

## Supporting Information

for

### **Mn<sup>2+</sup> complexes of 1-oxa-4,7-diazacyclononane based ligands: stability and relaxation studies**

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**Table S1.** Best fit parameters obtained from the simultaneous analysis of  $^{17}\text{O}$  NMR and  $^1\text{H}$  NMRD data for the  $[\text{Mn}(\text{L}^1)(\text{H}_2\text{O})_x]$  and  $[\text{Mn}(\text{L}^2)(\text{H}_2\text{O})]^{2-}$  complexes and parameters fixed during the fitting procedure.

Best fit parameters	$[\text{Mn}(\text{L}^1)(\text{H}_2\text{O})_x]$	$[\text{Mn}(\text{L}^2)(\text{H}_2\text{O})]^{2-}$	
$k_{\text{ex}}^{298} / 10^7 \text{ s}^{-1}$	$119 \pm 22$	$1.20 \pm 0.1$	water exchange rate
$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$11.7 \pm 0.8$	$38.8 \pm 1.1$	activation enthalpy for the exchange
$\Delta S^\ddagger / \text{J mol}^{-1} \text{K}^{-1}$	$-32 \pm 5$	$23 \pm 3$	activation entropy for the exchange
$E_{\text{rH}} / \text{kJ mol}^{-1}$	$12 \pm 1$	$23 \pm 2$	activation energy for the rotational motion
$\tau_{\text{rH}}^{298} / \text{ps}$	$22 \pm 1$	$103 \pm 3$	rotational correlation time
$\tau_{\text{v}}^{298} / \text{ps}$	$12.4 \pm 0.6$	$33.7 \pm 0.8$	correlation time for the modulation of ZFS
$\Delta^2 / 10^{18} \text{ s}^{-2}$	$79 \pm 5$	$53 \pm 4$	trace of the square of the transient ZFS tensor
Fixed parameters	$[\text{Mn}(\text{L}^1)(\text{H}_2\text{O})_x]$	$[\text{Mn}(\text{L}^2)(\text{H}_2\text{O})]^{2-}$	
$A_{\text{O}}/\hbar / 10^6 \text{ rad s}^{-1}$	$33.3^{\text{a}}$	$33.3^{\text{a}}$	hyperfine (scalar) coupling constant
$E_{\text{v}} / \text{kJ mol}^{-1}$	1	1	the activation energy of the modulation of the zero-field splitting
$D_{\text{MnH}} / 10^{-10} \text{ m}^2 \text{ s}^{-1}$	23	23	diffusion coefficient
$E_{\text{MnH}} / \text{kJ mol}^{-1}$	18	18	activation energy of diffusion
$r_{(\text{MnO})} / \text{Å}$	2.139	2.139	Mn–O <sub>w</sub> (coordinated) distance
$r_{(\text{MnH})\text{in}} / \text{Å}$	2.75	2.75	Mn–H <sub>w</sub> (inner-sphere) distance
$r_{(\text{MnH})\text{out}} / \text{Å}$	3.20	3.20	Mn–H <sub>w</sub> (outer-sphere) distance

**Table S2** Experimental values of overall protonation constants ( $\log\beta_{hlm}$ ) of  $\text{H}_2\text{L}^1\text{--H}_2\text{L}^4$  (25 °C,  $I = 0.1$  M  $(\text{NMe}_4)\text{Cl}$ , standard deviations in parenthesis as calculated by OPIUM);  $\beta_{hlm} = [\text{H}_h\text{L}_l\text{M}_m] / [\text{H}]^h[\text{L}]^l[\text{M}]^m$ . Charges were omitted for clarity.

