

Electronic Supporting Information (ESI)

Dinuclear Seven-Coordinate Mn(II) Complexes. Effect of Manganese(II)-Hydroxo Species on Water Exchange and Superoxide Dismutase Activity

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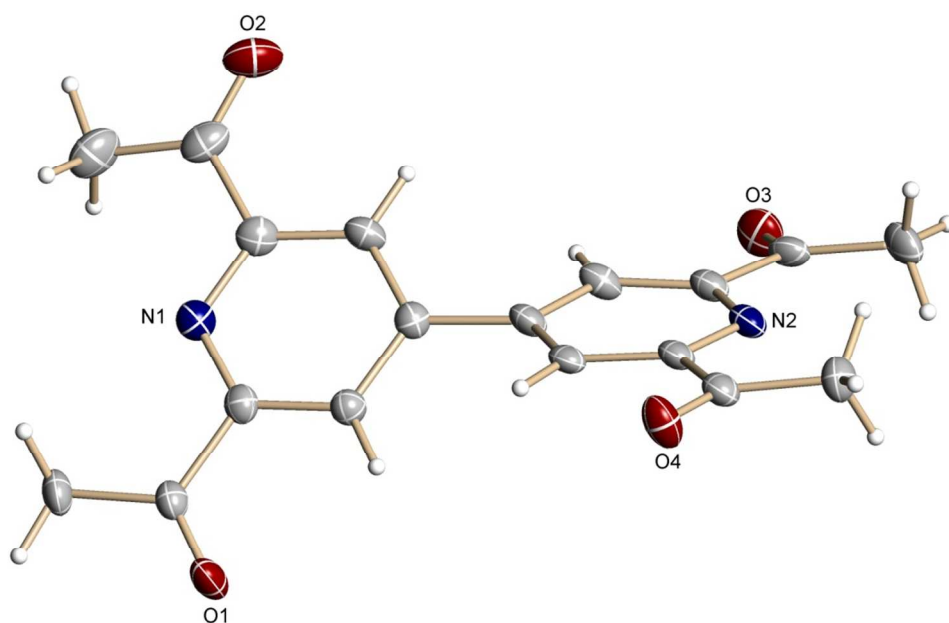


Figure S1. ORTEP drawing for tabpy with labeling and 50% probability ellipsoids for the non-hydrogen atoms.

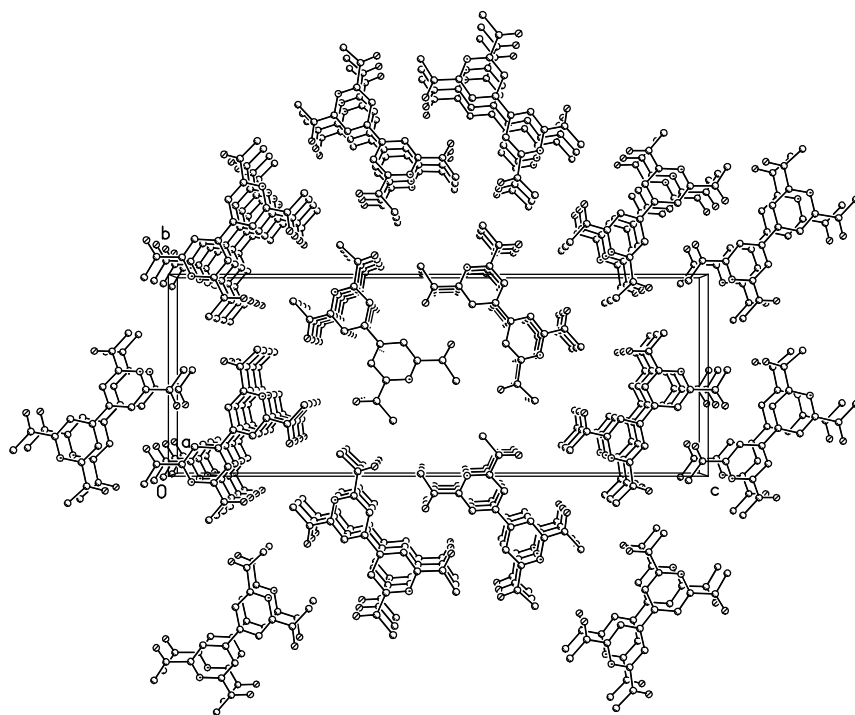


Figure S2. Packing diagram for tabpy along the crystallographic *a* axis.

Table S1. Crystallographic data for 2,2',6,6'-Tetraacetyl-4,4'-bipyridine (tabpy).

Empirical formula	C ₁₈ H ₁₆ N ₂ O ₄
Formula weight	324.33
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 3.8912(4) Å alpha = 90 deg. b = 12.3171(13) Å beta = 90 deg. c = 32.947(4) Å gamma = 90 deg.
Volume	1579.1(3) Å ³
Z	4
Calculated density	1.364 Mg/m ³
Absorption coefficient	0.098 mm ⁻¹
F(000)	680
Crystal size	0.41 x 0.10 x 0.08 mm
Theta range for data collection	1.77 to 27.13 deg.
Limiting indices	-4<=h<=4, -15<=k<=14, -42<=l<=41
Reflections collected / unique	9823 / 2085
[R(int) = 0.0488]	
Completeness to theta =	25.00 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.585
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2085 / 0 / 221
Goodness-of-fit on F ²	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0563, wR2 = 0.1436
R indices (all data)	R1 = 0.0652, wR2 = 0.1475
Largest diff. peak and hole	0.267 and -0.276 e.Å ⁻³

Discussion of crystal packing of [Mn₂(L1)Cl₄] and [Mn₂(L2)Cl₄]

The crystal packing is very similar for both compounds and is characterized by stacks of dinuclear complex molecules arranged along the crystallographic *b* axis (figure S3 and figure S4). Neighbored stacks of molecules are linked *via* hydrogen bonds between the hydroxyl groups of the co-crystallized methanol solvate molecules and chlorido ligands with D–H···A (donor-hydrogen···acceptor) distances ranging from 2.74 to 3.24 Å. Additional N–H···O and N–H···Cl

hydrogen bonds are observed in the case of the amine complex $[\text{Mn}_2(\text{L2})\text{Cl}_4]$, where the NH donors of the macrocyclic complex unit can interact with either a hydroxyl group of a solvent molecule or with a chlorido ligand of a neighbored complex molecule.

