolytic derivatives are reduced by one-electron steps. We have verified that $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ very rapidly reduces $[(\text{bipy})_2\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$ to Mn^{II} under the present reaction conditions and hence the change $\text{Mn}^{\text{IV}}_2 \rightarrow \text{Mn}^{\text{III,IV}}_2$ seems to be the only rate determining step. Nevertheless, none of these observations and arguments, can firmly discard the possibility of a two-electron reduction of $\text{Mn}^{\text{IV}}_2 \rightarrow \text{Mn}^{\text{III}}_2$ followed by a fast comproportionation reaction, $\text{Mn}^{\text{III}}_2 + \text{Mn}^{\text{IV}}_2 \rightarrow 2\text{Mn}^{\text{III,IV}}_2$. Such a reaction has a remarkably high ($10^{15.6}$) comproportionation constant.^{27c}

The immediate (one-electron) oxidation product of NH_3OH^+ is NH_2OH^+ which is known to generate N_2O via HNO^{\cdot} . Trace metal ions³¹ in solution strongly catalyse the oxidation of hydroxylamine and affects both rate and the oxidation product. Ambient light also sometimes plays a definite role. In our experiments use of excess bipyridyl sequestered trace metal ions, if any, and we observed no effect of diffuse light in our system, or if the reaction medium is purged with dinitrogen.

The observed sequence of rate constants $k_1 < k_2 < k_3$ indicates that the redox reactivity of the Mn^{IV}_2 complexes increases with the increased number of water molecules in the coordination sphere of a Mn centre. This trend is, however, not a speciality for the binuclear complexes, it is also well documented for higher valent mononuclear manganese complexes.^{44,48} In our system, the maximum number (3) of water molecules at each Mn^{IV} centre is found in $\mathbf{3}^{3+}$, which is oxidised with the highest rate. It is likely that increased aquation makes the oxidant more electron deficient with a concomitant increase in the electron affinity of the metal centres. Moreover, replacement of the rigid chelate rings with monodentate aqua ligands makes the complex more flexible with reduced Franck–Condon⁴⁹ barrier to electron transfer. Also removal of bulky chelating agents reduces the effective volume of the complex; the internuclear distance between the redox partners in the activated state is thus reduced. It was reported that electron transfer from hydroxylamine to Ir^{IV} in $[\text{IrCl}_6]^{2-}$ occurs via a weak outer-sphere association complex.⁵⁰ The self-exchange rate constant between the perfect octahedral couple $[\text{IrCl}_6]^{2-}/[\text{IrCl}_6]^{3-}$ is high ($2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)⁵¹ and is expected to exceed those for the more rigid molecules $\mathbf{1}^{3+}$, $\mathbf{2}^{4+}$ and $\mathbf{3}^{3+}$. The self-exchange rate for $[\text{IrCl}_6]^{3-}$ may thus be taken to be an upper limit for the self-exchange rate of species $\mathbf{1}^{3+}$.

The self-exchange rate constant for the couple $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}^+$ may roughly be taken as that for $\text{NH}_2\text{OH}/\text{NH}_2\text{OH}^+$ couple (5×10^{-13}).¹⁹ Using the Marcus cross-relation,⁵² the equilibrium constant (K) for the cross-reaction $k_{12} = (k_{11}k_{22}K)^{1/2}$ can then be estimated. Hence, for the species $\mathbf{1}^{3+}$, from the estimated K value, the lower limit of E°_{ox} for $\mathbf{1}^{3+}$ becomes ~ 1 V. However, the cyclic voltammogram of $\mathbf{1}^{3+}$ in CH_3CN shows an irreversible wave at 0.33 V versus SCE corresponding to the (IV,IV)/(III,III) couple.^{6b} Hence, the E°_{ox} value calculated from Marcus relation refutes an outer sphere pathway. Stated simply, the remarkably low self-exchange rate of the $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}^+$ couple and a poor reducing character of NH_3OH^+ disfavours outer-sphere reactions.

In the presence of $\sim 6\%$ (v/v) acrylonitrile no cloudiness in the solution due to polymerisation was observed during the reactions which might suggest that the radicals generated by the one-electron oxidation of NH_3OH^+ rapidly reduce the successor complex before they can escape into the bulk solvent. This perhaps indicates the inner-sphere nature of the reactions where the radicals are generated and consumed within the coordination sphere of the metal complex.

