Supporting information

for

Seven-coordinate Mn(II) complex with a pyridine-based 15-membered macrocyclic ligand containing one acetate pendant arm: structure, stability and relaxation properties

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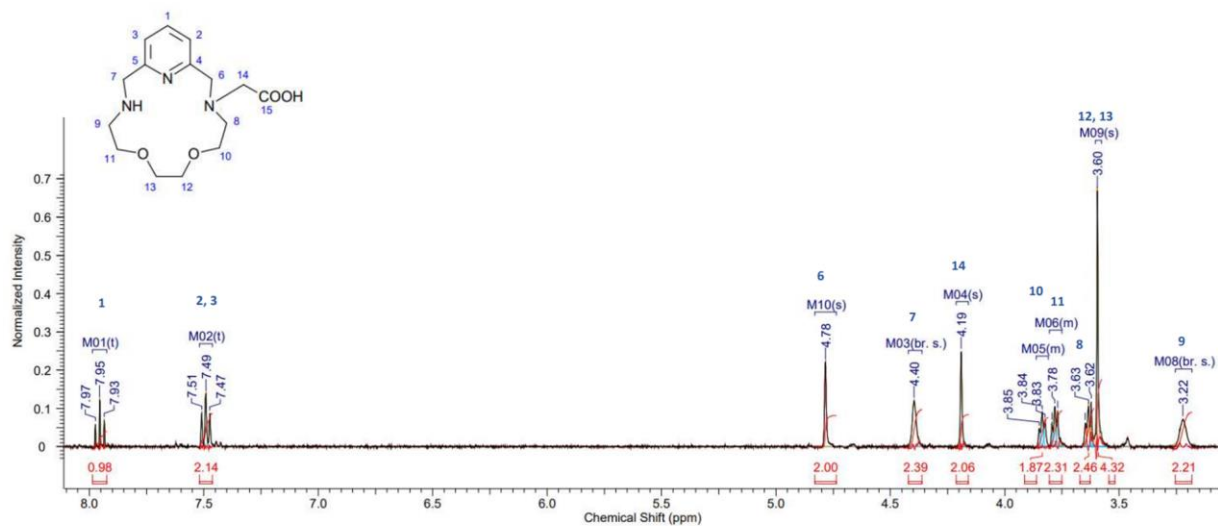
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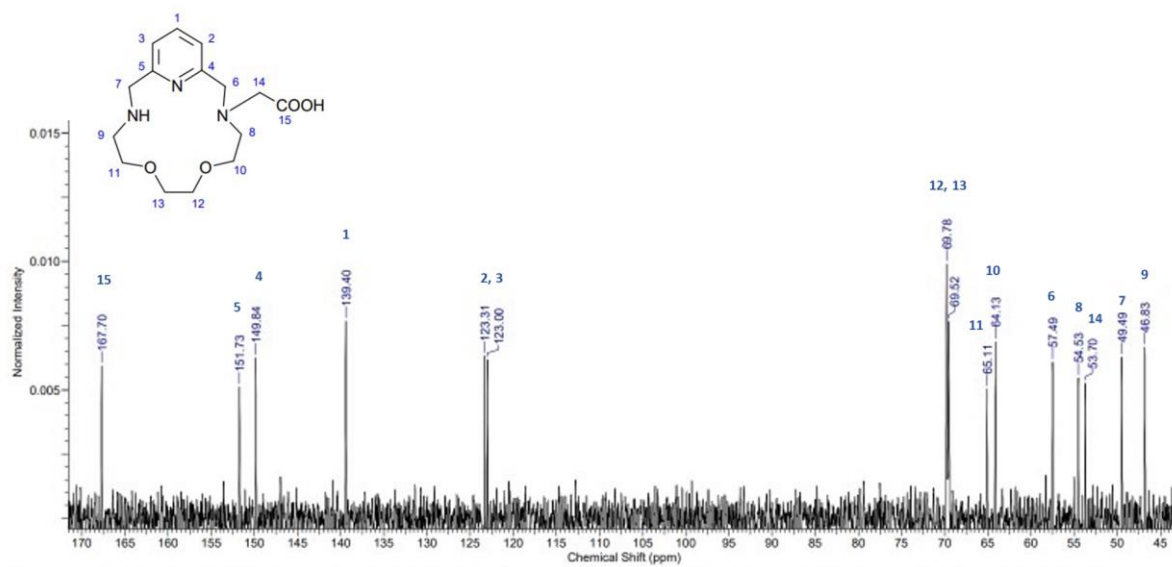
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