SUPPLEMENTARY MATERIAL

Manganese(II) Oxazolidine Nitrooxide Chelates; Structure, Magnetism and Redox Properties

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Figure S1. Plot of $\chi_M T$ vs T for 1 and best fit (red lines) with values shown inset.

Figure S2. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.00$. Residual value capped at 3.9.
Figure S3. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.00$. Residual value capped at 7.8.
Figure S4. Plot of $\chi_M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.

$$
g = 2.01 \\
J_1 = -69.8 \text{ cm}^{-1} \\
J_2 = 0.84 \text{ cm}^{-1}
$$

Figure S5. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.01$. Residual value capped at 3.9.
Figure S6. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.01$. Residual value capped at 7.8.
Figure S7. Plot of $\chi_M T$ vs T for 1 and best fit (red lines) with values shown inset.

$g = 2.02$
$J_1 = -71.4 \text{ cm}^{-1}$
$J_2 = 0.82 \text{ cm}^{-1}$

Figure S8. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.02$. Residual value capped at 3.9.
Figure S9. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.02$. Residual value capped at 7.8.
Figure S10. Plot of $\chi_M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.

Figure S11. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.03$. Residual value capped at 3.9.
Figure S12. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.03$. Residual value capped at 7.8.
Figure S13. Plot of $\chi M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.
**Figure S14.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.04$. Residual value capped at 3.9.

**Figure S15.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.04$. Residual value capped at 7.8.
Figure S16. Plot of $\chi_M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.
**Figure S17.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.05$. Residual value capped at 3.9.

**Figure S18.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.05$. Residual value capped at 7.8.
Figure S19. Plot of $\chi_M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.
**Figure S20.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.06$. Residual value capped at 3.9.

**Figure S21.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.06$. Residual value capped at 7.8.
Figure S22. Plot of $\chi_M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.

- $g = 2.07$
- $J_1 = -80.2$ cm$^{-1}$
- $J_2 = 0.87$ cm$^{-1}$
**Figure S23.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.07$. Residual value capped at 3.9.

**Figure S24.** Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.07$. Residual value capped at 7.8.
Figure S25. Plot of $\chi_M T$ vs $T$ for 1 and best fit (red lines) with values shown inset.

$g = 2.08$

$J_1 = 82.1 \text{ cm}^{-1}$

$J_2 = 1.02 \text{ cm}^{-1}$
Figure S26. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.08$. Residual value capped at 3.9.

Figure S27. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.08$. Residual value capped at 7.8.
Figure S28. Plot of $\chi_M T$ vs T for 1 and best fit (red lines) with values shown in inset.

$g = 2.09$
$J_1 = -84.0 \text{ cm}^{-1}$
$J_2 = 0.67 \text{ cm}^{-1}$
Figure S29. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.09$.

Residual value capped at 3.9.
Figure S30. Contour plot of $J_1$ vs $J_2$ in cm$^{-1}$ for complex 1 with lowest residual in blue with a fixed value of $g = 2.09$. Residual value capped at 7.8.
Figure S31. Plot of $M(N\beta)$ vs field (0 - 50000 G) for 1 at (top), 3, 4, 5.5, 10 and 20 K (bottom) with $g$ fixed at 2.00 and $S = 3/2$. The solid red lines represent fits of the experimental data with the parameters shown and in the text.

Figure S32. Plot of $M(N\beta)$ vs field (0 - 50000 G) for 1 at (top), 3, 4, 5.5, 10 and 20 K (bottom) with $g$ fixed at 2.02 and $S = 3/2$. The solid red lines represent fits of the experimental data with the parameters shown and in the text.
Figure S33. Plot of $M(N\beta)$ vs field (0 - 50000 G) for 1 at (top), 3, 4, 5.5, 10 and 20 K (bottom) with $g$ fixed at 2.04 and $S = 3/2$. The solid red lines represent fits of the experimental data with the parameters shown and in the text.

Figure S34. Plot of $M(N\beta)$ vs field (0 - 50000 G) for 1 at (top), 3, 4, 5.5, 10 and 20 K (bottom) with $g$ fixed at 2.06 and $S = 3/2$. The solid red lines represent fits of the experimental data with the parameters shown and in the text.
**Figure S35.** Plot of $M(\sqrt{\beta})$ vs field (0 - 50000 G) for I at (top), 3, 4, 5.5, 10 and 20 K (bottom) with $g$ fixed at 2.08 and $S = 3/2$. The solid red lines represent fits of the experimental data with the parameters shown and in the text.