In order to further explore the mechanism, we measured k_0 in aqueous media partially substituted with D_2O . The ratio of

Table 3 Comparison of k_1 , k_2 and k_3 in H₂O and in H₂O–D₂O (1 : 9)

Rate constant/dm ³ mol ⁻¹ s ⁻¹	H ₂ O	H ₂ O–D ₂ O (1 : 9)	$k_{\text{H}_2\text{O}}/k_{\text{H}_2\text{O-D}_2\text{O}}$ (1 : 9)
k_1	0.287 ± 0.015	0.013 ± 0.003	22.1
k_2	13.1 ± 0.350	1.45 ± 0.051	9.03
k_3	25.1 ± 0.501	2.54 ± 0.072	9.88

k_0 in pure H₂O (at pH 4.40) to that in a 90% D₂O–water mixture [$c_{\text{bipy}} = 0.005 \text{ mol dm}^{-3}$, $c_{\text{OAc}} = 0.1 \text{ mol dm}^{-3}$ and at $c_{\text{R}} = 1.0 \text{ mmol dm}^{-3}$, $\text{pH}_{\text{measured}} = 4.40$] is substantial (13 : 1). Variations in rate resulting from substitution of D₂O for solvent H₂O are expected to be slight for simple electron transfer reactions. However, dramatic rate retardation is expected when such transfer is coupled with the movement of a proton which is in equilibrium with solvent protons.⁵³ It is also noticeable that the plot of k_0 versus mol fraction of D₂O is linear (regression coefficient, $r > 0.99$) (Fig. 4). According to Albery and Davies⁵⁴ this is indicative of the transfer of just a single proton in the redox process.

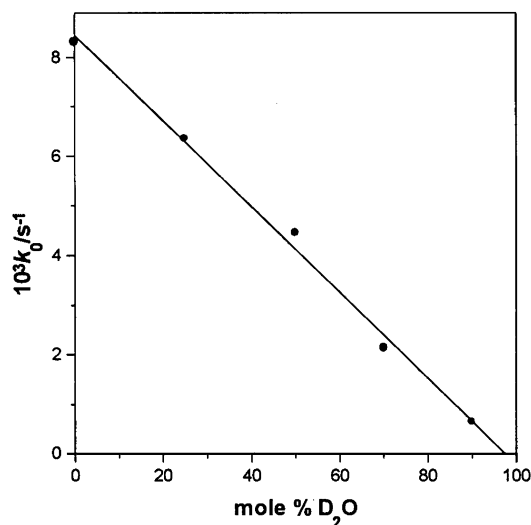


Fig. 4 Effect of mol% D₂O on k_0 ; [complex] = 0.1 mmol dm⁻³, $c_{\text{bipy}} = 0.005 \text{ mol dm}^{-3}$, $c_{\text{OAc}} = 0.1 \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, $c_{\text{R}} = 1.0 \text{ mmol dm}^{-3}$, $T = 25^\circ\text{C}$, $\text{pH}_{\text{measured}} = 4.40$.

We cannot conclude from Fig. 4 that D₂O retards either or all the reaction paths, but further kinetic studies in 90 mol% D₂O medium demonstrates unequal retardation for the three paths. The rate constants k_1 , k_2 and k_3 in 90% D₂O have been compared with those in H₂O in Table 3. This demonstrates that replacement of H₂O by D₂O most strongly affects the k_1 path (22.1× rate retardation). The effects on k_2 and k_3 are relatively modest (9–10× rate retardation), though large in itself.

The observed difference in solvent isotope effect probably reflects a difference in the basicity of the oxo-bridge in the species 1^{3+} , 2^{4+} and 3^{3+} . Replacement of more basic ligands like ethanoate and bipy with less basic aqua ligands⁵⁵ should render the manganese centre more electron accepting and the oxo-bridges less basic. Ghosh *et al.*^{5a} established an electroprotic pathway for the reduction of [(bipy)₂Mn^{IV}(μ-O)₂Mn^{III}(bipy)₂]³⁺ to [(bipy)₂Mn^{III}(μ-O)(μ-OH)Mn^{III}(bipy)₂]³⁺ by ascorbate and hydroquinone. Some electrochemical and chemical investigation further established the oxo-bridge to be a potential basic site for protonation in multinuclear manganese complexes.^{27a,c,36,41,56} Hence reduced basicity of the oxo-bridge is a likely cause for reduced solvent isotope effect.

