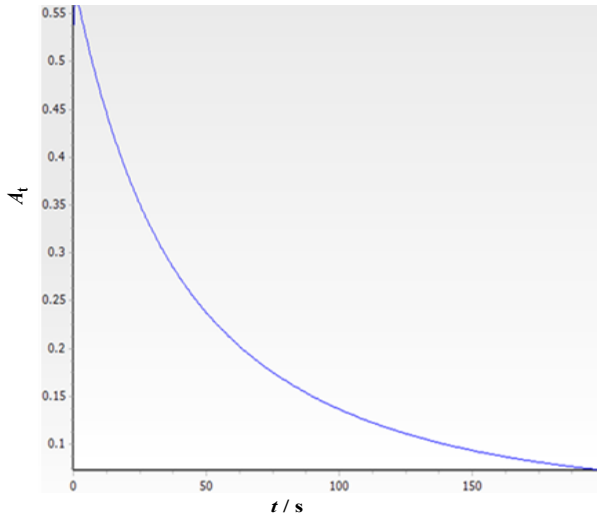
Supplementary Material (Electronic Supplementary Information)

Figure S1(a). Absorbance (A_t)-time (t/s) plot at 40^0C. $[HClO_4]$=0.05, $[OX]_T$ = 0.15, $[Mn^{III}(salen)(OH_2)_2^+]$ =1.285 x 10^{-4} mol dm^{-3}, λ = 380 nm.



1

2 Figure S1(b)- Absorbance (A_t) –time (t/s) plot at 30^oC. $[HClO_4]$=0.02,

3 $[OX]_T$ = 0.3, $[Mn^{III}(salen)(OH_2)_2^+]$=1.258 x$10^{-4}$ mol dm^{-3} , λ = 380 nm.

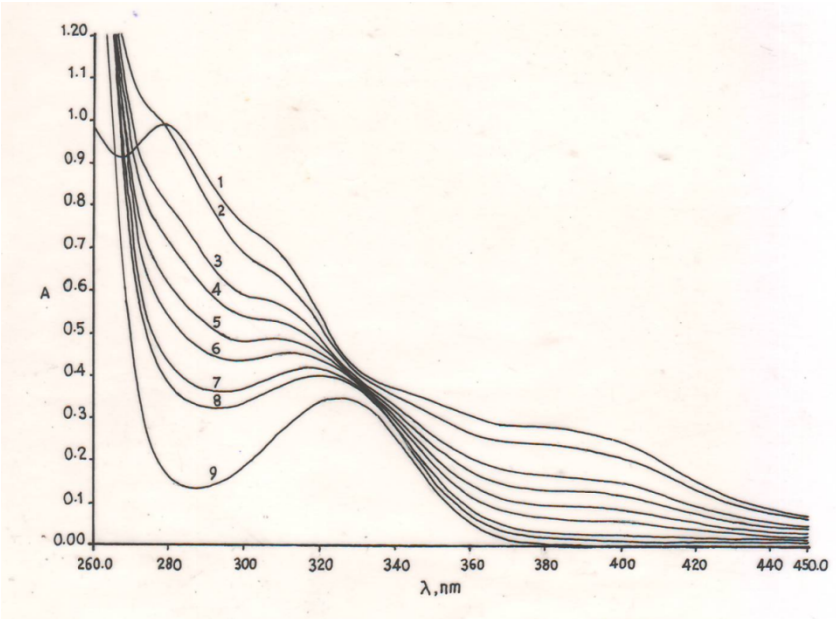


Figure S2- Successive Spectral Scans for Reduction of *trans*-$Mn^{III}(salen)(OH_2)_2^+$ by Oxalate. [complex]= 6.315 x 10^{-5} , $[OX]_T$ = 0.02 mol dm^{-3}, pH = 4.17, 30°C; curve no (time, s) : 1(in absence of OX), 2(60), 3(240), 4(480), 5(780), 6(1080), 7(1860), 8(2580), and 9(4200)

