Supporting Information

Two Nanosized 3d-4f Clusters Featuring Four Ln₆ Octahedrons Encapsulating a Zn₄ Tetrahedron

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Materials and General Procedures

All reagents were of commercial origin and were used as received. Gadolinium oxide, Samarium oxide and Zn(OAc)₂ were purchased from Alfa Aesar (China) Chemical Co., Ltd. Perchloric acid, Sodium acetate and NaOH were purchased from Sinopharm Chemical Reagent Co.,Ltd(SCRC). But perchlorates are potentially explosive. Only a small amount should used and handled with great care. Aqueous solutions of lanthanide perchlorates were prepared by digesting lanthanide oxides in concentrated perchloric acid. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyser. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curve was prepared on a SDT Q600 Thermal Analyzer. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID).

Preparation of aqueous solutions of Gd(ClO₄)₃ (1.0 mol L⁻¹). Gadolinium oxide (0.125 mol, 45.313 g) was dissolved by slowly adding perchloric acid aqueous solution (70.0% - 72.0%, 64.0 mL) at about 80 °C. Aqueous solution of Gd(ClO₄)₃ (1.0 mol L⁻¹) was obtained by diluting the concentrated solution to 250.00 mL with

deionized water.

Preparation of aqueous solutions of Sm(ClO₄)₃ (1.0 mol L⁻¹). Samarium oxide (0.125 mol, 43.590 g) was dissolved by slowly adding perchloric acid aqueous solution (70.0% - 72.0%, 64.0 mL) at about 80 °C. Aqueous solution of Sm(ClO₄)₃ (1.0 mol L⁻¹) was obtained by diluting the concentrated solution to 250.00 mL with deionized water.

Synthesis of compound 1. Sodium acetate (136.0 mg, 1.0 mmol), $Zn(OAc)_2$ (183.5 mg, 1.0 mmol) and $Gd(ClO_4)_3$ (4.0 mL, 4.0 mmol) was added to a mixture of 10 mL anhydrouse ethanol and 5 mL deionized water. The resulting solution was heated to about 80°C and a freshly prepared NaOH solution (aq. 1.0 M) was added dropwise to the point of incipient but permanent precipitation. The mixture than brought to and maintained under reflux for 2 hours. The resulting mixture was filtered. Evaporation of the filtrate under ambient conditons afforded colourless crystals as the product after one week (yield 30% based on Gd). Anal. Calcd. For $Gd_{24}Zn_4C_{24}O_{217}H_{256}Cl_{14}$ (FW = 8550.07): C, 3.37; H, 3.01. Found: C, 3.18; H, 2.88. IR (KBr,cm⁻¹): 3439 (vs), 1630 (ms), 1561 (w), 1429(w), 1384(vs), 1122 (ms), 1109 (w), 1084(w), 636(ms), 627(ms).

Synthesis of compound 2. This compound was prepared using the same procedure as described above for the synthesis of its Gd(III) cognate but using $Sm(ClO_4)_3$ in place of $Gd(ClO_4)_3$. The product was obtained as block-shaped pale-yellow crystals in about 40% yield.

Single crystal X–ray structure determination: Data of compounds 1 and 2 were collected on an Oxford Gemini S Ultra CCD area detector with monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 123 K. Absorption corrections were applied by using the multi-scan program CrysAlis Red.¹ The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F² using the SHELXTL–97 program.² The hydrogen atoms of the organic ligand were generated geometrically (C–H, 0.96 Å). Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1. Selected bond are showed in Table S2. CCDC contains the supplementary crystallographic data

for this paper with a deposition number of no.1055333 for **1** and no.1055334 for **2**. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>http://www.ccdc.cam.ac.uk/data_request/cif</u>.

According to the charge balance, there are 4 disordered ClO_4^- counter anions per formula units for **1** and **2**. Based on the EA and TGA analysis, there are 40 disordered guest water molecules per formula units for **1** and **2**. However, they are severely disordered and were therefore removed by SQUEEZE in structural refinement.³ The SQUEEZE analyses estimate the electron count to be 3625 within 23257 Å³ void per formula unit for **1**, and 3920 electron counts within 24467 Å³ void per formula unit for **2**. According to the electron counts and voids per formula unit, the numbers of guest water are ca. 40 for **1** and **2**, which are consistent with the one calculated from EA and TGA results.

