Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2021

# Single-Molecule Magnet Behavior and Magnetic Refrigeration of Carbonyl Oxygen Bridged Tetranuclear Lanthanide Complexes

**Chen Yang,[a] Yu-Heng Wei,[a] Shuang Xu,[a] Hao-Yu Zhang,[a] Yue-Qi Yang,[a] Bo Zhang,[a] Ming Fang,[a,b] ***

*a Department of Chemistry, Hebei Normal University of Science & Technology, Qinhuangdao 066004, Hebei province, P. R.China. E-mail:fangmingchem@163.com*
*c Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry , MOE, and TKL of Metal and Molecule Based Material Chemistry, Nankai University, Tianjin 300071, China.. E-mail: zhaobin@nankai.edu.cn*

## Electronic supplementary information

### Synthesis of Methyl 6-(Hydroxymethyl) Picolinate.

65 mmol $NaBH_4$ (2.46 g) was added in small portions over a period of 1 h to a stirred suspension of dimethyl pyridine-2,6-dicarboxylate (40 mmol, 7.81 g) in 200 mL MeOH at 0 °C. This mixture was stirred at room temperature for another 3 h and then MeOH was removed in a rotary evaporator (Scheme 1). A saturated $NaHCO_3$ aqueous solution (200 mL) was added to the residue and the resulting aqueous solution was extracted with $CHCl_3$ (5×100 mL). The combined organic layers were dried by anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo to dryness. The resulting crude residue was purified by column chromatography (n-hexane/EtOAc; 1:1, then 1:2) giving the desired product as a white solid. Anal. Calcd (%) for $C_8H_9NO_3$: C, 57.49; H, 5.39; N, 8.38. Found: C, 57.90; H, 5.26; N, 8.50.

*a Department of Chemistry, Hebei Normal University of Science & Technology, Qinhuangdao 066004, Hebei province, P. R.China. E-mail: fangmingchem@163.com*
*b Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China.*

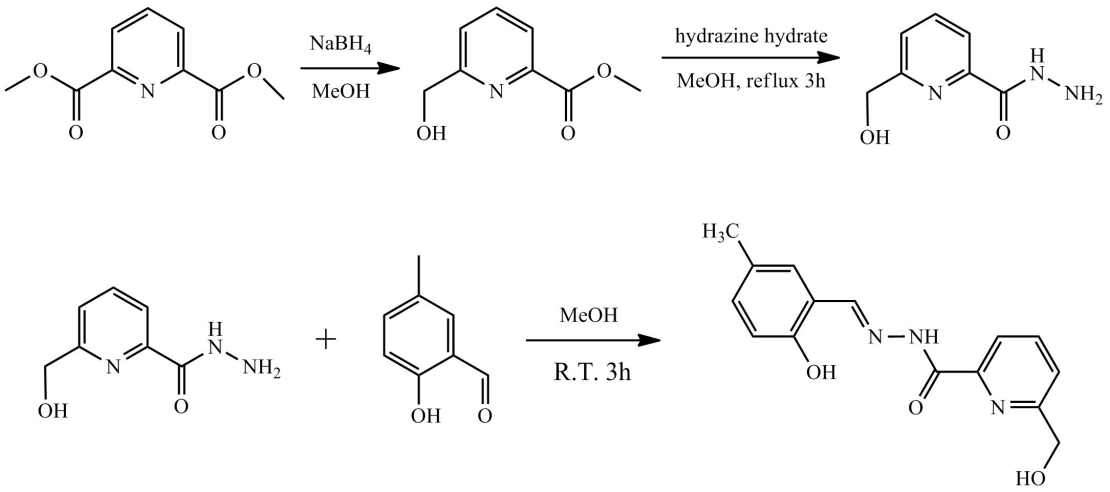
† Electronic Supporting Information Available: Crystallographic data in CIF format; tables of selected bond lengths and angles for compounds **1–3**, other magnetic data and plots. CCDC reference numbers 1862672-1862674 refer to compounds **1–3** respectively. This material is available free of charge via the Internet at See DOI: 10.1039/b000000x/.

