Synthesis, Structures and Magnetism of series of Binuclear and one-dimensional Ni-Ln Complexes: Single-molecule Magnetic Behavior in one-dimensional Nitrate-bridged Dy Analogue

Min-Xia Yao,* Xing-Yun Lu, Zhao-Xia Zhu, Xiao-Wei Deng, and Su Jing*

College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, 211816, P. R. China.

Supporting information

Table S1 Selected bond lengths (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th></th>
<th>Bond Length (Å)</th>
<th></th>
<th>Bond Length (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd(1)-O(2)</td>
<td>2.3414(18)</td>
<td>Gd(1)-O(5)</td>
<td>2.3494(19)</td>
<td></td>
</tr>
<tr>
<td>Gd(1)-O(14)</td>
<td>2.484(2)</td>
<td>Gd(1)-O(7)</td>
<td>2.485(2)</td>
<td></td>
</tr>
<tr>
<td>Gd(1)-O(10)</td>
<td>2.495(3)</td>
<td>Gd(1)-O(13)</td>
<td>2.511(3)</td>
<td></td>
</tr>
<tr>
<td>Gd(1)-O(6)</td>
<td>2.546(2)</td>
<td>Gd(1)-O(11)</td>
<td>2.549(3)</td>
<td></td>
</tr>
<tr>
<td>Gd(1)-O(8)</td>
<td>2.555(3)</td>
<td>Gd(1)-O(1)</td>
<td>2.653(2)</td>
<td></td>
</tr>
<tr>
<td>Gd(1)-Ni(1)</td>
<td>3.4798(6)</td>
<td>Ni(1)-O(1)</td>
<td>2.011(2)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)-O(5)</td>
<td>2.0213(19)</td>
<td>Ni(1)-O(2)</td>
<td>2.0357(18)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)-N(2)</td>
<td>2.053(2)</td>
<td>Ni(1)-N(4)</td>
<td>2.088(3)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)-N(3)</td>
<td>2.134(3)</td>
<td>O(2)-Gd(1)-O(5)</td>
<td>68.46(6)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Gd(1)-O(14)</td>
<td>88.22(7)</td>
<td>O(5)-Gd(1)-O(14)</td>
<td>77.53(7)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Gd(1)-O(7)</td>
<td>79.30(7)</td>
<td>O(5)-Gd(1)-O(7)</td>
<td>90.91(7)</td>
<td></td>
</tr>
<tr>
<td>O(14)-Gd(1)-O(7)</td>
<td>165.49(8)</td>
<td>O(2)-Gd(1)-O(10)</td>
<td>134.07(9)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Gd(1)-O(10)</td>
<td>146.45(9)</td>
<td>O(14)-Gd(1)-O(10)</td>
<td>120.65(9)</td>
<td></td>
</tr>
<tr>
<td>O(7)-Gd(1)-O(10)</td>
<td>73.76(9)</td>
<td>O(2)-Gd(1)-O(13)</td>
<td>76.27(8)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Gd(1)-O(13)</td>
<td>117.39(8)</td>
<td>O(14)-Gd(1)-O(13)</td>
<td>50.83(8)</td>
<td></td>
</tr>
<tr>
<td>O(7)-Gd(1)-O(13)</td>
<td>131.23(8)</td>
<td>O(10)-Gd(1)-O(13)</td>
<td>94.49(10)</td>
<td></td>
</tr>
</tbody>
</table>

* To whom correspondence should be addressed. Email: yaomx@njtech.edu.cn ; sjing@njtech.edu.cn. Fax: +86-25-58139528. Nanjing Tech University.
Table S2 Selected bond lengths (Å) and angles (°) for 2.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb(1)-O(4)</td>
<td>2.3283(15)</td>
</tr>
<tr>
<td>Tb(1)-O(11)</td>
<td>2.4703(17)</td>
</tr>
<tr>
<td>Tb(1)-O(13)</td>
<td>2.478(2)</td>
</tr>
<tr>
<td>Tb(1)-O(5)</td>
<td>2.5395(19)</td>
</tr>
<tr>
<td>Tb(1)-O(10)</td>
<td>2.549(2)</td>
</tr>
<tr>
<td>Tb(1)-Ni(1)</td>
<td>3.4695(7)</td>
</tr>
<tr>
<td>Ni(1)-O(1)</td>
<td>2.0158(15)</td>
</tr>
<tr>
<td>Ni(1)-N(1)</td>
<td>2.0562(19)</td>
</tr>
<tr>
<td>Ni(1)-N(4)</td>
<td>2.133(2)</td>
</tr>
<tr>
<td>O(4)-Tb(1)</td>
<td>79.23(6)</td>
</tr>
<tr>
<td>O(4)-Tb(1)-O(11)</td>
<td>90.77(6)</td>
</tr>
<tr>
<td>O(4)-Tb(1)-O(7)</td>
<td>88.14(6)</td>
</tr>
<tr>
<td>O(11)-Tb(1)-O(7)</td>
<td>165.39(6)</td>
</tr>
<tr>
<td>O(1)-Tb(1)</td>
<td>146.22(7)</td>
</tr>
</tbody>
</table>