Compound	1	2	
Formula	$Gd_{24}Zn_4C_{24}H_{256}O_{217}Cl_{14}$	Sm ₂₄ Zn ₄ C ₂₄ H ₂₅₆ O ₂₁₇ Cl ₁₄	
Mr	8550.07	8024.15	
Crystal system	Cubic	Cubic	
Space group	Fm-3m	Fm-3m	
a/Å	37.4763(2)	37.8651(4)	
b/Å	37.4763(2)	37.8651(4)	
c/Å	37.4763(2)	37.8651(4)	
$V/\text{\AA}^3$	52634.4(5)	54289.7(10)	
Z	8	8	
$\rho_{calc}[g/cm^3]$	2.158	1.963	
μ (Mo K α)/mm ⁻¹	6.560	5.678	
F(000)	32240.0	30256	
$\theta/^{\mathrm{o}}$	3.22 - 25.0	3.18-25.00	
Observed reflections	34444	11055	
Independent reflections	2017	1815	
Data/parameters	2314/120	2382/120	
GOF	1.111	1.077	
$R_1[I > 2\sigma(I)]^a$	0.0467	0.0558	
wR_2 (All data) ^b	0.1375	0.1737	

 Table S1. Crystal data as well as details of data collection and refinement for 1 and 2.

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

2.454(3)	Gd2-O7	2.395(4)
2,676(5)		
2.0,0(3)	Gd2-O1W	2.475(4)
2.386(3)	Gd2-O2W	2.464(5)
2.392(4)	Zn1-O1	2.0722(19)
2.397(5)	Zn1-O2	1.964(5)
2.431(4)	Gd1-Gd1#1	3.7634(6)
2.635(4)	Gd1-Gd2	3.7548(5)
2.398(5)	Gd2-Gd2#1	3.7497(7)
2.375(3)		
109.5	Gd(1)#1-O(5)-Gd(1)	103.8(2)
117.44(15)	Gd(2)#1-O(6)-Gd(2)	104.3(2)
101.13(19)	Gd(2)-O(6)-Gd(1)	103.80(15)
90.7(2)	Gd(2)#1-O(7)-Gd(2)	103.0(2)
179.0(3)	Gd(1)-O(4)-Gd(2)	103.40(15)
89.966(9)		
	2.386(3) 2.392(4) 2.397(5) 2.431(4) 2.635(4) 2.398(5) 2.375(3) 109.5 117.44(15) 101.13(19) 90.7(2) 179.0(3) 39.966(9)	2.370(3) $Gd2-O1W$ $2.386(3)$ $Gd2-O2W$ $2.392(4)$ $Zn1-O1$ $2.392(4)$ $Zn1-O2$ $2.397(5)$ $Zn1-O2$ $2.431(4)$ $Gd1-Gd1#1$ $2.635(4)$ $Gd1-Gd2$ $2.398(5)$ $Gd2-Gd2#1$ $2.375(3)$ $Gd(2)-Gd(2)$ 109.5 $Gd(1)#1-O(5)-Gd(1)$ $117.44(15)$ $Gd(2)#1-O(6)-Gd(2)$ $101.13(19)$ $Gd(2)-O(6)-Gd(1)$ $90.7(2)$ $Gd(2)#1-O(7)-Gd(2)$ $179.0(3)$ $Gd(1)-O(4)-Gd(2)$ $39.966(9)$ $Sd2-Gd2$

Table S2 Selected bonds distances(Å) and angles(deg^o) for compound 1.

Symmetry transformations used to generate equivalent atoms:

#1 -z+1/2,-x+1/2,y #2 -y+1/2,-x+1/2,z #3 -x+1/2,-y+1/2,z

Sm1-O2	2.485(7)	Sm2-O7	2.427(7)
Sm1-O3	2.709(9)	Sm2-O1W	2.483(9)
Sm1-O4	2.416(6)	Sm2-O2W	2.505(9)
Sm1-O5	2.420(7)	Zn1-O1	2.067(4)
Sm1-O6	2.424(10)	Zn1-O2	1.979(11)
Sm1-O8	2.473(8)	Sm1-Sm1#1	3.8044(13)
Sm2-O3	2.664(9)	Sm1-Sm2	3.7985(9)
Sm2-O4	2.432(10)	Sm2-Sm2#1	3.7948(15)
Sm2-O6	2.404(6)		
Zn(1)-O(1)-Zn(1)#3	109.5	Sm(1)-O(3)-Sm(1)#1	89.2(4)
Zn(1)-O(2)-Sm(1)	117.3(3)	Sm(1)-O(4)-Sm(2)	103.1(3)
Sm(1)-O(2)-Sm(1)#3	100.5(4)	Sm(1)-O(5)-Sm(1)#1	103.6(4)
Sm(2)-O(3)-Sm(2)#1	90.9(4)	Sm(2)-O(6)-Sm(2)#1	104.2(4)
Sm(2)-O(3)-Sm(1)	89.973(19)	Sm(2)-O(6)-Sm(1)	103.8(3)
Sm(2)-O(3)-Sm(1)#1	178.8(6)	Sm(2)-O(7)-Sm(2)#1	102.9(4)

Table S3 Selected bonds distances(Å) and angles(deg^o) for compound 2.

