

## Reactions of sulfur(IV) with an octahedral manganese(IV) complex of 1,8-bis(2-hydroxy benzamido)-3,6-diaza octane: the role of phenolate–amide–amine coordination

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### Abstract

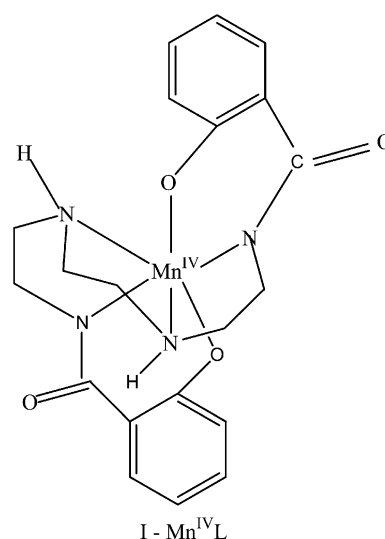
The  $\text{Mn}^{\text{IV}}$  complex of tetra-deprotonated 1,8-bis(2-hydroxybenzamide)-3,6-diazaoctane ( $\text{Mn}^{\text{IV}}\text{L}$ ) engrossed in phenolate-amido-amine coordination is reduced by  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  in the pH range 3.15–7.3 displaying biphasic kinetics, the  $\text{Mn}^{\text{III}}\text{L}^-$  being the reactive intermediate. The  $\text{Mn}^{\text{III}}\text{L}^-$  species has been characterized by u.v.–vis. spectra  $\{\lambda_{\text{max}}, (\epsilon, \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})\}$ : 285(15 570), 330 sh (7570), 469(6472), 520 sh (5665), pH = 5.42}.  $\text{SO}_4^{2-}$  was the major oxidation product of  $\text{S}^{\text{IV}}$ ; dithionate is also formed ( $18 \pm 2\%$  of  $[\text{Mn}^{\text{IV}}]_{\text{T}}$ ) which suggests that dimerisation of  $\text{SO}_3^{\bullet-}$  is competitive with its fast oxidation by  $\text{Mn}^{\text{IV/III}}$ . The rates and activation parameters for  $\text{Mn}^{\text{IV}}\text{L} + \text{HSO}_3^- (\text{SO}_3^{2-}) \rightarrow \text{Mn}^{\text{III}}\text{L}^-$ ;  $\text{Mn}^{\text{III}}\text{L}^- + \text{HSO}_3^- (\text{SO}_3^{2-}) \rightarrow \text{Mn}^{\text{II}}\text{L}^{2-}$  are reported at 28.5–45.0 °C ( $I = 0.3 \text{ mol dm}^{-3}$ , 10% (v/v) MeOH +  $\text{H}_2\text{O}$ ). Reduction by  $\text{SO}_3^{2-}$  is *ca.* eight times faster than by  $\text{HSO}_3^-$  both for  $\text{Mn}^{\text{IV}}\text{L}$  and  $\text{Mn}^{\text{III}}\text{L}^-$ . There was no evidence of  $\text{HSO}_3^-/\text{SO}_3^{2-}$  coordination to the Mn centre indicating an outer sphere (ET) mechanism which is further supported by an isokinetic relationship. The self exchange rate constant ( $k_{22}$ ) for the redox couple,  $\text{Mn}^{\text{III}}\text{L}^-/\text{Mn}^{\text{IV}}\text{L}$  ( $1.5 \times 10^6 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  at 25 °C) is reported.

### Introduction

This work stems from our research activity on the reactions of sulfur(IV) with transition metal ions and their complexes in solution [1]. Manganese is a trace metal ion with potential biological activity as it is present in several oxido-reductase and hydrolytic enzymes [2].

One of the most important biological reactions is water oxidation which is brought about by a polymeric manganese complex (dimer of dimers) involving the metal ion in higher oxidation states in the photosystem II [2, 3]. The biomimetic chemistry of water oxidation has, therefore, aroused great concern and has led to tremendous advancement of our knowledge on synthetic, structural and kinetic studies of polynuclear manganese complexes involving the metal ion in +2, +3 and +4 oxidation states [1–4]. However, there are scanty reports on the synthesis and structural aspects of mononuclear  $\text{Mn}^{\text{III/IV}}$  complexes [5]. The reports on their kinetic investigations are also very limited [6]. We have chosen an octahedral  $\text{Mn}^{\text{IV}}$  complex of 1,8-bis(2-hydroxybenzamido)-3,6-diazaoctane ( $\text{LH}_4$ ), with potential  $\text{N}_4\text{O}_2$  donor functions *i.e.* two amido, two phenolate and two *sec*-NH in the ligand frame. The complex  $\text{Mn}^{\text{IV}}\text{L}$  (I) in which the amide and phenol groups are deprotonated has been fully structurally characterized by Chakra-

vorty *et al.* [5f]. Our intention was to investigate the kinetics and mechanism of the reactions of sulfur(IV) ( $\text{SO}_2$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ) with this  $\text{Mn}^{\text{IV}}$  complex in order to examine the role of the *phenolate-amide-amine* coordination on the stability of the +4 oxidation state of Mn in its complex. We also hoped that this study would further our knowledge of the possible reactions of sulfur(IV) on Mn based biologically active molecules.



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## Experimental

### Materials

Mn<sup>III</sup> acetate, Mn(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> · 2H<sub>2</sub>O, was a Merck-Schuchardt (Germany) product.

MeOH was G.R. grade (Merck, purity 99.8%). Double distilled H<sub>2</sub>O was used; the second distillation was made from alkaline KMnO<sub>4</sub> using all-glass distillation apparatus. All other chemicals used in the kinetic study were of analytical grade. Sodium  $\mu$ -oxo-tetraoxodisulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, was the source of S<sup>IV</sup> which is very stable in the solid state and rapidly hydrolyses in aqueous medium to an equilibrium mixture of SO<sub>2</sub>-HSO<sub>3</sub><sup>-</sup>-SO<sub>3</sub><sup>2-</sup> · NaClO<sub>4</sub> was prepared by mixing freshly prepared and standardized stock solutions of NaOH and HClO<sub>4</sub> (each 2 mol dm<sup>-3</sup>) and digesting at ~70 °C in a water bath. The stock solution of NaClO<sub>4</sub> (1 mol dm<sup>-3</sup>) was adjusted to pH 6 and was estimated for Na<sup>+</sup> by a combined ion-exchange alkalimetric procedure. The resins Dowex 50W × 8 (Na<sup>+</sup>) and Amberlite IRA 400 (Cl<sup>-</sup>) used for ion-exchange experiments were pre-treated with alkaline H<sub>2</sub>O<sub>2</sub>. The cation and anion exchange resins were then converted into H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> forms, respectively, with HClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>.