**Figure S36.** Plot of $M(\sqrt{\beta})$ vs field (0 - 50000 G) for I at (top), 3, 4, 5.5, 10 and 20 K (bottom) with $g$ fixed at 2.10 and $S = 3/2$. The solid red lines represent fits of the experimental data with the parameters shown and in the text.
**Table S1** Summary of known mononuclear complexes containing a linear (L') – MnII - (L') arrangement and their magnetic data where L' = derivatives of Tempo, Proxyl and Iminoyl / Nitronyl nitroxides.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Plateaux χM T value (cm³ mol⁻¹ K)ᵃ</th>
<th>J₁ (cm⁻¹)ᵇ</th>
<th>J₂ (cm⁻¹)ᵇ</th>
<th>g</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnIII(hfac)₂(tempo)₂</td>
<td>1.79</td>
<td>-79</td>
<td>None</td>
<td>1.95</td>
<td>1,2</td>
</tr>
<tr>
<td>MnIII(hfac)₂(proxyl)₂</td>
<td>1.91</td>
<td>-105</td>
<td>None</td>
<td>2.02</td>
<td>1,2</td>
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<tr>
<td>MnIII(hfac)₂NITPh</td>
<td>1.90</td>
<td>-90</td>
<td>None</td>
<td>2.06</td>
<td>3</td>
</tr>
<tr>
<td>MnIII(Cl₂(NIT2-py)₂</td>
<td>1.84</td>
<td>-79.0</td>
<td>None</td>
<td>1.998</td>
<td>4</td>
</tr>
<tr>
<td>MnIII(4ImNNH)₂(NO₃)₂</td>
<td>1.80</td>
<td>-97.3</td>
<td>None</td>
<td>1.96</td>
<td>5</td>
</tr>
<tr>
<td>MnIII(4ImNNH)₂(Cl)₂</td>
<td>1.90</td>
<td>-121.6</td>
<td>None</td>
<td>2.01</td>
<td>5</td>
</tr>
<tr>
<td>MnIII(4ImNNH)₂(Br)₂</td>
<td>1.80</td>
<td>-108.4</td>
<td>None</td>
<td>1.95</td>
<td>5</td>
</tr>
<tr>
<td>MnIII(hfac)₂(L₁⁺)₂</td>
<td>2.01</td>
<td>-92.4</td>
<td>None</td>
<td>2.00</td>
<td>6</td>
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<tr>
<td>MnIII(hfac)₂(L₂⁺)₂</td>
<td>2.01</td>
<td>-102.2</td>
<td>None</td>
<td>2.00</td>
<td>6</td>
</tr>
<tr>
<td>MnIII(hfac)₂(L₃⁺)₂</td>
<td>N/Aᶜ</td>
<td>-311</td>
<td>11.1</td>
<td>2.0 (L₃⁺)</td>
<td>2.14 (Mn(II))</td>
</tr>
</tbody>
</table>

Abbreviations: hfac, hexafluoracetylacetonate; tempo, 2,2,6,6-tetramethylpiperidinyl-1-oxy; proxyl, 2,2,5,5-tetramethylpyrrolidinyl-1; NITPh, 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy 3-oxide; NIT2-py, 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy 3-oxide; 4ImNNH, (2-(4-imidazolyl)-4,4,5,5-tetramethylimidazolin-1-oxyl 3 oxide ; L1⁺, See Ref 6 (azobenzene tempo derivative); L2⁺ See Ref 6 (azobenzene derivative); L3⁺, 1-Iodo-3,5-bis(4',4',5',5'-tetramethyl-4',5'-dihydro-1H-imidazole-1’-oxy)benzene.
a The values have been converted to χM T units (cm³ mol⁻¹ K) and scaled to fit the appropriate spin Hamiltonian: 
\[ \hat{H} = -2J_1 \left( \mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 \right) - 2J_2 \left( \mathbf{S}_1 \cdot \mathbf{S}_3 \right) \] for a clearer comparison.
b These values corresponding to fits obtained using the spin Hamiltonian form as above.
c The (L') – MnIII - (L') moiety has an additional two non-interacting iminoylnitroxide radicals and one non interacting Mn(II) ion. The plateaux value in this case is 7.9 cm³ mol⁻¹ K but has been omitted from the table as it was not a direct comparison.