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Myo-inositol Supported Heterometallic $Dy_{24}M_2$ (M = Ni, Mn) Cages

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Da-Peng Liu, Jun-Bo Peng, Xin-Ping Lin, Que Huang, Xiang-Jian Kong,* La-Sheng Long,* Rong-Bin Huang, and Lan-Sun Zheng

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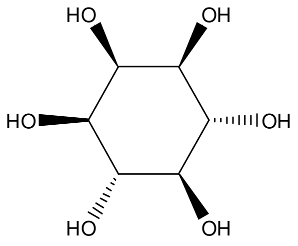
Two heterometallic cage-like $Dy_{24}M_2$ (M = Ni, Mn) cluster compounds have been synthesized through self-assembly of the metal ions and myo-inositol ligand templated by three ClO_4^- anions.

Recently considerable attention of coordination chemistry is focused on the synthesis and investigation of heterometallic 3d-4f polynuclear compounds owing to their fascinating architecture and their potential applications in a number of research fields, including biology, material science, and magnetism.[1-5] Up to now, a great variety of low-nuclearity 3d-4f compounds have been realized.[6-7] However high-nuclearity heterometallic 3d-4f clusters, especially including more than 20 metal ions, are rare, because of the repulsion of high positive charge of metal ions and the competitive reactions between 3d and 4f metals chelating to the same ligand.[8-10]

Recent studies have revealed that the anions template strategy is an effective approach to increase the nuclearity of heterometallic clusters, due to the dispersion action of anion-template for positive charge of clusters.[11-13] Over the course of these investigations, the use of simple single anion as template has been studied most extensively. However, compared with the single anion template, multiple anions template would be a better approach to construct high-nuclearity 3d-4f metal clusters, because of the multiple anions template dispersion action for positive charge of clusters.[11]

Polyalcohol ligands are favorite candidate for the synthesis of polynuclear 3d-4f clusters, and many polynuclear clusters have constructed from polyalcohol ligand, such as, single-molecule magnetisms (SMMs) of Mn-4f clusters.[14] Because of possessing six hydroxyl groups,[15] myo-inositol was selected to construct highnuclearity metal clusters in this work (scheme 1). Two high-nuclearity heterometallic 3d-4f cluster, formulated as $[Dy_{24}M_2(OH)_8(CH_3COO)_{12}(C_6H_{10}O_6)_6(C_6H_9O_6)_6(H_2O)_{51}][Dy(H_2O)_9](ClO_4)_{29}{\bullet}(H_2O)_{80}{\bullet}(C_2H_5OH)_4$ (M = Ni for **1**; M = Mn for **2**) were synthesized based on myo-inositol ligand. Structural analysis shows that three ClO_4^- anions, acting as templates, are located in the cage of the clusters. Compounds **1–2** were obtained from the reaction of $Dy(ClO_4)_3$, $M(CH_3COO)_2$, myo-inositol, and NaOH in a 10 mL mixture of anhydrous ethanol. They were found to be isomorphous, as revealed by single-crystal X-ray diffraction studies. As a representative, the structure of **1** is discussed to illustrate the structural features common to the two compounds. The cationic cluster of $[Dy_{24}M_2(OH)_8(CH_3COO)_{12}(C_6H_{10}O_6)_6(C_6H_9O_6)_6(H_2O)_{51}]^{26+}$ features a cage structure encapsulated three ClO_4^- anions, as shown in Figure 1.



Scheme 1. The myo-inositol ligand.

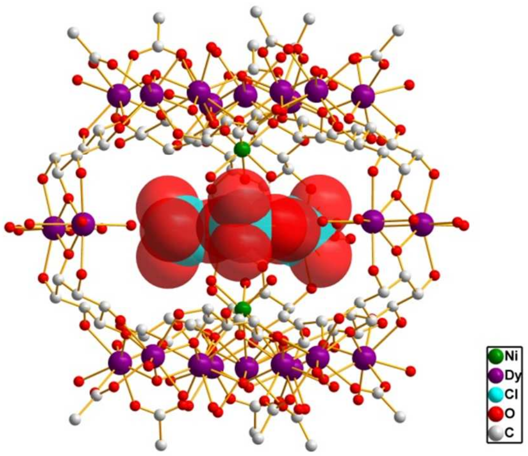


Figure 1. (a) Ball-and-stick view of the cationic $Dy_{24}Ni_2$ cluster in **1** along *a* axis.