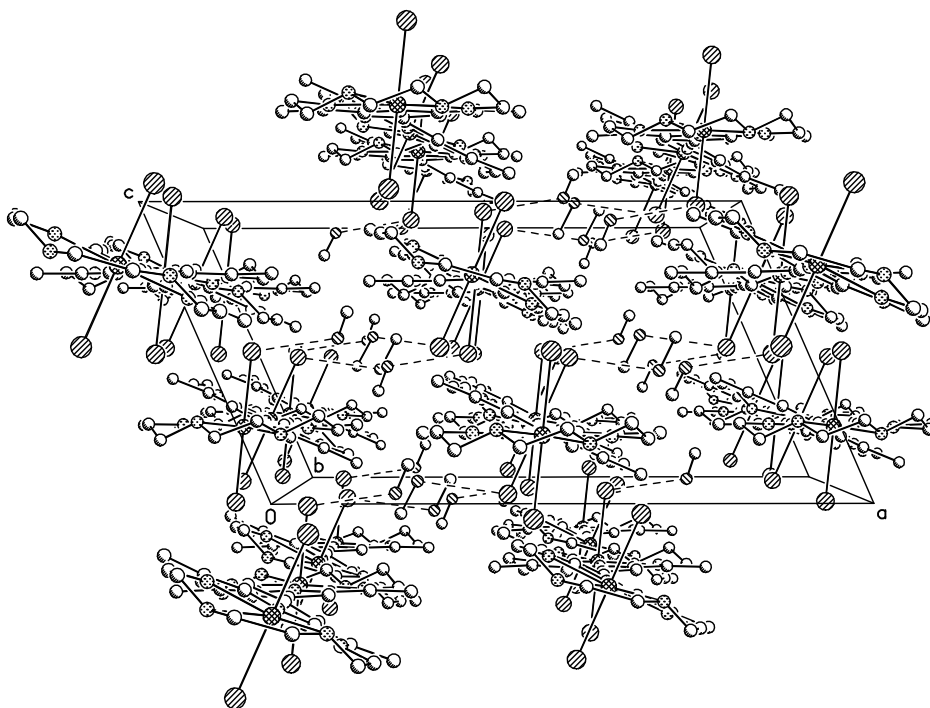


Figure S3. Packing diagram for $[\text{Mn}_2(\text{L1})\text{Cl}_4] \cdot 4\text{MeOH}$, view along the crystallographic *b* axis.

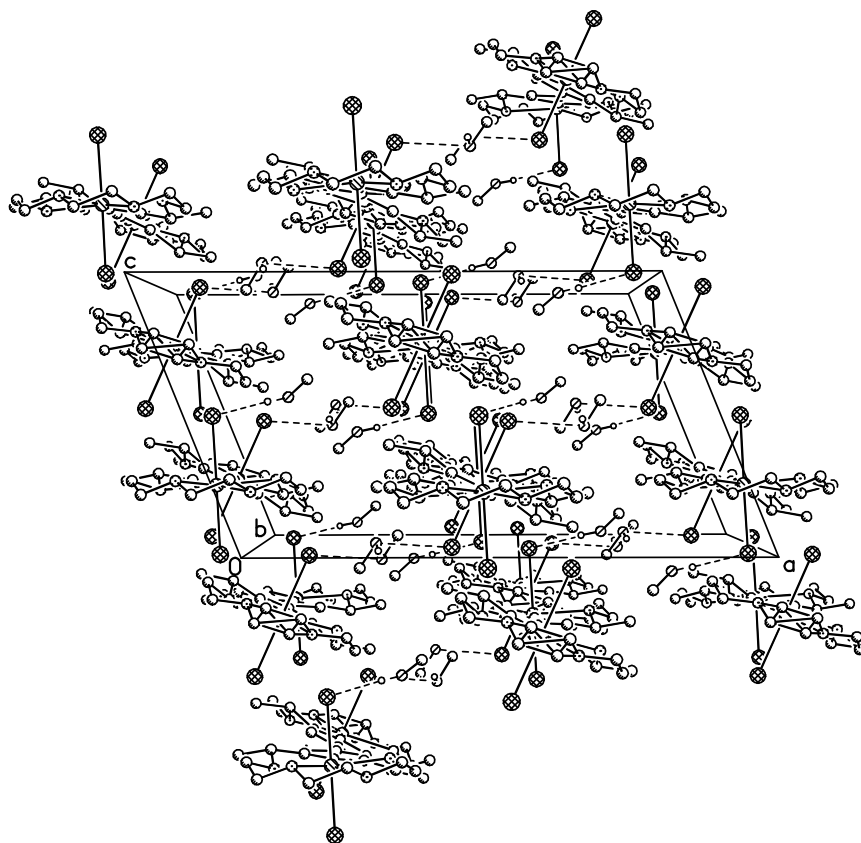


Figure S4. Packing diagram for $[\text{Mn}_2(\text{L2})\text{Cl}_4] \cdot 4\text{MeOH}$, view along the crystallographic b axis.

