Electronic Supplementary Information

Molybdate Templated Assembly of $Gd_{12}Mo_4$ and Related Clusters with a Truncated Tetrahedron Core

Yong Zheng,[a] Qian-Chong Zhang,[a] La-Sheng Long,*,[a] Rong-Bin Huang,[a] Achim Müller,[b] Jürgen Schnack,[c] Lan-Sun Zheng[a] and Zhiping Zheng[a]

[a] State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[b] Faculty of Chemistry, University of Bielefeld, P.O. Box 10 0131, D-33501 Bielefeld, Germany

[c] Faculty of Physics, University of Bielefeld, P.O. Box 10 0131, D-33501 Bielefeld, Germany

Email: lslong@xmu.edu.cn

1. General Experimental. All chemicals were of commercial origin and were used as received except (n-$Bu_4N)_4Mo_8O_{26}$ has been prepared using a literature procedure.[1] The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectrum (IR) was recorded on a Nicolet AVATAR FT-IR330 Spectrophotometer with pressed KBr pellets. Magnetic measurements were carried out with a Quantum Design SQUID MPMS magnetometer working in the 2-300 K range.

2. Syntheses of complexes 1-3. A mixture of *rac*-3-aminopropane-1,2-diol (23 mg, 0.25 mmol) and 2-hydroxybenzaldehyde (26 μL, 0.25 mmol) in methanol (18 mL) was refluxed for 2 hours. To the solution of Schiff-base (*rac*-H_3L) formed *in situ* was added $Ln(CH_3COO)_3\cdot 3H_2O$ (0.192 mg, 0.5 mmol), (n-$Bu_4N)_4Mo_8O_{26}$ (60 mg, 0.028 mmol) and triethylamine (109□μL, 0.75 mmol) under stirring at room temperature. The mixture was stirred for another 30 minutes, and subsequently sealed in a 23 ml Teflon lined Parr, heated to 90 °C for 12 hours. Slow evaporation of the filtrate afforded the products as pale-yellow, block-shaped crystals.

1, Yield: 38 % (based on Gd). Elemental analysis (%) calcd for $Gd_{12}Mo_4C_{96}H_{170}N_6O_{82}$ (FW= 4991.13): C 23.10, H 3.43, N 1.68; found: C 22.88, H 3.50, N 1.71; IR (KBr, cm^{-1}): 3471(b, s), 2889(w), 2359(w), 1630(s), 1570(s), 1449(s), 1346(m), 1279(m), 1149(w), 1128(w), 1054(w), 1033(w), 861(w), 812(s), 738(w), 674(m), 620(w), 589(w).

2, Yield: 45 % (based on Eu). Elemental analysis (%) calcd for $Eu_{12}Mo_4C_{96}H_{170}N_6O_{82}$ (FW= 4927.66): C 23.40, H 3.48, N 1.71; found: C 23.35, H 3.47, N 1.76; IR (KBr, cm^{-1}): 3468(b, s), 2889(w), 1631(s), 1570(s), 1448(s), 1344(m), 1280(m), 1150(w), 1128(w), 1055(w), 1033(w), 858(w), 809(s), 739(w), 672(m), 618(w), 589(w).

3, Yield: 35 % (based on Sm). Elemental analysis (%) calcd for $Sm_{12}Mo_4C_{96}H_{170}N_6O_{82}$ (FW= 4908.34): C 23.49, H 3.49, N 1.71; found: C 23.43, H 3.53, N 1.80; IR (KBr, cm^{-1}): 3462(b, s), 2891(w), 2362(w), 1632(s), 1570(s), 1448(s), 1344(m), 1280(m), 1151(w), 1128(w), 1055(w), 1033(w), 858(w), 809(s), 739(w), 672(m), 618(w), 589(w).

