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Two Three-Dimensional 2p−3d−4f Heterometallic Frameworks Featuring a $Ln_6Cu_{24}Na_{12}$ Cluster as a Node

Gui-Lin Zhuang, Wen-Xian Chen, Hai-Xia Zhao, Xiang-Jian Kong,* La-Sheng Long,* Rong-Bin Huang, and Lan-Sun Zheng

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

S *Supporting Information*

ABSTRACT: Two three-dimensional 2p−3d−4f heterometallic frameworks featuring a nanosized $Ln_6Cu_{24}Na_{12}$ (Ln = Gd, Dy) cluster as a node have been obtained under microwave irradiation conditions through the reaction of H_2ANMA (H_2ANMA = L-alanine-*N*-monoacetic acid), $Cu(NO_3)_2$, and $Ln(NO_3)_3$ (Ln = Gd for **1**, Dy for **2**) with NaOH in deionized water. Investigations on the magnetic properties show that **1** exhibits ferrimagnetic behavior. The electrical conductivity measurements reveal that **1** behaves as a proton conductor.

Heterometallic clusters have attracted enormous interest because of their extraordinary chemical and physical properties such as magnetism,[1,2] luminescence,[3] and electricity,[4] which could provide an impetus for application of these solids in the field of materials science. So far, a great variety of discrete heterometallic polynuclear complexes have been obtained either rationally or fortuitously.[5−7] Recently, the use of the heterometallic cluster as a building block to construct multidimensional frameworks is a most notable field.[8−11] Compared with single metal ions, heterometallic cluster-based polymers not only have larger pore sizes but also can incorporate desired functionalities from the clusters and frameworks. Nonetheless, owing to the synthetic difficulty, heterometallic cluster-based, especially high-nuclearity-based, frameworks are still very rare,[9−11] which obstructs further studies of their physical and chemical properties.

An effective synthetic strategy for heterometallic cluster-based frameworks is to select flexible and chelate-bridged ligands with an appropriate auxiliary group as the linker. Following this idea, we have obtained a series of 3d−4f heterometallic cluster-based frameworks based on the derivates of iminodiacetic acid under hydrothermal conditions.[11] Here, on the basis of the reaction of L-alanine-*N*-monoacetic acid (H_2ANMA), $Cu(NO_3)_2\cdot 3H_2O$, and $Ln(NO_3)_3\cdot 6H_2O$ (Ln = Gd for **1**, Dy for **2**) under microwave irradiation conditions, we report two novel three-dimensional (3D) 2p−3d−4f heterometallic coordination polymers, $[Ln_6Cu_{24}Na_{12}(ANMA)_{12}(\mu_3\text{-}OH)_{24}(\mu_5\text{-}O)_6Cl(H_2O)_{42}](NO_3)_{13}Cl_4(H_2O)_{48}$ (Ln = Gd for **1**, Dy for **2**). Notably, **1** and **2** are rare examples of 3D heterometallic frameworks constructed by high-nuclearity 2p−3d−4f clusters.[12]

Complex **1** was crystallized in the $R\bar{3}$ space group. Figure 1a shows the cation cluster core $Gd_6Cu_{24}Na_{12}$ of **1**, while the asymmetric unit is depicted in Figure 1b. The $Gd_6Cu_{24}Na_{12}$ core is composed of the Gd_6Cu_{12} octahedral inner core and six outer Na_2Cu_2 square units. The inner Gd_6Cu_{12} core can be well described as an octahedron with pseudocubic O_h symmetry, which is similar to those reported by the Chen and Wu groups.[5a,9] Six Gd^{3+} ions locate six vertexes of the octahedron, and 12 Cu^{2+} ions hold the midpoints of the octahedral edges. The Gd−Cu metal framework is interconnected by 24 μ_3-OH^- ligands, with each one bridging with two inner Cu^{2+} ions and one Gd^{3+} ion. Each face of the octahedron consists of three Gd^{3+} ions and three Cu^{2+} ions linked by three μ_3-OH^- groups.