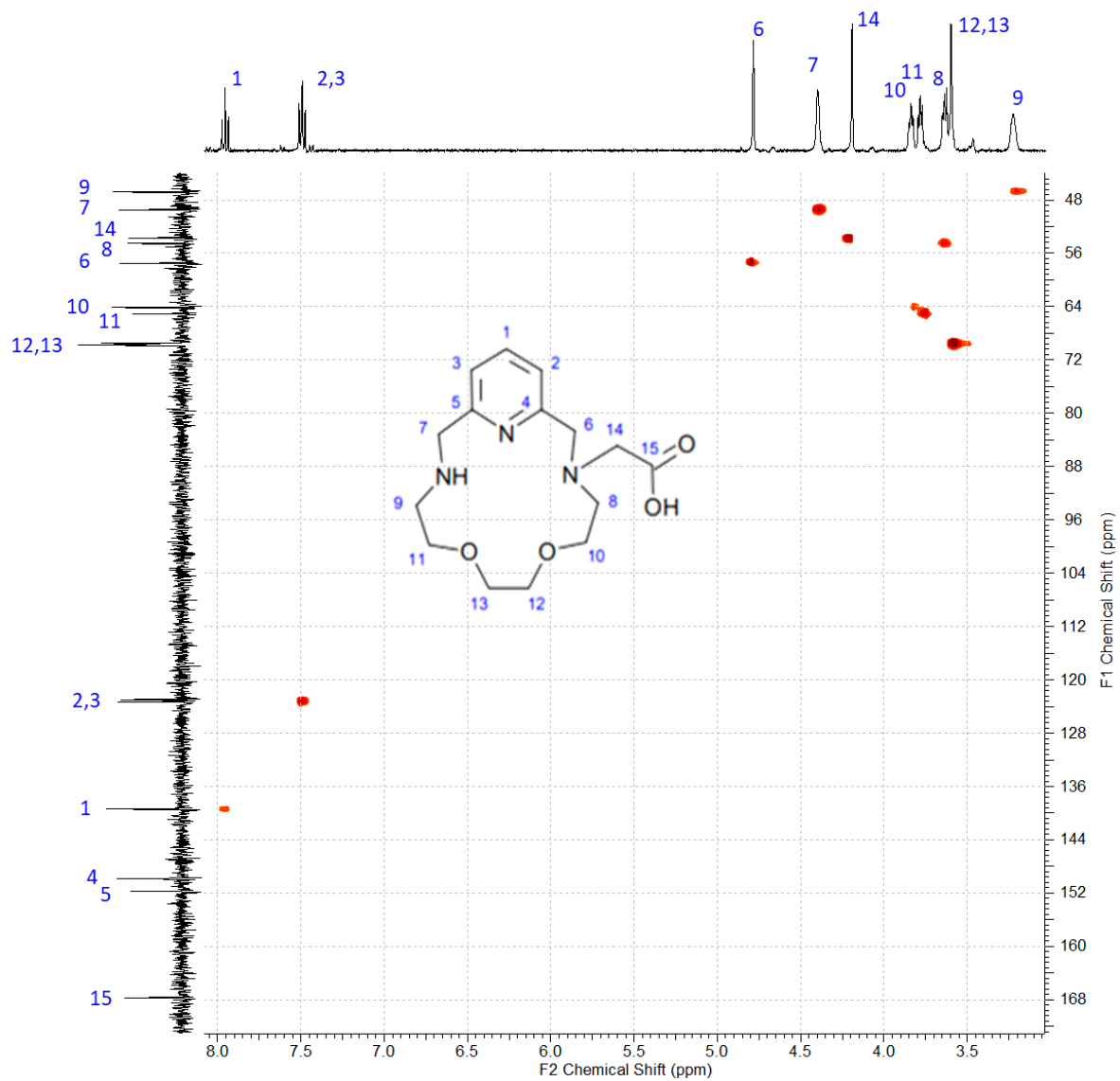
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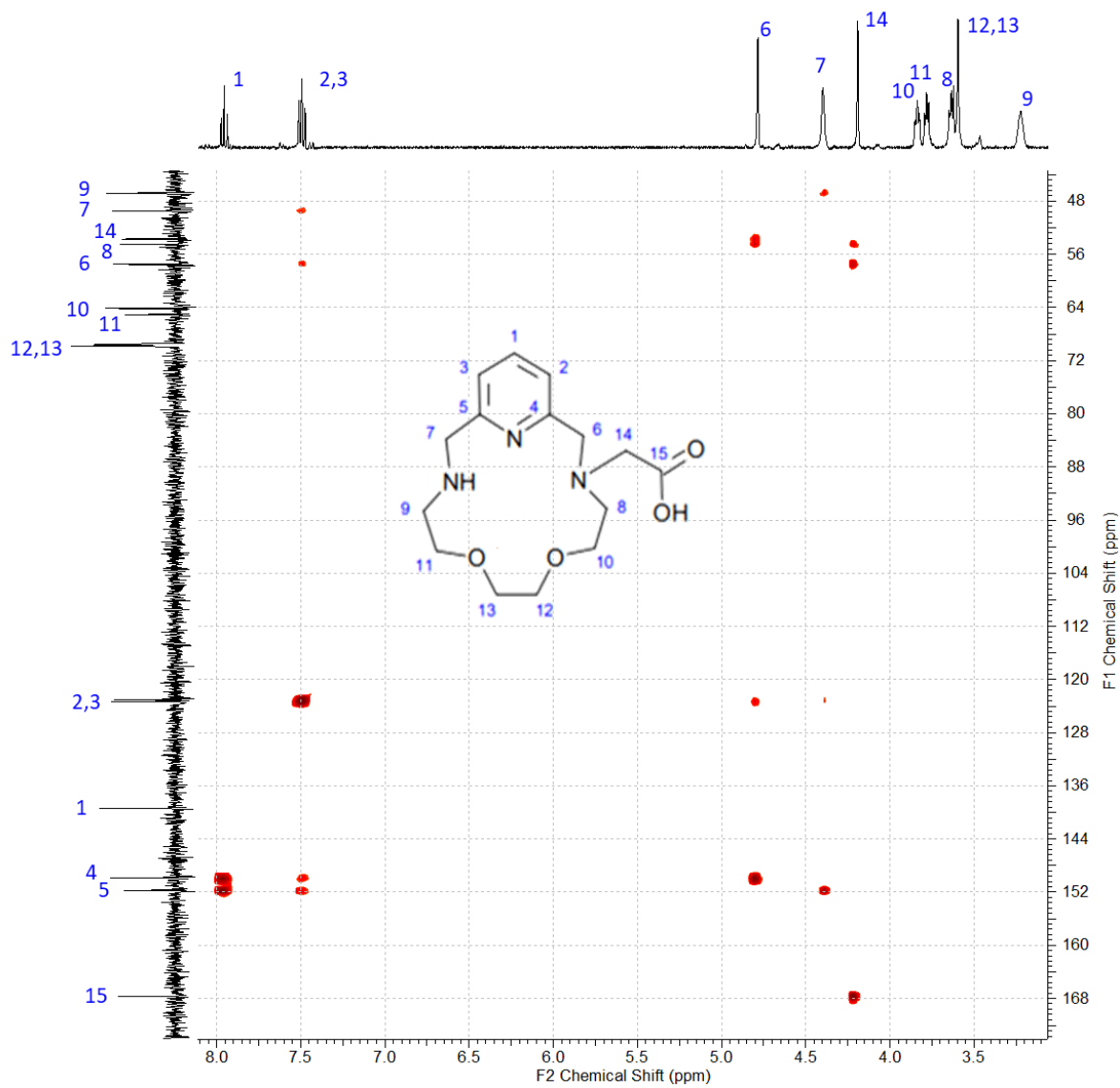
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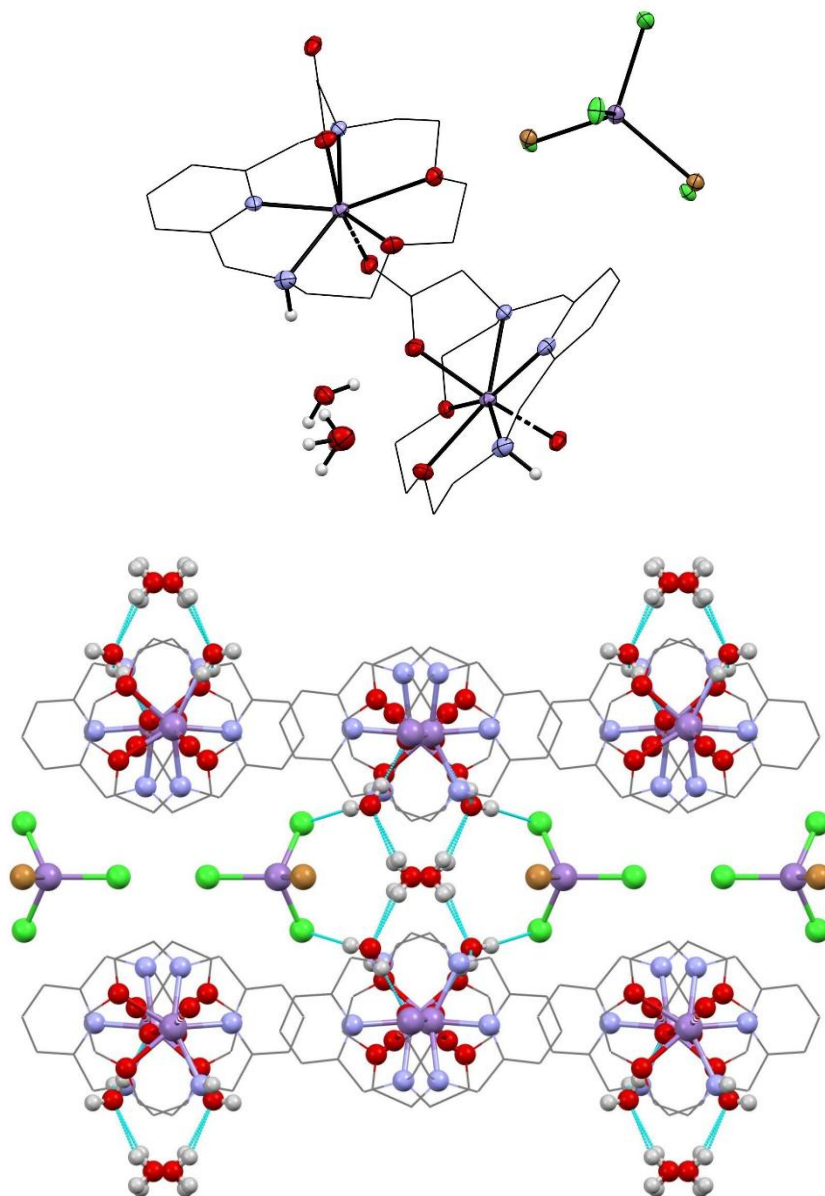
