Electronic Supplementary Information for :

Mn^{2+} complexes of open-chain ligands with a pyridine backbone: less donor atoms lead to higher kinetic inertness

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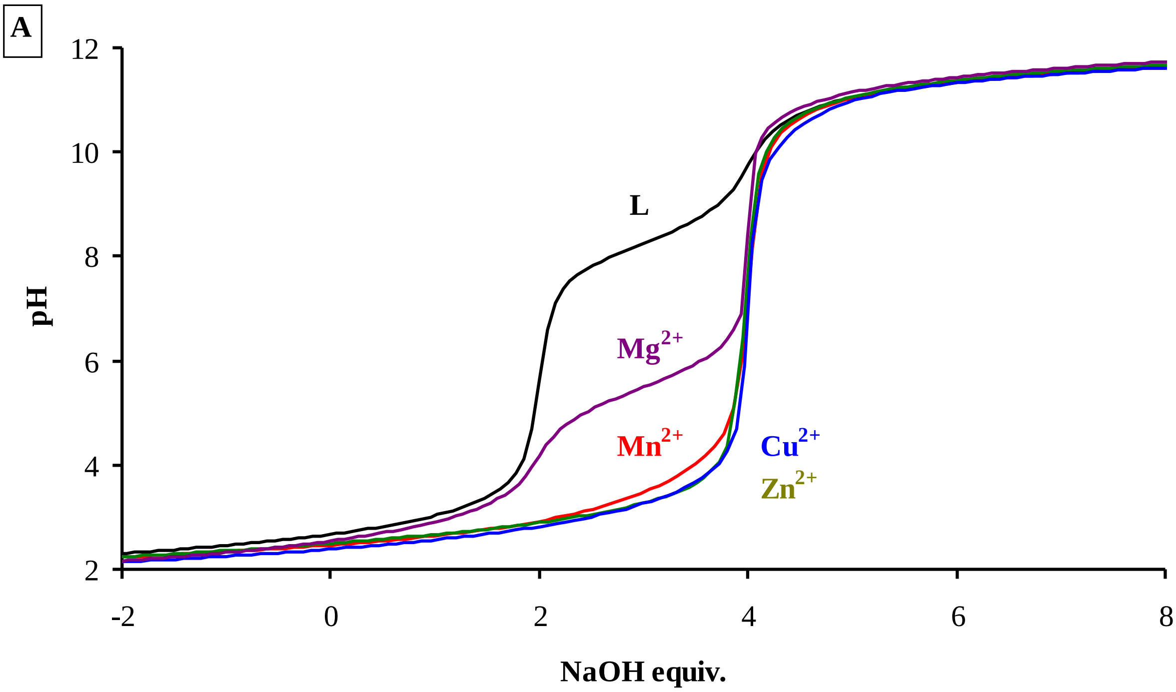