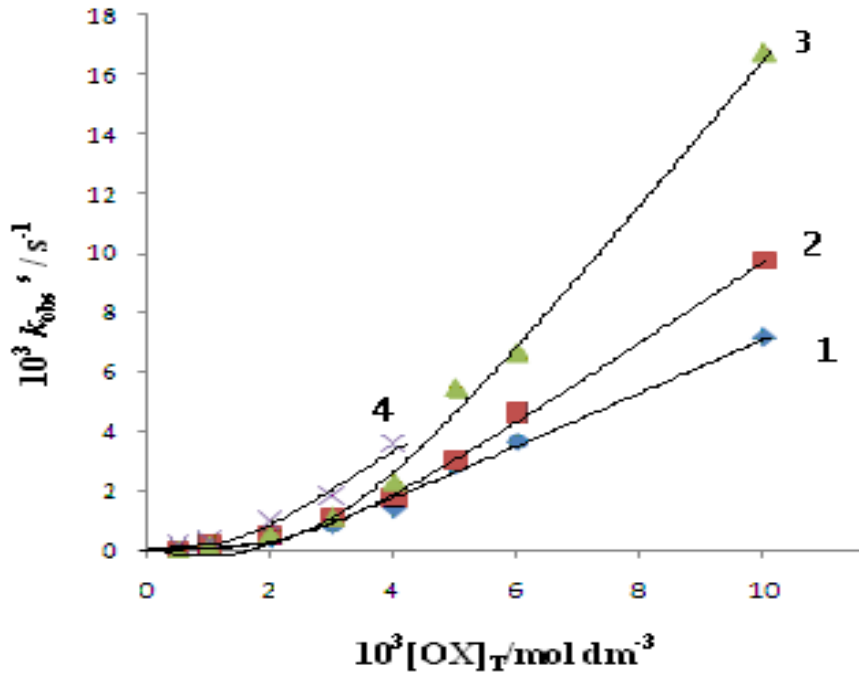


Figure S3a- $10^3 k_{obs}{}^s/s^{-1}$ versus $10^3[OX]_T$ plot at 25°(1), 30°(2), 35° (3), and 40°C (4) ; $[HClO_4]$ = 0.05 mol dm^{-3}.

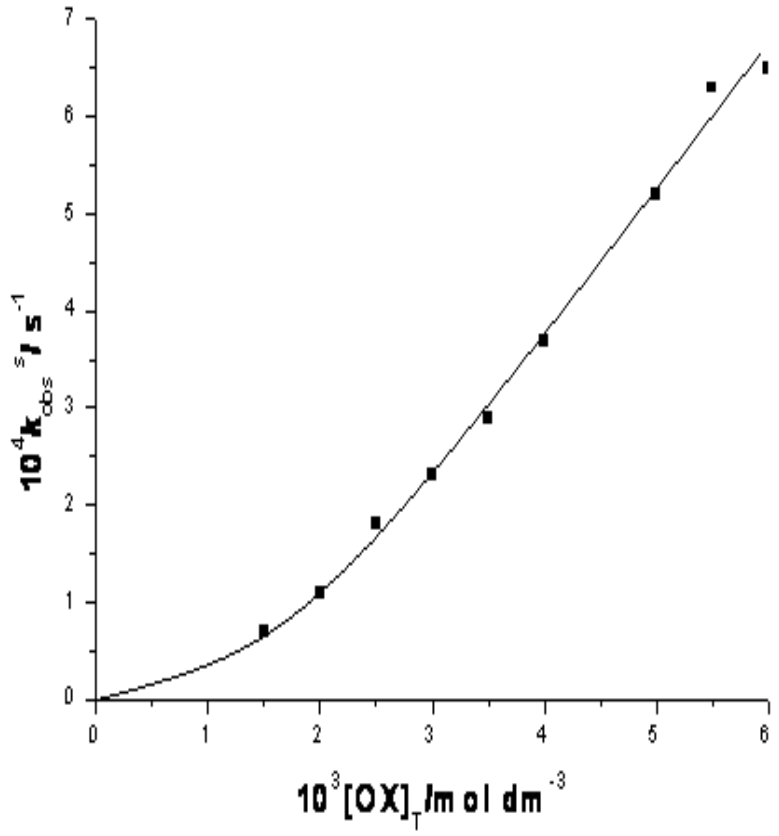


Figure S3b - $10^4 k_{obs}{}^s$ / s^{-1} vs. 10^3[OX]$_T$ plot at 35^{o}C, pH = 3.10 ± 0.09

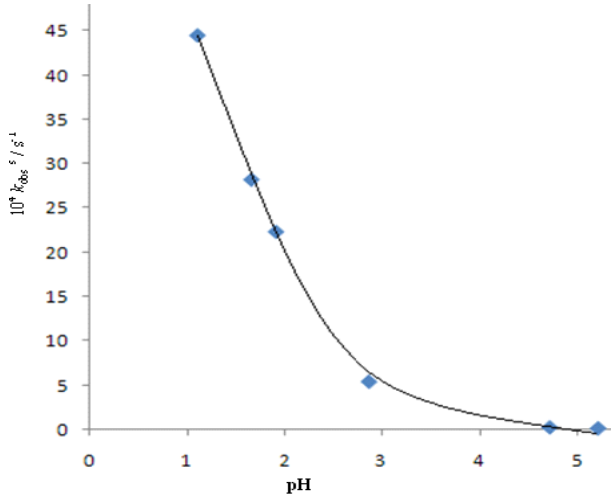
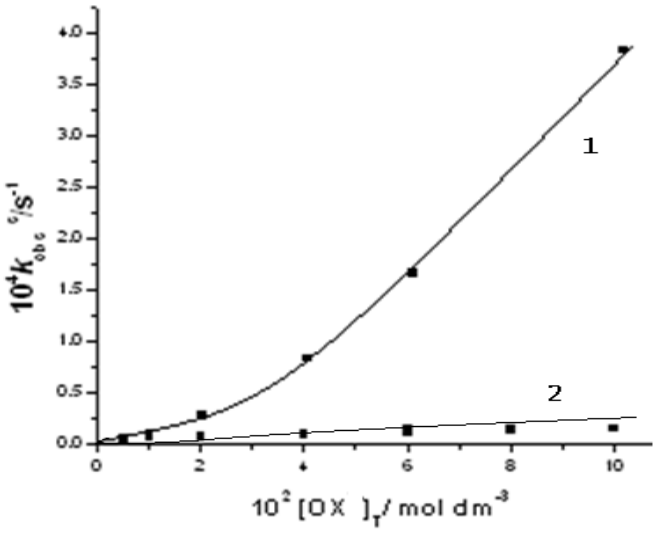