Equilibrium	stoichiometry			$\text{H}_2\text{L}^1$	$\text{H}_4\text{L}^2$	$\text{H}_2\text{L}^3$	$\text{H}_2\text{L}^4$
	$h$	$l$	$m$				
$\text{L} + \text{H}^+ \leftrightarrow \text{HL}$	1	1	0	10.59(1)	12.32(1)	8.42 (1)	9.23(1)
$\text{L} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{L}$	2	1	0	14.58(1)	20.21(1)	9.81 (2)	11.08(1)
$\text{L} + 3\text{H}^+ \leftrightarrow \text{H}_3\text{L}$	3	1	0	16.41(1)	25.65(1)	–	–
$\text{L} + 4\text{H}^+ \leftrightarrow \text{H}_4\text{L}$	4	1	0	–	27.53(1)	–	–

## Equations used for treatment of relaxometric data

$^{17}\text{O}$  NMR data have been fitted according to the Swift and Connick equations.<sup>1</sup> The reduced transverse  $^{17}\text{O}$  relaxation rates,  $1/T_{2r}$ , and reduced  $^{17}\text{O}$  chemical shifts,  $\omega_r$ , have been calculated from the measured relaxation rates  $1/T_2$  and angular frequencies  $\omega$  of the paramagnetic solutions and from the relaxation rates  $1/T_{2A}$  and angular frequencies  $\omega_A$  of the diamagnetic reference according to the Equations (S1) and (S2):

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left[ \frac{1}{T_2} - \frac{1}{T_{2A}} \right] = \frac{1}{\tau_m} \frac{T_{2m}^{-2} + \tau_m^{-1} T_{2m}^{-1} + \Delta\omega_m^2}{(\tau_m^{-1} + T_{2m}^{-1})^2 + \Delta\omega_m^2} \quad (\text{S1})$$

$$\Delta\omega_r = \frac{1}{P_m} (\omega - \omega_A) = \frac{\Delta\omega_m}{(1 + \tau_m T_{2m}^{-1})^2 + \tau_m^2 \Delta\omega_m^2} \quad (\text{S2})$$

$\Delta\omega_m$  is determined by the hyperfine or scalar coupling constant,  $A_O/\hbar$ , where  $B$  represents the magnetic field,  $S$  is the electron spin and  $g_L$  is the isotropic Landé  $g$  factor (Equation (S3)).

$$\Delta\omega_m = \frac{g_L \mu_B S(S+1) B A_O}{3k_B T \hbar} \quad (\text{S3})$$

The  $^{17}\text{O}$  transverse relaxation rate is mainly determined by the scalar contribution,  $1/T_{2sc}$ , and it is given by Equation (S4).

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

The exchange rate,  $k_{ex}$ , (or inverse binding time,  $\tau_m$ ) of the inner sphere water molecule is assumed to obey the Eyring equation (Equation (S5)) where  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  are the entropy and enthalpy of activation for the exchange, and  $^{298}k_{ex}$  is the exchange rate at 298.15 K.

$$\frac{1}{\tau_m} = k_{ex} = \frac{k_B T}{h} \exp \left\{ \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right\} = \frac{k_{ex}^{298} T}{298.15} \exp \left\{ \frac{\Delta H^\ddagger}{R} \left( \frac{1}{298.15} - \frac{1}{T} \right) \right\} \quad (\text{S5})$$

The electronic relaxation is mainly governed by modulation of the transient zero-field splitting, and for the electron spin relaxation rates,  $1/T_{1e}$  and  $1/T_{2e}$ , McMachlan has developed Equations (S6)–(S8)<sup>2</sup>:

$$\left( \frac{1}{T_{1e}} \right) = \frac{32}{25} \Delta^2 \left( \frac{\tau_v}{1 + \omega_s^2 \tau_v^2} + \frac{4\tau_v}{1 + 4\omega_s^2 \tau_v^2} \right) \quad (\text{S6})$$

$$\left( \frac{1}{T_{2e}} \right) = \frac{32}{50} \Delta^2 \left[ 3\tau_v + \frac{5\tau_v}{1 + \omega_s^2 \tau_v^2} + \frac{2\tau_v}{1 + 4\omega_s^2 \tau_v^2} \right] \quad (\text{S7})$$

$$\tau_v = \tau_v^{298} \exp \left\{ \frac{E_v}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right\} \quad (\text{S8})$$

where  $\Delta^2$  is the trace of the square of the transient zero-field-splitting (ZFS) tensor,  $\tau_v$  is the correlation time for the modulation of the ZFS with the activation energy  $E_v$ , and  $\omega_s$  is the Larmor frequency of the electron spin.