### Physical measurements

Electronic spectra were recorded on a Varian 1E u.v.-vis. spectrophotometer and a Systronic (India) spectrophotometer model 119 using 10 mm matched quartz cells. IR spectra were recorded on a Nicolet FT-IR spectrometer using a KBr disc. The micro analytical data were collected using a Perkin-Elmer 240C elemental analyzer. Manganese was estimated using a Varian AA 1475 atomic absorption spectrophotometer. The pH measurements were made by a Systronics (India) digital pH meter 335 equipped with a combined glass -Ag/AgCl, Cl<sup>-</sup> (2 mol dm<sup>-3</sup> NaCl) electrode. NBS buffers of pH 4.01, 6.86 and 9.20 were used to check the performance of the meter. The pH data were converted into p[H<sup>+</sup>] = (-log [H<sup>+</sup>]) by a calibration curve using HClO<sub>4</sub> in the range 3.0 ≤ p[H<sup>+</sup>] ≤ 6.0 [1a, 7]. The kinetic measurements were made spectrophotometrically using a Systronics spectrophotometer model 119.

### Preparation of the ligand and the complex

The ligand, 1,8-bis(2-hydroxybenzamido)-3,6-diazaoctane (LH<sub>4</sub>) and its complex, Mn<sup>IV</sup>L, 4H<sub>2</sub>O, were synthesized as described by Chandra and Chakravorty [5g], except that methyl salicylate was used instead of ethyl salicylate. (MnC<sub>20</sub>H<sub>30</sub>N<sub>4</sub>O<sub>8</sub> calcd.: Mn, 10.8; C, 47.2; H, 5.9; N, 11.0%. Found: Mn, 10.6; C, 47.4; H, 5.9; N, 10.8%).  $\lambda_{\text{max}}$  ( $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 525sh (5110), 465(5881), 335sh(7219), 286 (15270) (10% MeOH + H<sub>2</sub>O) in

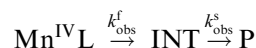
satisfactory agreement with the data reported by Chandra and Chakravorty [5g]. IR ( $\nu$ , cm<sup>-1</sup>): 3415, 3094 ( $\nu_{\text{str}}$ . for H<sub>2</sub>O, N-H of the sec. amine); 1595, 1571, 1515, 1466, 1447, [ $\nu_{\text{str}}$ (C=O) of the deprotonated sec. amide, bending mode of H<sub>2</sub>O and N-H (sec. amine), and C=C skeletal vibration of aromatic groups], 1359, 1235 [ $\nu_{\text{str}}$ (C-O of the coordinated phenolate),  $\nu_{\text{str}}$ (C-N, sec. amine)], 668 ( $\nu_{\text{str}}$ . Mn<sup>IV</sup>-O), 574 ( $\nu_{\text{str}}$ . Mn<sup>IV</sup>-N); 418 (deformation of C-N sec. amine) [8]. Absence of bands in the range 1700-1630 cm<sup>-1</sup> stands in support of the deprotonated amide coordinated to Mn<sup>IV</sup>.

### Kinetics

The kinetics of acid catalyzed decomposition and S<sup>IV</sup> oxidation of Mn<sup>IV</sup>L were investigated spectrophotometrically (469 nm) under pseudo-first order conditions; 10% (v/v) MeOH + H<sub>2</sub>O medium was used due to the solubility limitations of the complex in a fully aqueous medium. The stock complex solution was prepared in 40% MeOH + H<sub>2</sub>O and was protected from light. The concentration of the complex in the reaction mixture was varied within the limits {(6.5-8.5) × 10<sup>-5</sup> mol dm<sup>-3</sup>}. The acid catalyzed decomposition of Mn<sup>IV</sup>L was studied at 0.05 ≤ [H<sup>+</sup>]<sub>T</sub> mol dm<sup>-3</sup> ≤ 0.6 ( $I = 0.6$  mol dm<sup>-3</sup>, 28.50 °C). The S<sup>IV</sup> oxidation was studied as a function of pH (3.15 ≤ pH ≤ 7.3) and [S<sup>IV</sup>]<sub>T</sub> (0.005 ≤ [S<sup>IV</sup>]<sub>T</sub> mol dm<sup>-3</sup> ≤ 0.10) at  $I = 0.3$  mol dm<sup>-3</sup> (28.5 ≤  $t/^\circ\text{C} \leq 45.0$ ). Dilute AcONa/AcOH and MES buffers [9] were used to control pH. Some runs were also made using self-buffered HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> (pH > 6.5). The absorbance ( $A$ )-time ( $t/s$ ) curves (Figure 1) were bi-exponentials (Equation 1),

$$A_t = A_\infty + C_1 \exp(-k_{\text{obs}}^f t) + C_2 \exp(-k_{\text{obs}}^s t) \quad (1)$$

characteristic of consecutive reactions:



for which

$$C_1 = A_0 - A'_0 \frac{k_{\text{obs}}^f}{(k_{\text{obs}}^f - k_{\text{obs}}^s)} \quad \text{and} \quad C_2 = A'_0 \frac{k_{\text{obs}}^s}{(k_{\text{obs}}^f - k_{\text{obs}}^s)}$$

where  $A_0$  and  $A'_0$  denote the absorbances of Mn<sup>IV</sup>L and the intermediate (INT) respectively for the same total concentration [10]. Mn<sup>IV</sup>L and the intermediate were the absorbing species at the working wavelength with little contribution of absorbance from the end products.  $A_\infty$  was < 0.02 and  $A_0 - A_\infty$  was ~0.5 absorbance units (for [Mn<sup>IV</sup>L]<sub>T</sub> = 8.5 × 10<sup>-5</sup> mol dm<sup>-3</sup>). As a check a few runs were also made in nitrogen saturated solutions. There was practically no measurable effect on the kinetics and the values of  $k_{\text{obs}}$  agreed with those obtained for solutions under identical conditions which were not rigorously deaerated.

