Copper Complex Cation Templated Gadolinium(III)–Isophthalate Frameworks**

*You-Fu Zhou, Fei-Long Jiang, Da-Qiang Yuan,
Ben-Lai Wu, Rui-Hu Wang, Zheng-Zhong Lin,
and Mao-Chun Hong**

Crystal engineering provides a powerful tool for the design and construction of coordination frameworks with unique structural motifs and tunable physical properties.[1,2] Many heterometallic frameworks possess interesting physical properties,[3–7] which arise from the interactions between two distinct metal ions. However, 3D cavity lanthanide frameworks with trapped or bonded transition-metal complexes are rare. A typical strategy utilized to construct lanthanide–transition-metal frameworks is self-assembly from mixed metal ions and ligands containing hybrid donor atoms, such as carbonyl,[8] cyanide,[9] pyridine-carboxylate ligands.[6e] Herein we use isophthalate (ip) as the oxygen-donor ligand and 2,2′-bipyridine (bpy) as the nitrogen-donor ligand and Gd^{III} and Cu^{II} ions, to obtain two novel Gd–Cu frameworks, formulated as $[\{[Gd_4(ip)_7(H_2O)_2][Cu(bpy)_2]_2\}_n]$ (**1**) and $[\{Gd_3Cu(ip)_5(Hip)(bpy)\}_n]\cdot n\,H_2O$(**2**), we report their syntheses, crystal structures along with magnetic properties.

The hydrothermal reaction of Gd_2O_3, $Cu(NO_3)_2\cdot 3H_2O$, H_2ip, and bpy in a molar ratio of 1:2:1:2 at 170 °C yielded crystals of **1**. Single-crystal X-ray diffraction[10] reveals that the structure of **1** has charged cages containing two encapsulated $[Cu(bpy)_2]^+$ ions (Figure 1). There is a $[Cu(bpy)_2]^+$ ion, two Gd^{III} ions, three and a half ip ligands and a coordinated water in the asymmetric unit (Figure 2). Independent Gd^{III} ions (Gd1···Gd2 = 4.102 Å) are linked by two μ-oxygen atoms from separate carboxylate groups to form a Gd_2O_2 building unit, and each Gd^{III} ion is coordinated by eight oxygen atoms to furnish a dodecahedral geometry. Eight Gd_2O_2 units are linked by ip ligands to generate a large charged cage (ca. $11.5\times 14.9\times 16.5$ Å^3), in which two $[Cu(bpy)_2]^+$ ions with a distorted tetrahedral geometry are trapped as charge-compensating guests. The two trapped guests (about 11.0 Å in diameter) adopt encapsulated mode which is unusual because they are larger than the largest valid pore of the cage (ca. 9.78 Å in diameter). The cationic guests are further stabilized by the π–π stacking interaction between the pyridyl rings with a face-to-face separation of 3.47 Å and the van der Waals

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[*] Dr. Y.-F. Zhou, F.-L. Jiang, D.-Q. Yuan, B.-L. Wu, R.-H. Wang, Z.-Z. Lin, Prof. M.-C. Hong
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences, Fuzhou, Fujian, 350002 (China)
Fax: (+86) 591-8371-4946
E-mail: hmc@ms.fjirsm.ac.cn

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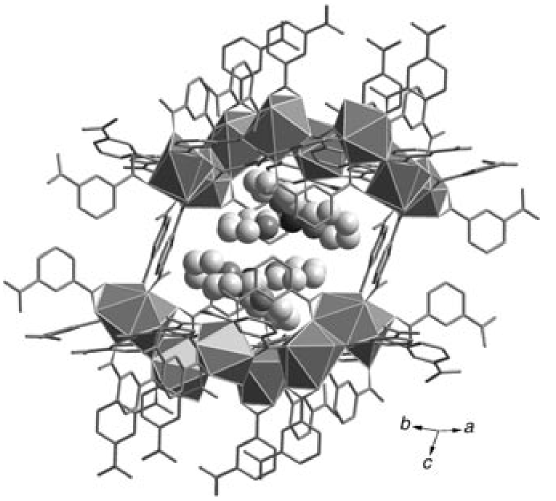

Figure 1. View of polymeric cage with two encapsulated $[Cu(bpy)_2]^+$ ions (space-filling representation) in **1**; Gd^{III} ions are shown as coordination dodecahedra and ip ligands as a stick model.

