Electronic Supplementary Information for Dalton Transactions

Supporting information

Synthesis, Structure and Magnetic Properties of Linear Heterobimetallic Trinuclear Mn_2Ln (Ln = Eu, Gd, Dy) Complexes

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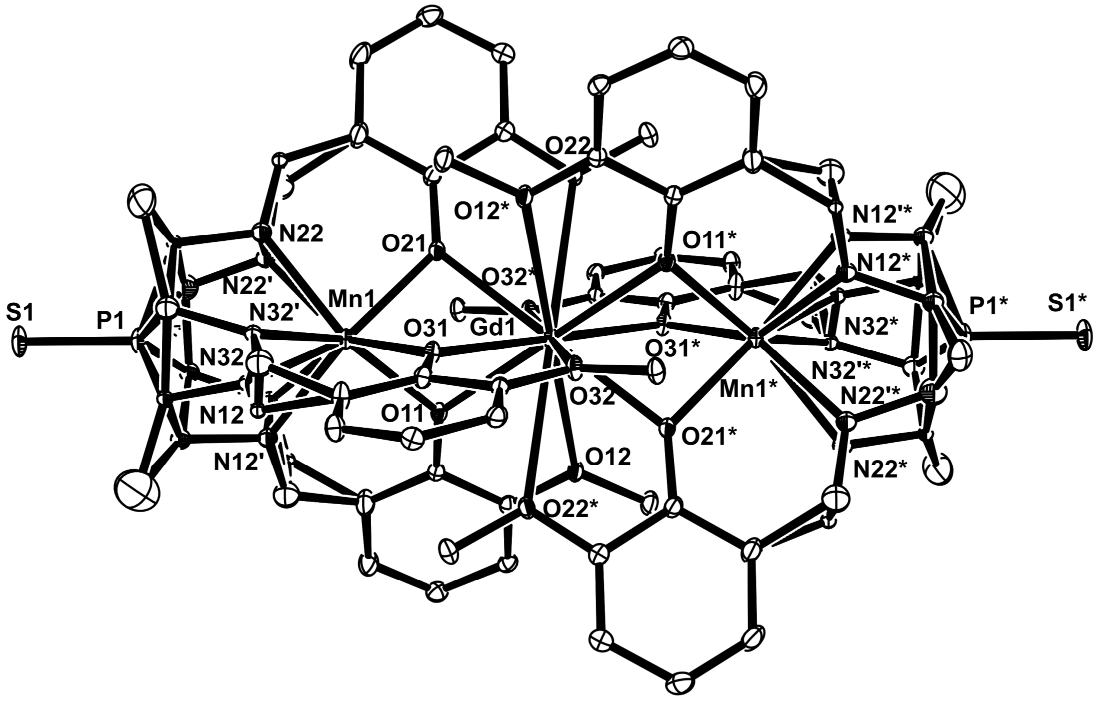

Figure S1. Cationic part, $[L_2Mn_2Gd]^+$, of **3**. Hydrogen atoms, nitrate anions and solvent molecules omitted for clarity