**Synthesis of 6-(Hydroxymethyl) Picolinohydrazide**

A methanolic solution of methyl 6-(hydroxymethyl) picolinate (10 mmol, 1.81 g) was added dropwise to a stirred solution of hydrazine hydrate (50 mmol) in 30 mL methanol at room temperature (Scheme 1). After the addition was over, the reaction mixture was heated under reflux for 3 h and subsequently allowed to come to room temperature before being kept in a refrigerator at 5 °C. A needle-shaped crystalline product was isolated which was suction-filtered, washed with a small amount of cold methanol, and air-dried. Anal. Calcd (%) for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.02; H, 5.16; N 24.86.

**Synthesis of N'-(2-hydroxy-5-methylbenzylidene)-6-(hydroxymethyl) picolinohydrazide ($H_2L$)**

A 10 mL methanolic solution of 2-hydroxy-5-methylbenzaldehyde (5 mmol, 0.68g) was added dropwise to a stirred suspension of 6-(hydroxymethyl) picolinohydrazide (5 mmol, 0.84g) in methanol (5 mL) at room temperature (Scheme 1). The reaction mixture was heated under reflux overnight, then cooled to room temperature and kept for 8 h without stirring. A precipitate formed was collected through filtration and washed with MeOH. Yield: 1.06 g (78.3%). Anal. Calcd (%) for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.80; N, 15.50. Found: C, 61.82; H, 4.93; N, 15.68.




Scheme 1. The synthesis of $H_2L$.