Table S2 Selected bond lengths (Å) and angles (°) for 2.
<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(7)-Tb(1)-O(13)</td>
<td>120.71(8)</td>
<td>O(4)-Tb(1)-O(8)</td>
</tr>
<tr>
<td>O(1)-Tb(1)-O(8)</td>
<td>117.66(7)</td>
<td>O(11)-Tb(1)-O(8)</td>
</tr>
<tr>
<td>O(7)-Tb(1)-O(8)</td>
<td>50.92(7)</td>
<td>O(13)-Tb(1)-O(8)</td>
</tr>
<tr>
<td>O(4)-Tb(1)-O(5)</td>
<td>130.99(5)</td>
<td>O(1)-Tb(1)-O(5)</td>
</tr>
<tr>
<td>O(11)-Tb(1)-O(5)</td>
<td>113.66(6)</td>
<td>O(7)-Tb(1)-O(5)</td>
</tr>
<tr>
<td>O(7)-Tb(1)-O(5)</td>
<td>69.52(6)</td>
<td>O(13)-Tb(1)-O(5)</td>
</tr>
<tr>
<td>O(8)-Tb(1)-O(5)</td>
<td>114.45(7)</td>
<td>O(8)-Tb(1)-O(10)</td>
</tr>
<tr>
<td>O(14)-Tb(1)-O(10)</td>
<td>97.38(9)</td>
<td>O(10)-Tb(1)-O(6)</td>
</tr>
<tr>
<td>N(2)-Ni(1)-O(1)</td>
<td>170.16(7)</td>
<td>N(2)-Ni(1)-O(4)</td>
</tr>
<tr>
<td>O(1)-Ni(1)-O(4)</td>
<td>80.91(6)</td>
<td>N(2)-Ni(1)-N(1)</td>
</tr>
<tr>
<td>O(1)-Ni(1)-N(1)</td>
<td>90.05(7)</td>
<td>O(4)-Ni(1)-N(1)</td>
</tr>
<tr>
<td>N(2)-Ni(1)-N(3)</td>
<td>87.71(8)</td>
<td>O(1)-Ni(1)-N(3)</td>
</tr>
<tr>
<td>O(4)-Ni(1)-N(3)</td>
<td>92.50(8)</td>
<td>N(1)-Ni(1)-N(3)</td>
</tr>
<tr>
<td>N(2)-Ni(1)-N(4)</td>
<td>93.19(8)</td>
<td>O(1)-Ni(1)-N(4)</td>
</tr>
<tr>
<td>O(4)-Ni(1)-N(4)</td>
<td>85.69(7)</td>
<td>N(1)-Ni(1)-N(4)</td>
</tr>
<tr>
<td>N(3)-Ni(1)-N(4)</td>
<td>177.98(8)</td>
<td>N(3)-Ni(1)-N(4)</td>
</tr>
</tbody>
</table>