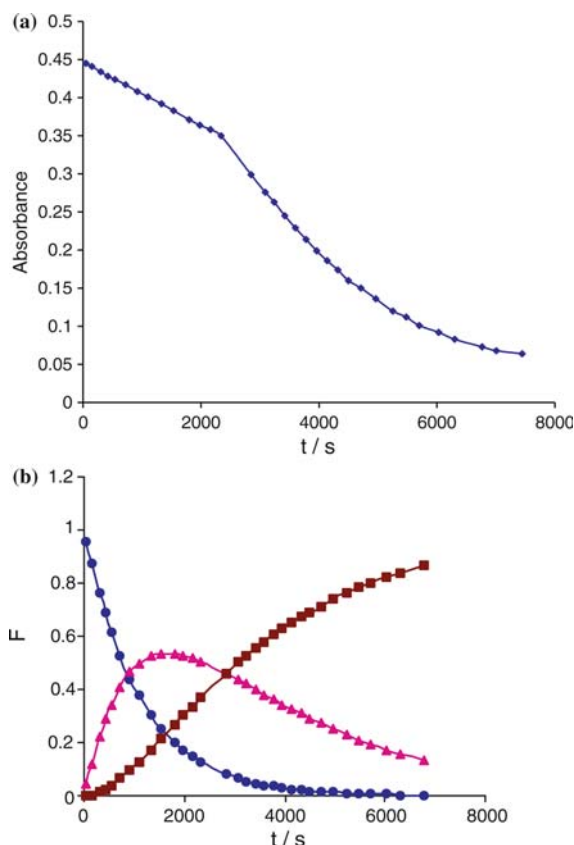


Fig. 1. (a) Absorbance (469 nm) versus time plot showing biphasic kinetics for the reduction of  $\text{Mn}^{\text{IV}}\text{L}$  by  $\text{S}^{\text{IV}}$ :  $[\text{Mn}^{\text{IV}}\text{L}]_{\text{T}} = 8.3 \times 10^{-5}$ ,  $[\text{S}^{\text{IV}}]_{\text{T}} = 0.03$ ,  $I = 0.3 \text{ mol dm}^{-3}$ ,  $\text{pH} = 5.3$  ( $28.5^\circ\text{C}$ , 10% (v/v) MeOH +  $\text{H}_2\text{O}$ ); (b) showing the decay of  $[\text{Mn}^{\text{IV}}\text{L}]_{\text{T}}$ , growth and decay of  $[\text{Mn}^{\text{III}}]_{\text{T}}$  and growth of  $[\text{Mn}^{\text{II}}]_{\text{T}}$  with time ( $t$ ):  $F = [\text{Mn}^{\text{IV}}]_{\text{T}}/[\text{Mn}^{\text{IV}}]_{\text{T}}$  (●),  $[\text{Mn}^{\text{III}}]_{\text{T}}/[\text{Mn}^{\text{IV}}]_{\text{T}}$  (▲),  $[\text{Mn}^{\text{II}}]_{\text{T}}/[\text{Mn}^{\text{IV}}]_{\text{T}}$  (■).

## Results and discussion

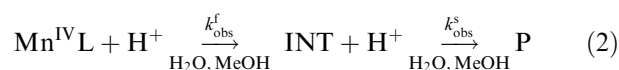
### Preliminary observations

Repetitive spectral scans of the complex  $\text{Mn}^{\text{IV}}\text{L}$  under ambient conditions at  $5.0 \times 10^{-4} \leq [\text{H}^+] \text{ (mol dm}^{-3}) \leq 5.0 \times 10^{-3}$  (10% (v/v) MeOH +  $\text{H}_2\text{O}$ ) over extended time showed that it does not undergo decomposition at  $\text{pH} > 3$ . However, the repetitive spectral scans at  $[\text{H}^+] \geq 0.05 \text{ mol dm}^{-3}$  indicated the slow acid catalyzed decomposition of the complex. In the process the  $\lambda_{\text{max}}$  of the complex at 286 nm is replaced by a maximum at 298 nm with complete disappearance of its absorption maxima at 335, 465 and 525 nm. There is apparently no indication of the build up of any stable intermediate. The final spectrum over long time intervals virtually agreed with the spectrum of the mixture of  $\text{Mn}^{\text{II}}$  and the ligand at the same acidity. It is also interesting to note that the final spectrum of the reaction mixture at  $[\text{H}^+] \geq 0.05 \text{ mol dm}^{-3}$  is not essentially different from that of the ligand alone which is diprotonated at the same acidity ( $\lambda_{\text{max}} = 298 \text{ nm}$  for  $\text{LH}_6^{2+}$ ). Since the spectrum of  $\text{Mn}^{\text{IV}}\text{L}$  is lost, and there is no evidence of residual  $\text{Mn}^{\text{III}}$  from the spectral features of the end product, we conclude that the acid catalyzed decomposition of

$\text{Mn}^{\text{IV}}\text{L}$  is essentially a redox process. Since the ligand concentration was not significantly affected, we were led to believe that  $\text{Mn}^{\text{IV}}\text{L}$  oxidized MeOH and/or water in moderate acidic conditions. This was further put to test by performing the following experiments. (1) The complex,  $\text{Mn}^{\text{IV}}\text{L}$ , was dissolved in fully aqueous medium and in 90% (v/v) MeOH +  $\text{H}_2\text{O}$  in the presence of  $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$  and its u.v.–vis. spectrum was scanned over an extended period. Strikingly the final spectrum in both cases displayed the same characteristic features as mentioned above ( $\lambda_{\text{max}} = 298 \text{ nm}$ ). (2) A known amount of the complex ( $\text{Mn}^{\text{IV}}\text{L}$ ) was dissolved in MeOH acidified with dilute  $\text{H}_2\text{SO}_4$  and the mixture was set aside until the reaction was complete as indicated by total fading of the yellowish brown color of the acidified solution. It was divided into two parts. One part was tested with Tollen's reagent (ammoniacal  $\text{AgNO}_3$ ) which indicated reduction of  $\text{Ag}^+$  (confirmed by dissolving the precipitated black particles after careful washing with distilled  $\text{H}_2\text{O}$ , in dilute  $\text{HNO}_3$  and then adding  $\text{NaCl}$  solution when a curdy white precipitate of  $\text{AgCl}$  was produced). The second part was treated with an acidified MeOH solution of 2,4-dinitrophenyl hydrazine which developed orange red colouration characteristic of the 2,4-dinitrophenyl hydrazone thereby indicating the formation of formaldehyde as an oxidation product of MeOH. (3)  $\text{Mn}^{\text{IV}}\text{L}$  ( $8.9 \times 10^{-5} \text{ mol dm}^{-3}$ ) was treated with hydroxylamine hydrochloride ( $^+\text{NH}_3\text{OH}$ ,  $\text{Cl}^-$ ) ( $0.01 \text{ mol dm}^{-3}$ ) at  $\text{pH} 5.9$  (10% MeOH +  $\text{H}_2\text{O}$ ). The reduction of  $\text{Mn}^{\text{IV}}\text{L}$  by hydroxylamine at this pH was slow as indicated by the repetitive spectral scans. However, the final spectrum (after 30 h) displayed only one absorption maximum at 298 nm with intensity comparable to that of ( $\text{Mn}^{\text{II}} + \text{LH}_4$ ) (each  $8.9 \times 10^{-5} \text{ mol dm}^{-3}$ ) in  $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$  as stated above. We feel that this is compelling evidence in favour of  $\text{H}^+$  promoted oxidation of both MeOH and  $\text{H}_2\text{O}$  by  $\text{Mn}^{\text{IV}}\text{L}$  and  $\text{Mn}^{\text{III}}$  intermediates. It is also important to note that  $\text{Mn}^{\text{II}}$ , the end product, is not oxidized by dissolved oxygen in the presence of the diprotonated ligand in moderately acidic medium ( $[\text{H}^+] \geq 0.05 \text{ mol dm}^{-3}$ ).

