Electronic Supplementary information

Catalase-like activity of the polyoxovanadate anion $[Mn^{IV}V_{13}O_{38}]^{7-}$: A mechanistic study.

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Table S1: Representative initial rates (V_i) for the catalyzed decomposition of H_2O_2. T_{OAc} = 0.15 M, T = 25ºC, I = 0.5 mol dm^{-3}

pH	10^3 [complex], mol dm^{-3}	10^3 [H_2O_2], mol dm^{-3}	$10^7 V_i$, mol dm^{-3} s^{-1}
3.5	0.05	1	2.57
4.0			0.93
4.3			0.6
4.6			0.67
4.9			0.54
5.2			0.47
5.4			0.42
3.5	0.05	0.25	0.95
		0.375	1.38
		0.5	1.98
3.5	0.01	1	0.42
	0.03	1	1.59
	0.075	1	3.3
4.3	0.05	0.375	0.35
		0.75	0.51
		3.0	0.63
4.3	0.02	1	0.39
	0.03		0.5
	0.075		1.29

Table S2: Stoichiometry Measurement

pH	10^3 complex, mole	10^3 H_2O_2, mole	10^3 $\Delta[O_2]$, mol	$\Delta[O_2] / \Delta[H_2O_2]$
3.5	30	0.6	0.28	0.47
4.1	40	0.8	0.37	0.46
4.5	30	1.0	0.5	0.5