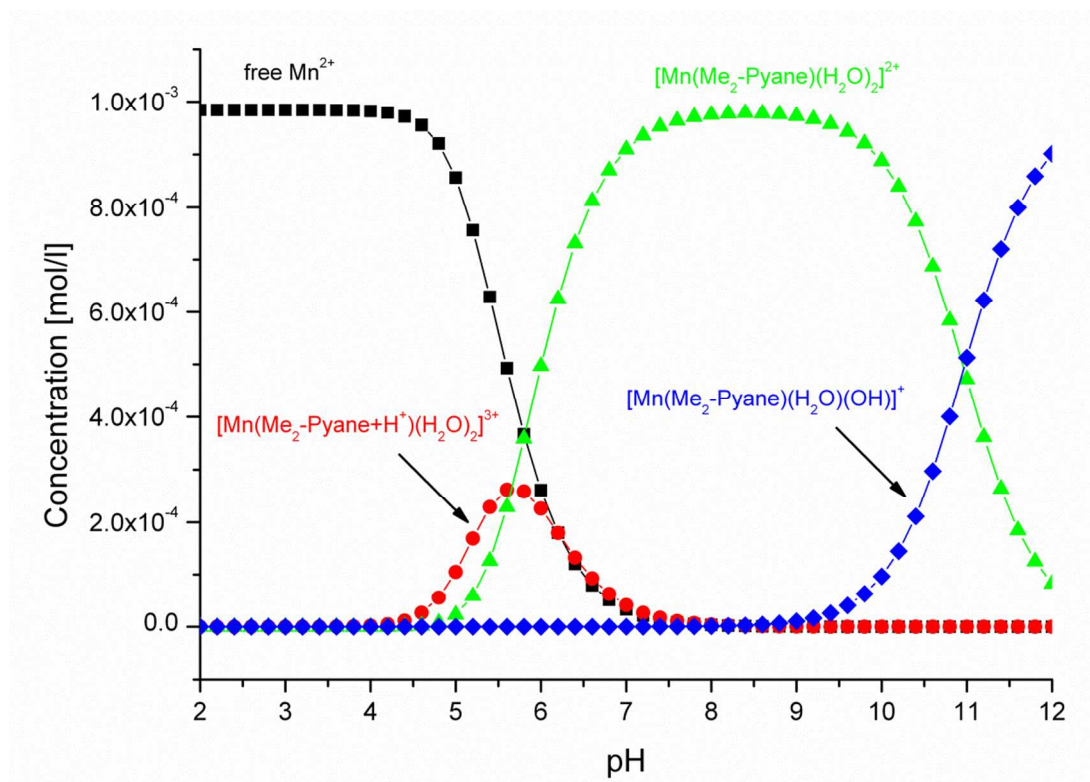


Figure S5. Species distribution for the complex $[\text{Mn}(\text{Me}_2\text{-Pyane})(\text{H}_2\text{O})_2]^{2+}$ as a function of pH at 25 °C and $[\text{complex}] = 1 \text{ mM}$.

Figure S6. High accuracy mass spectra of $[\text{Mn}_2(\text{L1})\text{Cl}_4]$ at 180 °C in aqueous solution pH 7.5
Main species at m/z 362.0919 is assigned to doubly charged $[\text{Mn}_2(\text{L1})\text{Cl}_3]^{2+}$. Species at m/z 524.1489 is a decomposition product due to harsh mass-spec conditions.

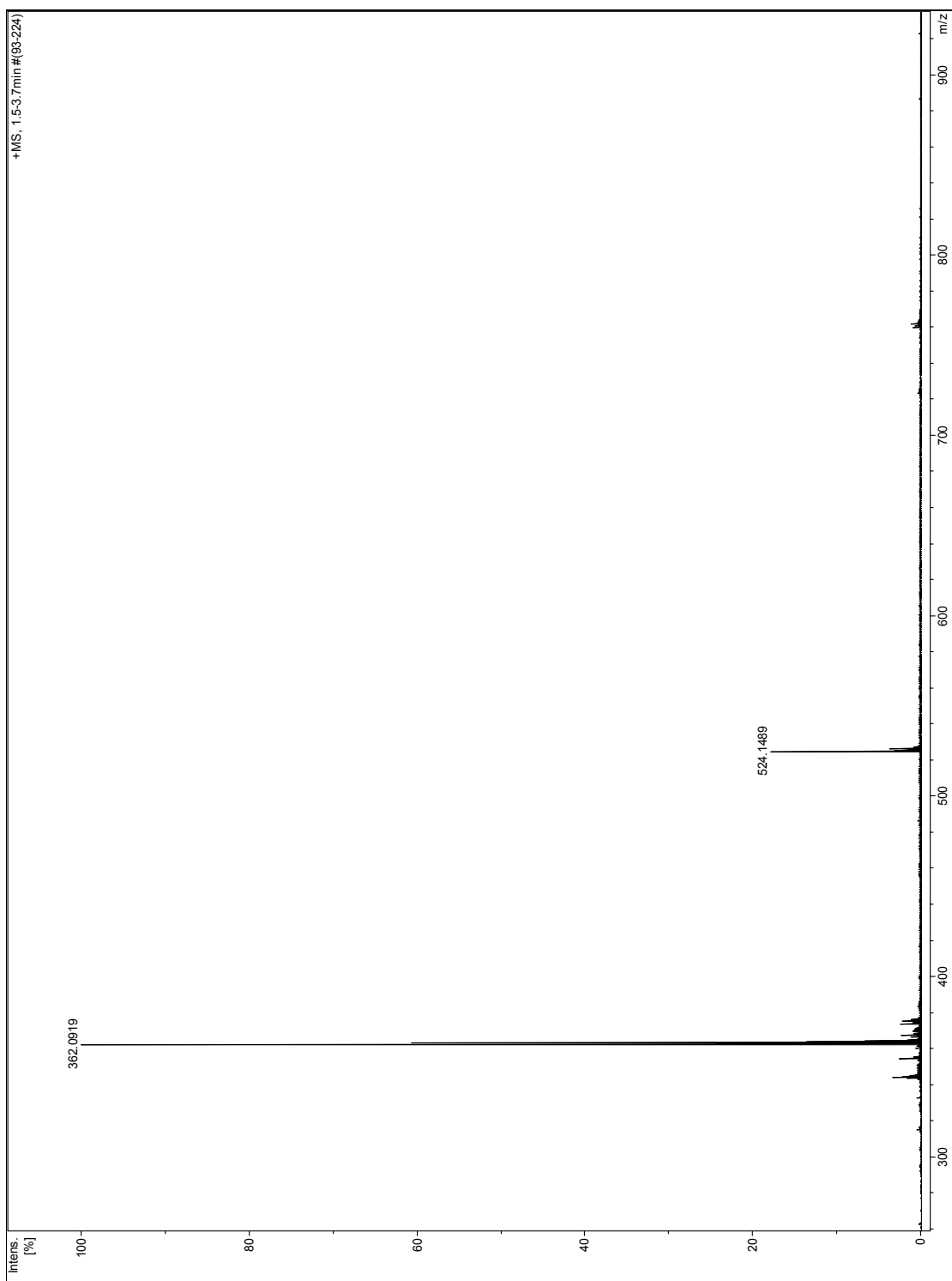
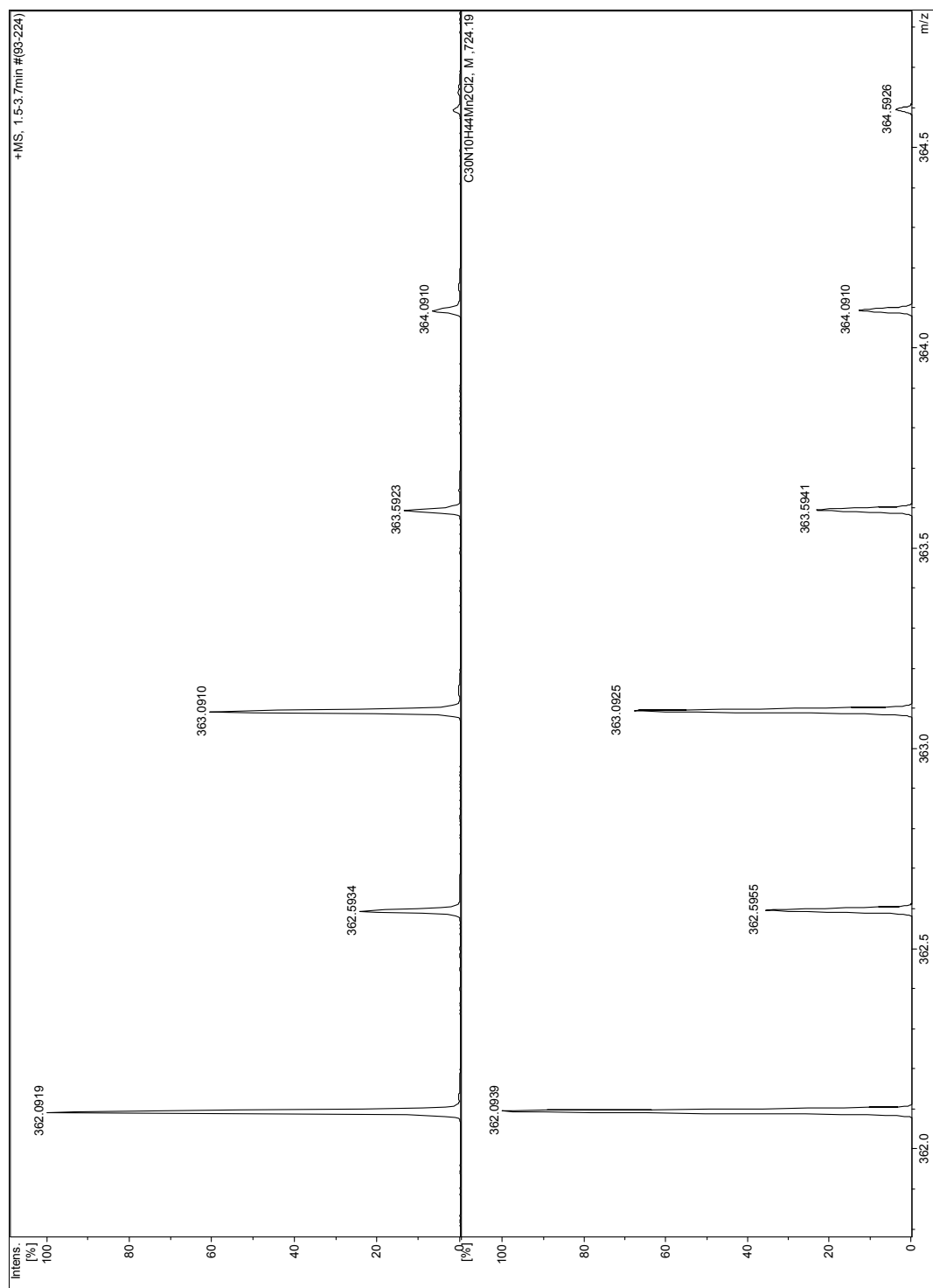