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References

- (a) K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1153; (b) J. B. Vincent and G. Christou, *Adv. Inorg. Chem.*, 1989, **33**, 197; (c) A. W. Rutherford, *Trends Biochem. Sci.*, 1989, **14**, 227; (d) G. W. Brudvig and R. H. Crabtree, *Prog. Inorg. Chem.*, 1989, **37**, 99; (e) V. L. Pecoraro, *Photochem. Photobiol.*, 1988, **48**, 249; (f) G. C. Dismukes, *Photochem. Photobiol.*, 1986, **43**, 99; (g) R. Manchanda, G. W. Brudvig and R. H. Crabtree, *Coord. Chem. Rev.*, 1995, **144**, 1; (h) L. Que, Jr. and A. E. True, *Prog. Inorg. Chem.*, 1990, **38**, 97.
- (a) B. Kok, B. Forbush and M. P. McGloin, *Photochem. Photobiol.*, 1970, **11**, 457; (b) P. Joliot, G. Barbieri and R. Chabaud, *Photochem. Photobiol.*, 1969, **10**, 302.
- (a) V. J. DeRose, V. K. Yachandra, Ann E. McDermott, R. D. Britt, K. Sauer and M. P. Klein, *Biochemistry*, 1991, **30**, 1335; (b) R. D. Guiles, J.-L. Zimmerman, Ann E. McDermott, V. K. Yachandra, J. L. Cole, S. L. Dexheimer, R. D. Britt, K. Wieghardt, U. Bossek, K. Sauer and M. P. Klein, *Biochemistry*, 1990, **29**, 471; (c) N. Tamura, M. Ikeuchi and Y. Inoue, *Biochim. Biophys. Acta*, 1989, **973**, 281; (d) Y. Takohashi and S. Katoh, *Biochim. Biophys. Acta*, 1986, **848**, 183; (e) V. K. Yachandra, R. D. Guiles, A. E. McDermott, R. D. Britt, S. L. Dexheimer, K. Sauer and M. P. Klein, *Biochim. Biophys. Acta*, 1986, **850**, 324.
- (a) G. Christou, *Acc. Chem. Res.*, 1989, **22**, 328; (b) G. Renger, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 643; (c) G. C. Dismukes, *Chem. Rev.*, 1996, **96**, 2909; (d) V. K. Yachandra, K. Sauer and M. P. Klein, *Chem. Rev.*, 1996, **96**, 2927; (e) W. Rüttinger and G. C. Dismukes, *Chem. Rev.*, 1997, **97**, 1; (f) M. Yagi and M. Kaneko, *Chem. Rev.*, 2001, **101**, 21.
- (a) M. C. Ghosh, J. W. Reed, R. N. Bose and E. S. Gould, *Inorg. Chem.*, 1994, **33**, 73; (b) S. Chaudhuri, S. Mukhopadhyay and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1995, 621; (c) S. Kundu, A. K. Bhattacharya and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1996, 3951; (d) A. K. Bhattacharya, A. B. Mondal and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1997, 2351; (e) R. Banerjee, B. Mondal and S. Kundu, *J. Chem. Soc., Dalton Trans.*, 1997, 4341; (f) A. K. Bhattacharya, A. B. Mondal, A. C. Dash, G. S. Brahma and R. Banerjee, *Can. J. Chem.*, 1999, **77**, 451; (g) D. Maji and R. Banerjee, *Transition Met. Chem.*, 2001, **26**, 544; (h) U. Roy Choudhury, S. Banerjee and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 2000, 589.
- (a) K. R. Reddy, M. V. Rajasekharan, S. Padhye, F. Dahan and J. P. Tuchagues, *Inorg. Chem.*, 1994, **33**, 428; (b) B. C. Dave, R. S. Czernuszewicz, M. R. Bond and C. J. Carrano, *Inorg. Chem.*, 1993, **32**, 3593.
- K. Wieghardt, *Adv. Inorg. Bioinorg. Mech.*, 1984, **3**, 213.
- R. A. Scott, G. P. Haight, Jr., and J. N. Cooper, *J. Am. Chem. Soc.*, 1974, **96**, 4136.
- In the absence of any concrete data on N–H bond energy of hydroxylamine, we anticipate that this will be close to the reported N–H bond energy in NH₃ or amines. See, for example: (a) E. A. Moelwyn-Hughes, *Physical Chemistry*, Pergamon Press, New York, 2nd revised edn., 1961, p. 1042; (b) J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Addison-Wesley Publishing Company, New York, 4th edn., 1993.
- (a) M. T. Caudle and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1997, **119**, 3415; (b) M. R. A. Blomberg, P. E. M. Siegbahn, S. Strying, G. T. Babcock, B. Akermark and P. Korall, *J. Am. Chem. Soc.*, 1997, **119**, 8285.
- A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis*, The English Language Book Society and Longmans, Green & Co Ltd, London, 3rd edn., 1964, p. 391.
- (a) S. Mukhopadhyay and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1994, 1349; (b) S. Banerjee, U. Roy Choudhury, B. C. Ray, R. Banerjee and S. Mukhopadhyay, *Anal. Lett.*, 2001, **34**, 2797.