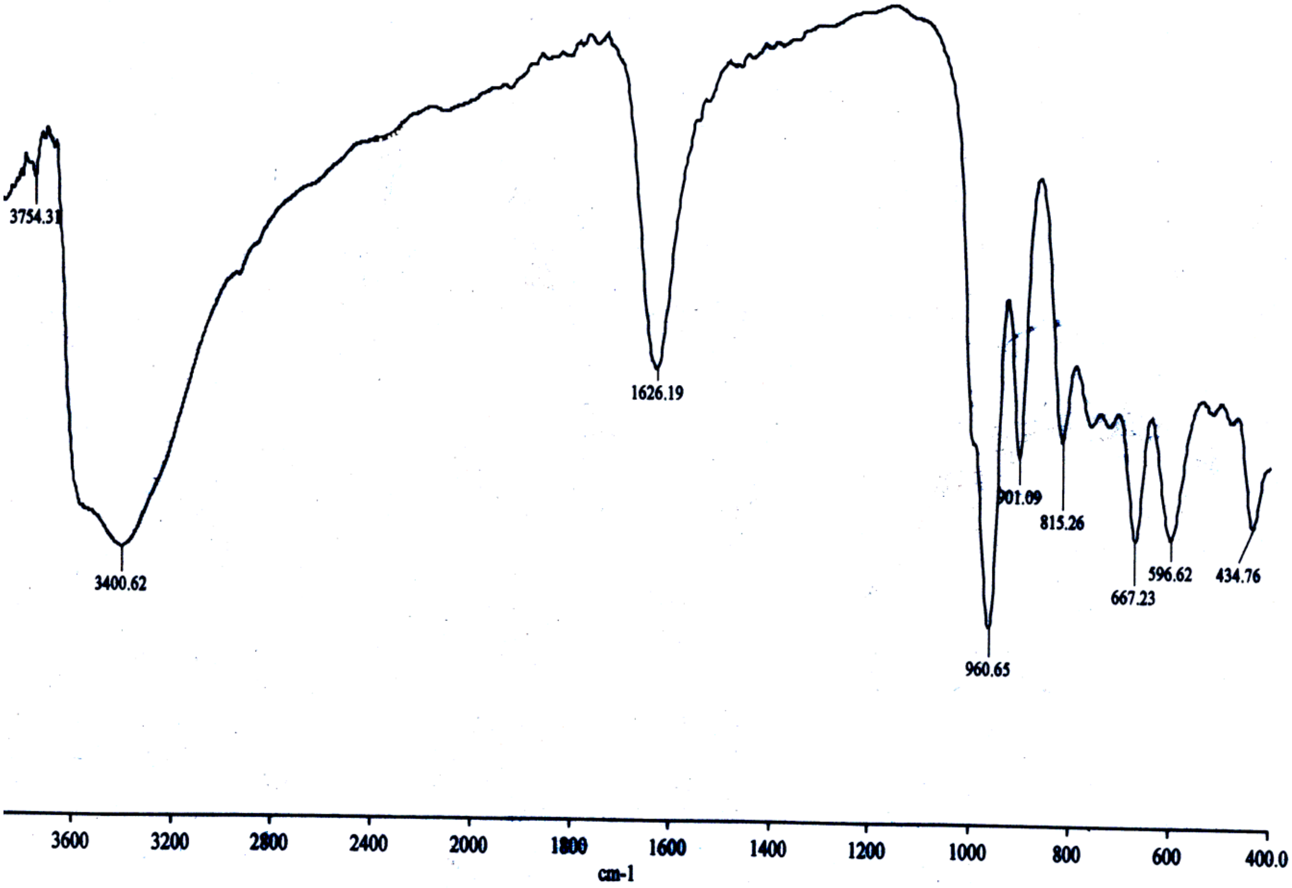

Fig. S1: IR spectra of the complex **1**

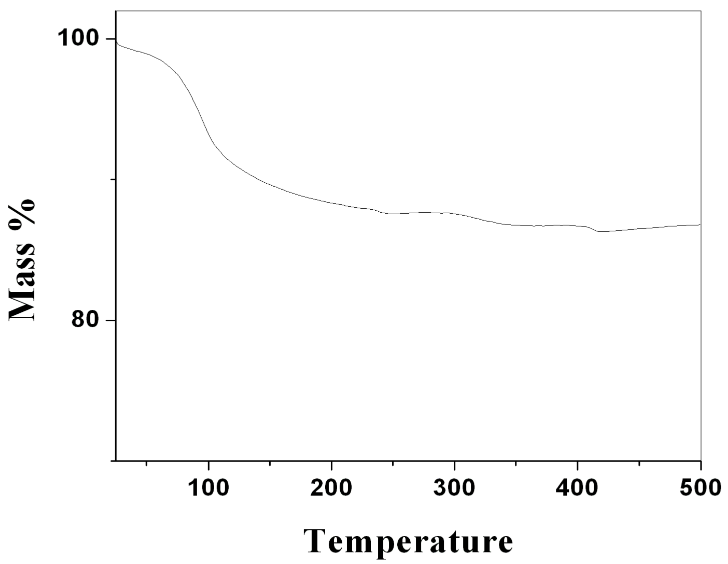

Fig. S2: TG/ DTA curve of the complex **1**

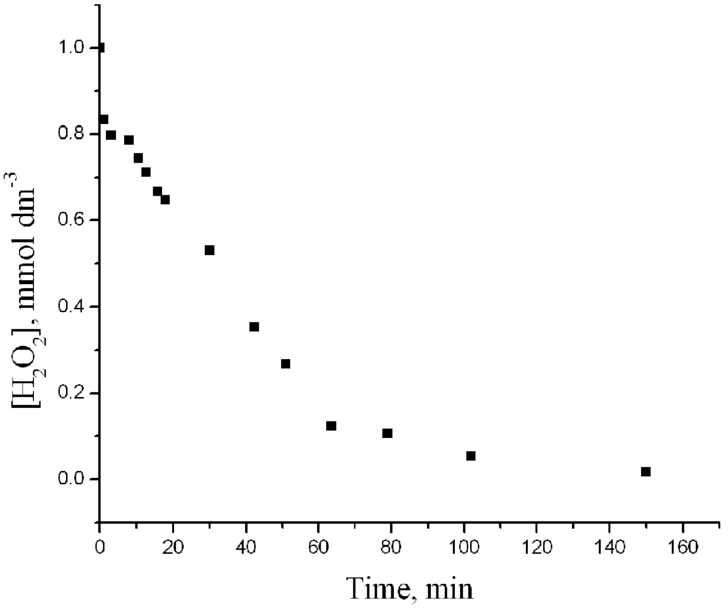

Fig. S3: decomposition of H_2O_2 with time. [**1**] = 5 ×10^{-5} mol dm^{-3}, [H_2O_2] = 1.0 ×10^{-3} mol dm^{-3}, pH = 3.8, T_{Oac} = 0.15 mol dm^{-3}, I = 0.5 mol dm^{-3}, T 25±.1°C