**Table S1** Selected bond lengths (Å) and angles (°) for complex **1**[a]

| | | | |
|---|---|---|---|
| Gd(2)-O(24)#1 | 2.304(4) | Gd(2)-O(7) | 2.314(4) |
| Gd(2)-O(3) | 2.320(4) | Gd(2)-O(2) | 2.382(4) |
| Gd(2)-O(5) | 2.395(4) | Gd(2)-O(4) | 2.496(4) |
| Gd(2)-N(3) | 2.580(5) | Gd(2)-N(4) | 2.588(5) |
| Gd(1)-O(7) | 2.309(4) | Gd(1)-O(24) | 2.318(4) |
| Gd(1)-O(6)#1 | 2.331(4) | Gd(1)-O(5)#1 | 2.403(4) |
| Gd(1)-O(2) | 2.406(4) | Gd(1)-O(1) | 2.473(4) |
| Gd(1)-N(6)#1 | 2.584(5) | Gd(1)-N(1) | 2.618(5) |
| Gd(2)-Gd(1) | 3.8723(4) | Gd(2)-Gd(1)#1 | 3.8997(4) |
| | | | |
| O(24)#1-Gd(2)-O(7) | 101.25(14) | O(24)#1-Gd(2)-O(3) | 92.49(14) |
| O(7)-Gd(2)-O(3) | 160.92(14) | O(24)#1-Gd(2)-O(2) | 81.12(14) |
| O(7)-Gd(2)-O(2) | 67.17(14) | O(3)-Gd(2)-O(2) | 128.77(14) |
| O(24)#1-Gd(2)-O(5) | 67.00(13) | O(7)-Gd(2)-O(5) | 89.67(14) |
| O(3)-Gd(2)-O(5) | 83.54(14) | O(2)-Gd(2)-O(5) | 136.14(13) |
| O(24)#1-Gd(2)-O(4) | 169.30(14) | O(7)-Gd(2)-O(4) | 80.41(14) |
| O(3)-Gd(2)-O(4) | 88.55(15) | O(2)-Gd(2)-O(4) | 89.93(14) |
| O(5)-Gd(2)-O(4) | 123.69(14) | O(24)#1-Gd(2)-N(3) | 99.80(15) |
| O(7)-Gd(2)-N(3) | 120.10(14) | O(3)-Gd(2)-N(3) | 69.59(15) |
| O(2)-Gd(2)-N(3) | 61.78(14) | O(5)-Gd(2)-N(3) | 149.83(15) |
| O(4)-Gd(2)-N(3) | 70.60(15) | O(24)#1-Gd(2)-N(4) | 128.40(15) |
| O(7)-Gd(2)-N(4) | 90.64(14) | O(3)-Gd(2)-N(4) | 70.38(14) |
| O(2)-Gd(2)-N(4) | 147.30(15) | O(5)-Gd(2)-N(4) | 63.02(14) |
| O(4)-Gd(2)-N(4) | 61.85(14) | N(3)-Gd(2)-N(4) | 117.02(15) |
| O(24)#1-Gd(2)-Gd(1) | 83.31(9) | O(24)#1-Gd(2)-Gd(1)#1 | 32.59(10) |
| O(7)-Gd(1)-O(24) | 101.40(14) | O(7)-Gd(1)-O(6)#1 | 92.92(14) |
| O(24)-Gd(1)-O(6)#1 | 162.11(14) | O(7)-Gd(1)-O(5)#1 | 79.98(14) |
| O(24)-Gd(1)-O(5)#1 | 66.64(13) | O(6)#1-Gd(1)-O(5)#1 | 127.22(13) |
| O(7)-Gd(1)-O(2) | 66.86(13) | O(24)-Gd(1)-O(2) | 91.04(13) |
| O(6)#1-Gd(1)-O(2) | 84.73(14) | O(5)#1-Gd(1)-O(2) | 135.51(13) |
| O(7)-Gd(1)-O(1) | 171.47(13) | O(24)-Gd(1)-O(1) | 79.41(14) |
| O(6)#1-Gd(1)-O(1) | 88.03(14) | O(5)#1-Gd(1)-O(1) | 92.69(13) |
| O(2)-Gd(1)-O(1) | 121.68(14) | O(7)-Gd(1)-N(6)#1 | 100.81(15) |
| O(24)-Gd(1)-N(6)#1 | 118.12(14) | O(6)#1-Gd(1)-N(6)#1 | 68.74(14) |
| O(5)#1-Gd(1)-N(6)#1 | 61.69(14) | O(2)-Gd(1)-N(6)#1 | 150.52(14) |
| O(1)-Gd(1)-N(6)#1 | 71.63(15) | O(7)-Gd(1)-N(1) | 127.22(14) |
| O(24)-Gd(1)-N(1) | 91.95(14) | O(6)#1-Gd(1)-N(1) | 70.70(15) |
| O(5)#1-Gd(1)-N(1) | 149.55(14) | O(2)-Gd(1)-N(1) | 62.02(14) |
| O(1)-Gd(1)-N(1) | 61.02(14) | N(6)#1-Gd(1)-N(1) | 117.16(15) |