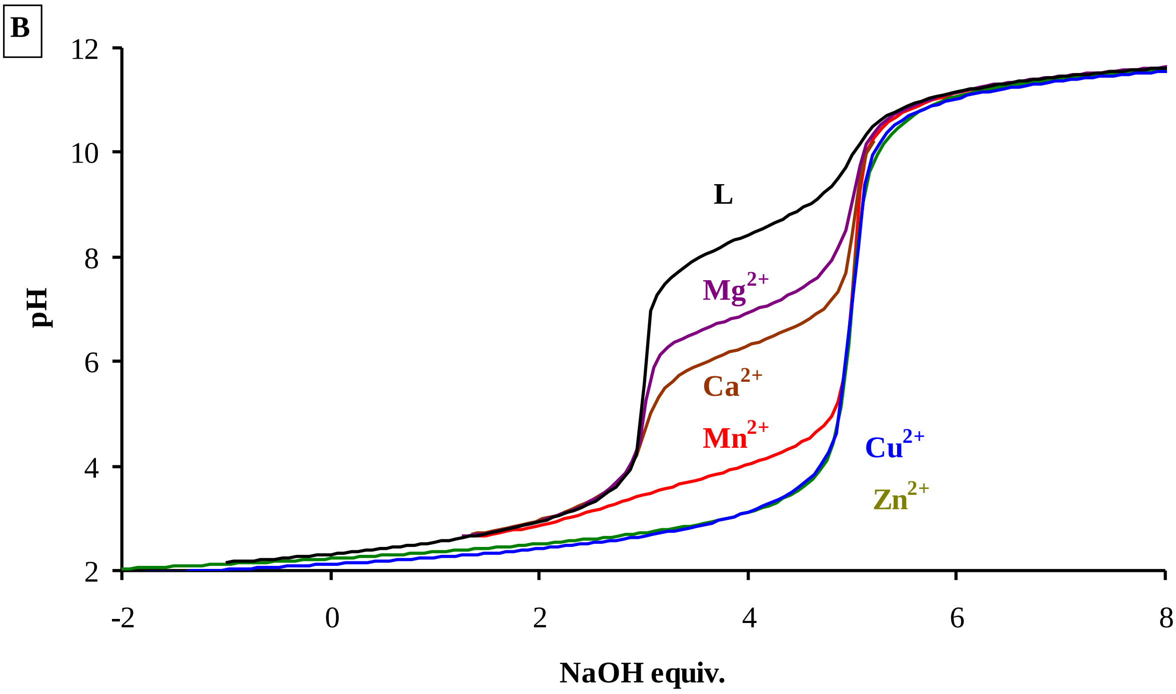


Figure S1: Potentiometric titration curves of solutions containing **L^1** (1.87mM) (A) and **L^3** (2.33mM) (B), with 0 and 1 equivalent of $MgCl_2$, $CaCl_2$, $MnCl_2$, $ZnCl_2$ and $CuCl_2$. I = 0.15M NaCl, 298K.

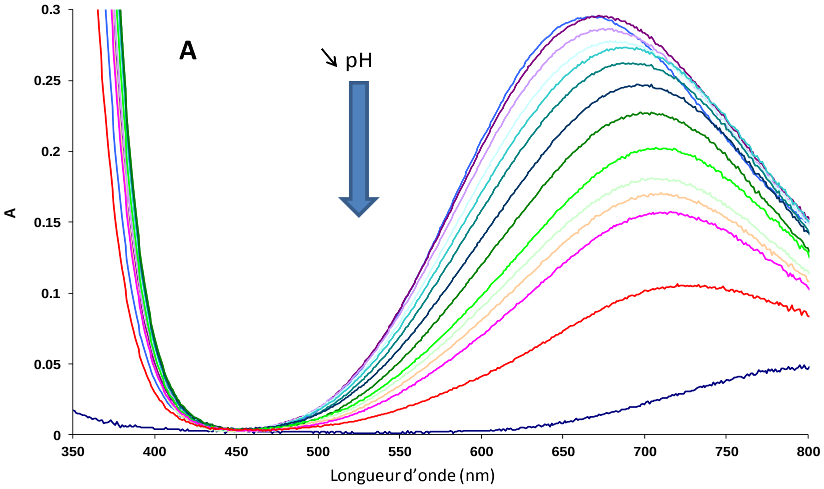


Figure S2. UV-visible spectra recorded in a solution containing 2.63 mM Cu^{2+} and 2.63 mM L^1 at increasing concentrations of H^+ (from 0.01362 to 0.9852 M) 25°C, 1.0 M NaCl.