**Table S3** Selected bond lengths (Å) and angles (°) for 3.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy(1)-O(2)</td>
<td>2.283(3)</td>
<td>Dy(1)-O(5)</td>
<td>2.293(3)</td>
<td></td>
</tr>
<tr>
<td>Dy(1)-O(15)</td>
<td>2.372(3)</td>
<td>Dy(1)-O(9)</td>
<td>2.429(3)</td>
<td></td>
</tr>
<tr>
<td>Dy(1)-O(12)</td>
<td>2.430(3)</td>
<td>Dy(1)-O(11)</td>
<td>2.476(3)</td>
<td></td>
</tr>
<tr>
<td>Dy(1)-O(1)</td>
<td>2.488(3)</td>
<td>Dy(1)-O(6)</td>
<td>2.497(3)</td>
<td></td>
</tr>
<tr>
<td>Dy(1)-O(8)</td>
<td>2.517(3)</td>
<td>Dy(1)-N(1)</td>
<td>3.4538(6)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)-O(5)</td>
<td>2.005(3)</td>
<td>Ni(1)-O(2)</td>
<td>2.010(3)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)-N(1)</td>
<td>2.023(4)</td>
<td>Ni(1)-N(2)</td>
<td>2.037(4)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)-N(6)</td>
<td>2.117(4)</td>
<td>Ni(1)-O(13)</td>
<td>2.161(3)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Dy(1)-O(5)</td>
<td>67.27(9)</td>
<td>O(2)-Dy(1)-O(15)</td>
<td>148.23(10)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Dy(1)-O(15)</td>
<td>135.16(10)</td>
<td>O(2)-Dy(1)-O(9)</td>
<td>91.95(11)</td>
<td></td>
</tr>
<tr>
<td>Bond</td>
<td>Length (Å)</td>
<td>Bond</td>
<td>Length (Å)</td>
<td>Bond</td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------</td>
<td>-----------------------</td>
<td>------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>O(5)-Dy(1)-O(9)</td>
<td>80.22(10)</td>
<td>O(15)-Dy(1)-O(9)</td>
<td>74.50(10)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Dy(1)-O(12)</td>
<td>124.36(11)</td>
<td>O(5)-Dy(1)-O(12)</td>
<td>121.80(11)</td>
<td></td>
</tr>
<tr>
<td>O(15)-Dy(1)-O(11)</td>
<td>68.21(10)</td>
<td>O(9)-Dy(1)-O(12)</td>
<td>141.85(11)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Dy(1)-O(11)</td>
<td>81.77(11)</td>
<td>O(5)-Dy(1)-O(11)</td>
<td>80.32(10)</td>
<td></td>
</tr>
<tr>
<td>O(15)-Dy(1)-O(11)</td>
<td>119.57(11)</td>
<td>O(9)-Dy(1)-O(11)</td>
<td>160.49(11)</td>
<td></td>
</tr>
<tr>
<td>O(12)-Dy(1)-O(11)</td>
<td>51.74(11)</td>
<td>O(2)-Dy(1)-O(1)</td>
<td>65.67(10)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Dy(1)-O(1)</td>
<td>129.22(10)</td>
<td>O(15)-Dy(1)-O(1)</td>
<td>95.53(10)</td>
<td></td>
</tr>
<tr>
<td>O(9)-Dy(1)-O(1)</td>
<td>118.97(11)</td>
<td>O(12)-Dy(1)-O(1)</td>
<td>73.38(11)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Dy(1)-O(6)</td>
<td>75.23(12)</td>
<td>O(2)-Dy(1)-O(6)</td>
<td>131.23(9)</td>
<td></td>
</tr>
<tr>
<td>O(9)-Dy(1)-O(6)</td>
<td>64.48(9)</td>
<td>O(15)-Dy(1)-O(6)</td>
<td>77.53(10)</td>
<td></td>
</tr>
<tr>
<td>O(11)-Dy(1)-O(6)</td>
<td>86.73(11)</td>
<td>O(12)-Dy(1)-O(6)</td>
<td>77.87(11)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Dy(1)-O(8)</td>
<td>83.71(11)</td>
<td>O(11)-Dy(1)-O(8)</td>
<td>150.93(10)</td>
<td></td>
</tr>
<tr>
<td>O(15)-Dy(1)-O(8)</td>
<td>73.36(10)</td>
<td>O(1)-Dy(1)-O(8)</td>
<td>104.69(10)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Dy(1)-O(10)</td>
<td>75.82(10)</td>
<td>O(1)-Dy(1)-O(10)</td>
<td>114.99(10)</td>
<td></td>
</tr>
<tr>
<td>O(15)-Dy(1)-O(10)</td>
<td>123.00(11)</td>
<td>O(1)-Dy(1)-O(10)</td>
<td>141.27(12)</td>
<td></td>
</tr>
<tr>
<td>O(1)-Dy(1)-O(12)</td>
<td>67.67(10)</td>
<td>O(6)-Dy(1)-O(12)</td>
<td>134.94(10)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Ni(1)-O(2)</td>
<td>87.78(13)</td>
<td>O(5)-Ni(1)-N(1)</td>
<td>165.19(14)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Ni(1)-N(1)</td>
<td>88.03(14)</td>
<td>O(5)-Ni(1)-N(1)</td>
<td>91.37(13)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Ni(1)-N(2)</td>
<td>168.75(13)</td>
<td>O(5)-Ni(1)-N(2)</td>
<td>102.67(16)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Ni(1)-N(6)</td>
<td>87.98(14)</td>
<td>O(5)-Ni(1)-N(6)</td>
<td>95.75(13)</td>
<td></td>
</tr>
<tr>
<td>N(1)-Ni(1)-N(6)</td>
<td>87.78(13)</td>
<td>O(2)-Ni(1)-N(6)</td>
<td>88.19(14)</td>
<td></td>
</tr>
<tr>
<td>O(5)-Ni(1)-O(13)</td>
<td>98.37(11)</td>
<td>O(2)-Ni(1)-O(13)</td>
<td>84.83(12)</td>
<td></td>
</tr>
<tr>
<td>N(1)-Ni(1)-O(13)</td>
<td>85.88(13)</td>
<td>N(2)-Ni(1)-O(13)</td>
<td>92.40(13)</td>
<td></td>
</tr>
<tr>
<td>N(6)-Ni(1)-O(13)</td>
<td>173.81(13)</td>
<td>N(2)-Ni(1)-O(13)</td>
<td>92.40(13)</td>
<td></td>
</tr>
</tbody>
</table>