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

**Table S2** Selected bond lengths (Å) and angles (°) for complex **2**[a]

| | | | |
|---|---|---|---|
| Tb(2)-O(7) | 2.294(5) | Tb(2)-O(8)#1 | 2.301(4) |
| Tb(2)-O(1)#1 | 2.314(5) | Tb(2)-O(2)#1 | 2.381(5) |
| Tb(2)-O(5) | 2.382(5) | Tb(2)-O(6) | 2.483(5) |
| Tb(2)-N(6) | 2.574(6) | Tb(2)-N(1)#1 | 2.577(6) |
| Tb(1)-O(8) | 2.289(5) | Tb(1)-O(7) | 2.308(5) |
| Tb(1)-O(4) | 2.321(5) | Tb(1)-O(2) | 2.382(5) |
| Tb(1)-O(5) | 2.387(5) | Tb(1)-O(3) | 2.460(5) |
| Tb(1)-N(4) | 2.583(6) | Tb(1)-N(3) | 2.609(6) |
| Tb(2)-Tb(1)#1 | 3.8498(5) | Tb(2)-Tb(1) | 3.8792(6) |
| | | | |
| O(7)-Tb(2)-O(8)#1 | 101.34(17) | O(7)-Tb(2)-O(1)#1 | 92.04(17) |
| O(8)#1-Tb(2)-O(1)#1 | 160.99(18) | O(7)-Tb(2)-O(2)#1 | 81.04(17) |
| O(8)#1-Tb(2)-O(2)#1 | 66.85(17) | O(1)#1-Tb(2)-O(2)#1 | 129.33(17) |
| O(7)-Tb(2)-O(5) | 66.90(17) | O(8)#1-Tb(2)-O(5) | 89.96(17) |
| O(1)#1-Tb(2)-O(5) | 82.88(17) | O(2)#1-Tb(2)-O(5) | 135.94(16) |
| O(7)-Tb(2)-O(6) | 168.67(17) | O(8)#1-Tb(2)-O(6) | 80.66(17) |
| O(1)#1-Tb(2)-O(6) | 88.87(18) | O(2)#1-Tb(2)-O(6) | 89.64(17) |
| O(5)-Tb(2)-O(6) | 124.40(17) | O(7)-Tb(2)-N(6) | 128.76(18) |
| O(8)#1-Tb(2)-N(6) | 90.64(17) | O(1)#1-Tb(2)-N(6) | 70.40(18) |
| O(2)#1-Tb(2)-N(6) | 146.98(18) | O(5)-Tb(2)-N(6) | 63.46(18) |
| O(6)-Tb(2)-N(6) | 62.02(18) | O(7)-Tb(2)-N(1)#1 | 99.31(19) |
| O(8)#1-Tb(2)-N(1)#1 | 120.30(18) | O(1)#1-Tb(2)-N(1)#1 | 69.85(18) |
| O(2)#1-Tb(2)-N(1)#1 | 62.09(17) | O(5)-Tb(2)-N(1)#1 | 149.26(18) |
| O(6)-Tb(2)-N(1)#1 | 70.43(19) | N(6)-Tb(2)-N(1)#1 | 117.02(19) |
| O(7)-Tb(2)-Tb(1)#1 | 83.36(11) | O(8)#1-Tb(2)-Tb(1)#1 | 32.91(12) |
| O(8)-Tb(1)-O(7) | 101.66(17) | O(8)-Tb(1)-O(4) | 92.71(17) |
| O(7)-Tb(1)-O(4) | 161.71(17) | O(8)-Tb(1)-O(2) | 67.02(17) |
| O(7)-Tb(1)-O(2) | 91.28(17) | O(4)-Tb(1)-O(2) | 83.90(17) |
| O(8)-Tb(1)-O(5) | 80.14(17) | O(7)-Tb(1)-O(5) | 66.60(17) |
| O(4)-Tb(1)-O(5) | 127.84(17) | O(2)-Tb(1)-O(5) | 135.83(16) |
| O(8)-Tb(1)-O(3) | 170.92(17) | O(7)-Tb(1)-O(3) | 79.53(17) |
| O(4)-Tb(1)-O(3) | 88.07(17) | O(2)-Tb(1)-O(3) | 122.04(17) |
| O(5)-Tb(1)-O(3) | 92.24(17) | O(8)-Tb(1)-N(4) | 100.30(18) |
| O(7)-Tb(1)-N(4) | 118.28(18) | O(4)-Tb(1)-N(4) | 69.29(18) |
| O(2)-Tb(1)-N(4) | 150.11(19) | O(5)-Tb(1)-N(4) | 61.61(18) |
| O(3)-Tb(1)-N(4) | 71.53(18) | O(8)-Tb(1)-N(3) | 127.40(17) |
| O(7)-Tb(1)-N(3) | 91.91(18) | O(4)-Tb(1)-N(3) | 70.23(18) |
| O(2)-Tb(1)-N(3) | 62.04(17) | O(5)-Tb(1)-N(3) | 149.32(18) |
| O(3)-Tb(1)-N(3) | 61.27(17) | N(4)-Tb(1)-N(3) | 117.27(18) |