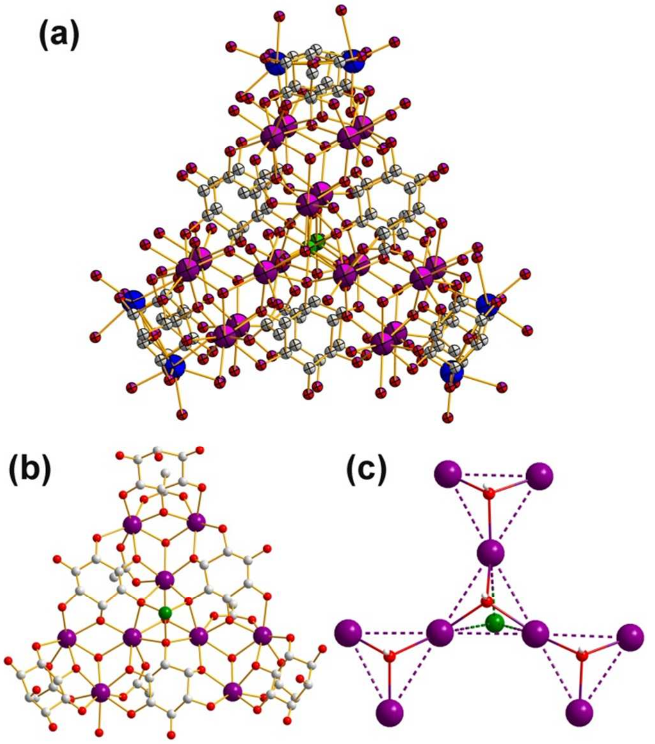


Figure 2. Ball-and-stick view of the cationic $Dy_{24}Ni_2$ core for **1** along c axis (a), the structure of $[Dy_9Ni(OH)_4(CH_3COO)_6(C_6H_{10}O_6)_3(C_6H_9O_6)_3]^{4+}$ unit (b) and the structure of $[Dy_9Ni(OH)_4]$ unit (c). Purple and blue for Dy, green for Ni, red for O, and grey for C.

The cage-like cluster core of **1** can be viewed as being constructed from two $[Dy_9Ni(OH)_4(CH_3COO)_6(C_6H_{10}O_6)_3(C_6H_9O_6)_3(H_2O)_{15}]^{4+}$ unit and three $[Dy_2(H_2O)_7]^{6+}$ unit (Figure 2). As shown in Figure 2b, each of $[Dy_9Ni(OH)_4(CH_3COO)_6(C_6H_{10}O_6)_3(C_6H_9O_6)_3(H_2O)_{15}]^{4+}$ unit is made up of one $[Dy_9Ni(OH)_4]^{25+}$ core, six acetate, three $[C_6H_{10}O_6]^{2-}$, three $[C_6H_9O_6]^{3-}$ anions, and fifteen aqua ligands. The $[Dy_9Ni(OH)_4]^{25+}$ core can be viewed as three $[Dy_3OH]^{8+}$ were connected by one OH^- and one Ni^{2+} ion (Figure 2c). The adjacent $[Dy_3OH]^{8+}$ units are also connected by one $[C_6H_9O_6]^{3-}$ ligand, which links four Dy^{3+} and one Ni^{2+} in a $\mu_5:\eta^1:\eta^2:\eta^3:\eta^2:\eta^1:\eta^0$ fashion (Figure S1), forming a $[Dy_9Ni(OH)_4(C_6H_9O_6)_3]^{16+}$ units. The $[Dy_9Ni(OH)_4(C_6H_9O_6)_3]^{16+}$ unit further coordinated by 6 acetate, 15 aqua ligands and three $[C_6H_{10}O_6]^{2-}$ ligands, resulting the bowl-like structure of $[Dy_9Ni(OH)_4(CH_3COO)_6(C_6H_{10}O_6)_3(C_6H_9O_6)_3(H_2O)_{15}]^{4+}$. The cage-like cluster core is made up of the two bowl-like units linked by three $[Dy_2(H_2O)_7]^{6+}$ unit through the coordination of three $[C_6H_{10}O_6]^{2-}$ ligands, which bridges four Dy^{3+} ions in a $\mu_4:\eta^1:\eta^2:\eta^1:\eta^2:\eta^1$ fashion (Figure S1). Structural analysis shows that polyalcohol is better candidate ligand to construct high-nuclearity 3*d*-4*f* metal clusters. Three templating ClO_4^- anions are found in the center of the cage.