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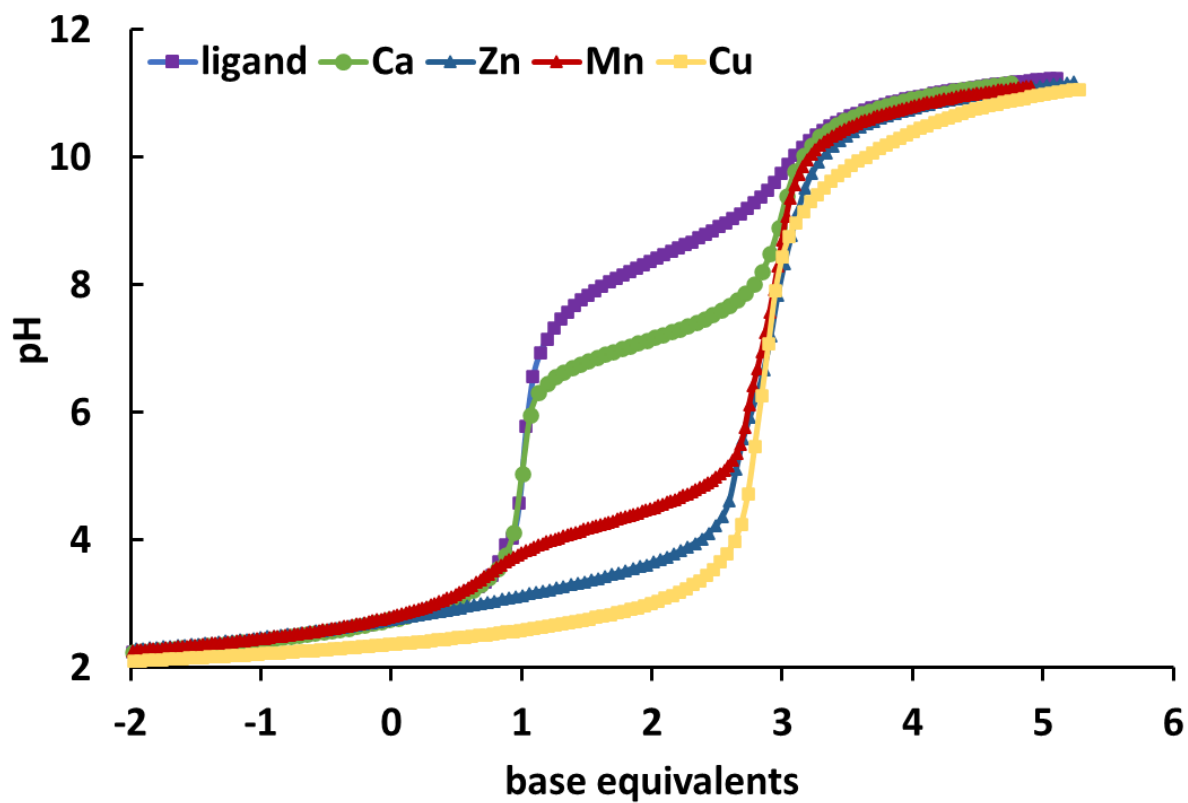
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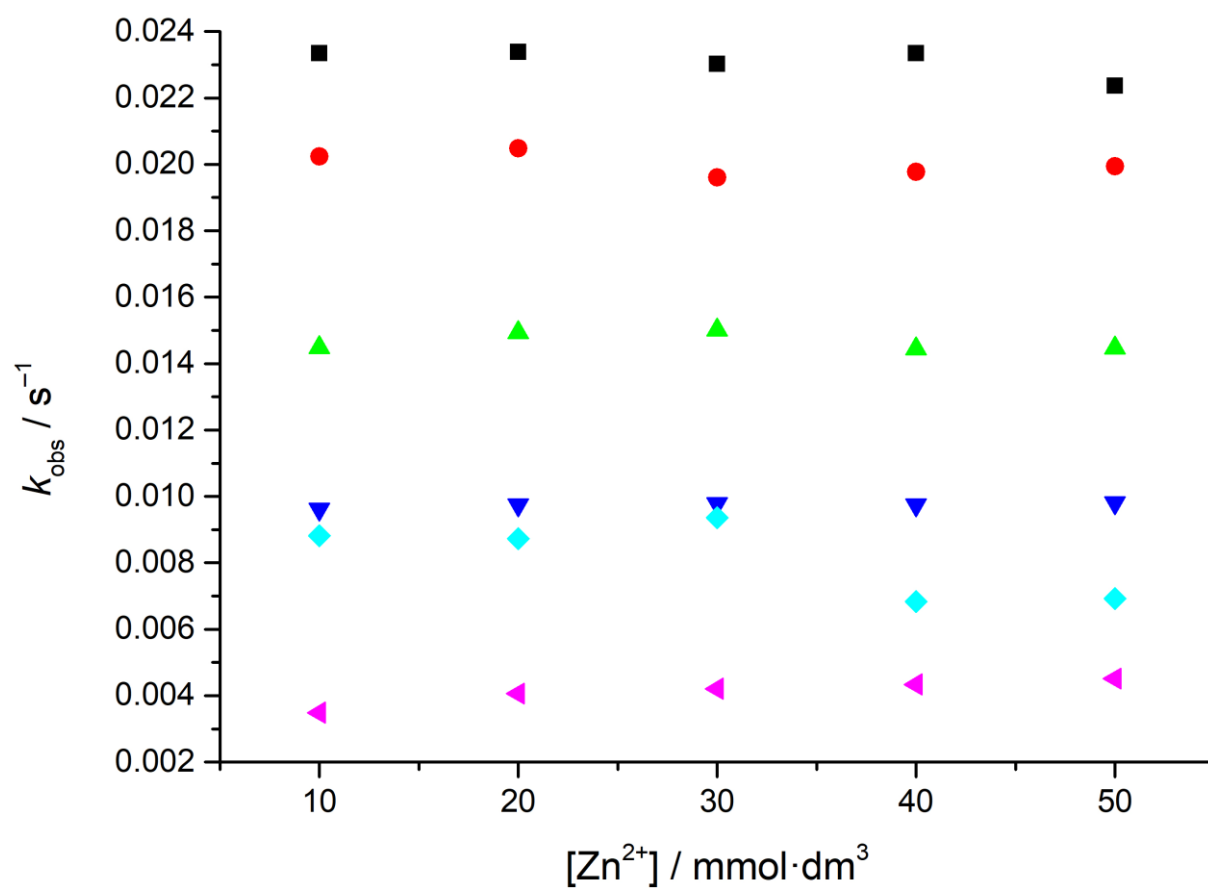
Figure S8. Dependence of the observed dissociation rate constants for **MnL1** on Zn^{2+} concentration. pH readings from the top are 4.9 (*black*), 5.0 (*red*), 5.2 (*green*), 5.5 (*dark blue*), 5.7 (*light blue*) and 6.1 (*pink*).