**Table S4** Selected bond lengths (Å) and angles (°) for 4.
<table>
<thead>
<tr>
<th>Bond or Angle</th>
<th>Value</th>
<th>Bond or Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(14)-Tb(1)-O(9)</td>
<td>146.21(11)</td>
<td>O(12)-Tb(1)-O(9)</td>
<td>75.05(11)</td>
</tr>
<tr>
<td>O(5)-Tb(1)-O(15)</td>
<td>91.13(12)</td>
<td>O(2)-Tb(1)-O(15)</td>
<td>75.87(11)</td>
</tr>
<tr>
<td>O(14)-Tb(1)-O(15)</td>
<td>52.31(13)</td>
<td>O(12)-Tb(1)-O(15)</td>
<td>127.99(13)</td>
</tr>
<tr>
<td>O(9)-Tb(1)-O(15)</td>
<td>149.10(12)</td>
<td>O(5)-Tb(1)-O(1)</td>
<td>136.30(9)</td>
</tr>
<tr>
<td>O(2)-Tb(1)-O(1)</td>
<td>66.29(8)</td>
<td>O(14)-Tb(1)-O(1)</td>
<td>78.05(11)</td>
</tr>
<tr>
<td>O(12)-Tb(1)-O(1)</td>
<td>77.09(10)</td>
<td>O(9)-Tb(1)-O(1)</td>
<td>78.88(10)</td>
</tr>
<tr>
<td>O(15)-Tb(1)-O(1)</td>
<td>86.45(12)</td>
<td>O(5)-Tb(1)-O(11)</td>
<td>83.03(10)</td>
</tr>
<tr>
<td>O(2)-Tb(1)-O(11)</td>
<td>138.38(10)</td>
<td>O(14)-Tb(1)-O(11)</td>
<td>103.42(13)</td>
</tr>
<tr>
<td>O(15)-Tb(1)-O(11)</td>
<td>51.83(11)</td>
<td>O(9)-Tb(1)-O(11)</td>
<td>71.11(11)</td>
</tr>
<tr>
<td>O(15)-Tb(1)-O(1)</td>
<td>137.98(13)</td>
<td>O(1)-Tb(1)-O(11)</td>
<td>125.34(10)</td>
</tr>
<tr>
<td>O(5)-Tb(1)-O(6)</td>
<td>64.91(9)</td>
<td>O(2)-Tb(1)-O(6)</td>
<td>124.41(9)</td>
</tr>
<tr>
<td>O(14)-Tb(1)-O(6)</td>
<td>74.17(11)</td>
<td>O(12)-Tb(1)-O(6)</td>
<td>100.07(11)</td>
</tr>
<tr>
<td>O(9)-Tb(1)-O(6)</td>
<td>127.97(10)</td>
<td>O(15)-Tb(1)-O(6)</td>
<td>73.19(12)</td>
</tr>
<tr>
<td>O(1)-Tb(1)-O(6)</td>
<td>151.87(10)</td>
<td>O(11)-Tb(1)-O(6)</td>
<td>66.65(11)</td>
</tr>
<tr>
<td>O(5)-Ni(1)-N(1)</td>
<td>169.94(12)</td>
<td>O(5)-Ni(1)-O(2)</td>
<td>81.52(10)</td>
</tr>
<tr>
<td>O(2)-Ni(1)-O(2)</td>
<td>88.52(12)</td>
<td>N(1)-Ni(1)-N(2)</td>
<td>87.24(12)</td>
</tr>
<tr>
<td>O(16)-Ni(1)-O(8)</td>
<td>102.76(13)</td>
<td>O(2)-Ni(1)-N(2)</td>
<td>168.56(11)</td>
</tr>
<tr>
<td>O(5)-Ni(1)-O(16)</td>
<td>89.45(12)</td>
<td>N(1)-Ni(1)-O(16)</td>
<td>89.53(13)</td>
</tr>
<tr>
<td>O(2)-Ni(1)-O(16)</td>
<td>92.33(11)</td>
<td>N(2)-Ni(1)-O(16)</td>
<td>89.71(12)</td>
</tr>
<tr>
<td>O(5)-Ni(1)-O(8)</td>
<td>92.22(10)</td>
<td>N(1)-Ni(1)-O(8)</td>
<td>88.71(12)</td>
</tr>
<tr>
<td>O(2)-Ni(1)-O(8)</td>
<td>87.31(10)</td>
<td>N(2)-Ni(1)-O(8)</td>
<td>90.99(12)</td>
</tr>
<tr>
<td>O(16)-Ni(1)-O(8)</td>
<td>178.21(12)</td>
<td>N(2)-Ni(1)-O(8)</td>
<td>90.99(12)</td>
</tr>
</tbody>
</table>