Each of the Ni^{2+}/Mn^{2+} ions is hexa-coordinated by six O atoms with three O from $[C_6H_{10}O_6]^{3-}$ and three O from three aqua ligands, displaying distorted octahedral coordination geometry. Dy1, Dy2, Dy3 and Dy4 are octa-coordinate and forms dicapped trigonal prism geometry, Dy5 is hepta-coordinate, while Dy6 is nona-coordinate (Figure S2). The Ni1/Mn1 and Cl1 atoms lie on a threefold axis. The Dy4 and Dy5 lie on mirror planes, while the Dy6 atom of the $[Dy(H_2O)_9]$ species lies at a site with bar-6 symmetry. The Dy–O distances range from 2.250(8) to 2.541(12) Å, and the Ni–O distances are in the range of 2.062(7) – 2.127(7) Å, which are comparable to those in reported compounds.[16] The Dy···Dy and Dy···Ni separations are 3.760(1) – 3.905(1) Å and 3.491(2) Å, respectively.

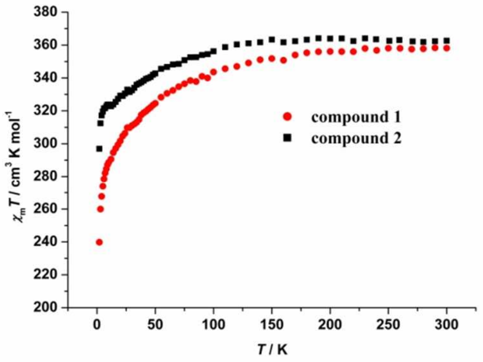


Figure 3. Plots of the temperature dependence of $\chi_M T$ for **1** and **2** under a 1000 Oe field between 2 and 300 K.

The temperature-dependent magnetic susceptibilities for the crystalline sample of compounds **1** and **2** was investigated between 2 K and 300 K under a direct-current (DC) field of 1 KOe, as shown in Figure 3. At 300 K, the $\chi_M T$ value is 357.4 cm^3 K mol^{-1} (calcd 356.25 cm^3 K mol^{-1} for 25 Dy^{3+} ions with S = 5/2, $^6H_{15/2}$, g = 4/3 and 2 Ni^{2+} with S = 1, g = 2.0) for **1** and 358.7 cm^{-3} K mol^{-1} (calcd 358.63 cm^3 K mol^{-1} for 25 Dy^{3+} ions with S = 5/2, $^6H_{15/2}$, g = 4/3 and 2 Mn^{2+} with S = 5/2, g = 2.0) for **2**. The $\chi_M T$ decreases gradually with the lowering of temperature from 300 to 100K and then falls abruptly down to the value of 238.2 cm^3 K mol^{-1} for **1** and 297.0 cm^3 K mol^{-1} for **2** at 2 K. The decrease of the $\chi_M T$ curve is attributed to a combination of intramolecular antiferromagnetic interactions and depopulation of Stark sublevels of the Dy^{3+} ions.[17]

The field dependence of magnetization of compounds **1** and **2** are shown in Figure S6. The magnetization at 2 K increases very fast below 1 T, and then slowly and linearly increases and is even saturated at 7 T. The maximum value for M is 141.1 μ_B for **1** and 155.8 μ_B for **2** at 7 T, which are smaller than the expected value for 25 ferromagnetically aligned Dy^{3+} ions and 2 Ni^{2+}/Mn^{2+}, which suggest the presence of a significant anisotropy and/or low-lying excited states.[7]