The proton relaxivities (normalized to 1 mM  $\text{Mn}^{2+}$  concentration) originate from inner- and outer-sphere contributions (Equation (S9)):

$$r_1 = r_{1is} + r_{1os} \quad (\text{S9})$$

The inner-sphere term is given by Equation (S10), where  $q$  is the number of inner-sphere water molecules.

$$r_{1is} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m}^H + \tau_m} \quad (\text{S10})$$

In the longitudinal relaxation rate of inner sphere water protons,  $1/T_{1m}^H$ , the dipolar contribution dominates (Equation (S11)):

$$\frac{1}{T_{1m}^H} \cong \frac{1}{T_1^{DD}} = \frac{2}{15} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_S^2 \gamma_I^2}{r_{MnH}^6} S(S+1) \left[ \frac{3\tau_{d1H}}{1 + \omega_1^2 \tau_{d1H}^2} + \frac{7\tau_{d2H}}{1 + \omega_S^2 \tau_{d2H}^2} \right] \quad (S11)$$

Here  $r_{MnH}$  is the effective distance between the  $Mn^{2+}$  electron spin and the water protons,  $\omega_1$  is the proton resonance frequency,  $\tau_{d1H}$  is given by Eq. 12, where  $\tau_{RH}$  is the rotational correlation time of the  $Mn^{2+}-H_{water}$  vector (Equation (S12)):

$$\frac{1}{\tau_{diH}} = \frac{1}{\tau_m} + \frac{1}{\tau_{RH}} + \frac{1}{T_{ie}} \quad i = 1, 2; \quad (S12)$$

The outer-sphere contribution to the overall relaxivity is described by Equation (S13), where  $N_A$  is the Avogadro constant, and  $J_{os}$  is a spectral density function (Equation (S14)).

$$r_{1os} = \frac{32N_A \pi}{405} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_S^2 \gamma_I^2}{a_{MnH} D_{MnH}} S(S+1) [3J_{os}(\omega_1, T_{1e}) + 7J_{os}(\omega_S, T_{2e})] \quad (S13)$$

$$J_{os}(\omega, T_{je}) = \text{Re} \left[ \frac{1 + \frac{1}{4} \left( i\omega\tau_{MnH} + \frac{\tau_{MnH}}{T_{je}} \right)^{1/2}}{1 + \left( i\omega\tau_{MnH} + \frac{\tau_{MnH}}{T_{je}} \right)^{1/2} + \frac{4}{9} \left( i\omega\tau_{MnH} + \frac{\tau_{MnH}}{T_{je}} \right) + \frac{1}{9} \left( i\omega\tau_{MnH} + \frac{\tau_{MnH}}{T_{je}} \right)^{3/2}} \right] \quad j = 1, 2 \quad (S14)$$

The diffusion coefficient for the diffusion of a water proton away from a  $Mn^{2+}$  complex,  $D_{MnH}$ , obeys the exponential temperature dependence described by Equation (S15), with activation energy  $E_{MnH}$ :

$$D_{MnH} = D_{MnH}^{298} \exp \left\{ \frac{E_{MnH}}{R} \left( \frac{1}{298.15} - \frac{1}{T} \right) \right\} \quad (S15)$$

<sup>1</sup> J. T Swift, T. J. and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307–320.

<sup>2</sup> A. D. McLachlan, *Proc. R. Soc. London, Ser. A.*, 1964, **280**, 271–288.