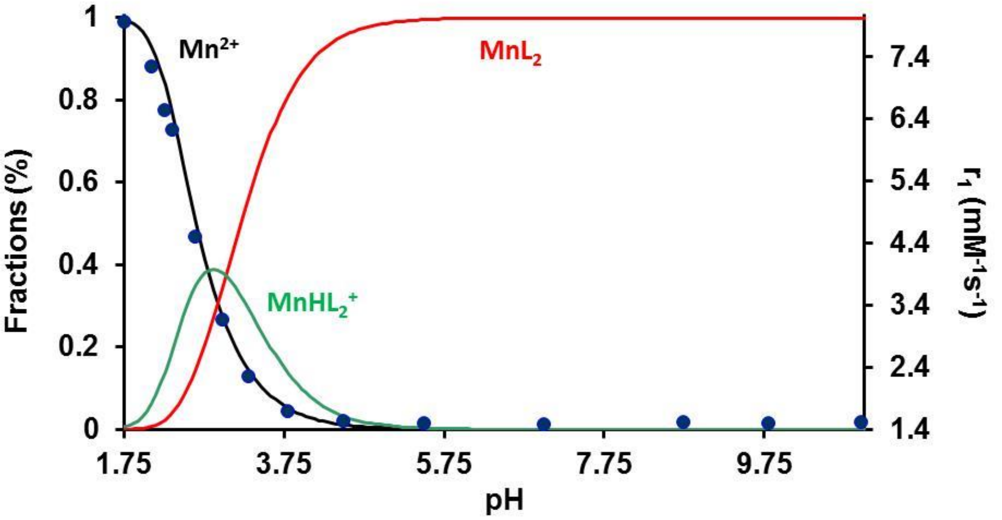
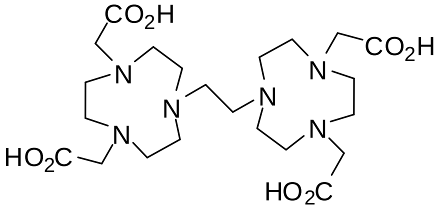


Figure S3. pH-dependent relaxivities (blue dots) measured in a solution containing equimolar quantities of Mn^{2+} and L^2 (20 MHz, 25 °C) and species distribution curves (solid lines) calculated by using the stability constants presented in Table 2 of the manuscript.



ENOTA

Scheme S1. Structure of ENOTA

Equations used for the treatment of the relaxometric data

^{17}O NMR data have been fitted according to the Swift and Connick equations [1]. The reduced transverse ^{17}O relaxation rates, $1/T_{2r}$, have been calculated from the measured relaxation rates $1/T_2$ of the paramagnetic solutions and from the relaxation rates $1/T_{2A}$ of the diamagnetic reference:

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

$\Delta\omega_m$ 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 (S2)).

$$\Delta\omega_m = \frac{g_L \mu_B\, S(S+1)B}{3k_B T}\,\frac{A_O}{\hbar} \qquad \text{(S2)}$$

The ^{17}O transverse relaxation rate is mainly determined by the scalar contribution, $1/T_{2sc}$, and it is given by Equation (S3).

$$\frac{1}{\tau_s} = \frac{1}{\tau_m} + \frac{1}{T_1} \qquad \text{(S3)}$$

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 (S4)) 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.

$$\frac{1}{\tau_m} = k_{ex} = \frac{k_B T}{h}\exp\left\{\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right\} = \frac{k_{ex}^{298} T}{298.15}\exp\left\{\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \qquad \text{(S4)}$$

For the fit of the ^{17}O T_2 data, we used an exponential function to treat the temperature dependency of $1/T_{1e}$:

$$\frac{1}{T_{1e}} = \frac{1}{T_{1e}^{298}}\exp\left\{\frac{E_v}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \qquad \text{(S5)}$$

The proton relaxivities (normalized to 1 mM Mn(II) concentration) originate from inner- and outer-sphere contributions (Equation (S6)):

$$r_1 = r_{1\mathrm{is}} + r_{1\mathrm{os}} \tag{S6}$$

The inner-sphere term is given by Equation (S7), where q is the number of inner-sphere water molecules.

$$r_{1\mathrm{is}} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1\mathrm{m}}^{\mathrm{H}} + \tau_{\mathrm{m}}} \tag{S7}$$