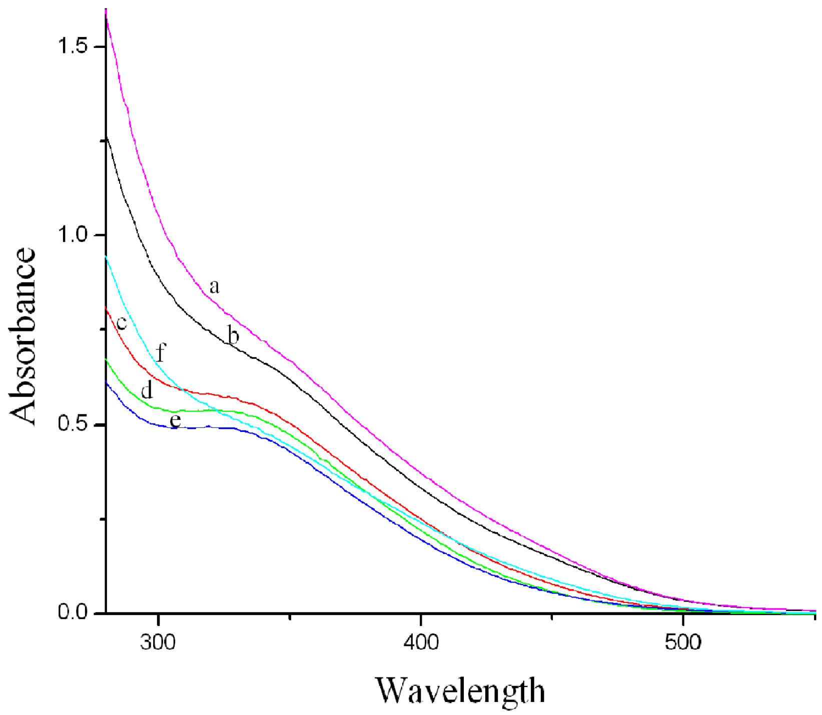

Fig. S4: (a-e) Decrease in absorbance of **1** on addition of H_2O_2 at 0, 0.50, 5, 20, and 75 min respectively, followed by (f) slow rise in the absorbance. [1] = 5 $\times 10^{-5}$ mol dm^{-3}, [H_2O_2] = 1 $\times 10^{-3}$ mol dm^{-3}, pH = 3.5, (T_{OAc} = 0.15 M) I = 0.5 mol dm^{-3}, T = 25.± 0.1 °C.

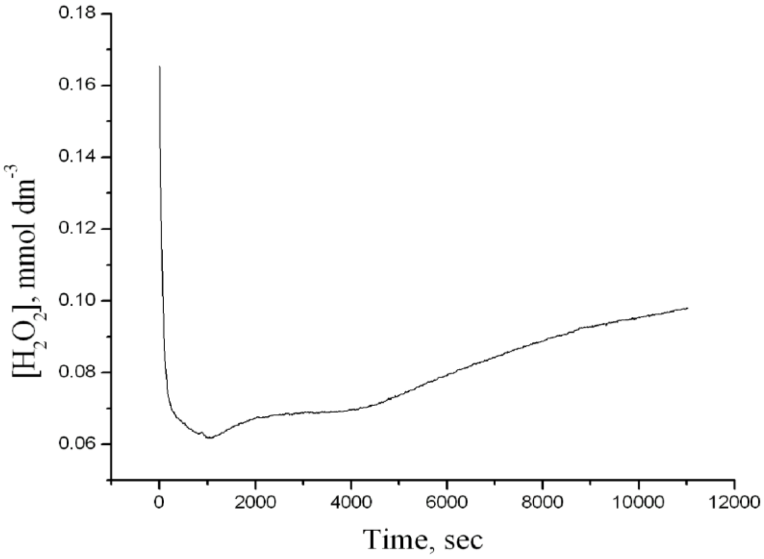

Fig. S5: decay in absorbance of 1, on addition of H_2O_2 fol1owed by a slow rise at 450 nm. ([1] = 5 ×10^{-5} mol dm-3, [H2O2] = 1.0 ×10^{-3} mol dm-3, pH = 3.16, *I* = 0.5 mol dm^{-3}, T_{OAc} = 0.2 mol dm^{-3}, T = 25±1^0C

