Supplementary Information

for

Two co-crystalline M(hfac)$_2$(IPhIN)$_2$•M(hfac)$_2$ (M = Mn, Co) compounds with a bis(iminoyl nitroxide) biradical: structure and magnetism

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Table S1. Selected angles (deg) for compounds 1 and 2.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M=Mn)</td>
<td>(M=Co)</td>
</tr>
<tr>
<td><strong>Bond angles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O6A—M1A—O2A</td>
<td>81.78(12)</td>
<td>82 (3)</td>
</tr>
<tr>
<td>O6A—M1A—O3A</td>
<td>108.92(12)</td>
<td>92 (4)</td>
</tr>
<tr>
<td>O2A—M1A—O3A</td>
<td>95.40(12)</td>
<td>102 (4)</td>
</tr>
<tr>
<td>O6A—M1A—O1A</td>
<td>92.96(9)</td>
<td>106 (4)</td>
</tr>
<tr>
<td>O2A—M1A—O1A</td>
<td>105.32(9)</td>
<td>94 (3)</td>
</tr>
<tr>
<td>O3A—M1A—O1A</td>
<td>151.86(9)</td>
<td>158 (4)</td>
</tr>
<tr>
<td>O6A—M1A—O4A</td>
<td>170.18(12)</td>
<td>93 (4)</td>
</tr>
<tr>
<td>O2A—M1A—O4A</td>
<td>93.40(12)</td>
<td>173 (4)</td>
</tr>
<tr>
<td>O3A—M1A—O4A</td>
<td>79.95(12)</td>
<td>83 (4)</td>
</tr>
<tr>
<td>O1A—M1A—O4A</td>
<td>80.01(8)</td>
<td>84 (4)</td>
</tr>
<tr>
<td>O6A—M1A—O5A</td>
<td>91.76(9)</td>
<td>172 (4)</td>
</tr>
<tr>
<td>O2A—M1A—O5A</td>
<td>170.41(9)</td>
<td>93 (3)</td>
</tr>
<tr>
<td>O3A—M1A—O5A</td>
<td>79.94(9)</td>
<td>83 (4)</td>
</tr>
<tr>
<td>O1A—M1A—O5A</td>
<td>82.0</td>
<td>80 (3)</td>
</tr>
<tr>
<td>N1A—O2A—M1A</td>
<td>119.9(2)</td>
<td>121 (7)</td>
</tr>
<tr>
<td>N5A—O6A—M1A</td>
<td>119.7(2)</td>
<td>120(8)</td>
</tr>
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<td><strong>Torsion angles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1A—C17A—C18A—C23A</td>
<td>43.0(2)</td>
<td>41(20)</td>
</tr>
<tr>
<td>N4A—C24A—C22A—C21A</td>
<td>-24.7(1)</td>
<td>-27(21)</td>
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<tr>
<td>N5A—C37A—C38A—C39A</td>
<td>48.8(5)</td>
<td>48(23)</td>
</tr>
<tr>
<td>N7A—C44A—C40A—C39A</td>
<td>-24.1(6)</td>
<td>-22(24)</td>
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</table>
**Figure S1.** Crystal packing of compound 1. (a) Closest contacts $N-O^{\cdot}\cdot N_{\text{imino}}$ and (b) Short contacts $F^{\cdot}\cdot F$ and hydrogen bonding among nitrooxide oxygen atom, imino nitrogen atom and coordinated water molecules to Mn1B ($vii=1.5-x, 1/2-y, -z$). Fluorine, hydrogen and carbon atoms of hfac$^{-}$ ligands were omitted for sake of clarity.