Figure S3c-$10^4 k_{obs}{}^s$/s^{-1} vs pH plot at 35^{o}C; [OX]$_T$ = 0.005 mol dm^{-3}

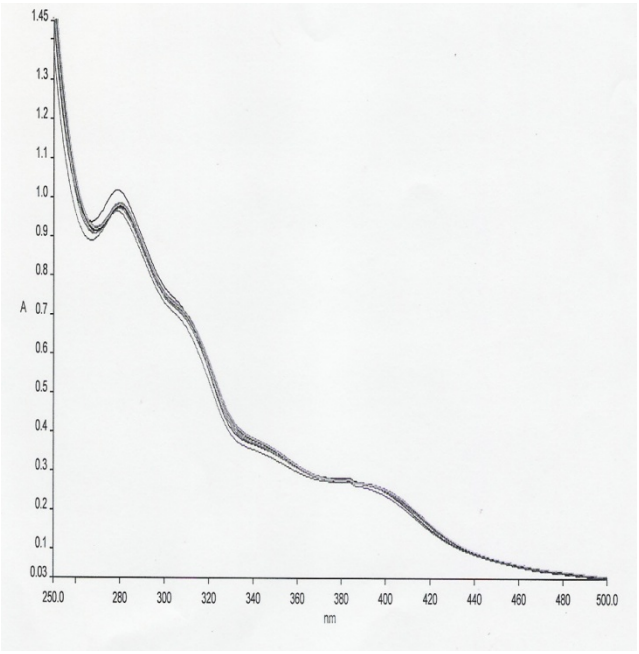


17

18 Figure S3d - $10^4 k_{obs}{}^s$ / s^{-1} vs. $[OX]_T$/ mol dm^{-3} plot at 35°C at pH = 5.26 ± 0.15 (1),

19 5.70 – 6.72 (2)

20



21

22 Figure S4a - Absorption spectra of *trans*-$Mn^{III}(salen)(OH_2)_2^+$: $[complex]_T = 5.708 \times 10^{-5}$,

23 $[HClO_4] = 1.0 \times 10^{-4}$, $[SDS]_T = 0, 0.01, 0.015, 0.02, 0.03, 0.05, 0.08, 0.1$ mol dm^{-3},

24 absorbance reading down wards at 280 nm with increasing $[SDS]_T$

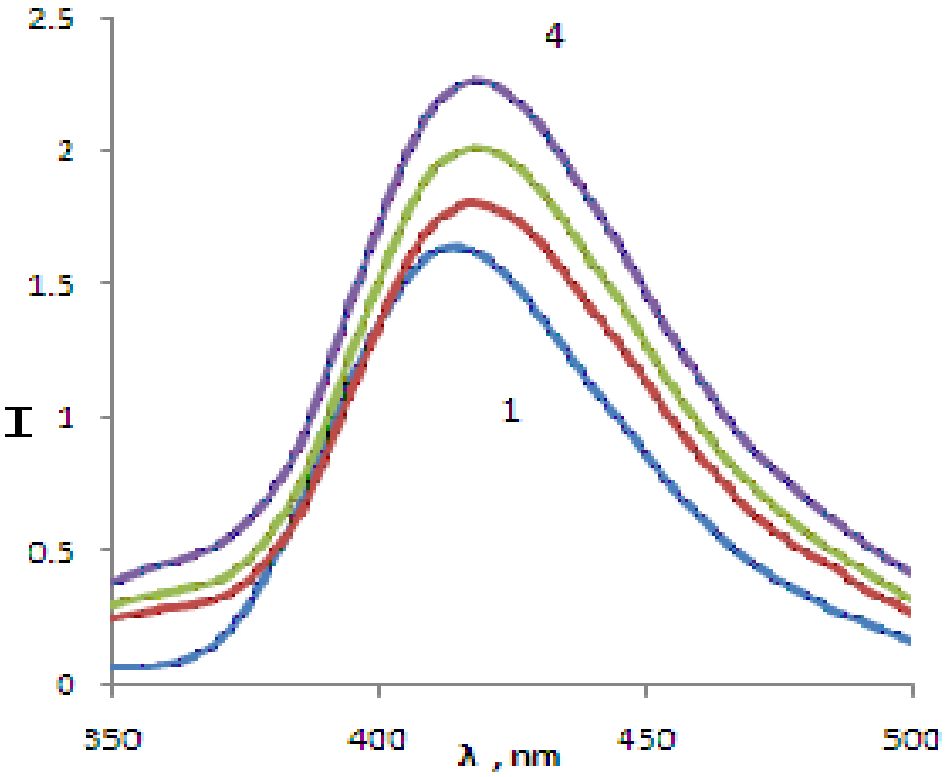


Figure S4b - Emission spectra of *trans*-$Mn^{III}(salen)(OH_2)_2^+$: $[complex]_T = 1.029 \times 10^{-4}$, $[HClO_4] = 1.0 \times 10^{-4}$, $[SDS]_T = 0(1), 0.02(2), 0.03(3), 0.05(4)$ mol dm^{-3}, $\mathbf{I} = \mathbf{I}_\lambda/\mathbf{I}^w_{\lambda max}$, $\mathbf{I}^w_{\lambda max}$ denotes Intensity at wave length maximum in absence of SDS.