Symmetry transformations used to generate equivalent atoms:

#1 -z+1/2,-x+1/2,y #2 -y+1/2,-x+1/2,z #3 -x+1/2,-y+1/2,z



Figure S1. Ball and stick view of the coordination mode of Gd1 and Gd2.



Figure S2. Ball and stick view of the coordination geometry of $[Zn_4(\mu_4-O)(\mu_3-OH)_{12}]^{6-}$ tetrahedron.



Figure S3. Ball and stick view of the shell 1 of Zn_4 tetrahedron and followed by shell 2 of Gd_{12} pseudo-truncated-tetrahedron structure.



 $\label{eq:Figure S4. Ball and stick view of the ([Zn_4(\mu_4-O)(\mu_3-OH)_{12}]^{6-})@([Gd_6(\mu_6-O)(\mu_3-OH)_8]^{8+})_4 \ units.$



Figure S5. The 3D packing structure of $Gd_{24}Zn_4$ viewed along 111(top and 100(down) plane.



Figure S6. TG Curves for compounds 1 and 2.



Figure S7. IR spectra in 500-4000 cm^{-1} for compounds 1 and 2.



Figure S8. Plots of temperature dependence of $\chi_M T$ and ${\chi_M}^{-1}$ for **1** under 1000 Oe dc field between 2 and 300 K.



Figure S9. Magnetization versus H/T for 1 at 2.0 K and at indicated fields.



Figure S10. (top) Field dependence of the magnetization plots for 2 at the indicated temperatures; (bottom) $\Delta S_{\rm m}$ calculated by using the magnetization data at various fields and temperatures.



Figure S11. Plots of temperature dependence of $\chi_M T$ for 2 under 1000 Oe dc field between 2 and 300 K.



Figure S12. Magnetization versus H/T for 2 at 2.0 K and at indicated fields.

Simulated method

QMC simulation was performed using a designed fitting program based on the ALPS package,⁴ where SSE and loop algorithm was conducted instead of the usual ITO method. For each site, 2×10^6 Monte Carlo steps and 2×10^5 Monte Carlo sweeps for thermalization were performed. In the process of post-treatment, TIP and R parameters were induced to my fitting program.

$$\begin{split} H &= -2J_1[(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1 + S_1S_5 + S_1S_6 + S_2S_5 + S_2S_6 + S_3S_5 + S_3S_6 + S_4S_5 + S_4S_6) \\ &+ (S_7S_8 + S_8S_9 + S_9S_{10} + S_{10}S_7 + S_7S_{11} + S_7S_{12} + S_8S_{11} + S_8S_{12} + S_9S_{11} + S_9S_{12} + S_{10}S_{11} + S_{10}S_{12}) \\ &+ (S_{13}S_{14} + S_{14}S_{15} + S_{15}S_{16} + S_{16}S_{13} + S_{13}S_{17} + S_{13}S_{18} + S_{14}S_{17} + S_{14}S_{18} + S_{15}S_{17} + S_{15}S_{18} + S_{16}S_{17} + S_{16}S_{18}) \\ &+ (S_{19}S_{20} + S_{20}S_{21} + S_{21}S_{22} + S_{22}S_{19} + S_{19}S_{23} + S_{19}S_{24} + S_{20}S_{23} + S_{20}S_{24} + S_{21}S_{23} + S_{21}S_{24} + S_{22}S_{23} + S_{22}S_{24}) \\ &+ (S_{15}T_7 + S_8S_{13} + S_2S_{14} + S_5S_{23} + S_{11}S_{20} + S_{17}S_{19})] - 2J_2[(S_1S_3 + S_2S_4 + S_5S_6) + (S_7S_9 + S_8S_{10} + S_{11}S_{12}) \\ &+ (S_{13}S_{15} + S_{14}S_{16} + S_{17}S_{18}) + (S_{19}S_{21} + S_{20}S_{22} + S_{23}S_{24})] \end{split}$$

Scheme S1 Hamilton operator of 24 Gd(III) ions.

References

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