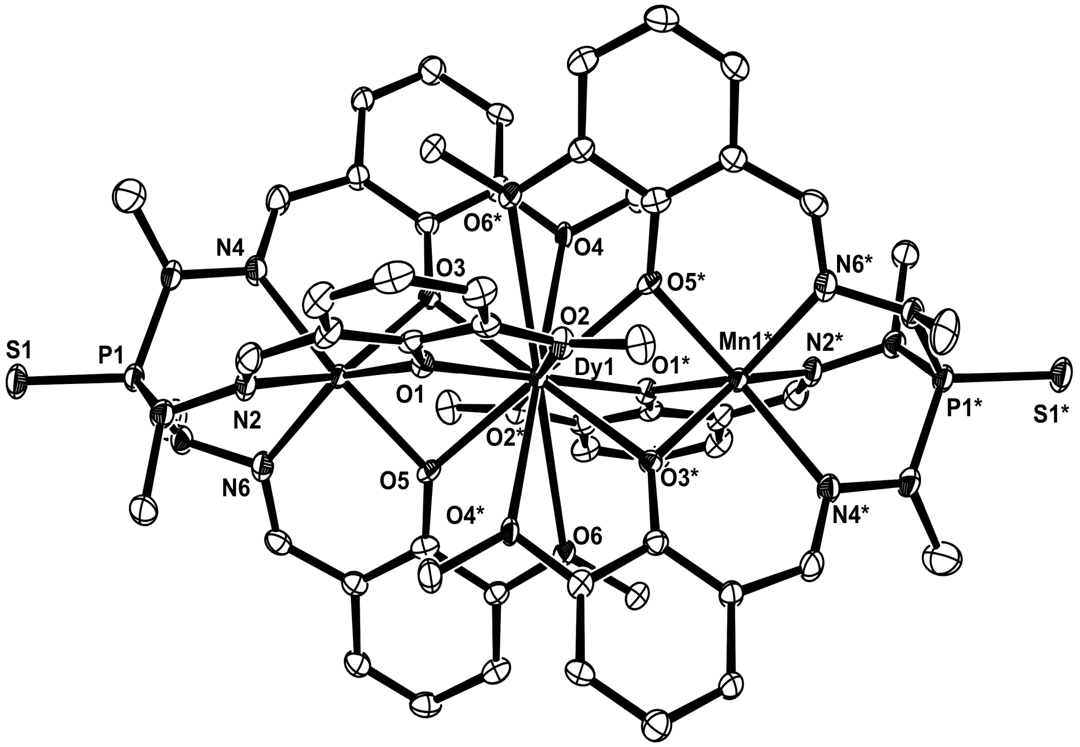

Figure S2. Cationic part, $[L_2Mn_2Dy]^+$, of **4.** Hydrogen atoms, nitrate anions and solvent molecules omitted for clarity.

Preparation of $[\{(S)P[N(Me)N=CH\text{-}C_6H_3\text{-}\,\mathit{2}\text{-}O\text{-}\mathit{3}\text{-}OMe]_3\}_2Mn_2Eu]Cl\cdot CHCl_3\cdot CH_3OH\cdot 3H_2O$ (2)

The ligand LH_3[1] (0.20 g; 0.333 mmol) was taken in a mixture of chloroform 30 mL and methanol 30 mL. $Mn(OAc)_2\cdot 4H_2O$ (0.082g; 0.333 mmol) and triethylamine was added to this solution, finally $EuCl_3\cdot 6H_2O$ (0.061 g; 0.167 mmol) was added to above solution and the reaction mixture was stirred for 12 h to afford a clear solution. It was filtered and the filtrate evaporated to dryness. The residue obtained was washed with *n*-hexane and dried. Compound **2** was purified by slow evaporation of chloroform/methanol mixture of the compound. Yield: 0.210g, 74.31 %. Mp: >280°C. FT-IR ν/cm^{-1}: 1591 (C=N). ESI-MS: 1457.13(M)$^+$. Anal. Calcd for

$C_{56}H_{71}Cl_4EuMn_2N_{12}O_{16}P_2S_2$: C, 39.62; H, 4.21; N, 9.91; S, 3.78 Found: C, 39.52; H, 4.22; N, 9.89; S, 3.73.

Preparation of **[{(S)P[N(Me)N=CH-C_6H_3-*2*-O-*3*-OMe]$_3$}$_2$$Mn_2Gd$]$NO_3$·2$CHCl_3$·3$H_2O$ (3)**

The ligand LH_3 (0.20 g; 0.333 mmol) was taken in a mixture of chloroform 30 mL and methanol 30 mL. $Mn(OAc)_2 \cdot 4H_2O$ (0.082 g; 0.333 mmol) and triethylamine was added to this solution, finally $Gd(NO_3)_3 \cdot 6H_2O$ (0.076 g; 0.167 mmol) was added to above solution and the reaction mixture was stirred for 12 h to afford a clear solution. It was filtered and the filtrate evaporated to dryness. The residue obtained was washed with *n*-hexane and dried. Compound (**3**) was purified by slow evaporation of chloroform/methanol mixture of the compound. Yield: 0.230g, 75.17 %. Mp: >280°C. FT-IR ν/cm^{-1}: 1591(C=N). ESI-MS: 1465.12(M)$^+$. Anal. Calcd for $C_{56}H_{68}Cl_6GdMn_2N_{13}O_{18}P_2S_2$: C, 37.05; H, 3.78; N, 10.04; S, 3.53 Found: C, 36.92; H, 3.81; N, 9.32; S, 3.50.

[{(S)P[N(Me)N=CH-C_6H_3-*2*-O-*3*-OMe]$_3$}$_2$$Mn_2Dy$]$ClO_4$·$CHCl_3$·$H_2O$ (4)

The ligand LH_3 (0.20 g 0.333 mmol) was taken in a mixture of chloroform 30 mL and methanol 30 mL. $Mn(ClO_4)_2 \cdot 6H_2O$ (0.121 g, 0.333 mmol) and triethylamine was added to this solution, finally $Dy(NO_3)_3 \cdot 5H_2O$ (0.073 g, 0.167 mmol) was added to above solution and the reaction mixture was stirred for 12 h to afford a clear solution. It was filtered and the filtrate evaporated to dryness. The residue obtained was washed with *n*-hexane and dried. Compound (**4**) was purified by slow evaporation of chloroform/methanol mixture of the compound **4**.