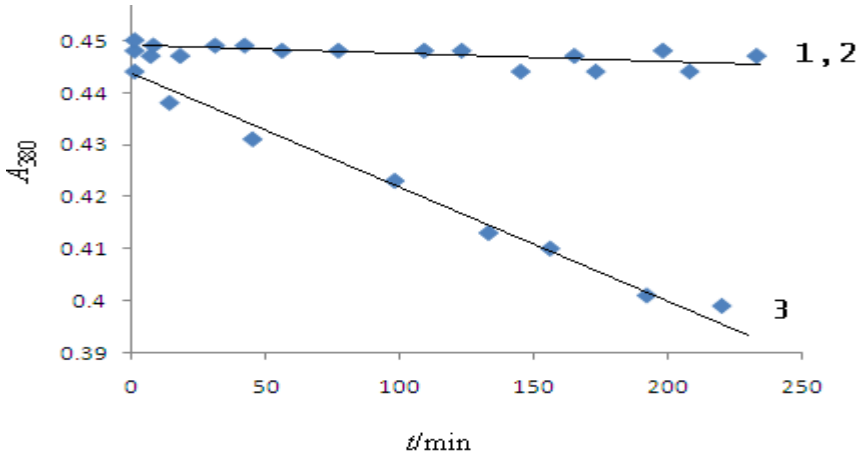


Figure S5- Absorbance ($A_{380\ nm}$) versus *t*/min plot at 40°C, $[Mn^{III}(salen)(OH_2)_2^+] = 1.285 \times 10^{-4}$,

$I = 0.3$ mol dm^{-3}, $[NaN_3]_T$/ mol dm^{-3} (pH)[run no.] : 0.01 (4.56)[1], 0.1 (4.41)[2], 0.24 (4.40)[3].

Table **S**1(a) : Rate data for the reversible formation of $Mn^{III}(salen)(OH_2)(HOX)$. [a]

Temp., °C	$[OX]_T$/ mol dm^{-3}	$[HClO_4]$/mol dm^{-3}		
		0.02	0.05	0.10
		k^f / s^{-1} obs. (calc.)	k^f / s^{-1} obs. (calc.)	k^f / s^{-1} obs (calc.)
20.0	0.05	0.424 (0.422)	0.412 (0.385)	0.329 (0.341)
	0.10	0.603 (0.611)	0.553 (0.559)	0.473 (0.491)
	0.15	0.789 (0.768)	0.694 (0.706)	0.620 (0.624)
	0.20	0.914 (0.905)	0.820 (0.837)	0.767 (0.743)
	0.25	1.02 (1.03)	0.948 (0.956)	0.862 (0.853)
	0.30	1.15 (1.14)	1.06 (1.06)	0.962 (0.956)
25.0	0.05	0.753 (0.645)	0.602 (0.594)	0.512 (0.533)
	0.10	0.968 (0.934)	0.756 (0.860)	0.731 (0.765)
	0.15	1.17 (1.17)	1.09 (1.09)	0.970 (0.970)
	0.20	1.38 (1.39)	1.25 (1.29)	1.18 (1.16)
	0.25	1.56 (1.58)	1.46 (1.47)	1.36 (1.33)
	0.30	1.78 (1.76)	1.67 (1.65)	1.50 (1.49)
30.0	0.05	1.23 (1.03)	1.00 (0.95)	0.784 (0.854)
	0.10	1.45 (1.44)	1.28 (1.33)	1.14 (1.18)
	0.15	1.80 (1.78)	1.59 (1.65)	1.41 (1.46)
	0.20	2.08 (2.08)	1.94 (1.93)	1.74 (1.72)
	0.25	2.30 (2.34)	2.14 (2.18)	1.91 (1.96)
	0.30	2.68 (2.58)	2.45 (2.42)	2.18 (2.18)
40.0	0.05	2.49 (2.05)	2.12 (1.87)	1.56 (1.65)
	0.10	3.01 (2.94)	2.62 (2.68)	2.06 (2.35)
	0.15	3.56 (3.67)	3.47 (3.37)	2.69 (2.97)
	0.20	4.08 (4.30)	4.14 (3.98)	3.18 (3.52)
	0.25	4.88 (4.88)	4.62 (4.53)	3.95 (4.03)
	0.30	5.72 (5.41)	-	4.61 (4.51)

[a] $\lambda = 380$ nm; $[Mn^{III}(salen)(OH_2)_2]^+ = (7.72\text{-}9.05) \times 10^{-5}$; $I = 0.3$ mol dm^{-3} ($NaClO_4$).