### Acid catalyzed decomposition of $\text{Mn}^{\text{IV}}\text{L}$

The rate of  $\text{H}^+$  promoted decomposition of  $\text{Mn}^{\text{IV}}\text{L}$  was studied at  $[\text{H}^+] = 0.05 - 0.6$  and  $I = 0.6 \text{ mol dm}^{-3}$  (10% (v/v) MeOH +  $\text{H}_2\text{O}$ ,  $28.5^\circ\text{C}$ ). The biphasic nature of the reaction is interpreted as  $\text{H}^+$  promoted reduction of  $\text{Mn}^{\text{IV}}\text{L}$  by  $\text{H}_2\text{O}$  and MeOH as shown in Equation (2) where INT is a protonated  $\text{Mn}^{\text{III}}$  complex,  $\text{Mn}^{\text{III}}\text{LH}$  and the product P is the corresponding  $\text{Mn}^{\text{II}}$  complex,



$k_{\text{obs}}^f$  and  $k_{\text{obs}}^s$  denote the observed pseudo-first order rate constants for the fast and slow phases of the overall reactions respectively. The product P is, however, expected to be equilibrated between the free ligand, its protonated forms and intermediate  $\text{Mn}^{\text{II}}$  complexes ( $\text{Mn}^{\text{II}}\text{LH}^-$ ,  $\text{Mn}^{\text{II}}\text{LH}_2$  etc.) as also  $\text{Mn}(\text{OH}_2)_6^{2+}$ . The radicals generated in the oxidation of  $\text{H}_2\text{O}/\text{MeOH}$  are rapidly mopped up by  $\text{Mn}^{\text{IV/III}}$ . The  $\text{H}^+$  dependence of  $k_{\text{obs}}^f$  ( $k_{\text{obs}}^s$ ) (see Table 1) conform to  $k_{\text{obs}}^{f(s)} = k_o^{f(s)} + k_H^{f(s)}[\text{H}^+]$  (Figure 2), and yielded  $10^3 k_o^f (10^4 k_o^s) = -0.25 \pm 0.20$  ( $-0.0012 \pm 0.064$ )  $\text{s}^{-1}$  and  $10^3 k_H^f (10^4 k_H^s) = 9.3 \pm 0.6$  ( $2.0 \pm 0.2$ )  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . This further confirmed that there is virtually no acid-independent reaction of  $\text{Mn}^{\text{IVL}}$  as well as the intermediate (INT).

### $\text{Mn}^{\text{IVL}}-\text{S}^{\text{IV}}$ reactions

Repetitive spectral scans of the mixtures of  $\text{Mn}^{\text{IVL}} (1.04 \times 10^{-4} \text{mol dm}^{-3})$  and  $\text{S}^{\text{IV}} ([\text{S}^{\text{IV}}]_{\text{T}} = 0.010 \text{mol dm}^{-3}, 34.0 \text{ }^\circ\text{C}, \text{pH} = 4, 10\% \text{ (v/v) MeOH} + \text{H}_2\text{O})$  displayed a decrease of absorbance with time at

Table 1. Observed rate constants for the acid catalyzed decomposition of  $\text{Mn}^{\text{IVL}}$ <sup>a</sup>

$[\text{HClO}_4]$ ( $\text{mol dm}^{-3}$ )	$10^3 k_{\text{obs}}^f$ ( $\text{s}^{-1}$ )	$10^4 k_{\text{obs}}^s$ ( $\text{s}^{-1}$ )
0.05	$0.20 \pm 0.01$	$0.14 \pm 0.01$
0.10	$0.53 \pm 0.01$	$0.20 \pm 0.01$
0.20	$1.96 \pm 0.02$	$0.38 \pm 0.01$
0.30	$2.60 \pm 0.05$	$0.65 \pm 0.01$
0.40	$3.20 \pm 0.10$	$0.78 \pm 0.02$
0.50	$4.07 \pm 0.06$	$0.88 \pm 0.03$
0.60	$5.63 \pm 0.07$	$1.35 \pm 0.03$

$$\begin{array}{ll} 10^3 k_o^{f,b,c} & -0.25 \pm 0.20; & 10^4 k_o^{s,b,d} & -0.001 \pm 0.06 \\ 10^3 k_H^{f,b,c} & 9.3 \pm 0.6; & 10^4 k_H^{s,b,d} & 2.0 \pm 0.2 \end{array}$$

<sup>a</sup> $28.5 \pm 0.1 \text{ }^\circ\text{C}$ ,  $[\text{Mn}^{\text{IVL}}]_{\text{T}} = 8.29 \times 10^{-5}$ ,  $I = 0.6 \text{ mol dm}^{-3}$ , 10% (v/v) MeOH +  $\text{H}_2\text{O}$ ,  $\lambda = 469 \text{ nm}$ .

<sup>b</sup>units:  $\text{s}^{-1}$  and  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$  for  $k_o$  and  $k_H$ , respectively.

<sup>c,d</sup>Corr. coeff. 0.99(c), 0.98(d).

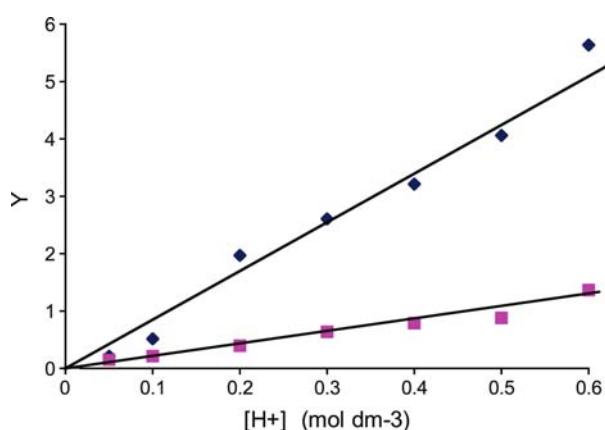


Fig. 2. The plots showing the dependence of  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on  $[\text{H}^+]$  ( $\text{mol dm}^{-3}$ ) for the acid catalyzed decomposition of  $\text{Mn}^{\text{IVL}}$  { $\blacklozenge$ :  $Y = 10^3 k_{\text{obs}}^f (\text{s}^{-1})$ } and  $\text{Mn}^{\text{III}}\text{L}^-$  { $\blacksquare$ :  $Y = 10^4 k_{\text{obs}}^s (\text{s}^{-1})$ } at  $28.5 \text{ }^\circ\text{C}$ .  $[\text{Mn}^{\text{IVL}}]_{\text{T}} = 8.3 \times 10^{-5}$ ,  $I = 0.6 \text{ mol dm}^{-3}$ , 10% (v/v) MeOH +  $\text{H}_2\text{O}$ .