An outer tetranuclear Na_2Cu_2 cluster unit can be well described as a square. Two outer Cu^{2+} ions locate two adjacent vertexes of the square and two Na^+ ions positioned at the other two vertexes. One μ_5-O^{2-} ligand locates in the square center linking four outer metal ions and one inner Gd^{3+} ion. Four μ_2-H_2O ligands locate outboard of the square and link adjacent metal ions. Each outer Cu^{2+} ion links one Gd^{3+} ion and one inner Cu^{2+} ion by the carboxyl of the $ANMA^{2-}$ ligand in a syn−anti mode. Each Na^+ ion is connected with one Gd^{3+} ion by one μ_2-H_2O bridge. It is noteworthy that a chlorine ion, which plays an important role as a template, is enveloped in the center of the octahedral cage.

The coordination geometry of the nonacoordinate Gd^{3+} ion is well described as a monocapped square antiprism, featuring coordination by four μ_3-OH^- groups, two carboxylate oxygen atoms, one μ_5-O^{2-} atom, and two μ_2-H_2O ligands. The inner Cu^{2+} ion is pentacoordinated, featuring quadrilateral pyramid coordination symmetry by four μ_3-OH^- groups and one carboxyl oxygen atom, while the coordination mode of the outer Cu^{2+} ion is regarded as octahedron, which derives from the contribution of one $ANMA^{2-}$ ligand in a tridentate fashion, two μ_2-H_2O ligands, and one μ_5-O^{2-} atom. The Na^+ ion is hexacoordinated, featuring the contribution of five aqua ligands and one μ_5-O^{2-} atom. The bond lengths of Gd−O, Na−O, Cu−O, and Cu−N in **1** are 2.424(4)−2.571(8), 1.851(5)−2.716(13), 1.927(5)−2.386(9), and 1.958(12)−2.040(12) Å, respectively, comparable to those in the reported compounds.[5e,7b,14] The distances of $Gd^{3+}\cdots Cu^{2+}$ and $Cu^{2+}\cdots Cu^{2+}$ are 3.4818(7)−3.5037(7) and 3.2286(2)−3.3731(9) Å, respectively, and each pair of Gd^{3+} ions is separated by a distance of 6.9812(4) Å. Each $ANMA^{2-}$ ligand chelates one outer Cu^{2+} in a tridentate fashion and links one Na^+ ion from an adjacent building block.

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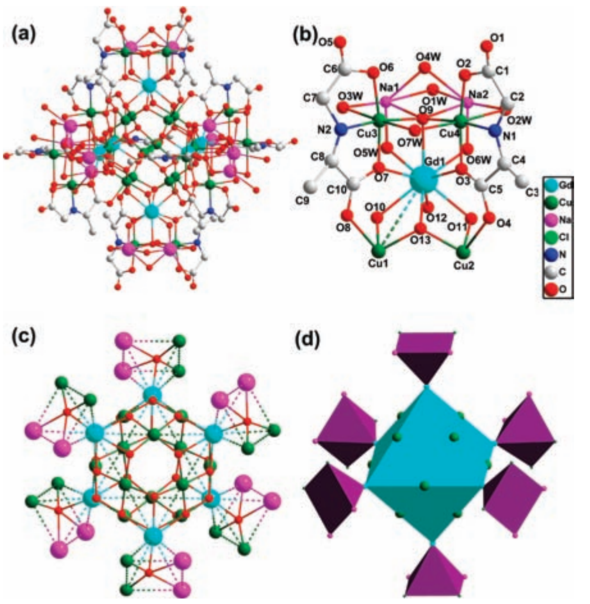

Figure 1. (a) Crystal structure of $[Gd_6Cu_{24}Na_{12}]$ cation. (b) Asymmetric unit of **1**. (c) $[Gd_6Cu_{24}Na_{12}(\mu_3\text{-}OH)_{24}(\mu_5\text{-}O)_6]$ cation core of **1**. (d) Polyhedron view of $[Gd_6Cu_{24}Na_{12}]$.