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

**Table S3** Selected bond lengths (Å) and angles (°) for complex **3**[a]

| | | | |
|---|---|---|---|
| Dy(2)-O(2)#1 | 2.376(3) | Dy(2)-O(5) | 2.375(3) |
| Dy(2)-O(7)#1 | 2.285(3) | Dy(2)-O(8) | 2.282(3) |
| Dy(2)-O(6) | 2.307(3) | Dy(2)-O(1)#1 | 2.456(3) |
| Dy(2)-N(6) | 2.573(4) | Dy(2)-N(1)#1 | 2.596(4) |
| Dy(1)-O(2) | 2.361(3) | Dy(1)-O(5) | 2.376(3) |
| Dy(1)-O(7) | 2.284(3) | Dy(1)-O(8) | 2.292(3) |
| Dy(1)-O(3) | 2.291(3) | Dy(1)-O(4) | 2.475(3) |
| Dy(1)-N(3) | 2.566(4) | Dy(1)-N(4) | 2.573(4) |
| Dy(2)-Dy(1) | 3.8670(4) | Dy(2)-Dy(1)#1 | 3.8375(3) |
| | | | |
| O(2)#1-Dy(2)-O(1)#1 | 122.60(11) | O(2)#1-Dy(2)-N(6) | 150.05(13) |
| O(2)#1-Dy(2)-N(1)#1 | 62.43(11) | O(5)-Dy(2)-O(2)#1 | 134.81(11) |
| O(5)-Dy(2)-O(1)#1 | 92.74(12) | O(5)-Dy(2)-N(6) | 61.82(12) |
| O(5)-Dy(2)-N(1)#1 | 149.78(12) | O(7)#1-Dy(2)-O(2)#1 | 66.58(11) |
| O(7)#1-Dy(2)-O(5) | 79.70(12) | O(7)#1-Dy(2)-O(6) | 92.44(12) |
| O(7)#1-Dy(2)-O(1)#1 | 170.79(11) | O(7)#1-Dy(2)-N(6) | 99.88(12) |
| O(7)#1-Dy(2)-N(1)#1 | 127.26(12) | O(8)-Dy(2)-O(2)#1 | 90.96(11) |
| O(8)-Dy(2)-O(5) | 66.64(11) | O(8)-Dy(2)-O(7)#1 | 101.69(12) |
| O(8)-Dy(2)-O(6) | 161.93(12) | O(8)-Dy(2)-O(1)#1 | 79.81(12) |
| O(8)-Dy(2)-N(6) | 118.51(12) | O(8)-Dy(2)-N(1)#1 | 91.90(12) |
| O(6)-Dy(2)-O(2)#1 | 84.33(12) | O(6)-Dy(2)-O(5) | 127.80(12) |
| O(6)-Dy(2)-O(1)#1 | 88.04(12) | O(6)-Dy(2)-N(6) | 69.15(13) |
| O(6)-Dy(2)-N(1)#1 | 70.45(13) | O(1)#1-Dy(2)-N(6) | 71.70(12) |
| O(1)#1-Dy(2)-N(1)#1 | 61.45(12) | N(6)-Dy(2)-N(1)#1 | 117.65(12) |
| O(2)-Dy(1)-O(5) | 135.18(11) | O(2)-Dy(1)-O(4) | 89.95(12) |
| O(2)-Dy(1)-N(3) | 62.37(12) | O(2)-Dy(1)-N(4) | 147.27(12) |
| O(5)-Dy(1)-O(4) | 124.81(11) | O(5)-Dy(1)-N(3) | 149.26(12) |
| O(5)-Dy(1)-N(4) | 63.69(12) | O(7)-Dy(1)-O(2) | 66.85(11) |
| O(7)-Dy(1)-O(5) | 89.55(12) | O(7)-Dy(1)-O(8) | 101.37(11) |
| O(7)-Dy(1)-O(3) | 160.83(12) | O(7)-Dy(1)-O(4) | 81.00(12) |
| O(7)-Dy(1)-N(3) | 120.61(12) | O(7)-Dy(1)-N(4) | 90.62(12) |
| O(8)-Dy(1)-O(2) | 80.95(12) | O(8)-Dy(1)-O(5) | 66.48(11) |
| O(8)-Dy(1)-O(4) | 168.65(11) | O(8)-Dy(1)-N(3) | 99.13(13) |
| O(8)-Dy(1)-N(4) | 128.48(12) | O(3)-Dy(1)-O(2) | 129.51(11) |
| O(3)-Dy(1)-O(5) | 83.33(12) | O(3)-Dy(1)-O(8) | 92.09(12) |
| O(3)-Dy(1)-O(4) | 88.48(12) | O(3)-Dy(1)-N(3) | 69.71(12) |
| O(3)-Dy(1)-N(4) | 70.26(12) | O(4)-Dy(1)-N(3) | 70.46(13) |
| O(4)-Dy(1)-N(4) | 62.20(12) | N(3)-Dy(1)-N(4) | 117.24(13) |
| Dy(1)-O(2)-Dy(2)#1 | 108.21(12) | Dy(2)-O(5)-Dy(1) | 108.95(12) |
| Dy(1)-O(7)-Dy(2)#1 | 114.24(13) | Dy(2)-O(8)-Dy(1) | 115.47(14) |