$200 \leq \lambda \text{ nm} \leq 700$ . The intensity of absorption at  $\lambda_{\text{max}}$  ca. 300 nm steadily decreased to a minimum, while the maxima at  $\lambda > 300 \text{ nm}$  completely vanished. Similar observations were also made at higher pH and  $[\text{S}^{\text{IV}}]_{\text{T}}$ . The lack of isosbestic point(s) showed that the reaction engendered no stable  $\text{Mn}^{\text{III}}$  intermediate in the presence of an excess of  $\text{S}^{\text{IV}}$ . The spectrum of the end product matched with that of the mixture of  $\text{Mn}^{\text{II}}$ ,  $[\text{S}^{\text{IV}}]$  and the ligand under similar conditions, thus suggesting that  $\text{Mn}^{\text{IV}}$  complex was reduced by  $\text{S}^{\text{IV}}$ .

### Stoichiometry

The reaction mixture ( $10 \text{ cm}^3$ ,  $[\text{Mn}^{\text{IVL}}]_{\text{T}} = 1.0 \times 10^{-3}$ ,  $[\text{S}^{\text{IV}}]_{\text{T}} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} = 4$ , 0, 10% (v/v) MeOH +  $\text{H}_2\text{O}$ ,  $30 \text{ }^\circ\text{C}$ ) was allowed to undergo complete reduction of  $\text{Mn}^{\text{IV}}$  to  $\text{Mn}^{\text{II}}$  after which it was acidified with  $\text{HClO}_4$  to pH 1 and subjected to cation exchange with Dowex 50W  $\times 8$  resin ( $\text{H}^+$ ) to remove  $\text{Mn}^{\text{II}}$  and the diprotonated ligand. The resulting solution was then flushed with  $\text{N}_2$  to remove dissolved  $\text{SO}_2$  and then  $\text{BaCl}_2$  solution was added which resulted in the formation of a white precipitate, insoluble in hot HCl, thus confirming the presence of  $\text{SO}_4^{2-}$ . Simultaneously a blank experiment in the absence of  $\text{Mn}^{\text{IVL}}$  was also performed for the sake of comparison. Quantitative estimation of  $\text{S}_2\text{O}_6^{2-}$  was done as follows. In another experiment the reaction mixture, after completion of reduction and removal of  $\text{SO}_2$ , was subjected to anion exchange with IRA 400 ( $\text{SO}_4^{2-}$  form) resin. The resin was then thoroughly washed with distilled  $\text{H}_2\text{O}$  and then eluted with  $0.4 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ . The collected effluent ( $100 \text{ cm}^3$ ) was treated with an excess of  $\text{Cr}^{\text{VI}}$  in  $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and heated on a water bath at  $70 \text{ }^\circ\text{C}$  for 4 h, and then made up to a required volume with  $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . The unreacted  $\text{Cr}^{\text{VI}}$  was estimated spectrophotometrically (348 nm) as reported by Carlyle [11]. A calibration curve using a known amount of sodium dithionate was also made. Replica experiments indicated that dithionate was produced to the extent of  $18 \pm 2\%$  of  $[\text{Mn}^{\text{IV}}]_{\text{T}}$ . A quantitative estimation of  $\text{SO}_4^{2-}$  by the  $\text{BaSO}_4$  precipitation method always yielded a high value of  $\text{SO}_4^{2-}$  even after making blank correction. This is attributed to the dissolved oxygen interference on the overall stoichiometry. However, oxygen interference was insignificant as regards the kinetics of  $\text{Mn}^{\text{IVL}}/\text{Mn}^{\text{III}}\text{L} + \text{S}^{\text{IV}}$  reaction. Thus the overall stoichiometry of  $\text{S}^{\text{IV}}$  reduction does not conform to a simple relation as shown in Equation (3).



Rather, the oxidation of the  $\text{SO}_3^{\bullet-}$  intermediate by  $\text{Mn}^{\text{IVL}}/\text{Mn}^{\text{III}}\text{L}$  is competitive with its dimerisation.

### Rate data

The rate data are collected in Table 2(a, b). It can be seen that the plots of  $k_{\text{obs}}^f$  and  $k_{\text{obs}}^s$  versus  $[\text{S}^{\text{IV}}]_{\text{T}}$  at a given

Table 2. Rate data for the reactions of Mn<sup>IV</sup>L with S<sup>Iva</sup>

[S <sup>IV</sup> ] <sub>T</sub> mol dm <sup>-3</sup>	pH <sup>b</sup>	10 <sup>3</sup> k <sub>obs</sub> <sup>f</sup> (10 <sup>4</sup> k <sub>obs</sub> <sup>s</sup> ) <sup>c</sup> s <sup>-1</sup>
(a) 28.5 ± 0.1 °C		
0.03	3.15	0.68 (2.40)
0.03	3.41	0.52 (2.25)
0.03	3.71	0.65 (2.83)
0.03	4.15	0.59 (2.15)
0.03	4.44	0.44 (2.33)
0.03	4.74	0.62 (2.68)
0.03	5.07	0.67 (2.22)
0.03	5.30	0.69 (3.12)
0.03	5.70	0.88 (4.10)
0.05	4.86	1.12 (4.30)
0.06	4.90	1.27 (4.56)
0.08	4.86	1.70 (6.14)
0.10	4.84	1.89 (10.2)
0.005	6.13	0.35 (1.17)
0.01	6.71	0.81 (3.94)
0.015	7.13	2.21 (8.00)
0.02	7.13	3.01 (10.9)
0.03	6.73	3.37 (12.8)
0.03	7.19	3.23 (18.1)
0.05	7.33	6.49 (30.5)
0.06	7.30	7.25 (35.1)
0.07	7.31	8.05 (40.0)
35.0 ± 0.1 °C		
0.03	3.27	4.05 (6.41)
0.03	3.50	3.58 (5.83)
0.03	4.12	3.22 (5.11)
0.03	4.26	3.59 (5.45)
0.03	4.46	3.76 (5.74)
0.03	4.57	4.10 (5.65)
0.03	5.10	5.02 (5.76)
0.03	5.35	4.85 (5.82)
0.03	5.50	5.61 (6.48)
0.03	5.78	5.27 (7.52)
0.03	5.99	6.02 (8.44)
0.005	5.43	0.78 (1.67)
0.01	5.30	1.94 (2.32)
0.02	5.53	2.13 (4.29)
0.04	5.47	6.70 (8.29)
0.01	4.79	1.11 (2.57)
0.02	4.53	1.83 (3.16)
0.04	4.53	1.83 (3.16)
0.05	4.27	6.02 (8.30)
0.06	4.17	7.82 (11.2)
0.005	5.60	0.84 (1.64)
0.03	6.39	– (12.6)
0.03	6.61	– (16.4)
0.05	5.57	– (9.77)
0.06	5.37	– (10.4)
0.07	5.45	– (12.1)
0.09	3.80	– (16.5)
0.01	6.54	3.12 (9.38)
0.01	6.84	4.08 (10.8)
0.01	7.04	4.67 (14.5)
(b) 45.0 ± 0.1 °C		
0.005	3.50	4.50 (1.36)
0.005	4.14	4.30 (2.54)
0.005	4.78	4.57 (3.32)
0.005	5.25	3.40 (3.25)
0.005	6.20	4.70 (3.81)
0.005	6.50	5.00 (5.74)
0.005	6.85	7.90 (7.30)
0.01	3.35	8.75 (5.40)