Table S1 Selected non-covalent contact parameters (Å, °) for complexes 1.

D	H	A	d(D–H)	d(H···A)	d(D···A)	<(D-H-A)
O5	H5A	O3	0.87	1.91	2.771(4)	169.9
O5	H5B	Cl1[1]	0.87	2.33	3.194(3)	171.9
O6	H6C	O5	0.87	2.21	2.918(3)	138.9
O6	H6D	O5[2]	0.87	2.22	2.918(3)	136.8
N3	H3	O5[3]	1.00	2.06	2.991(4)	153.7

Symmetry transformations used to generate equivalent atoms:
[1] 1/2-X,-1/2+Y,-1/2+Z; [2] +X,1/2-Y,+Z; [3] 1/2+X,+Y,3/2-Z

Analysis of the ^{17}O NMR and ^{1}H NMRD data[1]

The reduced transverse ^{17}O relaxation rates, $1/T_{2r}$, and reduced ^{17}O chemical shifts, ω_r, are calculated from the measured relaxation rates $1/T_2$ and angular frequencies ω of the paramagnetic solutions and from the relaxation rates $1/T_{2A}$ and angular frequencies ω_A of the diamagnetic reference according to the Equations (S1) and (S2)[2]:

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

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

$\Delta\omega_m$ 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)).

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

The chemical shifts are measured with high errors (given the large linewidths) and the reduced chemical shifts were not further used in the fit.

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

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

The exchange rate, k_{ex}, (or inverse binding time, τ_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 k_{ex}^{298} is the exchange rate at 298.15 K.

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

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):

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

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

$$\tau_{\mathrm{v}} = \tau_{\mathrm{v}}^{298} \exp\left\{\frac{E_{\mathrm{v}}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \tag{S8}$$

where Δ^2 is the trace of the square of the transient zero-field-splitting (ZFS) tensor, τ_{v} is the correlation time for the modulation of the ZFS with the activation energy E_{v}, and ω_{s} is the Larmor frequency of the electron spin.

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

$$r_1 = r_{1is} + r_{1os} \tag{S9}$$

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

$$r_{1is} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m}^{H} + \tau_{m}} \tag{S10}$$

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

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

Here r_{MnH} is the effective distance between the Mn^{2+} electron spin and the water protons, ω_I is the proton resonance frequency, τ_{diH} is given by Eq. S12, where τ_{RH} is the rotational correlation time of the Mn^{2+}–H_{water} vector:

$$\frac{1}{\tau_{diH}} = \frac{1}{\tau_m} + \frac{1}{\tau_{RH}} + \frac{1}{T_{ie}} \qquad i = 1, 2; \tag{S12}$$

No scalar relaxation term was included in the analysis, as the NMRD profiles did not present a second, low-field dispersion, typical of an important scalar contribution to relaxivity.[1]

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)).

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

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

$$j = 1, 2 \tag{S14}$$

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}:

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

In the fitting procedure, some parameters have been fixed to common values: the distance between the metal ion and the inner and outer sphere water protons ($r_{MnH} = 2.83$ Å and $a_{MnH} = 3.6$ Å, respectively); the diffusion coefficient and its activation energy ($D_{MnH} = 26\times10^{-10}$ m^2s^{-1} and $E_{MnH} = 20$ kJ mol^{-1}).

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[1] E. Balogh, Z. He, W. Hsieh, S. Liu, É. Tóth; *Inorg. Chem.* 2007, **46**, 238-250.
[2] T. J. Swift, R. E. Connick, *J.Chem.Phys.* 1962, *37,* 2, 307-320.