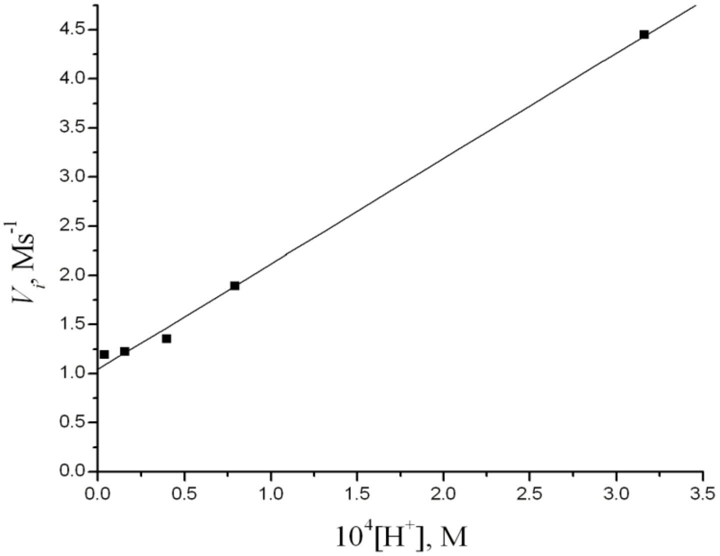

Fig. S6: V_i vs. [H^+] plot (Slope = 0.67 s^{-1} and intercept = 3.9×10^{-8}mol dm^{-3} s^{-1}). [1] = 5 ×10^{-5} mol dm^{-3}, [H_2O_2] = 1.0 ×10^{-3} mol dm^{-3} , T_{OAc} = 0.15 M, I = 0.5 mol dm^{-3}, T = 25±1ºC

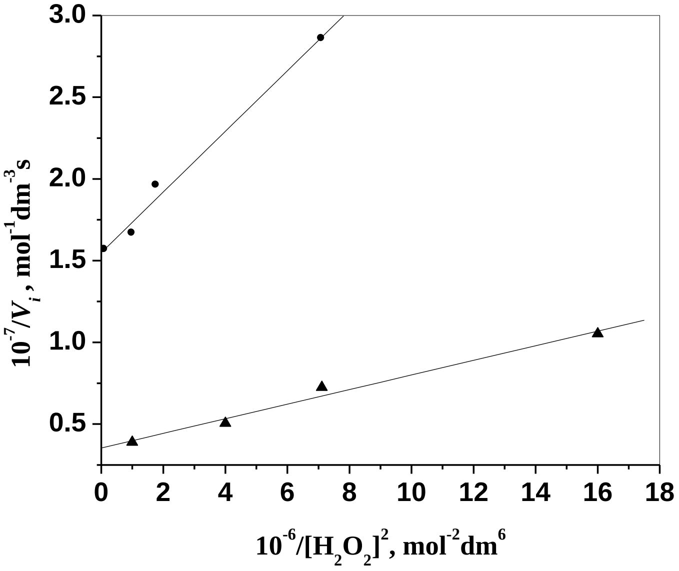

Fig. S7: $1/V_i$ *vs* $1/[H_2O_2]^2$ (●) at pH = 4.3 (Slope = 1.8 ×10^{-4} mol dm^{-3} s and intercept = 1.54 ×10^3 mol^{-1} dm^3 s; and (▲) at pH = 3.5, Slope = 4 ×10^{-5} mol dm^{-3} s and intercept = 3.5 ×10^2 mol^{-1} dm^3 s). [**1**] = 5 ×10^{-5} mol dm^{-3} pH = 3.8 (T_{OAc} = 0.15 M), I = 0.5 mol dm^{-3}, T = 25±1ºC