Table 2. (Continued)

[S <sup>IV</sup> ] <sub>T</sub> mol dm <sup>-3</sup>	pH <sup>b</sup>	10 <sup>3</sup> k <sub>obs</sub> <sup>f</sup> (10 <sup>4</sup> k <sub>obs</sub> <sup>s</sup> ) <sup>c</sup> s <sup>-1</sup>
0.01	3.88	7.81 (4.59)
0.01	4.29	7.50 (4.00)
0.01	4.91	8.50 (3.93)
0.01	5.35	7.95 (4.50)
0.01	6.16	14.1 (8.54)
0.01	6.58	15.6 (10.8)

<sup>a</sup>10% (v/v) MeOH + H<sub>2</sub>O, *I* = 0.3 mol dm<sup>-3</sup>, each entry of *k*<sub>obs</sub> is from single run,  $\sigma(k_{\text{obs}})/k_{\text{obs}} \leq 0.05$ .

<sup>b</sup>pH = -Log [H<sup>+</sup>], AcONa/AcOH buffer for 3.50 ≤ pH ≤ 5.50 ([AcO<sup>-</sup>]<sub>T</sub> = 0.05 mol dm<sup>-3</sup>), MES buffer ([MES]<sub>T</sub> = 0.05 mol dm<sup>-3</sup>) for pH = 5.50 ≤ pH ≤ 6.61.

<sup>c</sup>Values in parentheses are for 10<sup>4</sup>k<sub>obs</sub><sup>s</sup>.

pH are linear and extrapolate to zero at [S<sup>IV</sup>]<sub>T</sub> = 0. This further confirms that there is no detectable [S<sup>IV</sup>]<sub>T</sub> independent reaction of Mn<sup>IV</sup>L and Mn<sup>III</sup>L<sup>-</sup> intermediate at pH ≥ 3. The observed pH dependence of *k*<sub>obs</sub><sup>f</sup> and *k*<sub>obs</sub><sup>s</sup> at constant [S<sup>IV</sup>]<sub>T</sub> is consistent with HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> as reducing S<sup>IV</sup> species in which form [S<sup>IV</sup>]<sub>T</sub> is predominantly speciated at 3.1 ≤ pH ≤ 7.3. The acid dissociation equilibria of SO<sub>2</sub> are represented by Equations (4) and (5) where S(H)O<sub>3</sub><sup>-</sup> denote the equilibrium mixture of H-SO<sub>3</sub><sup>-</sup> and H-O-SO<sub>2</sub><sup>-</sup>, with the latter predominating in solution [12]. However, no distinction is made regarding the redox reactions of these two forms of bisulfite.



Scheme 1 is proposed for which *k*<sub>obs</sub><sup>f</sup> and *k*<sub>obs</sub><sup>s</sup> are given by Equations (6) and (7), respectively.

$$k_{\text{obs}}^f = \frac{\left( \frac{k_{\text{HSO}_3} [\text{S}^{\text{IV}}]_{\text{T}} + k_{\text{SO}_3} K_2 [\text{S}^{\text{IV}}]_{\text{T}}}{[\text{H}^+]} \right)}{\left( \frac{1+K_2}{[\text{H}^+]} \right)} \quad (6)$$

$$k_{\text{obs}}^s = \frac{\left( \frac{k'_{\text{HSO}_3} [\text{S}^{\text{IV}}]_{\text{T}} + k'_{\text{SO}_3} K_2 [\text{S}^{\text{IV}}]_{\text{T}}}{[\text{H}^+]} \right)}{\left( \frac{1+K_2}{[\text{H}^+]} \right)} \quad (7)$$

where *K*<sub>2</sub> is the acid dissociation constant of S(H)O<sub>3</sub><sup>-</sup> and [S<sup>IV</sup>]<sub>T</sub> = [S(H)O<sub>3</sub><sup>-</sup>] + SO<sub>3</sub><sup>2-</sup>.

The values of p*K*<sub>1</sub> and p*K*<sub>2</sub> of S<sup>IV</sup> are 1.8 and 6.8 (*I* = 0.3 mol dm<sup>-3</sup>, 35 °C, 10% MeOH + H<sub>2</sub>O) [1d]. The *k*<sub>obs</sub><sup>f</sup> (and *k*<sub>obs</sub><sup>s</sup>) data in Table 2(a, b) were fitted to Equations (6) and (7) by varying (*k*<sub>HSO<sub>3</sub></sub>), (*k*<sub>SO<sub>3</sub></sub>, *K*<sub>2</sub>), *K*<sub>2</sub> [and the corresponding parameters of Equation (7)]. The values of *K*<sub>2</sub> turned out to be essentially constant {10<sup>7</sup> *K*<sub>2</sub> (mol dm<sup>-3</sup>): 4.7 ± 1.7, 2.5 ± 1.2 (28.5 °C); 1 ± 3 (35 °C); 4.0 ± 3.5, 1.8 ± 1.3 (45 °C)}. Hence a constant value of *K*<sub>2</sub> = 2.5 × 10<sup>-7</sup> was chosen for data fitting. The calculated values of the parameters are collected in Table 3. The rate constants and



Table 4. A comparison of rate and activation parameters for Mn<sup>III</sup>L/Mn<sup>IV</sup>L reduction by sulfur(IV)

