Electronic Supplementary Information for:

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

Sophie Laine,\(^a\) Célia S. Bonnet,\(^a\) Ferenc K. Kálmán,\(^b\) Zoltán Garda,\(^b\) Agnès Pallier,\(^a\) Fabien Caillé,\(^a,c\) Franck Suzenet,\(^c\) Gyula Tircsó\(^b\) \(^*\) and Éva Tóth\(^a\) \(^*\)

\(^a\) Centre de Biophysique Moléculaire, CNRS, Université d’Orléans, rue Charles Sadron, 45071 Orléans, Cedex 2, France
\(^b\) Department of Inorganic and Analytical Chemistry, Faculty of Science and Technology, University of Debrecen, Debrecen, Egyetem tér 1, H-4010, Hungary.
\(^c\) Institut de Chimie Organique et Analytique, UMR 7311 CNRS, Université d’Orléans, rue de Chartres, 45067 Orléans, France

![Graph showing pH versus NaOH equiv. for different metal ions](image-url)
Figure S1: Potentiometric titration curves of solutions containing \(L^1\) (1.87 mM) (A) and \(L^3\) (2.33 mM) (B), with 0 and 1 equivalent of \(\text{MgCl}_2\), \(\text{CaCl}_2\), \(\text{MnCl}_2\), \(\text{ZnCl}_2\) and \(\text{CuCl}_2\). \(I = 0.15 \text{M NaCl}, 298K\).

Figure S2. UV-visible spectra recorded in a solution containing 2.63 mM \(\text{Cu}^{2+}\) 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.

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:

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

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

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

$$\frac{1}{T_{2sc}} = \frac{1}{\tau_s} + \frac{1}{\tau_m} \frac{1}{T_1}$$  \hspace{1cm} (S3)

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 (S4)) where $\Delta S^\dagger$ and $\Delta H^\dagger$ are the entropy and enthalpy of activation for the exchange, and $k_{ex}^{298}$ is the exchange rate at 298.15 K.

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

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

$$\frac{1}{T_{1e}} = \frac{1}{T_{1e}^{298}} \exp \left\{ \frac{E_c}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right\}$$  \hspace{1cm} (S5)

The proton relaxivities (normalized to 1 mM Mn(II) concentration) originate from inner- and outer-sphere contributions (Equation (S6)):
The inner-sphere term is given by Equation (S7), where \( q \) is the number of inner-sphere water molecules.

\[
\begin{equation}
\begin{aligned}
    r_{\text{is}} &= \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m}^H + \tau_m} \\
    \text{(S7)}
\end{aligned}
\end{equation}
\]

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

\[
\begin{equation}
\begin{aligned}
    \frac{1}{T_{1m}^H} &\approx \frac{1}{T_1^{\text{DB}}} = 2 \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\eta^2 \gamma_s^2 \gamma_r^2}{r_{\text{MnH}}^6} S(S + 1) \left[ \frac{3 \tau_{d1H}}{1 + \omega_s^2 \tau_{d1H}^2} + \frac{7 \tau_{d2H}}{1 + \omega_s^2 \tau_{d2H}^2} \right] \\
    \text{(S8)}
\end{aligned}
\end{equation}
\]

Here \( r_{\text{MnH}} \) is the effective distance between the Mn\(^{2+} \) electron spin and the water protons, \( \omega_h \) is the proton resonance frequency, \( \tau_{dH} \) is given by Eq. 9, where \( \tau_{RH} \) is the rotational correlation time of the Mn(II)–H\text{water} vector:

\[
\begin{equation}
\begin{aligned}
    \frac{1}{\tau_{dH}} &= \frac{1}{\tau_m} + \frac{1}{\tau_{RH}} + \frac{1}{T_e} \\
    \text{(S9)}
\end{aligned}
\end{equation}
\]

\[
\begin{equation}
\begin{aligned}
    \tau_{RH} &= \tau_{RH}^{298} \exp \left\{ \frac{E_R}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right\} \\
    \text{(S10)}
\end{aligned}
\end{equation}
\]

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 (S11)–(S13) which were used in the fit of the NMRD data [2]:

\[
\begin{equation}
\begin{aligned}
    \left( \frac{1}{T_{1e}} \right) &= \frac{32}{25} \Delta^2 \left( \frac{\tau_v}{1 + \omega_s^2 \tau_v^2} + \frac{4 \tau_v}{1 + 4 \omega_s^2 \tau_v^2} \right) \\
    \text{(S11)}
\end{aligned}
\end{equation}
\]

\[
\begin{equation}
\begin{aligned}
    \left( \frac{1}{T_{2e}} \right) &= \frac{32}{50} \Delta^2 \left[ 3 \tau_v + \frac{5 \tau_v}{1 + \omega_s^2 \tau_v^2} + \frac{2 \tau_v}{1 + 4 \omega_s^2 \tau_v^2} \right] \\
    \text{(S12)}
\end{aligned}
\end{equation}
\]

\[
\begin{equation}
\begin{aligned}
    \tau_v &= \tau_v^{298} \exp \left\{ \frac{E_v}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right\} \\
    \text{(S13)}
\end{aligned}
\end{equation}
\]
where $\Lambda^2$ 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 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)).

$$r_{1os} = \frac{32N_A\pi}{405} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\eta^2 S^2 S}{a_{MnH} D_{MnH}} S(S+1) \left[ 3J_{os}(\omega_1, T_{je}) + 7J_{os}(\omega_S, T_{2e}) \right]$$ (S14)

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

$$j = 1, 2$$ (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 $E_{MnH}$:

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

References