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

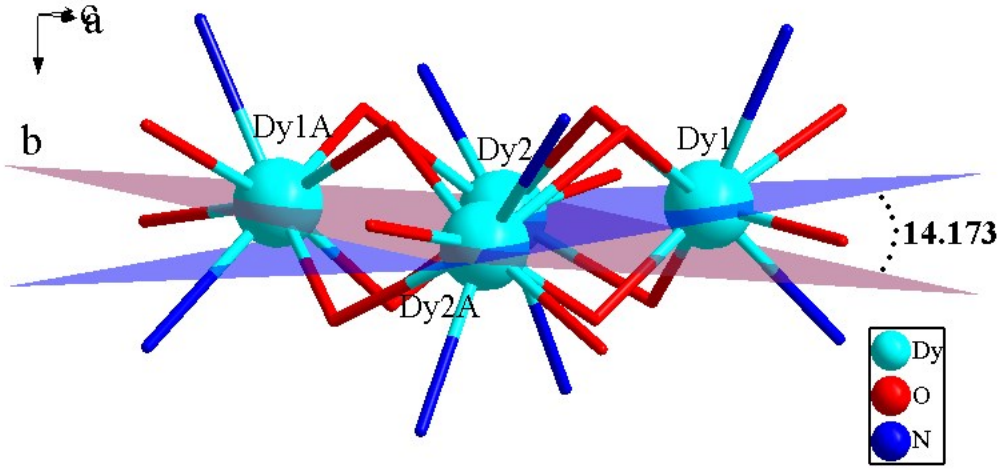



Figure S1 The dihedral angle between the two planes (two Dy2−Dy2−Dy1) of **3** (all hydrogen atoms are omitted for clarity).