Reaction	Conditions t [°C]/I/medium	$k$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )	Ref.
HOMn <sup>III</sup> – OMn <sup>II</sup> + HSO <sub>3</sub> <sup>-</sup> → 2Mn <sup>II</sup> + SO <sub>3</sub> <sup>-</sup>	25/1.0/aq	$1.5 \times 10^6$			a
Mn <sup>III</sup> (cdta)OH <sub>2</sub> <sup>-</sup> + SO <sub>3</sub> <sup>2-</sup> → Mn <sup>II</sup> (cdta)OH <sub>2</sub> <sup>2-</sup> + SO <sub>3</sub> <sup>-</sup>	25/0.16/aq	$2.27 \times 10^5$	48 ± 1	17 ± 4	b
Mn <sup>III</sup> (cdta)OH <sub>2</sub> <sup>-</sup> + HSO <sub>3</sub> <sup>-</sup> → Mn <sup>II</sup> (cdta)OH <sub>2</sub> <sup>2-</sup> + SO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	30/0.2/aq	22	9 ± 4	-188 ± 42	c
Mn <sup>III</sup> (acac) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> + HSO <sub>3</sub> <sup>-</sup> → Mn <sup>II</sup> (acac) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> + SO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	30/1.0/aq	$2.1 \times 10^{-2}$			d
Mn <sup>III</sup> (acac) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> + SO <sub>3</sub> <sup>2-</sup> → Mn <sup>II</sup> (acac) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> + SO <sub>3</sub> <sup>-</sup>	30/1.0/aq	$3.5 \times 10^{-2}$			d
Mn <sup>III</sup> (acac) <sub>2</sub> (OH <sub>2</sub> )OH + SO <sub>3</sub> <sup>2-</sup> → Mn <sup>II</sup> (acac) <sub>2</sub> (OH <sub>2</sub> )OH <sup>-</sup> + SO <sub>3</sub> <sup>-</sup>	30/1.0/aq	0.41			d
Mn <sup>III</sup> (salen)(OH <sub>2</sub> )SO <sub>3</sub> <sup>-</sup> + HSO <sub>3</sub> <sup>-</sup> → Mn <sup>II</sup> (salen)(OH <sub>2</sub> )SO <sub>3</sub> <sup>2-</sup> + SO <sub>3</sub> <sup>-</sup>	30/0.3/aq	$3.9 \times 10^{-3}$	49 ± 5	-130 ± 20	e
Mn <sup>III</sup> (salen)(OH <sub>2</sub> )SO <sub>3</sub> <sup>-</sup> + SO <sub>3</sub> <sup>2-</sup> → Mn <sup>II</sup> (salen)(OH <sub>2</sub> )SO <sub>3</sub> <sup>2-</sup> + SO <sub>3</sub> <sup>-</sup>	30/0.3/aq	$2.4 \times 10^{-3}$	42 ± 7	-160 ± 20	e
Mn <sup>III</sup> L <sub>1</sub> <sup>+</sup> + HSO <sub>3</sub> <sup>-</sup> → Mn <sup>II</sup> L <sub>1</sub> + SO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	30/0.5/aq	0.13			f
Mn <sup>III</sup> L <sub>1</sub> <sup>+</sup> + SO <sub>2</sub> · H <sub>2</sub> O → Mn <sup>II</sup> L <sub>1</sub> + SO <sub>3</sub> + 2H <sup>+</sup>	30/0.5/aq	34.2			f
Mn <sup>IV</sup> L + HSO <sub>3</sub> <sup>-</sup> → Mn <sup>III</sup> L <sup>-</sup> + SO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	30/0.3/ 10%MeOH + H <sub>2</sub> O	$4.0 \times 10^{-2}$	162 ± 27	262 ± 88	g
Mn <sup>IV</sup> L + SO <sub>3</sub> <sup>2-</sup> → Mn <sup>III</sup> L <sup>-</sup> + SO <sub>3</sub> <sup>-</sup>		0.20	136 ± 12	192 ± 40	
Mn <sup>III</sup> L <sup>-</sup> + HSO <sub>3</sub> <sup>-</sup> → Mn <sup>II</sup> L <sup>2-</sup> + SO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>		$1.0 \times 10^{-2}$	79.7 ± 3.9	-21 ± 12	
Mn <sup>III</sup> L <sup>-</sup> + SO <sub>3</sub> <sup>2-</sup> → Mn <sup>II</sup> L <sup>2-</sup> + SO <sub>3</sub> <sup>-</sup>		$8.2 \times 10^{-2}$	50.3 ± 2.5	-100 ± 8	
[Mn <sup>IV</sup> Mo <sub>9</sub> <sup>VI</sup> O <sub>32</sub> ] <sup>6-</sup> + SO <sub>2</sub> · H <sub>2</sub> O → [Mn <sup>II</sup> Mo <sub>6</sub> <sup>VI</sup> O <sub>24</sub> ] <sup>-</sup> + HMo <sup>VI</sup> O <sub>4</sub> <sup>-</sup> + H <sup>+</sup> SO <sub>4</sub> <sup>2-</sup>	25/variable/aq	$3.6 \times 10^{-2}$	39.2	-141	h

<sup>a</sup>[4e]; <sup>b</sup>[6f]; <sup>c</sup>[6e]; <sup>d</sup>[6b]; <sup>e</sup>[6a]; <sup>f</sup>[6d].

L<sub>1</sub>-(1,8) bis(5-Br-Salicylidineiminato) 3,6-diazaoctane.

<sup>g</sup>This work; <sup>h</sup>[6g].

formation. The spectrum of Mn<sup>III</sup>L is strongly pH dependent { $\lambda_{\max}$ , nm ( $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 285(15 570), 330 sh(7570), 469 (6472), 520 sh(5665) at pH 5.42; 295 (8882), 415 sh (2313) in 0.5 mol dm<sup>-3</sup> HClO<sub>4</sub>}. The pH and ionic strength dependence of  $k_{\text{obs}}$ <sup>s</sup> and the [H<sup>+</sup>] dependence of the absorption spectrum of the intermediate Mn<sup>III</sup> complex lead us to suggest that it is most likely monoprotonated and still bears a negative charge conforming to the composition Mn<sup>III</sup>LH(OH)<sup>-</sup>. This could be possible if one of the coordinated amide functions is opened up during the electron transfer to Mn<sup>IV</sup>L followed by fast entry of water at the resulting Mn<sup>III</sup> centre.

It is worth noting that both Mn<sup>IV</sup>L and Mn<sup>III</sup>L<sup>-</sup> species are substantially inert to reduction by solvent (H<sub>2</sub>O + MeOH) at pH > 3. This further reflects the substantial stabilizing effect offered by the coordination environment of the phenolate-deprotonated amide-amine function of the hexadentate ligand (L) and protection offered by its bulky and hydrophobic skeleton. However, at moderate acidic conditions ([H<sup>+</sup>] ≥ 0.05 mol dm<sup>-3</sup>) Mn<sup>IV</sup>L is *ca.* 50 times more sensitive to H<sup>+</sup>-promoted reduction by solvent than Mn<sup>III</sup>L<sup>-</sup> ( $k_{\text{H}}^{\text{Mn}^{\text{IV}}\text{L}}/k_{\text{H}}^{\text{Mn}^{\text{III}}\text{L}^-} = 46 \pm 5$ ) despite the fact that the latter is expected to be relatively more prone to protonation than the former.