3. X-ray Structure Determination. Intensity data of **1** were collected on a Bruker SMART CCD with graphite monochromatic $Mo_{K\alpha}$ radiation □(λ= 0.71073 Å) radiation at 173 K. The frames were integrated with the Bruker SAINT© build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. In compound **1**, a total of 116 restraints were used in the structural refinement on the disorder atoms. Intensity data of **2** and **3** were collected on a Oxford Gemini S Ultra system with graphite monochromatic $Mo_{K\alpha}$□ radiation (λ= 0.71073 Å) at 133 K. Data reductions were performed using CrysAlis RED program. Structures were solved by direct methods and refined to convergence by least squares method on F^2 using the SHELXTL software suite.[2] Hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2□xUeq of the attached atom (1.5 x □Ueq for methyl hydrogen atoms). Non-hydrogen atoms (except for C8, C11, C17, C39, C49, C63, C71, C72, C79, C92, C93, N1, O24, O28, O36, O38, O53, O55, O68 and 1W in **1**, O1W and O2W in **2** and O1W,O2W and O3W in **3**) were refined anisotropically. The severely disordered guest molecules (2 methanol molecules and 7 water molecules per formula unit in **1**, 6 water molecules per formula unit in **2** and 5 water molecules per formula unit in **3**) were removed by SQUEEZE.[3] Other disordered atoms were refined with command of ISOR. CCDC 861086-861088 contains the supplementary crystallographic data for **1-3** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Tab. S3.1. Crystal data and structure refinements for **1-3**.

Complex	**1**	**2**	**3**
Formula	$Gd_{12}Mo_4C_{96}H_{170}N_6O_{82}$	$Eu_{12}Mo_4C_{96}H_{170}N_6O_{82}$	$Sm_{12}Mo_4C_{96}H_{170}N_6O_{82}$
Mr	4991.14	4927.66	4908.34
Temperature/K	173(2)	133(2)	133(2)
Crystal size/mm^3	0.20 x 0.15 x 0.15	0.60 x 0.40 x 0.30	0.40 x 0.35 x 0.35
Crystal system	Monoclinic	Monoclinic	Monoclinic

Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	22.539(3)	22.590(1)	22.588(1)
b/Å	27.768(4)	27.744(1)	27.831(1)
c/Å	28.619(3)	28.615(1)	28.672(1)
β/deg	121.92(1)	122.04(1)	121.97(1)
V/Å^3	15204(3)	15202(1)	15291(1)
Z	4	4	4
Dc/g cm^{-3}	2.181	2.153	2.132
μ/mm^{-1}	5.567	5.283	4.939
Data/restraints/params	26751/120/1642	26741/12/1759	30040/18/1767
θ /deg	1.06- 25.00	2.71-25.00	2.76-26.00
Obs reflns	17241	22377	25191
Goof on F^2	0.967	1.097	1.120
R_{int}	0.0819	0.0387	0.0373
$R_1[I > 2\sigma(I)]$[a]	0.0730	0.0438	0.0479
wR_2(All data)[b]	0.1989	0.1009	0.1047

[a] $R_1 = \sum||F_O| - |F_C||/\sum|F_O|$ [b] $wR_2 = \{\sum[w(F_O{}^2 - F_C{}^2)^2]/\sum[w(F_O{}^2)^2]\}^{1/2}$

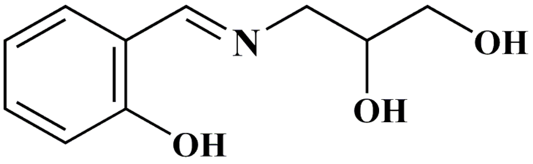
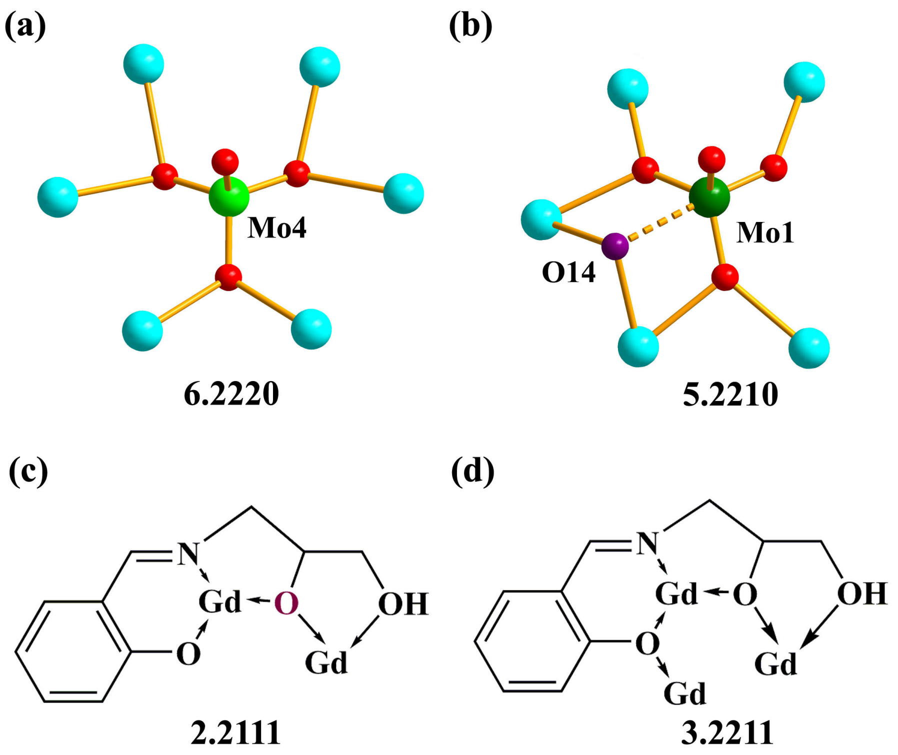


