Electronic Supplementary Information

Polymorphism and “reverse” spin transition in the spin crossover system
[Co(4-terpyridone)2](CF3SO3)2·1H2O


Table S1. Crystal data for 1 at 293 K and 120 K.

<table>
<thead>
<tr>
<th></th>
<th>293 K</th>
<th>120 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C32H24N6O9S2F6Co</td>
<td></td>
</tr>
<tr>
<td>Mr</td>
<td>873.62</td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.1020(5)</td>
<td>9.0803(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.2410(5)</td>
<td>9.1039(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.3860(18)</td>
<td>21.1499(7)</td>
</tr>
<tr>
<td>α (°)</td>
<td>94.896(2)</td>
<td>94.899(3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>94.487(2)</td>
<td>94.810(2)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.730(6)</td>
<td>91.322(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1786.4(2)</td>
<td>1735.05(9)</td>
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Selected bond lengths [Å] and angles [°] for 1 at 120 K.

<table>
<thead>
<tr>
<th>Bond</th>
<th>120 K</th>
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<tbody>
<tr>
<td>Co(1)-N(1)</td>
<td>2.099(9)</td>
</tr>
<tr>
<td>Co(1)-N(2)</td>
<td>1.922(9)</td>
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<tr>
<td>Co(1)-N(3)</td>
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<tr>
<td>Co(1)-N(4)</td>
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<tr>
<td>Co(1)-N(5)</td>
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<tr>
<td>Co(1)-N(6)</td>
<td>2.079(10)</td>
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<tr>
<td>N(1)-Co-N(2)</td>
<td>79.1(4)</td>
</tr>
<tr>
<td>N(1)-Co-N(3)</td>
<td>158.3(4)</td>
</tr>
<tr>
<td>N(1)-Co-N(4)</td>
<td>93.7(4)</td>
</tr>
<tr>
<td>N(1)-Co-N(5)</td>
<td>100.8(4)</td>
</tr>
<tr>
<td>N(1)-Co-N(6)</td>
<td>89.4(4)</td>
</tr>
<tr>
<td>N(2)-Co-N(3)</td>
<td>79.2(4)</td>
</tr>
<tr>
<td>N(2)-Co-N(4)</td>
<td>101.1(4)</td>
</tr>
<tr>
<td>N(2)-Co-N(5)</td>
<td>179.2(4)</td>
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<tr>
<td>N(2)-Co-N(6)</td>
<td>99.2(4)</td>
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<tr>
<td>N(3)-Co-N(4)</td>
<td>91.5(4)</td>
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<td>N(3)-Co-N(5)</td>
<td>100.9(4)</td>
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<td>N(3)-Co-N(6)</td>
<td>93.0(4)</td>
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<td>N(4)-Co-N(5)</td>
<td>79.7(4)</td>
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<td>N(4)-Co-N(6)</td>
<td>159.7(4)</td>
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<td>N(5)-Co-N(6)</td>
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Table S2. Crystal data for 2 at 293 K, 180 K and 120 K.

<table>
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<th>293 K</th>
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<th>120 K</th>
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<td>C_{32}H_{24}N_{6}O_{9}F_{6}S_{2}Co</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mr</td>
<td>873.62</td>
<td></td>
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<tr>
<td>Crystal system</td>
<td>triclinic</td>
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</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.5700(4)</td>
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<td>9.2500(4)</td>
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<td>b (Å)</td>
<td>14.3510(9)</td>
<td>14.2520(4)</td>
<td>14.2320(7)</td>
</tr>
<tr>
<td>c (Å)</td>
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<td>14.8710(5)</td>
<td>14.8280(10)</td>
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<td>α (°)</td>
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<td>75.246(2)</td>
<td>75.209(2)</td>
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<td>β (°)</td>
<td>71.982(4)</td>
<td>72.662(1)</td>
<td>72.982(3)</td>
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<td>γ</td>
<td>72.274(2)</td>
<td>72.439(1)</td>
<td>72.315(2)</td>
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<td>V (Å^3)</td>
<td>1832.19(17)</td>
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