The relatively faster reduction of Mn<sup>IV</sup>L by HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> in comparison to that for Mn<sup>III</sup>L<sup>-</sup>, may be contrasted with the water exchange rates of Mn<sup>IV</sup> and Mn<sup>III</sup> ( $k_{\text{ex}}^{\text{w}} = 10^{-2}$  and  $10^5$  s<sup>-1</sup> for Mn<sup>IV</sup> and Mn<sup>III</sup>, respectively) [18]. However, in either case HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> in large excess at pH > 3 did not disturb the coordination environment of Mn<sup>IV</sup>L and Mn<sup>III</sup>L<sup>-</sup> as we were unsuccessful in detecting mixed ligand complexes, Mn<sup>IV</sup>L(SO<sub>3</sub>)<sup>2-</sup> or Mn<sup>III</sup>L(SO<sub>3</sub>)<sup>3-</sup> (or their protonated forms) in which entry of SO<sub>3</sub><sup>2-</sup> could have occurred by partial opening of Mn–L bond. A comparison of the rate and activation parameters for the redox reactions of S<sup>IV</sup> with Mn<sup>IV</sup>/Mn<sup>III</sup> complexes are presented in Table 4. A linear plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  { $\Delta H^\ddagger$  (kJ mol<sup>-1</sup>) = 83.8(± 1.6) + 0.289(± 0.010)  $\Delta S^\ddagger$  (J K<sup>-1</sup> mol<sup>-1</sup>)} excluding the data for Mn<sup>III</sup>(cdta)OH<sub>2</sub><sup>-</sup> (corr. coeff. 0.994) irrespective of the oxidation states of Mn and the reducing species, SO<sub>2</sub>/HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup>, is consistent with a common mechanism. It is to be noted that Mn<sup>III</sup>(cdta)OH<sub>2</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> and Mn<sup>III</sup>(cdta)OH<sub>2</sub><sup>-</sup>/HSO<sub>3</sub><sup>-</sup> deviate remarkably from such a plot. While Mentasti and coworkers [6e] proposed an inner sphere mechanism for the Mn<sup>III</sup>(cdta)OH<sub>2</sub><sup>-</sup>/HSO<sub>3</sub><sup>-</sup>, Mehrotra and coworkers [6f] suggested an outer sphere mechanism for Mn<sup>III</sup>(cdta)OH<sub>2</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup>, assigning the observed deviation in the Marcus plot to the specifics of the

complex. However, the validity of the compensation/isokinetic plot for most of the complexes (see Table 4), for which evidence of direct coordination of  $S^{IV}$  species to the  $Mn^{III/IV}$  centre is lacking, is indicative of an outer sphere mechanism. Accordingly the wide variation of the rate and activation parameters reflect substantially a large reorganization energy in attaining the transition state for electron transfer. This energy requirement is very well compensated by the entropy gain due to metal-ligand bond readjustments and consequent restructuring of the solvation shell.

Based on an outer sphere mechanism with little adiabaticity (transmission coefficient 1) it is possible to calculate the self exchange rate constant ( $k_{22}$ ) for the  $Mn^{IV}L/Mn^{III}L^-$  couple in the present case, using the available data the same as for  $SO_3^{\bullet-}/SO_3^{2-}$  ( $k_{11} = 4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , 25 °C) [19] and *ca.*  $K_{12}$ , the equilibrium constant of the reaction:  $Mn^{IV}L + SO_3^{2-} = Mn^{III}L^- + SO_3^{\bullet-}$  ( $K_{12}$ ), from the relevant potential data  $\{SO_3^{\bullet-} + e = SO_3^{2-}$ , 0.72 V *versus* NHE [19];  $Mn^{IV}L + e = Mn^{III}L^-$ , 0.251 V *versus* NHE); the value of  $Mn^{III}L^-/Mn^{IV}L$  was calculated from  $E_{1/2}$  data (= 0.01 V *versus* SCE) reported by Chandra and Chakravorty [5 g]) using 0.241 V as the potential of SCE. Setting  $k^{SO_3} = (k_{11} k_{22} K_{12} f_{12})^{1/2}$  where  $\log f_{12} = (\log K_{12})^2 / [4 \log(k_{11}k_{22}/Z^2)]$  [20],  $Z = 10^{11} \text{ s}^{-1}$  ( $K_{12} = 1.2 \times 10^{-8}$ ,  $k^{SO_3} = 8.1 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C), the values of  $k_{22}$  and  $f_{12}$  were iteratively calculated as  $1.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $9.3 \times 10^{-2}$ , respectively (25 °C,  $I = 0.3 \text{ mol dm}^{-3}$ , 10% (v/v) MeOH + H<sub>2</sub>O). This appears to be a reasonable estimate considering the literature values of the self exchange rate constants ( $k_{22}$ ,  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of Mn in different oxidation states for the reactions:  $MnO_4^- + Mo(CN)_6^{4-}$  (or  $Fe(CN)_6^{4-}$ ) ( $3 \times 10^3$ ),  $Mn^{III} + Fe(phen)_3^{2+}$  ( $3 \times 10^{-4}$ ) and  $Mn^{III}(cdta) + Fe(edta)^{2-}$  (1.2) [21].

## Conclusion

The present work highlights the stabilization of the +4 and +3 oxidation states of Mn by a tetradeprotonated ligand ( $L^{4-}$ ) offering an octahedral coordination environment by the diphenolate-diamido-diamine donor set. It is observed that  $Mn^{IV}L$  and  $Mn^{III}L^-$  are only stable to reduction by solvent (H<sub>2</sub>O + MeOH) at pH > 3 while at  $[H^+] > 0.05 \text{ mol dm}^{-3}$   $Mn^{IV}L$  is reduced by solvent *via* one electron transfer engendering  $Mn^{III}$  intermediate which in turn is further reduced to  $Mn^{II}$ . These slow reactions exhibit first-order dependence in  $[H^+]$  in the range  $[H^+] = 0.05\text{--}0.6 \text{ mol dm}^{-3}$ . The reactivity trend,  $k_H^{Mn^{IV}L}/k_H^{Mn^{III}L^-} = 40$  reflects the relative kinetic instability of the two Mn complexes in contrast with the reported faster water exchange rate for  $Mn^{III}$  as compared to that for  $Mn^{IV}$  ( $k_{ex}^w = 10^5$  and  $10^{-2} \text{ s}^{-1}$  for  $Mn^{3+}$  and  $Mn^{4+}$ , respectively) [18]. The reduction of  $Mn^{IV}L$  by  $HSO_3^-/SO_3^{2-}$  occurred *via*

consecutive steps involving  $Mn^{III}L^-$  as intermediate. Despite the high concentration of  $[S^{IV}]_T$  used ( $50 < [S^{IV}]_T/[Mn^{IV}L]_T < 1000$ ) at  $3.2 \leq \text{pH} \leq 7.3$  (28.5–45 °C) there was no evidence of  $S^{IV}$  incorporation into the coordination sphere of Mn in  $Mn^{IV}L$  and the intermediate  $Mn^{III}L^-$ . This is in favour of the outer sphere mechanism of electron transfer between  $Mn^{IV}L/Mn^{III}L^-$  and  $S^{IV}$  ( $HSO_3^-, SO_3^{2-}$ ) which is further supported by comparison with previous studies. By applying the Marcus relation we calculate the self exchange rate constant of the  $Mn^{III}L^-/Mn^{IV}L$  redox couple as  $1.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C.

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