Figure S7. High accuracy mass spectra of the $[\text{Mn}_2(\text{L1})\text{Cl}_3]^{2+}$ species. Top shows experimentally obtained spectra. Bottom shows simulated isotopic pattern.



Data Treatment for ^{17}O NMR Spectroscopy. The exchange rate of solvent molecules between the bulk and the coordination site of the different paramagnetic manganese(II) complexes were determined by ^{17}O -NMR from measurements of the transverse relaxation rates $1/T_{2r}$ of the bulk solvent nuclei. From the experimentally obtained NMR data, $\Delta\nu_{\text{obs}}$ and $\Delta\nu_{\text{sol}}$, the half widths of the ^{17}O -NMR lines for solvent in the bulk in the presence and absence of the Mn(II) complex, respectively, together with the mole fraction of the bound water P_m (eq S2), the reduced transverse relaxation rates ($1/T_{2r}$) can be calculated for each temperature and pressure via the mathematical equations set up by Swift and Connick.¹ According to this equation T_{2r} is related to the mean lifetime, τ_m , and to the transverse relaxation time T_{2m} of coordinated water in the inner sphere of Mn(II) in the absence of chemical exchange (eq 1). Thus, the relationship of the exchange rate, $k_{\text{ex}} = \frac{1}{\tau_m}$, between coordinated and bulk water and the NMR observable $1/T_{2r}$ is given by equation S1.

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left\{ \frac{1}{T_2} - \frac{1}{T_2^0} \right\} = \pi \frac{1}{P_m} (\Delta\nu_{\text{obs.}} - \Delta\nu_{\text{solvent}}) =$$

$$\frac{1}{\tau_m} \left\{ \frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2} \right\} + \frac{1}{T_{2os}} \quad (\text{S1})$$

P_m is the mole fraction of solvent in the exchanging site compared to the bulk solvent (eq S2, with n = number of coordinated water molecules on the paramagnetic center); $\Delta\omega_m$ is the difference between the resonance frequency of oxygen-17 nuclei of solvent in the metal ions first coordination sphere and in the bulk. The outer-sphere contributions to T_{2r} , arising from long-range interactions of the paramagnetic unpaired electron of the manganese complex with the water outside the first coordination sphere, are represented by T_{2os} . The contribution of $1/T_{2os}$ was found to be negligible in the studied systems, which is clearly seen in the shape of the

temperature dependence of T_{2r} , *i.e.* no changeover to positive slope in the slow exchange region at low temperatures.

$$P_m = \frac{n \times [\text{complex}]}{[H_2O]} \quad (\text{S2})$$

In the case of Mn(II) complexes the long electronic relaxations² cause T_{2m} to dominate in eq 1 so that $\Delta\omega_m$ is considered to be negligible. Therefore, the temperature dependence of T_{2r} for Mn(II) complexes is given by the reduced equation S3.^{3,4}