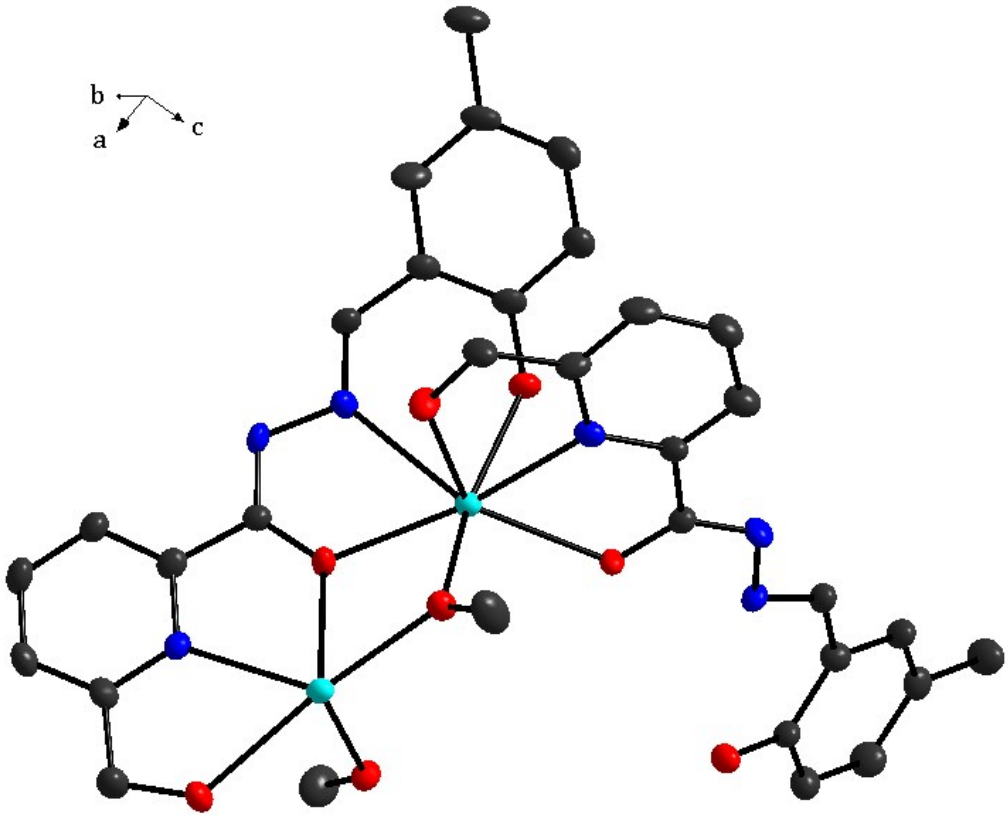



Figure S2 Coordination environments of $Gd^{3+}$ compound **1**. All hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are at 50% probability.