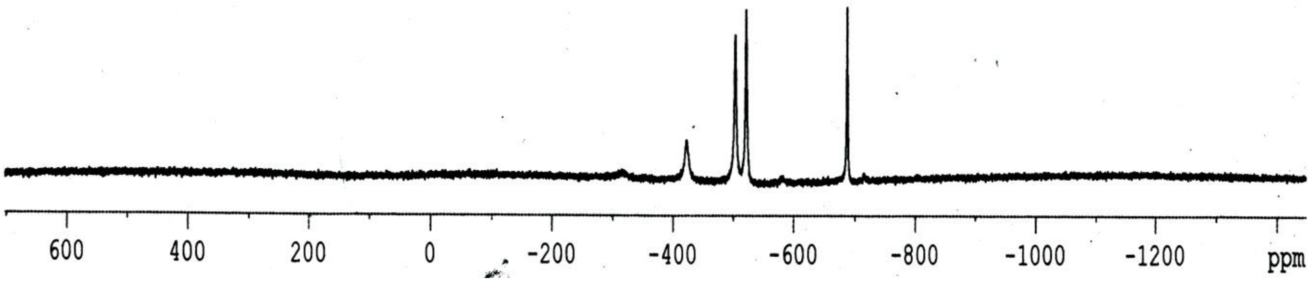

Fig. S8a: ^{51}V NMR spectra after addition of H_2O_2

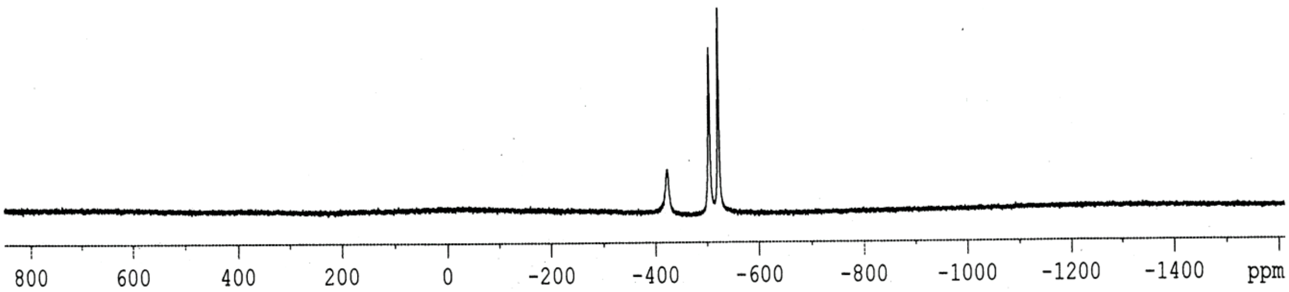

Fig. S8b: ^{51}V NMR of the complex

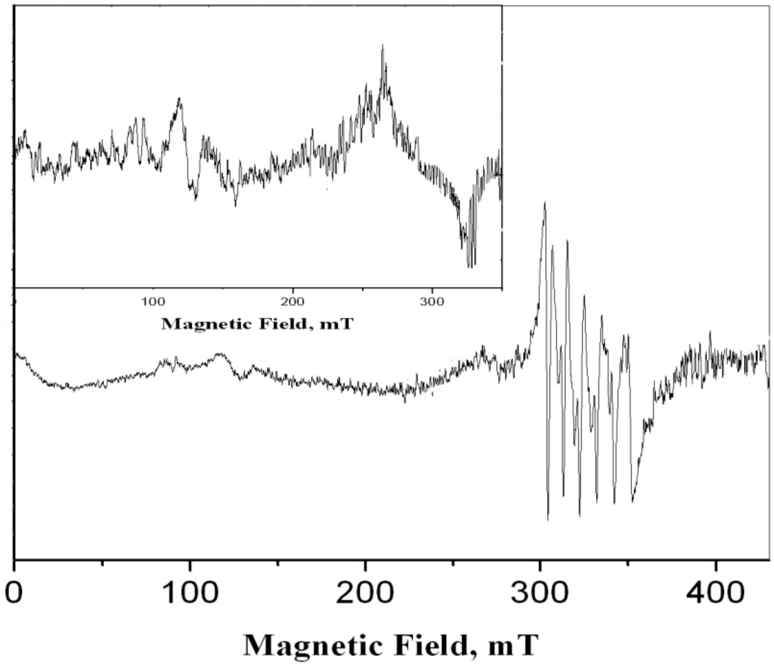

Fig. S9: epr spectra of the reaction mixture after addition of H_2O_2

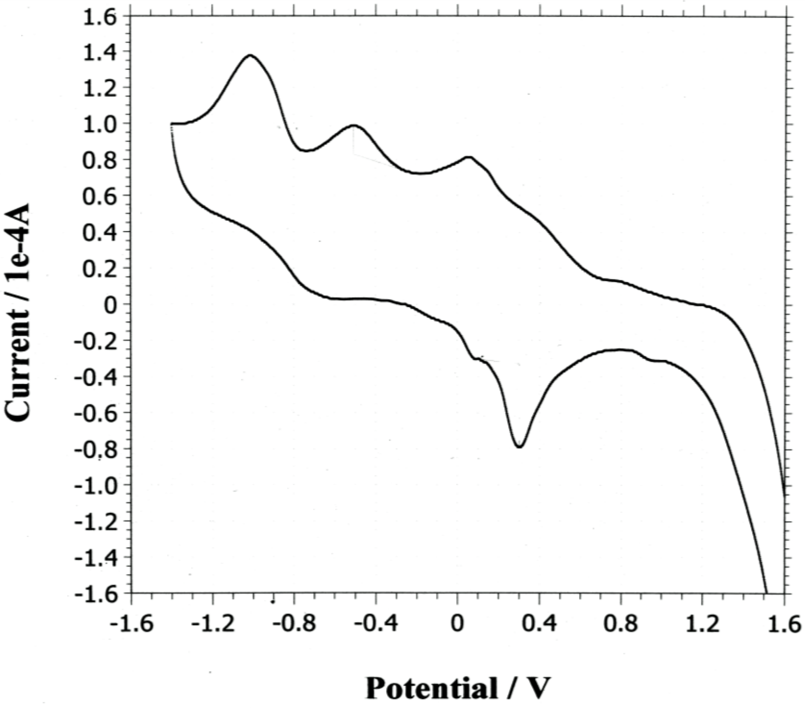