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m + T_{2m}} \quad (\text{S3})$$

In this reduced equation (eq S3), the transverse relaxation is dominated by the scalar relaxation mechanism, $1/T_{2sc}$ (eq S4), with the longitudinal electronic relaxation term $1/T_{1e}$ (given in eq 4a with $i = 1$) being the determining factor in transverse relaxation.^{3,4,5}

$$\frac{1}{T_{2m}} \cong \frac{1}{T_{2sc}} = \frac{1}{3} (S(S+1)) \left(\frac{A}{\hbar} \right)^2 \left(\tau_{s1} + \frac{\tau_{s2}}{1 + \tau_{s2}^2 \omega_s^2} \right) \quad (\text{S4})$$

$$\frac{1}{\tau_{si}} = \frac{1}{\tau_m} + \frac{1}{T_{ie}} \quad i = 1, 2 \quad (\text{S4a})$$

The electronic spin relaxation is mainly governed by the transient zero field splitting (ZFS) mechanism and for the longitudinal term $1/T_{1e}$ McLachlan has developed equation S5.⁶

$$\frac{1}{T_{1e}} = \frac{32}{25} \Delta^2 \left(\frac{\tau_v}{1 + \omega_s^2 \tau_v^2} + \frac{4\tau_v}{1 + 4\omega_s^2 \tau_v^2} \right) \quad (\text{S5})$$

$$\tau = \tau_v^{298} \exp \left\{ \frac{E_v}{R} \left(\frac{1}{T} - \frac{1}{298.2} \right) \right\} \quad (\text{S5a})$$

The parameters Δ^2 (eq S5) and τ_v (eq S5) are usually obtained through EPR measurements, but due to the very complex behavior of dinuclear manganese complexes in EPR⁷ values for Δ^2 , τ_v , which is dependent from τ_v *via* eq. S5a, were not directly accessible but were determined as

variables in the fitting process of the transverse relaxation with eq S7 as reported in the literature.^{8,9,10} The parameter E_v has been fixed to 1 kJ/mol for all measurements in order to improve the fit. However, we found the contribution of electronic relaxation rates in the fast exchanging systems to be small or negligible (between 3 and 21 % under experimental conditions).

The temperature dependence of the solvent exchange rate constant, k_{ex} , is given by the Eyring equation (eq S6).

$$\frac{1}{\tau_m} = k_{ex} = \frac{k_b T}{h} \exp\left(\frac{\Delta S^\#}{R} - \frac{\Delta H^\#}{RT}\right) \quad (S6)$$

A combination of the significant contributions to T_{2r} for Mn(II) species leads to equation S7 and the reduced transverse relaxation values $1/T_{2r}$, obtained from $\Delta\nu_{obs}$ with ^{17}O -NMR line broadening at various temperatures, were fitted with this eq S7 to obtain the parameters (A/h), $\Delta H^\#$, $\Delta S^\#$, Δ^2 and τ_v all of which are summarized in Table 6.¹¹ From $\Delta H^\#$ and $\Delta S^\#$ the water exchange rate constant is calculated eventually *via* eq. S6.¹²

$$\frac{1}{T_{2r}} = \left(\tau_m + \frac{1}{C} \left(\frac{1}{\tau_m} + \frac{1}{T_{1e}} \right) \right)^{-1} \quad (S7)$$

$$C = \frac{1}{3} (S(S+1)) \left(\frac{A}{h} \right)^2 \quad (S7a)$$

Table S2. Temperature dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L1})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M PIPES buffer, pH 7.5, [complex] = 10 mM, and B = 9.4 T. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Temperature [K]	$1000 / T [K^{-1}]$	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
274.2	3.65	1.44×10^{-3}	168.8	1048.8	15.221
278.2	3.60	1.44×10^{-3}	150.6	1119.5	15.311
283.2	3.53	1.44×10^{-3}	131.9	1362.5	15.537
288.2	3.47	1.44×10^{-3}	114.0	1690.2	15.773
293.2	3.41	1.44×10^{-3}	89.4	2052.1	15.979
298.2	3.35	1.44×10^{-3}	75.8	2343.6	16.119
303.2	3.30	1.44×10^{-3}	67.3	2790.7	16.299
308.2	3.24	1.44×10^{-3}	58.6	3062.0	16.395
313.2	3.19	1.44×10^{-3}	51.6	3319.5	16.478
318.2	3.14	1.44×10^{-3}	45.7	3495.5	16.531
323.2	3.09	1.44×10^{-3}	40.5	3223.5	16.451
328.2	3.05	1.44×10^{-3}	36.3	3061.7	16.399
333.2	3.00	1.44×10^{-3}	32.5	3040.2	16.393
338.2	2.96	1.44×10^{-3}	29.2	2796.9	16.310

Table S3. Pressure dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L1})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M PIPES buffer, pH 7.5, [complex] = 10 mM, and B = 9.4 T and T = 290.2 K. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Pressure [MPa]	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
2	1.44×10^{-3}	113.5	1699.0	15.75
30	1.44×10^{-3}	113.2	1617.5	15.70
60	1.44×10^{-3}	113.2	1559.4	15.66
90	1.44×10^{-3}	113.0	1469.8	15.59
120	1.44×10^{-3}	112.9	1420.5	15.56
150	1.44×10^{-3}	112.9	1334.2	15.49

Table S4. Temperature dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L1})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M CAPS buffer, pH 9.3, [complex] = 20 mM, and B = 9.4 T. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Temperature [K]	$1000 / T [K^{-1}]$	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
274.2	3.65	1.44×10^{-3}	114.5	1416.8	14.860
278.2	3.60	1.44×10^{-3}	97.2	1591.4	14.997
283.2	3.53	1.44×10^{-3}	80.5	2132.7	15.315
288.2	3.47	1.44×10^{-3}	68.1	2756.7	15.585
293.2	3.41	1.44×10^{-3}	58.2	3467.8	15.822
298.2	3.35	1.44×10^{-3}	50.0	4347.4	16.054
303.2	3.30	1.44×10^{-3}	44.2	5043.8	16.205
308.2	3.24	1.44×10^{-3}	39.1	5694.2	16.328
313.2	3.19	1.44×10^{-3}	34.7	6406.7	16.448
318.2	3.14	1.44×10^{-3}	31.2	6791.3	16.507
323.2	3.09	1.44×10^{-3}	28.1	6406.7	16.449
328.2	3.05	1.44×10^{-3}	25.5	6391.3	16.447
333.2	3.00	1.44×10^{-3}	23.4	5839.5	16.356
338.2	2.96	1.44×10^{-3}	21.1	5378.8	16.274