In the longitudinal relaxation rate of inner sphere water protons, $1/T_{1\mathrm{m}}{}^{\mathrm{H}}$, the dipolar contribution dominates (Equation (S8)):

$$\frac{1}{T_{1\mathrm{m}}^{\mathrm{H}}} \cong \frac{1}{T_1^{\mathrm{DD}}} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\eta^2 \gamma_{\mathrm{S}}^2 \gamma_{\mathrm{I}}^2}{r_{\mathrm{MnH}}^6} S(S+1)\left[\frac{3\tau_{\mathrm{d1H}}}{1+\omega_{\mathrm{I}}^2 \tau_{\mathrm{d1H}}^2} + \frac{7\tau_{\mathrm{d2H}}}{1+\omega_{\mathrm{S}}^2 \tau_{\mathrm{d2H}}^2}\right] \tag{S8}$$

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. 9, where τ_{RH} is the rotational correlation time of the Mn(II)–$\mathrm{H}_{\mathrm{water}}$ vector:

$$\frac{1}{\tau_{\mathrm{d}iH}} = \frac{1}{\tau_{\mathrm{m}}} + \frac{1}{\tau_{\mathrm{RH}}} + \frac{1}{T_{ie}} \qquad i = 1\,,\,2; \tag{S9}$$

$$\tau_{RH} = \tau_{\mathrm{RH}}^{298} \exp\left\{\frac{E_{\mathrm{R}}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \tag{S10}$$

The electronic relaxation is mainly governed by modulation of the transient zero-field splitting, and for the electron spin relaxation rates, $1/T_{1\mathrm{e}}$ and $1/T_{2\mathrm{e}}$, McMachlan has developed Equations (S11)–(S13) which were used in the fit of the NMRD data [2]:

$$\left(\frac{1}{T_{1\mathrm{e}}}\right) = \frac{32}{25}\Delta^2\left(\frac{\tau_{\mathrm{v}}}{1+\omega_{\mathrm{S}}^2\tau_{\mathrm{v}}^2} + \frac{4\tau_{\mathrm{v}}}{1+4\omega_{\mathrm{S}}^2\tau_{\mathrm{v}}^2}\right) \tag{S11}$$

$$\left(\frac{1}{T_{2\mathrm{e}}}\right) = \frac{32}{50}\Delta^2\left[3\tau_v + \frac{5\tau_v}{1+\omega_{\mathrm{S}}^2\tau_{\mathrm{v}}^2} + \frac{2\tau_v}{1+4\omega_S^2\tau_v^2}\right] \tag{S12}$$

$$\tau_{\mathrm{v}} = \tau_{\mathrm{v}}^{298} \exp\left\{\frac{E_{\mathrm{v}}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \tag{S13}$$

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 outer-sphere contribution to the overall relaxivity is described by Equation (S14), where N_A is the Avogadro constant, and J_{os} is a spectral density function (Equation (S15)).

$$r_{1os} = \frac{32 N_A \pi}{405}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\eta^2 \gamma_S^2 \gamma_I^2}{a_{MnH} D_{MnH}} S(S+1)\left[3J_{os}(\omega_I, T_{1e}) + 7J_{os}(\omega_S, T_{2e})\right] \tag{S14}$$

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

$$j = 1, 2 \tag{S15}$$

The diffusion coefficient for the diffusion of a water proton away from a Mn(II) complex, D_{MnH}, obeys the exponential temperature dependence described by Equation (S16), with activation energy E_{MnH}:

$$D_{MnH} = D_{MnH}^{298} \exp\left\{\frac{E_{MnH}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \tag{S16}$$

References

[1] Swift T. J., Connick R. E., J.Chem.Phys. 1962, 37, 307-320.

[2] McLachlan A. D., Proc. R. Soc. London, Ser. A. 1964, 280, 271-288.