Supporting Information

for

Mn$^{2+}$ complexes of 1-oxa-4,7-diazacyclononane based ligands: stability and relaxation studies

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Content:

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

<table>
<thead>
<tr>
<th>Best fit parameters</th>
<th>[Mn(L$^1$)(H$_2$O)$_x$]</th>
<th>[Mn(L$^2$)(H$_2$O)]$^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ex}^{298}$ / 10$^7$ s$^{-1}$</td>
<td>119 ± 22</td>
<td>1.20 ± 0.1</td>
</tr>
<tr>
<td>$\Delta H^\ddagger$ / kJ mol$^{-1}$</td>
<td>11.7 ± 0.8</td>
<td>38.8 ± 1.1</td>
</tr>
<tr>
<td>$\Delta S^\ddagger$ / J mol$^{-1}$K$^{-1}$</td>
<td>$-32 \pm 5$</td>
<td>23 ± 3</td>
</tr>
<tr>
<td>$E_{\text{rot}}$ / kJ mol$^{-1}$</td>
<td>12 ± 1</td>
<td>23 ± 2</td>
</tr>
<tr>
<td>$\tau_{\text{rot}}^{298}$ / ps</td>
<td>22 ± 1</td>
<td>103 ± 3</td>
</tr>
<tr>
<td>$\tau_{v}^{298}$ / ps</td>
<td>12.4 ± 0.6</td>
<td>33.7 ± 0.8</td>
</tr>
<tr>
<td>$\Delta^2$ / 10$^{18}$ s$^{-2}$</td>
<td>79 ± 5</td>
<td>53 ± 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fixed parameters</th>
<th>[Mn(L$^1$)(H$_2$O)$_x$]</th>
<th>[Mn(L$^2$)(H$_2$O)]$^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_O/h$ / 10$^6$ rad s$^{-1}$</td>
<td>33.3$^a$</td>
<td>33.3$^a$</td>
</tr>
<tr>
<td>$E_v$ / kJ mol$^{-1}$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$D_{\text{MnH}}$ / 10$^{-10}$ m$^2$ s$^{-1}$</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>$E_{\text{MnH}}$ / kJ mol$^{-1}$</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>$r_{(\text{MnO})}$ / Å</td>
<td>2.139</td>
<td>2.139</td>
</tr>
<tr>
<td>$r_{(\text{MnH})_{\text{in}}}$ / Å</td>
<td>2.75</td>
<td>2.75</td>
</tr>
<tr>
<td>$r_{(\text{MnH})_{\text{out}}}$ / Å</td>
<td>3.20</td>
<td>3.20</td>
</tr>
</tbody>
</table>
Table S2 Experimental values of overall protonation constants (log\(\beta_{hlm}\)) of H₂L₁–H₂L₄ (25 °C, \(I = 0.1\) M (NMe₄)Cl, standard deviations in parenthesis as calculated by OPIUM); \(\beta_{hlm} = [H₄LₜMₘ] / [H]^{h}[L]^{l}[M]^{m}\). Charges were omitted for clarity.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>stoichiometry</th>
<th>H₂L¹</th>
<th>H₄L²</th>
<th>H₂L³</th>
<th>H₂L⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>L + H⁺ ↔ HL</td>
<td>1 1 0</td>
<td>10.59(1)</td>
<td>12.32(1)</td>
<td>8.42 (1)</td>
<td>9.23(1)</td>
</tr>
<tr>
<td>L + 2H⁺ ↔ H₂L</td>
<td>2 1 0</td>
<td>14.58(1)</td>
<td>20.21(1)</td>
<td>9.81 (2)</td>
<td>11.08(1)</td>
</tr>
<tr>
<td>L + 3H⁺ ↔ H₃L</td>
<td>3 1 0</td>
<td>16.41(1)</td>
<td>25.65(1)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L + 4H⁺ ↔ H₄L</td>
<td>4 1 0</td>
<td>–</td>
<td>27.53(1)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Equations used for treatment of relaxometric data

$^{17}$O NMR data have been fitted according to the Swift and Connick equations.\(^1\) The reduced transverse $^{17}$O relaxation rates, $1/T_{2r}$, and reduced $^{17}$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):

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

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

$\Delta \omega_m$ 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)).

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

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

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

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 $298k_{ex}$ is the exchange rate at 298.15 K.

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

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):

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

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

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

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 Mn$^{2+}$ concentration) originate from inner- and outer-sphere contributions (Equation (S9)):

\[
r_i = r_{iis} + r_{ion} \quad \text{(S9)}
\]

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

\[
r_{iis} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m} + \tau_m} \quad \text{(S10)}
\]
In the longitudinal relaxation rate of inner sphere water protons, $1/T_{1m}^H$, the dipolar contribution dominates (Equation (S11)):

$$
\frac{1}{T_{1m}^H} \equiv \frac{1}{T_{1}^{DD}} = \frac{2}{15} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{h^2 \gamma_s^2 I^2}{r_{MnH}^6} S(S + 1) \left[ \frac{3\tau_{diiH}^{diiH}}{1 + \omega_i^2 \tau_{diiH}^{diiH}} + \frac{7\tau_{diiH}^{diiH}}{1 + \omega_i^2 \tau_{diiH}^{diiH}} \right]
$$  \hspace{1cm} (S11)

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

$$
\frac{1}{\tau_{diiH}} = \frac{1}{\tau_m} + \frac{1}{\tau_{RH}} + \frac{1}{T_{ie}} \quad i = 1, 2;
$$  \hspace{1cm} (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)).

$$
r_{os} = \frac{32 N_A \pi}{405} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{h^2 \gamma_s^2 I^2}{a_{MnH} D_{MnH}} S(S + 1) \left[ 3J_{os} (\omega_1, T_{1e}) + 7J_{os} (\omega_2, T_{2e}) \right]
$$  \hspace{1cm} (S13)

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

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

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