**Table S5** Selected bond lengths (Å) and angles (°) for 5.
Table S6. Results of the Continuous Shape Measure Analysis

<table>
<thead>
<tr>
<th>Geometry</th>
<th>JSPC-10</th>
<th>SDD-10</th>
<th>TD-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.00</td>
<td>1.82</td>
<td>1.94</td>
</tr>
<tr>
<td>2</td>
<td>2.94</td>
<td>1.86</td>
<td>1.96</td>
</tr>
</tbody>
</table>

*JSPC-10 is the shape measure relative to the sphenocorona J87; SDD-10 is the shape measure relative to the staggered dodecahedron (2:6:2); TD-10 is the shape measure relative to the tetradecahedron (2:6:2).*

<table>
<thead>
<tr>
<th>Geometry</th>
<th>MFF-9</th>
<th>CSAPR-9</th>
<th>JCSAPR-9</th>
<th>TCTPR-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.64</td>
<td>2.72</td>
<td>3.90</td>
<td>2.38</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>1.70</td>
<td>3.02</td>
<td>2.82</td>
</tr>
<tr>
<td>5</td>
<td>2.09</td>
<td>1.77</td>
<td>3.08</td>
<td>2.86</td>
</tr>
</tbody>
</table>

*MFF-9 is the shape measure relative to the muffin; CSAPR-9 is the shape measure relative to the spherical capped square antiprism; JCSAPR-9 is the shape measure relative to the capped square antiprism; TCTPR-9 is the shape measure relative to the spherical tricapped trigonal prism. The number in bold corresponds to the closer ideal.
geometry to the real complexes.

**Figure S1.** Perspective drawing of the crystallographically structural unit of 2 showing the atom numbering. H atoms are omitted for clarity.

**Figure S2.** A view showing 3D structure formed by weak H-bonding interactions (black dash lines) in 1.
**Figure S3.** A view showing 3D structure formed by weak H-bonding interactions (black dash lines) in 2.

**Figure S4.** A view showing 2D structure formed by weak H-bonding interactions (black dash lines) in 3.
Figure S5. Perspective drawing of the crystallographically structural unit of 4 showing the atom numbering. H atoms and one solvated diethyl ether molecule are omitted for clarity.

Figure S6. A view showing 3D structure formed by weak H-bonding interactions and CH⋯π interactions (black dash lines) in 4.
Figure S7. A view showing 3D structure formed by weak H-bonding interactions and CH⋯π interactions (black dash lines) in 5.

Figure S8. Field dependence of magnetization for 1-5 at low temperatures.
Figure S9. Temperature dependence of the in-phase $\chi'$ and out-of-phase $\chi''$ in a 2 Oe ac field oscillating at 100 and 999 Hz with a zero applied dc field for 2.

Figure S10. Temperature dependence of the in-phase $\chi'$ and out-of-phase $\chi''$ in a 2 Oe ac field oscillating at 100 and 999 Hz with a zero applied dc field for 4.
**Figure S11.** Temperature dependence of the in-phase $\chi'$ and out-of-phase $\chi''$ at different frequencies in a 2 Oe ac field oscillating at 1–999 Hz with a zero applied dc field for 5.

**Figure S12.** the Arrhenius fit for the $\ln \tau$ vs $T^{-1}$ plot from ac-f data of 3. The red solid line represents the best fits of the data.
Figure S13. $\ln(\chi'T)$ vs $T^{-1}$ plots on a semi-logarithmic scale from polycrystalline samples of 3.