Yield: 0.200 g, 70.41 %. Mp: >280°C. FT-IR ν/cm^{-1}: 1593 (C=N). ESI-MS: 1468.02(M)$^+$. Anal. Calcd for $C_{55}H_{63}Cl_4DyMn_2N_{12}O_{17}P_2S_2$: C, 38.75; H, 3.73; N, 9.87; S, 3.75 Found: C, 38.92; H, 3.69; N, 9.82; S, 3.74.

X-ray crystallography. Single crystals suitable for X-ray crystallographic analyses were obtained by a slow evaporation of chloroform / methanol mixture of these compounds (**2-4**). The crystal data for compounds **2-4** have been collected on a Bruker SMART CCD diffractometer using a Mo Kα sealed tube. The program SMART[2a] was used for collecting frames of data, indexing reflection, and determining lattice parameters, SAINT[2a] for integration of the intensity of reflections and scaling, SADABS[2b] for absorption correction, and SHELXTL[2c, 2d] for space group and structure determination and least-squares refinements on F^2. All structures were solved by direct methods using the programs SHELXS-97[2e] and refined by full-matrix least squares methods against F^2 with SHELXL-97.[2e] Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The complex **2** one chloride ion and disordered solvent molecules, SQUEEZE/PLATON[3] was used to remove the disorder solvent molecule and anion. PLATON program show compound **2** contains solvent accessible void 2483.1 Å^3 and the electron count per cell is 492, it shows it contain 4 chloride, 4 chloroform, 4 methanol, and 12 water molecules in the unit cell. In complex **3** hydrazone nitrogen, imino carbon atom and methyl carbon atoms are present in the 50:50 disordered position and it contain one nitrate and two chloroform and three water molecules. Chloroform molecules are present in disordered and we resolved the disorder by splitting the atoms on two positions. In compound **3** N21, C22, C12, C1' atoms are showed as a non-positive definite therefore these atoms are refined isotropically. Compound **4** contain disordered perchlorate as anion and disordered solvent molecules, SQUEEZE/PLATON[3] program was used to remove the disordered solvent molecule and anion. PLATON program shows that the complex **4** contains solvent accessible void 528.2 Å^3 and the electron count per cell is 116, it shows it contain one perchlorate anion, one chloroform and one water molecules in the unit cell. The figures have been generated using *Diamond 3.1e* software.[2f]

Table S1: Important bond length (Å) for **2-4**

	2	**3**[a]	**4**
M n-N	2.189(4) 2.249(4) 2.251(4) 2.186(4) 2.202(4) 2.214(4) 2.215(4)avg	2.191(6) 2.201(6) 2.232(6) 2.152(6) 2.258(6) 2.179(6) 2.202(6)avg	2.176(4) 2.183(4) 2.243(4) 2.201(4)avg
Mn-O	2.092(3) 2.134(3) 2.147(3) 2.119(3) 2.130(3) 2.133(3) 2.126(3)avg	2.115(2) 2.126(2) 2.137(2) 2.126(2)avg	2.102(3) 2.130(3) 2.146(3) 2.126(3)avg
Ln-O(phenolic)	2.415(3) 2.421(3) 2.426(3) 2.429(3) 2.430(3) 2.450(3) 2.429(3)avg	2.416(2) 2.419(3) 2.421(2) 2.419(3)avg	2.371(3) 2.381(3) 2.401(3) 2.384(3)avg
Ln-O(ome)	2.830(3) 2.869(3) 2.879(3) 2.900(3)	2.884(2) 2.900(3) 2.900(2) 2.895(3)avg	2.891(3) 2.914(3) 2.914(3) 2.906(3)avg

	2.939(3) 2.944(3) 2.893(3)avg		
Mn-Ln	3.332(3)	3.3114(6)	3.286(2)
Mn-Mn	6.652(2)	6.623(9)	6.573(2)

For compound 3, Mn-N and Mn-N’ bond distances are given.

Reference

(1) V. Chandrasekhar, B. M. Pandian, R. Azhakar, J. J. Vittal and R. Clérac, *Inorg. Chem.* 2007, **46**, 5140.

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(3) P. Van der Sluis, A. L. Spek, *Acta Crystallogr.* 1990, **A46**, 194.