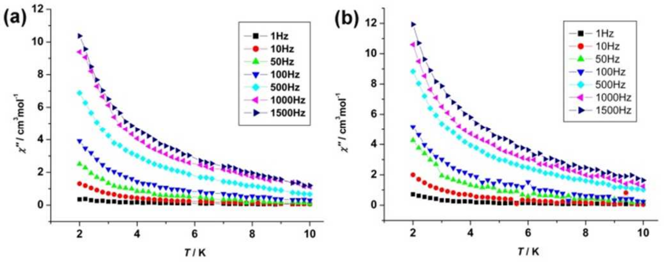


Figure 4. Temperature dependence of the out-of-phase (χ'') components of the ac susceptibility for **1** and **2** at different ac frequencies and in zero dc field.

In order to investigate the dynamic of these systems, alternative current susceptibilities were performed. As shown in Figure 4, the out-of-phase of **1** and **2** are strongly frequency-dependent, indicating the slow magnetic relaxation. However, because of the absence of frequency-dependent peaks in out-of-phase susceptibility signals, the energy barrier and characteristic relation time of the system cannot be obtained by fitting the peak temperatures to an Arrhenius-type expression. But assuming that there is only one characteristic relaxation process, the energy barrier and τ_0 values can be obtained from the relationship $\ln(\chi''/\chi') = \ln(\omega\tau_0) + Ea/K_BT$.[18] As shown in Figure S11 and S12, the extracted Ea = 1.24 K and $\tau_0 = 5.61 \times 10^{-5}$s for **1** and Ea = 0.98 K and $\tau_0 = 6.67 \times 10^{-5}$ s for **2**.

In conclusion, two heterometallic 3d-4f clusters based on myo-inositol ligand have been synthesized. The cluster core possesses a fascinating cage-like structure with two $[Dy_9Ni(OH)_4]^{25+}$ units templating three ClO_4^- anions. Magnetic studies revealed that the $Dy_{24}Ni_2$ and $Dy_{24}Mn_2$ display slow relaxation of magnetization. The present work demonstrates the validity of assembly high-nuclearity 3d-4f metal clusters based on multiple anions template approach.

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Notes and references

[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. E-mail: xjkong@xmu.edu.cn or lslong@xmu.edu.cn

† Synthesis of **1** and **2**. $Ni(CH_3COO)_2 \cdot 4H_2O$ (249 mg, 1.0 mmol) for **1** and $Mn(CH_3COO)_2 \cdot 4H_2O$ (245 mg, 1.0 mmol) for **2**，$Dy(ClO_4)_3$ (4 ml, 4.0 mmol) and myo-inositol (180 mg, 1.0 mmol) was added to a mixture of 10 mL anhydrous ethanol. The resulting solution was heated to about 70 °C and a freshly prepared NaOH solution (aq. 1.0 mol L^{-1}) was added dropwise to adjust the pH of the solution to 6 while stirring. Then the solution was refluxed for 2 hours and then filtered. Evaporation of the filtrate afforded block-shaped crystals in two weeks with 170 mg (yields 16 %) for **1** and 180 mg (yields 17 %) for **2**. Anal. calcd. for **1**: C, 9.80 H, 3.62; Found: C, 9.99; H, 3.51. Anal. calcd. for **2**: C, 9.81; H, 3.62; Found: C, 9.88; H, 3.55. Crystallographic data in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 983777 for **1** and 9837778 for **2**.

Electronic Supplementary Information (ESI) available: [details of synthesis of **1** and **2**, crystal data, Table S1-S3, and Figure S1-S12]. See DOI: 10.1039/c000000x/

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Myo-inositol Supported heterometallic $Dy_{24}M_2$ (M = Ni, Mn) Cages

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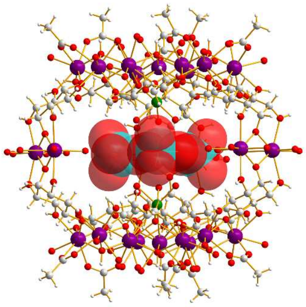

Two heterometallic cage-like $Dy_{24}M_2$ (M = Ni, Mn) cluster compounds have been synthesized through self-assembly of the metal ions and myo-inositol ligand templated by three ClO_4^- anions.