Fig. S1. The molecular structure of the Schiff-base ligand H_3L.



(a) 6.2220

(b) 5.2210

(c) 2.2111

(d) 3.2211

Fig. S2. (b) and (c) two different coordination environments of the MoO_4^{2-} ions with their coordination modes expressed using Harris notation (Mo2 and Mo3 have the same connection fashions as Mo1); (d) and (e) schematic presentation of the two different types of HL^{2-} ligands with their coordination modes expressed using Harris notation.

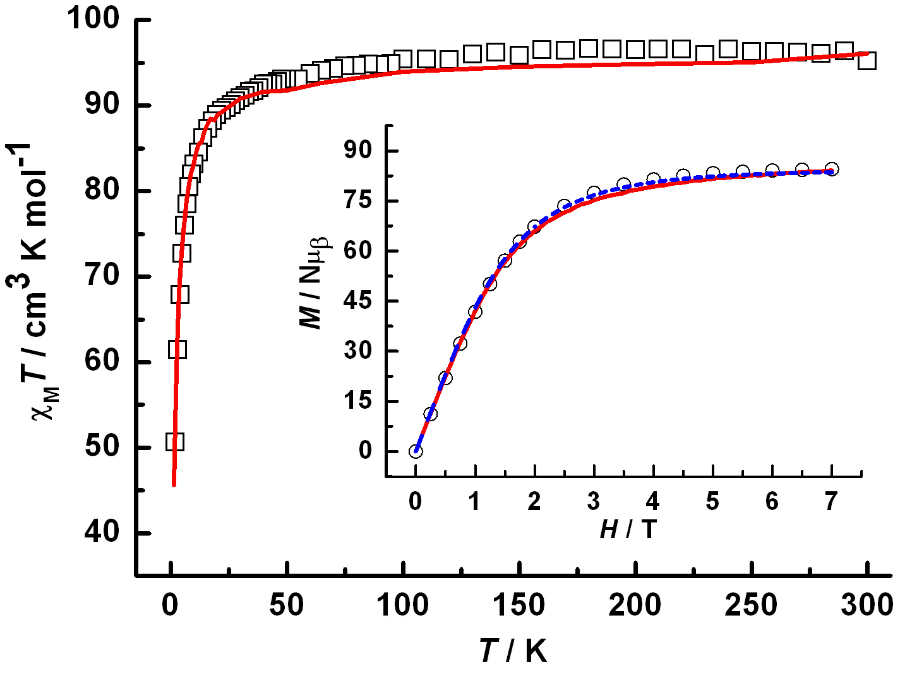


Fig. S3. Plots of temperature dependence of χ_MT for **1** under 1000 Oe DC field between 2 and 300 K; Inset: field-dependent magnetization plots of **1** at 2 K. The red solid curves display the result of classical Monte-Carlo calculations, the dashed blue one the results of the FTLM method. The magnetization is scaled to the saturation value.