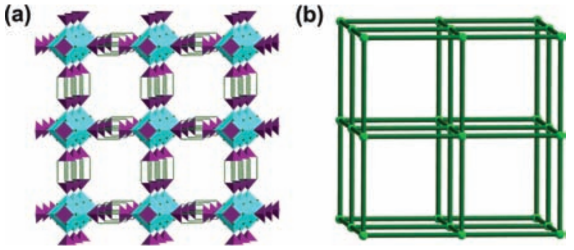

Figure 2. (a) Polyhedral view of the 3D metal framework of **1**. (b) Topology of the 3D structure.

The inspection of 3D frameworks of **1** reveals that $Gd_6Cu_{24}Na_{12}$ as a six-connected building block is linked to adjacent ones by the $ANMA^{2-}$ ligand, generating extended solids with the Schläfli symbol (4, 4) topology (Figure 2). Owing to disorder, 48 guest water molecules, 5 NO_3^-, and 4 Cl^- ions are removed by *SQUEEZE*.[13a] The pore volume of the framework **1** calculated through the *PLATON* program is approximately 15 685 Å^3 per unit cell volume (57.3%).[13b]

Complex **2** is isomorphic to **1**. The bond lengths of Dy–O, Na–O, Cu–O, and Cu–N in **2** are 2.392(5)–2.569(7), 1.863(5)–2.798(17), 1.934(4)–2.339(8), and 1.920(9)–1.987(10) Å, respectively, slightly shorter than those in **1**. The distances of $Dy^{3+}\cdots Cu^{2+}$ and $Cu^{2+}\cdots Cu^{2+}$ are 3.4577(6)–3.4910(6) and 3.2176(15)–3.3766(8) Å, and each pair of Dy^{3+} ions is separated by a distance of 6.9481(4) Å.

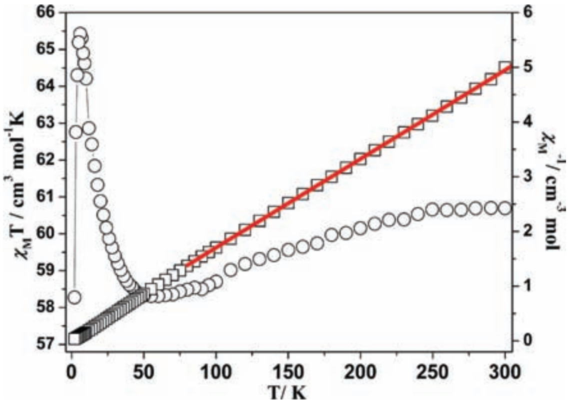

Figure 3. Plots of $\chi_M T$ vs T (denoted as ○) and a red solid line fitted for χ_M^{-1} vs T (denoted as □) of **1**.

The temperature dependence of the magnetic susceptibility of **1** was measured from 1.8 to 300 K with an applied magnetic field of 1000 Oe. As shown in Figure 3, the $\chi_M T$ value of **1** at room temperature is 60.69 cm^3 mol^{-1} K (300 K), which is consistent with the expected value of 56.25 cm^3 mol^{-1} K for 6 independent Gd^{3+} ions ($8S_{7/2}$, $g = 2.0$) and 24 independent Cu^{2+} ions ($g = 2.0$). As the temperature decreases, the value of $\chi_M T$ decreases slowly and reaches a value of 55.04 cm^3 mol^{-1} K at 50.0 K. Upon further lowering of the temperature, the value of $\chi_M T$ increases abruptly and reaches a maximum of 65.43 cm^3 mol^{-1} K at 6 K, in which **1** exhibits ferrimagnetic behavior. Inspection of the structure of **1** reveals that the overall ferrimagnetic behavior may be derived from the integrated result of ferromagnetic coupling between Gd^{3+} and inner Cu^{2+} ions,[5e,15] ferromagnetic coupling between inner and outer Cu^{2+} ions bridged by syn–anti carboxylate, and antiferromagnetic coupling between outer Cu^{2+} ions.[5e,16] Upon further lowering of the temperature, the value of $\chi_M T$ decreases rapidly and reaches a value of 58.27 cm^3 mol^{-1} K at 2 K, which may be ascribed to an antiferromagnetic interaction between the clusters. The data over the temperature range of 100–300 K fit well the Curie–Weiss law[17] with Weiss constant C = 12.38 cm^3 mol^{-1} K and Curie constant θ = −0.13 K, which is consistent with the overall weak antiferromagnetic behavior.[5e] Magnetization has come to saturation at an applied magnetic field of 4 T (Figure S1 in the Supporting Information, SI).