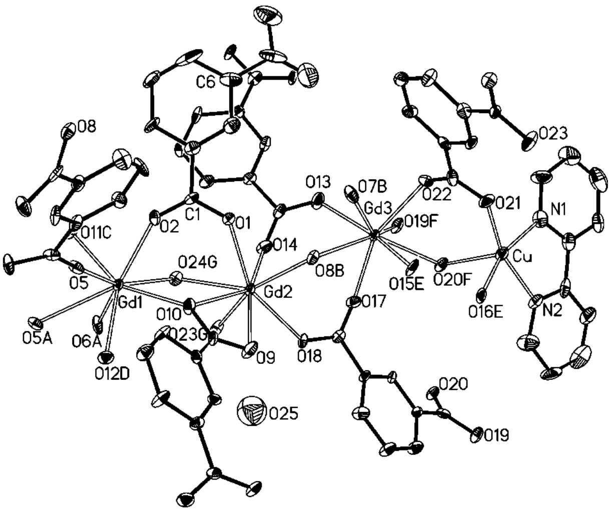

Figure 3. ORTEP plot (thermal ellipsoids set at 30% probability) of the asymmetric unit in **2**, symmetry codes: A: $-x+1$, $-y$, $-z+1$; B: $-x+1$, $-y+1$, $-z+1$; C: $x+1$, y, z; D $-x$, $-y$, $-z+1$; E: $x-1$, y, z, F: $-x+1$, $-y+1$, $-z+2$; G: x, $y-1$, z.

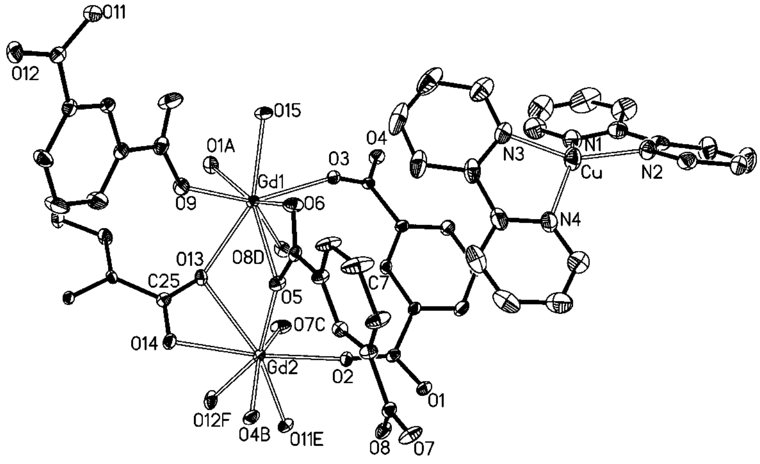

Figure 2. ORTEP plot (thermal ellipsoids set at 30% probability) of the asymmetric unit in **1**, symmetry codes: A,C: $-x+1/2$, $y+1/2$, $-z+1/2$; B: $-x+1/2$, $y-1/2$, $-z+1/2$; D: x, $-y+1$, $z-1/2$.

force between the guests and cage. The cages are connected by ip ligands to form a 3D cavity framework. To our knowledge, complex **1** is the first 3D framework containing multi encapsulated complex cations within a charged cage, being different from the reported inclusion complex that possesses a 3D framework containing only one encapsulated $[Gd(dmf)_8]^{3+}$ ion within a charged cage.[6b]