Table **S**1(b) . pK values of H_2OX at $\boldsymbol{I} = 0.3$ mol dm^{-3}.[a]

Temp.,^{o}C	pK_1	pK_2
20.0	1.00	3.59
25.0	1.01	3.60
30.0	1.02	3.62
35.0	1.03	3.63
40.0	1.03	3.64

[a] Values calculated using ΔH^0 and ΔS^0 data and were corrected to I = 0.3 mol dm^{-3}, ref. (21)

Table **S**1(c) . Calculated rate, equilibrium constants and activation parameters for the reversible formation of *trans*-Mn^{III}(Salen) OXH).

Temp, ^{o}C	k_1^f/dm^3 mol^{-1} s^{-1}	k_2^f/dm^3 mol^{-1} s^{-1}	Q_1^{-1}/mol dm^{-3}	k_{-1}^f [a]/ s^{-1}	F [b]
20.0	7.94 ± 0.26	0.013 ± 0.12	(2.052 ± 0.16) x 10^{-2}	0.163 ± 0.014	0.00339
25.0	11.8 ± 0.75	0.31 ± 0.34	(2.163 ± 0.32) x 10^{-2}	0.255 ± 0.020	0.029
30.0	17.5 ± 1.1	0.000023 ± 0.49	(2.690 ± 0.354) x 10^{-2}	0.471 ± 0.069	0.072
40.0 $\Delta H^{\neq}$ / kJ mol^{-1}[c] $\Delta S^{\neq}$/ J K^{-1} mol^{-1}	38.2 ± 3.8 54.6 ± 0.8	0.0018 ± 1.74	(2.173 ± 0.53) x 10^{-2}	0.830 ± 0.218 64.2 ± 6.7	0.781
$\Delta S^{\neq}$/ J K^{-1} mol^{-1}	—41.2 ± 2.6			—40.8 ± 22.7	

[a] $k_{-1}^f = k_1^f Q_1^{-1}$; Q_1/dm^3 mol^{-1} = 48.7 ± 3.9, 46.2 ± 6.9, 37.2 ± 4.9 and 46.0 ± 11.2 at 20.0^{o}, 25.0^{o}, 30.0^{o} and 40.0^{o} C respectively. [b] $\sum (k_{cal} - k_{obs})^2$

Table **S**2- Reduction of *trans*-Mn^{III}(salen)$(OH_2)_2^+$ by Oxalate species in the presence of $HClO_4$

$10^3[OX]_T$/ mol dm^{-3}	$[HClO_4]_T$ /mol dm^{-3}	$10^3 k^s$/s^{-1} obs [cal]	$10^3 k^s$/s^{-1} obs [cal]	$10^3 k^s$/s^{-1} obs [cal]	$10^3 k^s$/s^{-1} obs [cal]
		25.0 ± 0.1 ^{o}C	**30.0 ± 0.1 ^{o}C**	**35.0 ± 0.1 ^{o}C**	**40.0 ± 0.1 ^{o}C**
1.00	0.012	0.145 [0.23]	0.17 [0.22]	0.17 [0.13]	0.23 [0.17]
2.00	0.012	0.30[a] [0.55]	0.42[a] [0.57]	0.51 [0.50]	0.57 [0.66]
3.00	0.012	0.74 [0.74]	0.97 [1.05]	0.90 [1.09]	1.21 [1.47]
4.00	0.012	1.26 [1.44]	1.56 [1.64]	1.03 [1.91]	2.06 [2.60]

5.00	0.012	2.00 [2.02]	2.35 [2.35]	2.23 [2.96]	4.47 [4.04]
8.00	0.012	5.14 [4.20]	6.39 [5.14]	8.22 [7.37]	
1.00	0.025	0.16 [0.23]	0.23 [0.23]	0.23 [0.19]	0.30 [0.23]
2.00	0.025	0.30 [0.58]	0.41 [0.63]	0.54[a] [0.69]	1.08[a] [0.89]
3.00	0.025	1.03 [1.04]	0.82 [1.18]	1.27 [1.48]	1.55 [1.95]
4.00	0.025	1.55 [1.60]	1.78[a] [1.89]	2.92 [2.55]	2.95 [3.40]
5.00	0.025	2.20 [2.26]	2.19 [2.73]	3.82 [3.89]	5.49 [5.23]
0.50	0.05	0.047 [0.091]	0.050 [0.089]	0.082 [0.074]	0.22 [0.071]
1.00	0.05	0.13 [0.22]	0.20 [0.23]	0.21 [0.25]	0.34 [0.28]
2.00	0.05	0.40 [0.58]	0.52[b] [0.66]	0.61 [0.87]	1.00 [1.09]
3.00	0.05	0.85 [1.08]	1.09 [1.29]	1.17 [1.86]	1.88 [2.39]
4.00	0.05	1.43 [1.70]	1.82 [2.09]	3.36 [3.19]	3.62 [4.16]
5.00	0.05	2.87 [2.45]	3.07 [3.06]	5.50 [4.82]	
6.00	0.05	3.68 [3.30]	4.66 [4.19]	6.70 [6.75]	
10.0	0.05	7.21 [7.70]	9.78 [10.1]	16.8 [17.1]	

[a] average of duplicate runs, [b] average of five runs

Table **S**3- Reduction of $Mn^{III}(salen)(OH_2)_2^+$ by Oxalate species at 25°C and 30°C in self buffer medium.