Fig S10a: Cyclic voltammetry diagram of the complex in acetate buffer solution (pH=3.8, [**1**] = 1 x 10^{-3} mol dm^{-3}, scan rate = 50 mV/s using SCE as reference electrode)

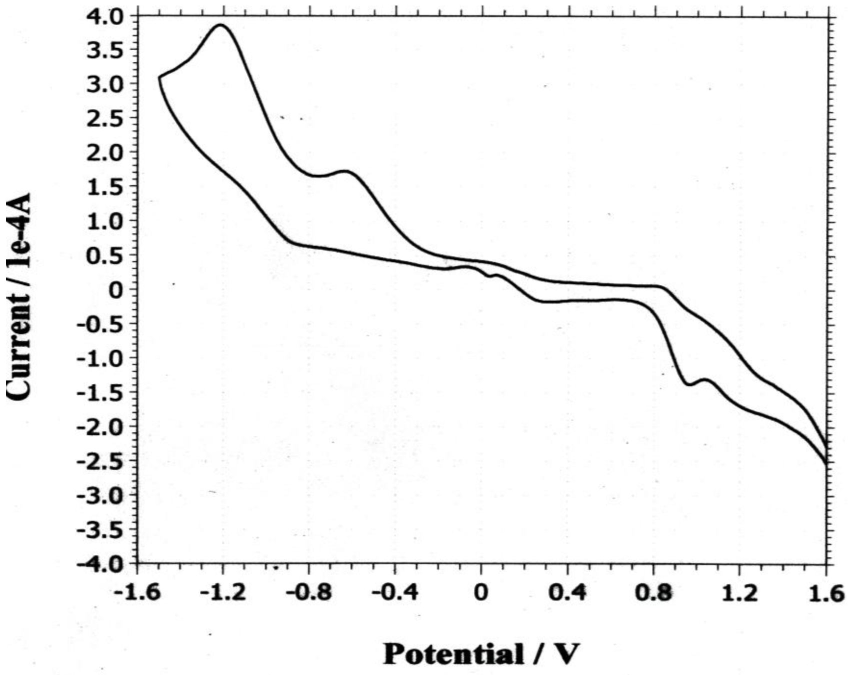

Fig S10b: Cyclic voltammetry diagram of the reaction mixture in acetate buffer solution (pH=3.8, [**1**] = 1 x 10^{-3} mol dm^{-3}, [H_2O_2] = 2 x 10^{-3} mol dm^{-3}, scan rate = 50 mV/s using SCE as reference electrode)