Table S5. Pressure dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L1})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M CAPS buffer, pH 9.3, [complex] = 20 mM, and B = 9.4 T and T = 290.2 K. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Pressure [MPa]	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
2	1.44×10^{-3}	68.1	2788	15.60
30	1.44×10^{-3}	67.5	2652	15.57
60	1.44×10^{-3}	67.6	2558	15.54
90	1.44×10^{-3}	67.4	2411	15.48
120	1.44×10^{-3}	67.5	2330	15.44
150	1.44×10^{-3}	67.2	2188	15.38

Table S6. Temperature dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M PIPES buffer, pH 7, [complex] = 10 mM, and B = 9.4 T. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Temperature [K]	$1000 / T [K^{-1}]$	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
274.2	3.65	7.2×10^{-4}	168.8	2539.4	16.152
278.2	3.60	7.2×10^{-4}	150.6	2913.6	16.305
283.2	3.53	7.2×10^{-4}	131.9	3432.8	16.483
288.2	3.47	7.2×10^{-4}	114.0	3811.6	16.597
293.2	3.41	7.2×10^{-4}	89.4	4191.1	16.700
298.2	3.35	7.2×10^{-4}	75.8	4295.1	16.728
303.2	3.30	7.2×10^{-4}	67.3	4284.5	16.728
308.2	3.24	7.2×10^{-4}	58.6	4164.7	16.701
313.2	3.19	7.2×10^{-4}	51.6	4101.6	16.688
318.2	3.14	7.2×10^{-4}	45.7	3813.1	16.615
323.2	3.09	7.2×10^{-4}	40.5	3520.4	16.536
328.2	3.05	7.2×10^{-4}	36.3	3186.6	16.436
333.2	3.00	7.2×10^{-4}	32.5	2900.1	16.342
338.2	2.96	7.2×10^{-4}	29.2	2532.5	16.206
343.2	2.91	7.2×10^{-4}	26.9	2233.0	16.080
348.2	2.87	7.2×10^{-4}	24.4	1943.6	15.941
353.2	2.83	7.2×10^{-4}	22.4	1681.1	15.795
358.2	2.79	7.2×10^{-4}	20.6	1497.6	15.679

Table S7. Pressure dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M PIPES buffer, pH 7, [complex] = 10 mM, and B = 9.4 T and T = 335.2 K. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Pressure [MPa]	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
2	1.44×10^{-3}	68.1	2890.4	16.32
30	1.44×10^{-3}	67.5	3022.1	16.37
60	1.44×10^{-3}	67.6	3107.5	16.40
90	1.44×10^{-3}	67.4	3261.3	16.45
120	1.44×10^{-3}	67.5	3369.2	16.48
150	1.44×10^{-3}	67.2	3453.0	16.51

Table S8. Temperature dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M CAPS buffer, pH 10, [complex] = 10 mM, and B = 9.4 T. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 2 water molecules attached to the two Mn(II) centers.

Temperature [K]	$1000 / T [\text{K}^{-1}]$	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
274.2	3.65	3.6×10^{-4}	114.5	1653.9	16.377
278.2	3.60	3.6×10	97.2	1871.6	16.525
283.2	3.53	3.6×10	80.5	2116.5	16.667
288.2	3.47	3.6×10	68.1	2300.6	16.764
293.2	3.41	3.6×10	58.2	2405.5	16.822
298.2	3.35	3.6×10	50.0	2419.2	16.834
303.2	3.30	3.6×10	44.2	2297.6	16.784
308.2	3.24	3.6×10	39.1	2120.6	16.706
313.2	3.19	3.6×10	34.7	1911.9	16.603
318.2	3.14	3.6×10	31.2	1688.7	16.478
323.2	3.09	3.6×10	28.1	1463.8	16.335
328.2	3.05	3.6×10	25.5	1269.8	16.192
333.2	3.00	3.6×10	23.4	1100.7	16.048
338.2	2.96	3.6×10	21.1	954.6	15.904
343.2	2.91	3.6×10	19.3	793.1	15.716
348.2	2.87	3.6×10	17.8	640.4	15.497
353.2	2.83	3.6×10	16.5	528.8	15.302
358.2	2.79	3.6×10	15.3	448.3	15.133

Table S9. Pressure dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_4]^{4+}$ in 0,2 M CAPS buffer, pH 10, [complex] = 10 mM, and B = 9.4 T and T = 335.2 K. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 4 water molecules attached to the two Mn(II) centers.

Pressure [MPa]	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
2	1.44×10^{-3}	22.0	1053	16.013
30	1.44×10^{-3}	19.4	1110	16.068
60	1.44×10^{-3}	19.4	1166	16.119
90	1.44×10^{-3}	19.2	1226	16.170
120	1.44×10^{-3}	19.1	1290	16.221
150	1.44×10^{-3}	19.0	1340	16.260