$10^3[OX]_T$/ mol dm^{-3}	pH[a]	$10^3 k^s$/ s^{-1} obs [cal]	pH[a]	$10^3 k^s$/ s^{-1} obs [cal]
	25.0 ± 0.1° C		**30.0 ± 0.1° C**	
1.50	2.88	0.047 [0.044]	3.01	0.079 [0.049]
2.00	2.87	0.075 [0.078]	3.01	0.12 [0.084]
2.50	2.89	0.11 [0.12]	2.96	0.13 [0.13]
3.00	2.82	0.16 [0.17]	2.96	0.22 [0.19]
3.00	3.76	0.036 [0.037]	3.50	0.092 [0.090]
3.00	4.57	0.0038 [0.002]	3.93	0.034 [0.029]
3.50	2.84	0.21 [0.23]	2.93	0.29 [0.26]
4.00	2.85	0.26 [0.28]	2.93	0.37 [0.33]
4.00	3.90	0.035 [0.040]	3.73	0.094 [0.090]
4.50	2.35	0.51 [0.43]	2.93	0.47 [0.41]

4.50	2.98	0.30 [0.32]		
5.00	2.35	0.62 [0.52]	2.91	0.55[b] [0.51]
5.00	2.96	0.33 [0.39]	2.92	0.56[b] [0.50]
5.00	4.81	0.0052 [0.002]	3.76	0.031 [0.030]
5.55	2.36	0.70 [0.62]	2.91	0.65 [0.60]
5.55	2.93	0.40 [0.48]		
6.00	2.91	0.46 [0.57]	2.90	0.76 [0.71]
6.00	3.57	0.16 [0.20]	3.47	0.33 [0.33]
6.00			3.42	0.32 [0.37]
6.00			3.41	0.33 [0.37]
6.00	4.25	0.030 [0.023]	3.88	0.093 [0.12]
9.00	3.49	0.37 [0.47]	3.39	0.80 [0.77]
10.0			3.64	0.48 [0.54]
10.0			4.14	0.080 [0.11]
10.0			4.43	0.012 [0.037]
12.0	3.48	0.73 [0.75]	3.37	1.27 [1.28]
12.0			3.88	0.27 [0.37]
12.0			4.20	0.072 [0.12]
15.0			4.10	0.15 [0.25]
18.0			3.84	0.64 [0.76]
19.0			4.08	0.26 [0.37]
20.0			3.59	1.68[b] [1.76]
25.0			4.51	0.036 [0.10]
25.0			4.80	0.022 [0.030]
26.0			4.50	0.072 [0.11]
28.0			4.22	0.27 [0.38]
30.0			4.10	0.55 [0.65]
32.0			3.97	1.01 [1.11]
34.0			3.88	1.78 [1.61]
35.0			4.51	0.057 [0.16]
36.0			3.86	1.89 [1.85]
45.0			4.53	0.081 [0.19]

[a] pH = – log [H^+]. [b] average of duplicate runs.

Table **S**4. Reduction of *trans*-$Mn^{III}(salen)(OH_2)_2^+$ by oxalate species at 35° and 40°C in self buffer medium.

$10^3[OX]_T$/mol dm^{-3}	pH[b]	$10^3 k^s/s^{-1}$ obs [cal]	pH[b]	$10^3 k^s/s^{-1}$ obs [cal]
	35.0 ± 0.1° C		**40.0 ± 0.1° C**	
1.50	3.13	0.069 [0.057]	2.92	0.12 [0.12]
2.00	3.05	0.11 [0.11]	2.92	0.20 [0.20]
2.50	3.07	0.18 [0.16]	2.93	0.31 [0.30]
3.00	3.02	0.23 [0.24]	2.92	0.42 [0.42]
3.00	3.69	0.067 [0.081]		
3.00	4.30	0.018 [0.012]		
3.50	3.10	0.29 [0.29]	2.94	0.57 [0.55]
4.00	3.03	0.37 [0.40]	2.93	0.66 [0.70]
4.00	3.79	0.085 [0.11]		
4.50	3.03	0.47 [0.50]	2.91	0.91 [0.88]
5.00	3.19	0.52 [0.52]	2.91	1.16 [1.06]
5.00	4.47	0.019 [0.016]		
5.00	4.66	0.0078 [0.007]		
5.50	3.13	0.63 [0.66]	2.89	1.26 [1.28]
6.00	3.25	0.65 [0.67]	2.90	1.77 [1.48]
6.00	3.66	0.29 [0.32]		
6.00	4.08	0.068 [0.093]		
9.00	3.67	0.63 [0.63]		
10.0	3.69	0.64 [0.72]	3.76	0.83 [0.90]
10.0	4.03	0.26[a] [0.27]	4.34	0.15 [0.13]
10.0	4.80	0.017 [0.014]	4.63	0.025 [0.043]
12.0	3.98	0.40 [0.43]	3.93	0.55 [0.73]
12.0	3.48	1.45 [1.55]	4.34	0.15 [0.18]
12.0	3.69	1.02 [0.98]		
15.0	4.26	0.24 [0.24]	4.28	0.29 [0.31]
18.0	3.90	0.94 [1.08]		