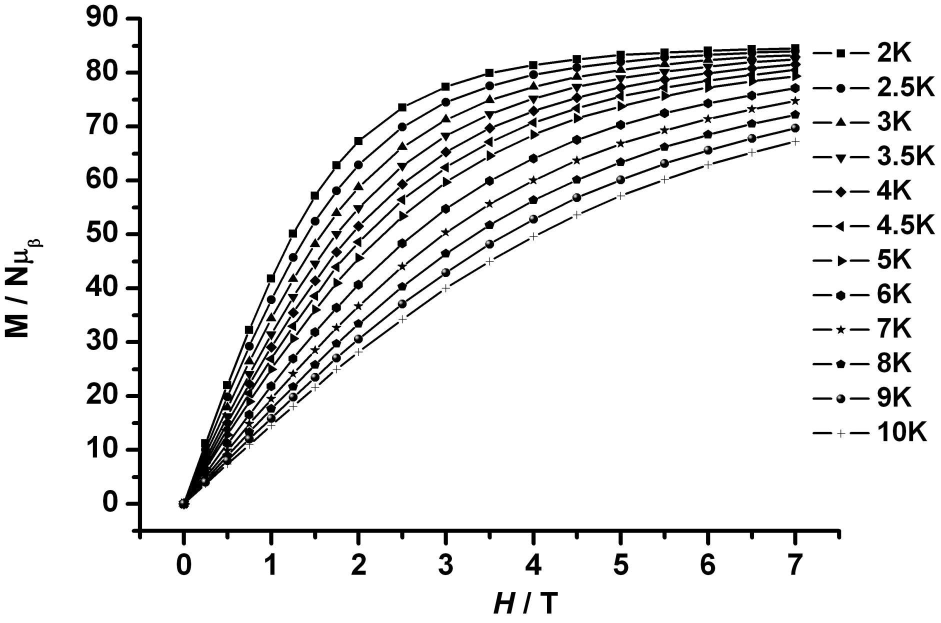


Fig. S4. Experimental field-dependent magnetization plots of **1** at indicated temperatures.

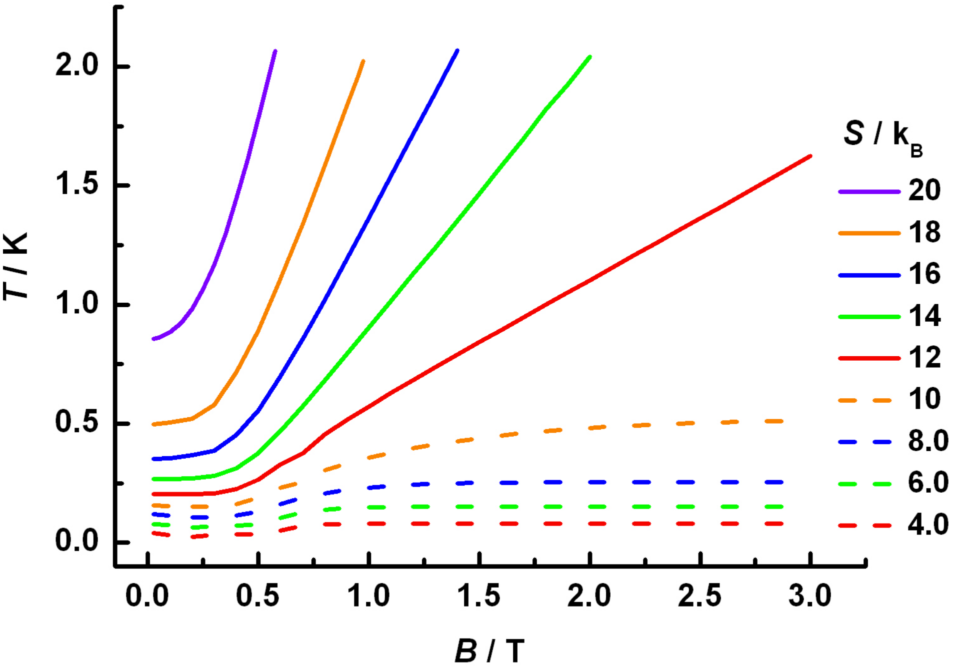


Fig. S5. Theoretical contour lines of constant entropy evaluated for the substitute system using FTLM.

[1] N. H. Hur, W. G. Klemperer and R.-C. Wang, *Inorg. Synth.*, 1990, **27**, 78.

[2] Bruker AXS SHELXTL version 6.12. Structure Determination Package. Bruker AXS 2000. Madison, WI, USA.

[3] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.