Magnetic analysis reveals that the antiferromagnetic coupling of outer Cu^{2+} ions in complex **2** are slightly stronger (Figure S2 in the SI),[16,18] which can be supported by slightly shorter $Cu^{2+}\cdots Cu^{2+}$ bond lengths.

In order to investigate the electrical property of **1**, alternating-current (ac) impedance measurements were performed. Figure 4 shows Nyquist plots of **1** at various temperatures. At low frequencies, the Nyquist plots show semicircles, which were fitted by a semicircular equation. The conductance value (σ) of **1** is 1.36 × 10^{-6} S cm^{-1} at 318 K. With an increase of the temperature, the conductance value decreases and reaches 0.84 × 10^{-6} S cm^{-1} at 328 K, 0.44 × 10^{-6} S cm^{-1} at 338 K, 0.16 × 10^{-6} S cm^{-1} at 348 K, and 0.04 × 10^{-6} S cm^{-1} at 358 K. The Nyquist plot almost becomes a beeline at 368 K. A powder X-ray diffraction study at different temperatures and thermogravimetric analysis (Figure S3 and S4 in the SI) reveal that the 3D framework of **1** is maintained during the ac impedance measurements. Thus, a decrease of the conductance value is attributed to the removal of guest water molecules. The origin of conductivity may be derived from transfer of a proton, where guest water molecules act as suppliers of protons.[19,20]

In summary, we reported two rare examples of 3D heterometallic frameworks constructed with a high-nuclearity $Ln_6Cu_{24}Na_{12}$ cluster as a node. Magnetic measurements suggest that **1** exhibits ferrimagnetic behavior. ac impedance measurements reveal that **1** exhibits proton conductivity. The results presented herein indicate that using the high-nuclearity cluster as a building

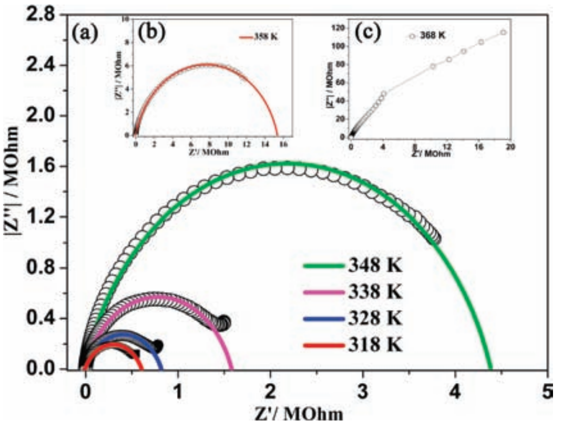

Figure 4. Nyquist plots of the ac impedance of **1** over the temperature range of 318–368 K. The solid line was fitted to experimental data (○) based on a semicircular equation.

block to construct multidimensional frameworks is a feasible synthetic approach to multifunctional materials.

■ ASSOCIATED CONTENT

Supporting Information. Figures S1–S5 and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xjkong@xmu.edu.cn (X.-J.K.), lslong@xmu.edu.cn (L.-S.L.).

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