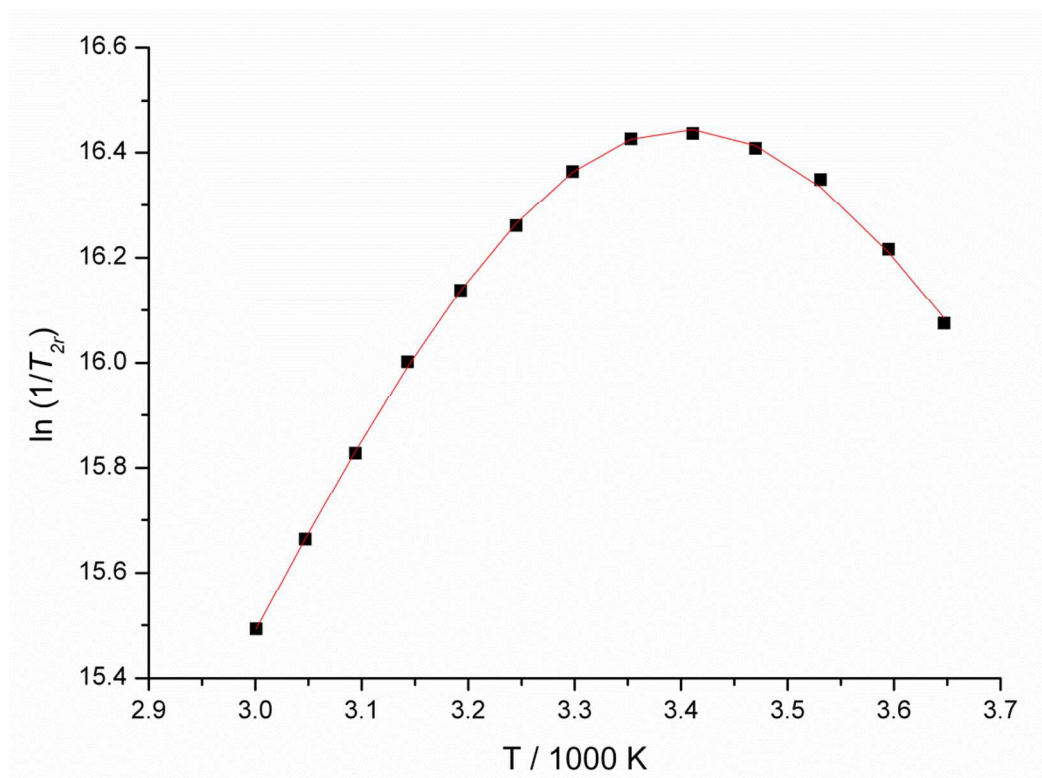


Figure S8. Temperature dependence of the reduced ^{17}O NMR relaxivity of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_4]^{4+}$ in 0.2 M CAPS buffer, pH 11.0, [complex] = 15 mM, $n = 2$, $B = 9.4$ T.

Table S10. Temperature dependent ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_2(\text{OH})_2]^{2+}$ in 0,2 M CAPS buffer, pH 10, [complex] = 15 mM, and B = 9.4 T. Reduced transverse relaxivity $1/T_{2r}$ calculated for n = 2 water molecules attached to the two Mn(II) centers.

Temperature [K]	$1000 / T [K^{-1}]$	P_m	$\Delta\nu_{\text{solvent}}$	$\Delta\nu_{\text{complex}}$	$\ln(1/T_{2r})$
274.2	3.65	3.6×10^{-4}	168.8	1814.4	16.075
278.2	3.60	3.6×10^{-4}	150.6	2045.9	16.216
283.2	3.53	3.6×10^{-4}	131.9	2296.0	16.349
288.2	3.47	3.6×10^{-4}	114.0	2410.4	16.408
293.2	3.41	3.6×10^{-4}	89.4	2450.6	16.436
298.2	3.35	3.6×10^{-4}	75.8	2413.1	16.426
303.2	3.30	3.6×10^{-4}	67.3	2266.2	16.364
308.2	3.24	3.6×10^{-4}	58.6	2042.2	16.261
313.2	3.19	3.6×10^{-4}	51.6	1805.6	16.138
318.2	3.14	3.6×10^{-4}	45.7	1575.8	16.002
323.2	3.09	3.6×10^{-4}	40.5	1326.3	15.828
328.2	3.05	3.6×10^{-4}	36.3	1127.6	15.664
333.2	3.00	3.6×10^{-4}	32.5	952.4	15.493

Table S11. Comparison of ^{17}O -NMR line widths ($\Delta\nu_{\text{complex}}$) of $[\text{Mn}_2(\text{L2})(\text{H}_2\text{O})_4]^{4+}$ in 0.2 M PIPES buffer with and without 300 mM sodium chloride, pH 7.0, [complex] = 10 mM, B = 9.4 T.

Temperature [K]	$\Delta\nu_{\text{complex}}$ without chloride	$\Delta\nu_{\text{complex}}$ with 300 mM NaCl
274.2	2539.4	2479.4
278.2	2913.6	2901.6
283.2	3432.8	3372.8
288.2	3811.6	3700.6
293.2	4191.1	4145.3
298.2	4295.1	4266.6
303.2	4284.5	4284.5
308.2	4164.7	4053.1
313.2	4101.6	4009.9
318.2	3813.1	3799.2
323.2	3520.4	3466.1
328.2	3186.6	3144.1
333.2	2900.1	2870.0
338.2	2532.5	2501.4
343.2	2233.0	2213.1
348.2	1943.6	1913.7

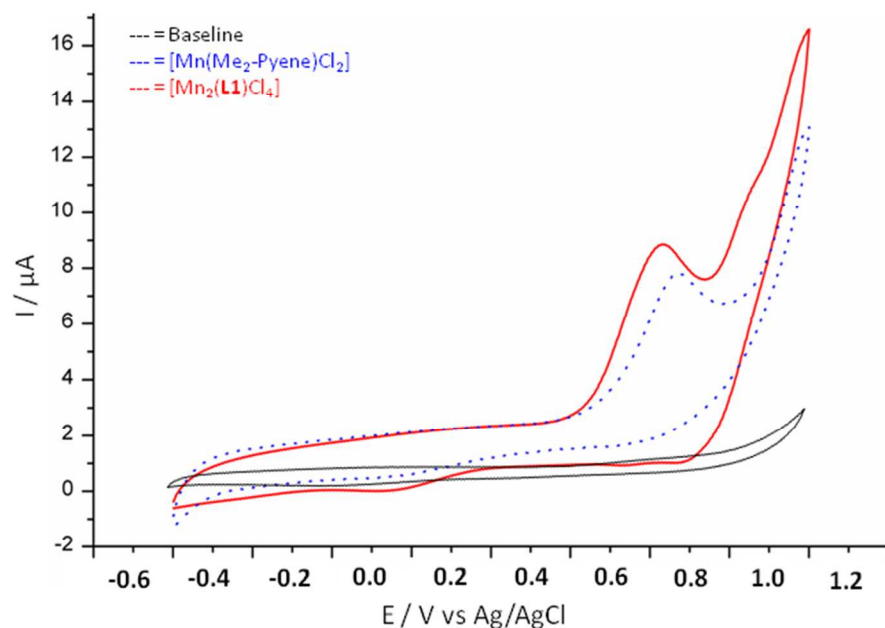


Figure S9. Cyclic Voltammogram of 1 mM [Mn(Me₂-Pyene)Cl₂] (dotted blue line) and 1 mM [Mn(L1)Cl₄] (solid red line) in DMSO with 0.1 M Bu₄NPF₆ as Electrolyte. Scan rate = 100 mV/s, Temperature = 20 °C.