19.0	4.26	0.40	[0.35]	4.26	0.50 [0.47]
20.0 20.0	3.66 3.69	2.70 2.21	[2.41] [2.24]	3.62	3.45 [3.72]
22.0				4.62	0.21 [0.14]
25.0	4.78	0.052	[0.065]	4.70	0.079 [0.012]
25.0	4.92	0.039	[0.035]	5.08	0.062 [0.024]
26.0	4.67	0.11	[0.12]	4.71	0.15 [0.12]
28.0	4.40	0.38[a]	[0.37]	4.42	0.48 [0.44]
30.0	4.21	0.82	[0.84]	4.21	1.09 [1.07]
32.0	4.09	1.39	[1.40]	4.06	1.75 [1.99]
34.0	3.96	2.33	[2.34]	3.96	2.60 [3.00]
35.0	4.80	0.078	[0.092]	4.69	0.12 [0.19]
36.0	3.83	3.61	[3.72]	3.94	4.13 [3.45]
45.0	4.83	0.11	[0.12]	4.73	0.17 [0.22]

[a] av of duplicate runs, [b] pH = – log [H^+].

Table **S**5. Reduction of *trans*-$Mn^{III}(salen)(OH_2)_2^+$ by oxalate species in $K_2C_2O_4$/KCl medium at 35°C.[a]

$[OX]_T$/ mol dm^{-3}	pH [b]	$10^4 k_{obs}$ s/ s^{-1}	$10^4 k_{cal}$ /s^{-1}
0.0025	5.04	0.032	0.018
0.005	5.25	0.045	0.039
0.005	5.38	0.037	0.029
0.005	5.41	0.045	0.027
0.010	5.30	0.10	0.11
0.020	5.27	0.27	0.38
0.040	5.26	0.83	1.07
0.060	5.24	1.67	1.90
0.080	5.21	2.83	2.93
0.100	5.26	3.83	3.40

0.010	5.70	0.053	0.048
0.010	5.71	0.055	0.047
0.020	6.00	0.066	0.084
0.020	6.00	0.068	0.084
0.040	6.26	0.086	0.15
0.040	6.30	0.085	0.14
0.060	6.45	0.11	0.20
0.080	6.61	0.12	0.25
0.10	6.72	0.14	0.30
Calculated parameters			
$(k_5Q_2 + k_7Q_1)^c$/ $dm^6\,mol^{-2}\,s^{-1}$	6.79 ± 0.39	$(k_5 \pm 0.91\ k_7)$/ $dm^3\,mol^{-1}\,s^{-1}$	0.148 ± 0.009
$k_6Q_2{}^c$/ $dm^6\,mol^{-2}\,s^{-1}$	(1.35 ± 1.18) × 10^{-2}	k_6/ $dm^3\,mol^{-1}\,s^{-1}$	(2.94 ± 2.57) × 10^{-4}
$k_4Q_2{}^c$/ $dm^3\,mol^{-1}\,s^{-1}$	(1.4 ± 699.1) × 10^{-6}	k_4/ s^{-1}	(0.03 ± 14) × 10^{-6}

[a] ***I*** = 0.3 ($K_2C_2O_4$ + KCl), $[Mn^{III}(salen)(OH_2)_2^+]$ = (0.6 – 1.3) x 10^{-4} mol dm^{-3}. [b] pH = – log $[H^+]$. [c] based on pK_1 = 1.03, pK_2 = 3.63, pK_M = 6.9, Q_1 = 42.0, Q_2 (= $Q_1K_2^{/}/K_1$) = 45.9 dm^3 mol^{-1}, k_1 = 1.16 $dm^3\,mol^{-1}\,s^{-1}$, $K_2^{/}$ = 2.56 x 10^{-4} mol dm^{-3}; $\sum[10^4(k_{cal} - k_{obs}{}^s)]^2$ = 0.386.

Table **S**6- Reduction of *trans*-$[Mn^{III}(salen)(OH_2)_2]^+$ by oxalate in the presence of sodium dodecyl sulphate (SDS).[a]

$[NaClO_4]$ / mol dm^{-3}	$[SDS]_T$/ mol dm^{-3}	pH[b]	$10^4k_{obs}{}^s/s^{-1}$[c]	$10^4k_{cal}/s^{-1}$
0.00	0.0005	3.96	3.34	
0.00	0.001	3.96	3.36,3.57	
0.00	0.002	3.97	3.37	
0.00	0.005	3.98	3.43	
0.00	0.0075	3.95	3.35	
0.00	0.010	3.98	2.68	2.59 (2.59)
0.00	0.012	3.98	1.87	1.91 (1.92)
0.00	0.015	4.00	1.24	1.35 (1.36)