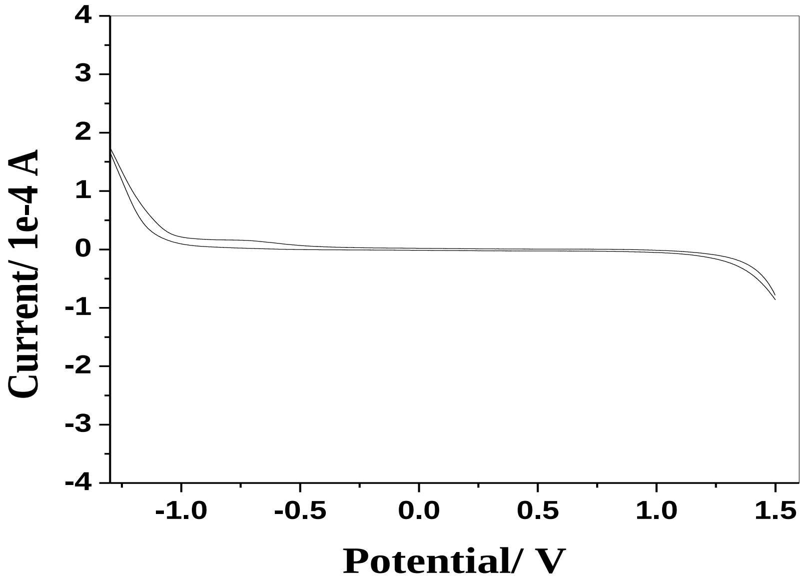

Fig S10c: Cyclic voltammetry diagram of H_2O_2 in acetate buffer solution (pH=3.8, $[H_2O_2] = 2 \times 10^{-3}$ mol dm^{-3}, scan rate = 50 mV/s using SCE as reference electrode)

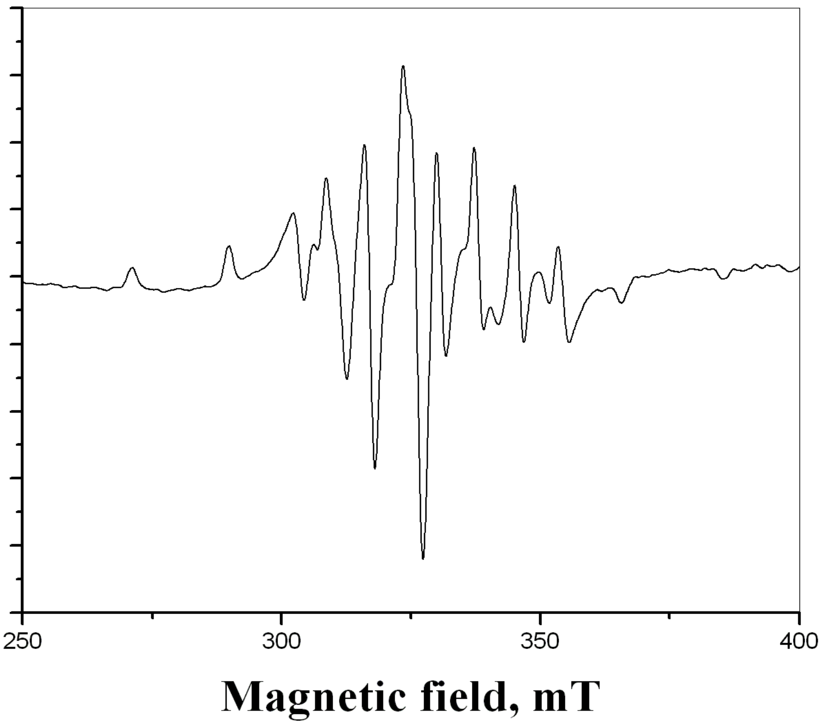

Fig. S11: epr spectra of the complex solution after coulometric reduction

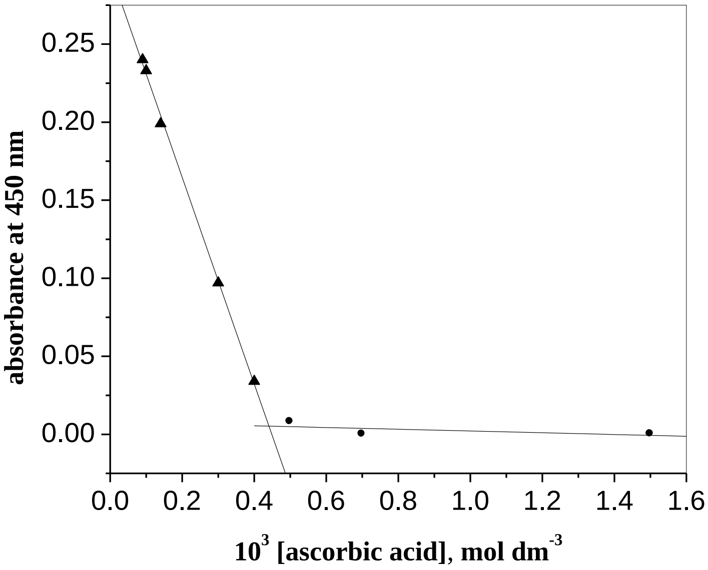

Fig. S12: Spectrophotometric titration of the complex by ascorbic acid

Derivation of the rate law:

Complex protonation:

$$[\mathrm{Mn^{IV}V_{13}O_{38}}]^{7-} + \mathrm{H^+} \xrightleftharpoons{K_\mathrm{H}} [\mathrm{HMn^{IV}V_{13}O_{38}}]^{6-} \qquad (1)$$

(**1**) (**1**)

Reactions of **1**

$$\mathbf{1} + 2\mathrm{H_2O_2} \xrightleftharpoons{K_1} [\mathrm{Mn^{IV}\text{-}dpv}]^{7-} \qquad (2)$$

$$[\mathrm{Mn^{IV}\text{-}dpv}]^{7-} + \mathrm{H_2O_2} \xrightarrow{k_1} [\mathrm{Mn^{II}\text{-}dpv}]^{9-} + \mathrm{O_2} + 2\mathrm{H^+} \qquad (3)$$

$$[\mathrm{Mn^{II}\text{-}dpv}]^{9-} + \mathrm{H_2O_2} + 2\mathrm{H^+} \longrightarrow [\mathrm{Mn^{IV}\text{-}dpv}]^{7-} + 2\mathrm{H_2O} \qquad (4)$$

Parallel reactions of $\mathbf{1_H}$

$$\mathbf{1_H} + 2\mathrm{H_2O_2} \xrightleftharpoons{K_{1\mathrm{H}}} \mathrm{H}[\mathrm{Mn^{IV}\text{-}dpv}]^{6-} \qquad (5)$$

$$\mathrm{H}[\mathrm{Mn^{IV}\text{-}dpv}]^{6-} + \mathrm{H_2O_2} \xrightarrow{k_2} \mathrm{H}[\mathrm{Mn^{II}\text{-}dpv}]^{8-} + \mathrm{O_2} + 2\mathrm{H^+} \qquad (6)$$

$$\mathrm{H}[\mathrm{Mn^{II}\text{-}dpv}]^{8-} + \mathrm{H_2O_2} + 2\mathrm{H^+} \longrightarrow \mathrm{H}[\mathrm{Mn^{IV}\text{-}dpv}]^{6-} + 2\mathrm{H_2O} \qquad (7)$$

Assuming, K_H to be small, the total concentration of the polyoxovanadate complex is

$T_c = [\mathbf{1}] + [\mathrm{Mn}^{IV}\text{-dpv}]^{7-}$ (8)

Now, $[\mathrm{Mn}^{IV}\text{-dpv}]^{7-} = K_1[H_2O_2]^2\,[\mathbf{1}]$ (from 3),

and $H[\mathrm{Mn}^{IV}\text{-dpv}]^{6-} = K_{1H}K_H\,[H^+]\,[H_2O_2]^2\,[\mathbf{1}]$ (from 6)

So, $T_c = ([\mathbf{1}] + K_1[\mathbf{1}][H_2O_2]^2)$

Or, $T_c = [\mathbf{1}]\{1 + K_1[H_2O_2]^2\}$

Or, $[\mathbf{1}] = T_c/\,(1 + K_1[H_2O_2]^2)$ (9)

Initial rate, $V_i = k_1[[\mathrm{Mn}^{IV}\text{-dpv}]^{7-}]_+\ k_2[H[\mathrm{Mn}^{IV}\text{-dpv}]^{6-}]$

Or, $V_i = (k_1K_1[H_2O_2]^2 + k_2\,K_{1H}K_H[H^+]\,[H_2O_2]^2)[\mathbf{1}]$

Substituting [**1**] from equation 9 we get

$V_i = \{(k_1K_1[H_2O_2]^2 + k_2\,K_{1H}K_H[H^+]\,[H_2O_2]^2)T_c\}/\,\{1 + K_1[H_2O_2]^2)$ (10)

Or, $1/V_i = [1/\,\{[H_2O_2]^2(k_1K_1+k_2K_{1H}K_H[H^+])T_c\}] + [K_1/\,\{T_c(k_1K_1+k_2K_{1H}K_H[H^+])\}]$ (11)