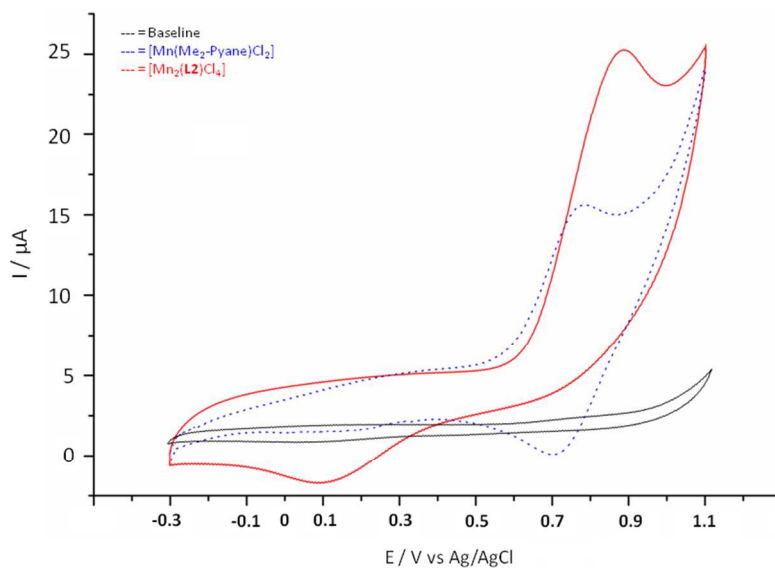


Figure S10. Cyclic Voltammogram of 1 mM [Mn(Me₂-Pyane)Cl₂] (dotted blue line) and 1 mM [Mn(L2)Cl₄] (solid red line) in DMSO with 0.1 M Bu₄NPF₆ as Electrolyte. Scan rate = 100 V/s, Temperature = 20 °C.

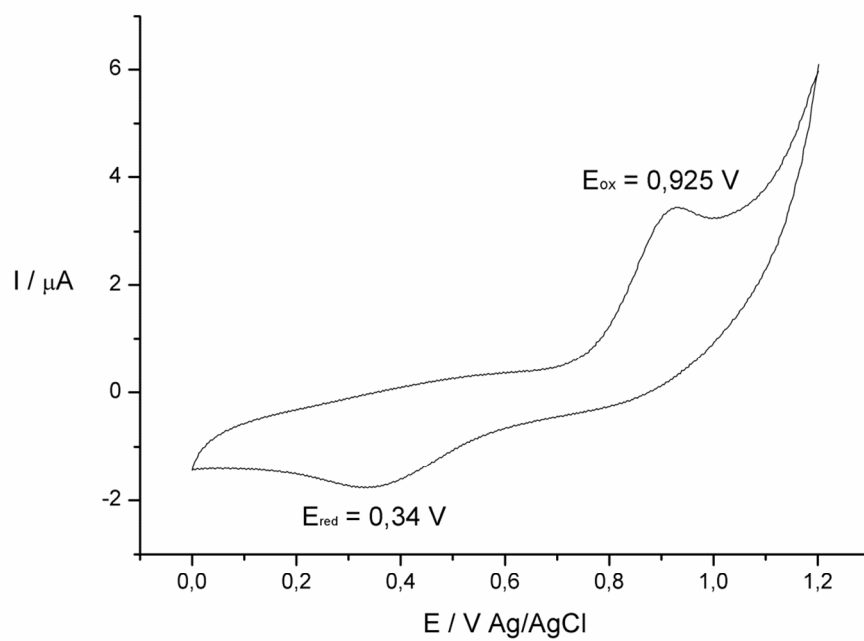


Figure S11. Cyclic voltammogram of $[\text{Mn}(\text{L2})\text{Cl}_4]$ in 60 mM CAPS buffer at pH 10.0 under tight nitrogen atmosphere. Scan rate = 100 mV/s, Temperature = 20 °C.

Table S12. Experimentally obtained k_{obs} values at 21 °C for decomposition of superoxide with $[\text{Mn}_2(\text{L2})\text{Cl}_4]$ in 60 mM Hepes buffer at pH 7.4. These result in a second order rate constant $k_{\text{cat}} = 4.70 \pm 0.21 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Complex concentration [M]	$k_{\text{obs}} [\text{s}^{-1}]$
2.81E-07	55±2
5.63E-07	73±4
1.13E-06	98±4
2.25E-06	149±7

Table S13. Experimentally obtained k_{obs} values at 21 °C for decomposition of superoxide with $[\text{Mn}_2(\text{L2})\text{Cl}_4]$ in 60 mM Hepes buffer at pH 8.1. These result in a second order rate constant $k_{\text{cat}} = 2.30 \pm 0.10 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Complex concentration [M]	$k_{\text{obs}} [\text{s}^{-1}]$
4.50E-07	26±2
9.00E-07	37±2
2.25E-06	65±5
4.50E-06	118±5

Table S14. Experimentally obtained k_{obs} values at 21 °C for decomposition of superoxide with $[\text{Mn}_2(\text{L2})\text{Cl}_4]$ in 60 mM Caps buffer at pH 10.0. These result in a second order rate constant $k_{\text{cat}} = 1.90 \pm 0.12 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Complex concentration [M]	$k_{\text{obs}} [\text{s}^{-1}]$
5.63E-07	8.1±0.3
1.13E-06	11.7±0.5
2.25E-06	39.9±3.0
4.50E-06	81.8±4.1

Table S15. Experimentally obtained k_{obs} values at 21 °C for decomposition of superoxide with $[\text{Mn}(\text{Me}_2\text{-Pyane})]$ in 60 mM Caps buffer at pH 10.0. These result in a second order rate constant $k_{\text{cat}} = 0.54 \pm 0.60 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Complex concentration [M]	$k_{\text{obs}} [\text{s}^{-1}]$
5.63E-07	2.4±0.2
1.13E-06	5.1±0.2
2.25E-06	10.5±0.5
4.50E-06	21.4±0.5
9.00E-06	47.6±1.0

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