- 13 (a) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, 1960, **64**, 188; (b) R. A. Binstead, M. E. McGuire, A. Dovletoglou, W. K. Seok, L. E. Roecker and T. J. Meyer, *J. Am. Chem. Soc.*, 1992, **114**, 173.
- 14 W. M. Banick and G. F. Smith, *Anal. Chim. Acta.*, 1958, **19**, 304.
- 15 J. N. Cooper and D. W. Margerum, *Inorg. Chem.*, 1993, **32**, 5905.
- 16 R. C. Beckwith, J. N. Cooper and D. W. Margerum, *Inorg. Chem.*, 1994, **33**, 5144.
- 17 G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, ELBS, Essex, UK, 5th edn., 1994, p. 702.
- 18 G. Charlot, *Colorimetric Determination of Elements: Principles and Methods*, Elsevier Publishing Company, New York, 1964, p. 324.
- 19 M.-L. Hung, M. L. McKee and D. M. Stanbury, *Inorg. Chem.*, 1994, **33**, 5108.
- 20 (a) R. M. Liu, M. R. McDonald and D. W. Margerum, *Inorg. Chem.*, 1995, **34**, 6093; (b) O. P. Strausz and H. F. Gunning, *Trans. Faraday Soc.*, 1964, **60**, 347; (c) D. Behar, D. Shapira and A. Treinin, *J. Phys. Chem.*, 1972, **76**, 180.
- 21 (a) W. A. Waters and I. R. Wilson, *J. Chem. Soc. A*, 1966, 534; (b) R. Swaroop and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, 1974, **36**, 169; (c) G. Rabai and M. T. Beck, *J. Chem. Soc., Dalton Trans.*, 1982, 573.
- 22 (a) J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, 1963, **39**, 1904; (b) J. Q. Adams, S. W. Nicksic and J. R. Thomas, *J. Chem. Phys.*, 1965, **45**, 654; (c) R. Stone and W. A. Waters, *Proc. Chem. Soc., London*, 1962, 253; (d) C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 1965, 751.
- 23 M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 2824.
- 24 J. R. Buchholz and R. E. Powell, *J. Am. Chem. Soc.*, 1963, **85**, 509; J. R. Buchholz and R. E. Powell, *J. Am. Chem. Soc.*, 1965, **87**, 2350.
- 25 D. S. Honig, K. Kustin and J. F. Martin, *Inorg. Chem.*, 1972, **11**, 1895.
- 26 J. E. Sarneski, L. J. Brzezinski, B. Anderson, M. Didiuk, R. Manchanda, R. H. Crabtree, G. W. Brudvig and G. K. Schulte, *Inorg. Chem.*, 1993, **32**, 3265.
- 27 (a) R. Manchanda, H. H. Thorp, G. W. Brudvig and R. H. Crabtree, *Inorg. Chem.*, 1991, **30**, 494; (b) R. Manchanda, H. H. Thorp, G. W. Brudvig and R. H. Crabtree, *Inorg. Chem.*, 1992, **31**, 4040; (c) S. R. Cooper and M. Calvin, *J. Am. Chem. Soc.*, 1977, **99**, 6623; (d) S. Pal, M. K. Chan and W. H. Armstrong, *J. Am. Chem. Soc.*, 1992, **114**, 6398.
- 28 K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols and J. J. Girerd, *J. Am. Chem. Soc.*, 1988, **110**, 7398.
- 29 W. Hillier, P. Lukins, M. Seibert and T. Wydrzynski, *Biochemistry*, 1997, **36**, 76.
- 30 K. J. Brewer, M. Calvin, R. S. Lumpkin, J. W. Otvos and L. O. Spreer, *Inorg. Chem.*, 1989, **28**, 4446.
- 31 G. Bengtson, *Acta Chem. Scand. Ser. A*, 1983, **37**, 639.
- 32 S. Menage, J. M. Vincent, C. Lambeaux, G. Chottard, A. Grand and M. Fontecave, *Inorg. Chem.*, 1993, **32**, 4766.
- 33 S. Pal, M. M. Olmstead and W. H. Armstrong, *Inorg. Chem.*, 1995, **34**, 4708.