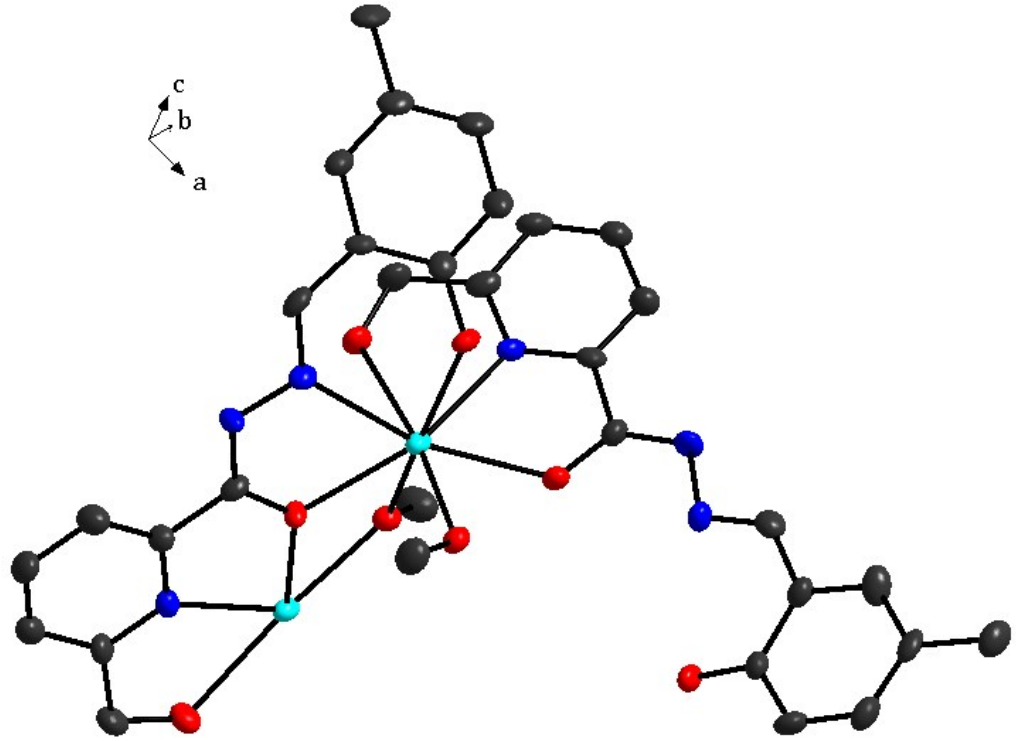



Figure S2 Coordination environments of $Tb^{3+}$ compound **2**. All hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are at 50% probability.

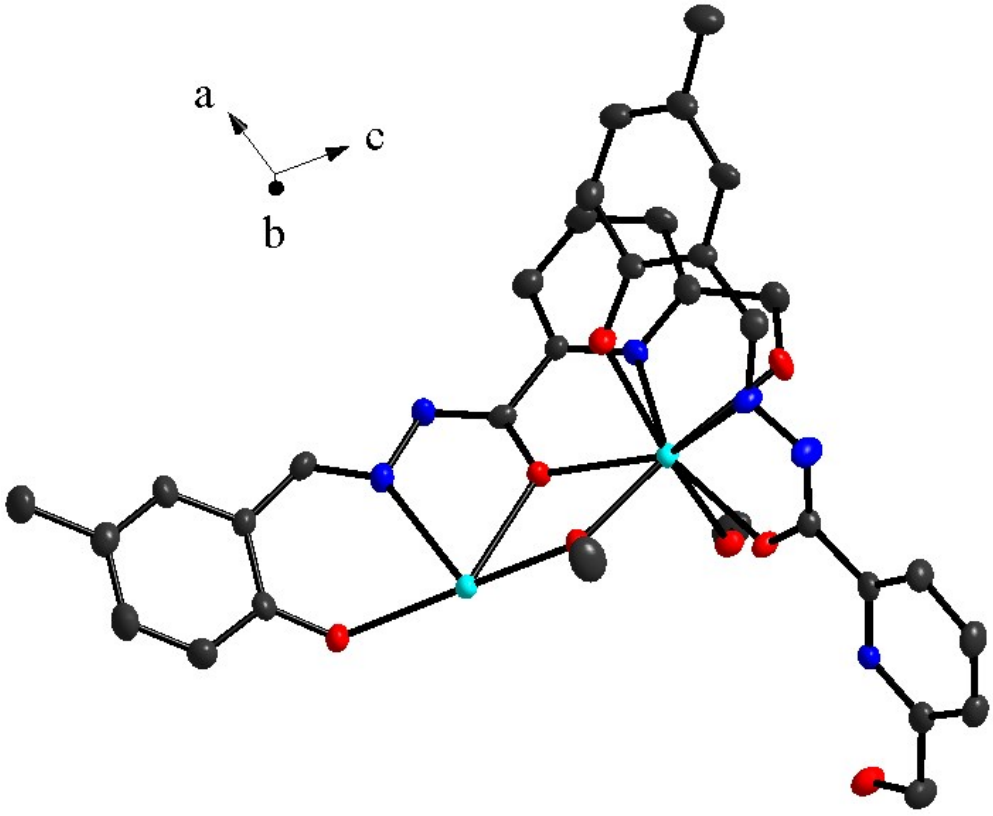



Figure S4 Coordination environments of $Dy^{3+}$ compound **3**. All hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are at 50% probability.