0.00	0.020	3.99	0.94	0.99 (0.99)
0.00	0.025	3.95	0.82	0.86 (0.87)
0.00	0.030	3.98	0.72	0.69 (0.70)
0.00	0.040	4.02	0.55	0.51 (0.51)
0.00	0.080	4.00	0.52	0.34 (0.34)
0.00	0.100	3.95	0.51	0.34 (0.34)
0.01	0.020	3.90	1.08	1.29 (1.30)
0.02	0.020	3.89	1.21	1.37 (1.38)
0.05	0.020	3.85	1.58	1.52 (1.53)
0.10	0.020	3.70	2.03	2.00 (2.00)
0.15	0.020	3.67	2.22	2.01 (2.02)
0.20	0.020	3.62	2.45	2.14 (2.15)
0.30	0.020	3.51	2.62	2.55 (2.55)
K_{ex}[d]	10.4 ± 0.8, (10.3 ± 1.2)	Q_m/dm^3 mol^{-1}	0, (0.0009 ± 53)	

[a] $[Na_2OX]_T$ = 0.002, $[NaHOX]_T$ = 0.004 mol dm^{-3}. [b] pH = –log[H$^+$]. [c] 30.0^{o}C, variable Ionic strength (*calc.* ***I*** = 0.0169 - 0.319 mol dm^{-3}).

[d] based on k_1^W = 0.87 dm^3 mol^{-1} s^{-1}, Q_1^0 = 72.7, pK_2^0 = 4.27, β = 0.6, cmc = 0.009 mol dm^{-3} ; $\sum[10^4(k_{cal}-k_{obs})]^2$ = 0.312 (0.313). All parenthesized values refer to data fitting using Q_m and K_{ex} as the two variables.

Table **S**7– Values of β *and* cmc used to compute K_{ex} and Q_m.

β	cmc/ mol dm^{-3}	K_{ex}[a]	Q_m[a] / mol dm^{-3}	$\sum[10^4(k_{cal}-k_{obs})]^2$ [a]
0.6	0.006	6.8 ± 0.8 [7.0 ± 1.3]	[0.042 ± 68]	1.006 [1.008]
0.6	0.007	7.7 ± 0.2 [7.2 ± 1.2]	[0.16 ± 64]	0.745 [0.746]
0.6	0.008	8.9 ± 0.8 [8.6 ± 1.2]	[0.004 ± 58]	0.482 [0.486]
0.6	0.009	10.4 ± 0.8 [10.3 ± 1.2]	[0.0009 ± 53]	0.312 [0.313]
0.6	0.0095	10. 8 ± 0.9 [10.9 ± 1.3]	[0.0005 ± 61]	0.381 [0.382]
0.7	0.006		[0.00012 ± 65]	1.02 [1.019]
0.7	0.007	5.5 ± 0.7 [5.4 ± 0.9]	[0.30 ± 63]	0.773 [0.776]

0.7	0.008	6.3 ± 0.7 [6.1 ± 1.0]	[0.0004± 60]	0.524 [0.524]
0.7	0.009	7.3 ± 0.7 [7.4 ± 1.0]	[0.012 ± 54]	0.335 [0.339]
0.7	0.0095	8.5 ± 0.7 [8.2 ± 0.9]	[0.003 ± 57]	0.349 [0.354]
		9.0 ± 0.7 [8.7 ± 1.0]		
0.8	0.006		[0.55 ± 64]	1.027 [1.028]
0.8	0.007	4.6 ± 0.6 [4.5 ± 0.8]	[0.004 ± 66]	0. 798 [0.819]
0.8	0.008	5.2 ± 0.6 [5.6 ± 0.9]	[0.073 ± 59]	0.562 [0.562]
0.8	0.009	6.0 ± 0.6 [6.0 ± 0.9]	[0.0009 ± 55]	0.373 [0.377]
0.8	0.0095	7.1 ± 0.6 [6.9 ± 0.8]	[0.33 ± 57]	0.359 [0.362]
0.8	0.010	7.6 ± 0.6 [7.4± 0.9]	[0.00002 ± 67]	0.493 [0.496]
		7.8 ± 0.7 [7.6 ± 1.0]		

[a] Q_m= 0 for values not shown under square brackets.

Table **S**8- Rate data for reduction of *trans*-$[Mn^{III}(salen)(OH_2)_2]^+$ by oxalate in the presence of azide (N_3^-).[a]

$[NaN_3]_T$/mol dm^{-3}	$10^3k_{obs}^s$/s^{-1}	10^3k_{cal}/s^{-1}	$[NaN_3]_T$/mol dm^{-3}	$10^3k_{obs}^s$/s^{-1}	10^3k_{cal}/s^{-1}
0	0.27		0.10	1.25	1.25
0.01	0.41	0.42	0.15	1.50	1.49
0.02	0.58	0.56	0.20	1.66	1.67
0.05	0.86	0.88			
$k_8Q_4^b$/dm^6 mol^{-2} s^{-1}	28.3 ± 1.1				
Q_4^b/dm^3 mol^{-1}	26.1 ± 1.8				
k_8/ dm^3 mol^{-1} s^{-1}	1.08 ± 0.09				
$\sum[10^3(k_{cal} - k_{obs})]^2$	0.001209				

[a] 40.0°C, –log[H$^+$] = 4.53 ± 0.03, ***I*** = 0.3, $[OX]_T$ = 0.022 moldm^{-3}.

[b] based on pK_d(N_3H) = 4.35, pK_2 = 3.64, Q_1 = 42, $K_2^{/}$= 3.57 x 10^{-4} mol dm^{-3}.