- 34 S. Ito, T. Okuno, H. Matsushima, T. Tokii and Y. Nishida, *J. Chem. Soc., Dalton Trans.*, 1996, 4037.
- 35 B. Mondal, S. Kundu and R. Banerjee, *Polyhedron*, 1997, **16**, 2199.
- 36 R. Manchanda, G. W. Brudvig and R. H. Crabtree, *New J. Chem.*, 1994, **18**, 561.
- 37 (a) J. Messinger, M. Badger and T. Wydrzynski, *Proc. Natl. Acad. Sci. USA.*, 1995, **92**, 3209; (b) J. Messinger, M. Hillier, M. Badger and T. Wydrzynski, in *Photosynthesis: From Light to Biosphere*, ed. P. Mathis, Kluwer, Dordrecht, The Netherlands, 1995, pp. 283–286.
- 38 (a) G. S. Waldo, S. Yu and J. E. Penner-Hahn, *J. Am. Chem. Soc.*, 1992, **114**, 5869; (b) S. Khangulov, M. Sivaraja, V. V. Barynin and G. C. Dismukes, *Biochemistry*, 1993, **32**, 4912; (c) M. Shank, V. Barynin and G. C. Dismukes, *Biochemistry*, 1994, **33**, 15433.
- 39 C. W. Hoganson and G. T. Babcock, *Science*, 1997, **227**, 1953.
- 40 A. B. Mondal, A. K. Bhattacharya, D. Maji and R. Banerjee, *Polyhedron*, 1998, **17**, 1693.
- 41 J. E. Sarneski, H. H. Thorp, G. W. Brudvig, R. H. Crabtree and G. K. Schulte, *J. Am. Chem. Soc.*, 1990, **112**, 7255.
- 42 G. H. Cartledge, *J. Am. Chem. Soc.*, 1951, **73**, 4416.
- 43 G. H. Cartledge, *J. Am. Chem. Soc.*, 1952, **74**, 6015.
- 44 S. Mukhopadhyay and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1993, 933.
- 45 D. D. Perrin, *J. Phys. Chem.*, 1958, **62**, 767.
- 46 (a) P. Krumholz, *Nature*, 1949, **163**, 724; (b) P. Krumholz, *J. Am. Chem. Soc.*, 1949, **71**, 3654; (c) M. Yasuda, K. Sane and K. Yamaski, *J. Phys. Chem.*, 1956, **60**, 1667.
- 47 J. B. Scarborough, *Numerical Mathematical Analysis*, John Hopkins Press, Baltimore, USA, 6th edn., 1966, ch. 12.
- 48 (a) R. Banerjee, R. Das and A. K. Chakraborty, *J. Chem. Soc., Dalton Trans.*, 1990, 3277; (b) S. Mukhopadhyay, S. Chaudhuri and R. Banerjee, *Can. J. Chem.*, 1993, **71**, 2155.
- 49 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley Eastern Limited, New Delhi, 2nd edn., 1977, ch. 6.
- 50 Ms. Rekha, A. Prakash and R. N. Mehrotra, *Can. J. Chem.*, 1993, **71**, 2164.
- 51 D. M. Stanbury, W. K. Wilmarth, S. Khalaf, H. N. Po and J. E. Byrd, *Inorg. Chem.*, 1980, **19**, 2715.
- 52 (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; (b) R. A. Marcus and N. Sutin, *Inorg. Chem.*, 1975, **14**, 213.
- 53 P. N. Dickson and D. W. Margerum, *Anal. Chem.*, 1986, **58**, 3153.
- 54 W. J. Albery and M. H. Davies, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 162.
- 55 (a) G. Charlot and D. Bezier, *Quantitative Inorganic Analysis*, (English Version of 3rd French edn.), John Wiley and Sons, Inc., New York, 1957, p. 23; (b) J. Waser, *Quantitative Chemistry A Laboratory Text*, W. A. Benjamin, Inc., New York, 1964, p. 208.
- 56 (a) J. M. Carroll and J. R. Norton, *J. Am. Chem. Soc.*, 1992, **114**, 8744; (b) E. J. Larson, P. J. Riggs, J. E. Penner-Hahn and V. L. Pecoraro, *J. Chem. Soc., Chem. Commun.*, 1992, 102.