Clearly, Cu^{II} was reduced to Cu^{I} by the excessive bpy during the hydrothermal synthesis of **1**.[1d,11] In an attempt to synthesize the Gd^{III}–Cu^{II} analogue by using less bpy, the similar reaction was carried out with the molar ratio of Gd:Cu:H_2ip:bpy (1:2:1:1), and green crystals of **2** were isolated. The asymmetric unit of **2** consists of three Gd^{III} ions, a Cu^{II} ion, a bpy ligand, six completely or partially deprotonated ip ligands, and a free water molecule (Figure 3). The valences of copper ions are supported by the calculated values of +1.3 (for **1**) and +1.8 (for **2**).[12] Each Gd^{III} ion is coordinated by eight carboxylate oxygen atoms (Gd–O 2.277(9)-2.84(1) Å) to furnish a dodecahedral geometry. The separations between adjacent metal ions are 3.89(1), 4.01(1), and 4.29(1) Å for Gd···Gd, 3.97(1) Å for Gd···Cu and 5.51(1) Å for Cu···Cu. The ip ligands link Gd^{III} and Cu^{II} ions to form a 3D open-framework containing irregular cavities (ca. 11.4 × 8.10 Å^2; Figure 4). Each Cu^{II} ion is coordinated by two nitrogen atoms from the chelating bpy ligand and three carboxylate oxygen atoms to furnish a square pyramidal geometry. Thus, the orientation of the $[Cu(bpy)]^{2+}$ ions bound the inner backbone of the cavity alternates(Figure 4). The structures of **1** and **2** imply that copper ions and bpy ligands form complex cations first, and then these complex cations serve as structure-directing templates during the formation of Gd–ip frameworks. Consequently, the different-sized complex cations result in the frameworks containing different cavities.[1c]

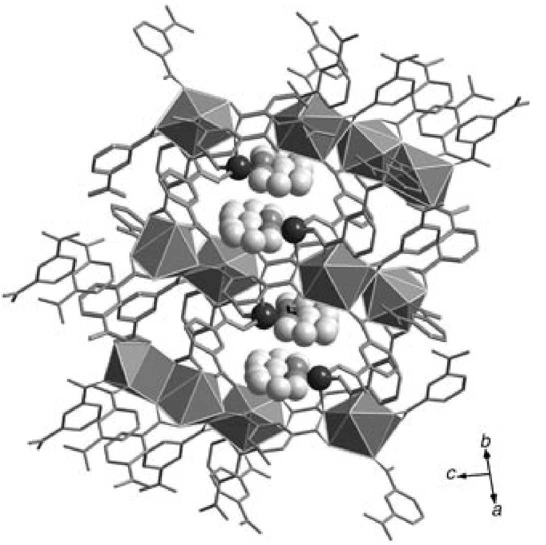

Figure 4. View of polymeric cavity with bound $[Cu(bpy)]^{2+}$ ions (space-filling models, Cu dark gray; N light gray) in **2**, Gd^{III} ions as coordination dodecahedra, and ip ligands as a stick model.

The magnetic properties of **1** and **2** were investigated over the temperature range 5–300 K. For **1**, the observed $\chi_M T$ values of 30.9 $cm^3 mol^{-1}$ K at 300 K is slightly smaller than the expected value of 31.5 $cm^3 mol^{-1}$ K for a $Gd^{III}{}_4Cu^{I}{}_2$ complex with noninteracting metal ions. The $\chi_M T$ value decreases slightly to 29.0 $cm^3 mol^{-1}$ K at 12 K, and then dramatically decreases to 25.8 $cm^3 mol^{-1}$ K at 5 K (see the Supporting Information). Considering the structure of **1** and no orbital angular momentum for the Gd^{III} ion, the spin-coupled dimer model ($H = -JS_{Gd} \cdot S_{Gd}$)[13] was applied to perform a quantitative analysis leading to $g = 2.08$ and $J = -0.09$ cm^{-1},[14] which indicates a very weak antiferromagnetic interaction between closest Gd^{III} ions. For **2**, the observed $\chi_M T$ values of 24.2 $cm^3 mol^{-1}$ K at 300 K is slightly larger than the expected value of 24.0 $cm^3 mol^{-1}$ K for a noninteracting $Gd^{III}{}_3Cu^{II}$ complex. The $\chi_M T$ plot is almost constant from 300 K to 50 K, increase as temperature is lowered further, reaches a maximum value of 24.4 $cm^3 mol^{-1}$ K around 10 K, and then decreases to 23.9 $cm^3 mol^{-1}$ K at 5 K (see the Supporting Information). Considering the separations between adjacent metal ions, a linear octanuclear model containing one spin-coupled Gd^{III}–Gd^{III} dimer(i), two spin-coupled Gd^{III}-Cu^{II} dimer (ii), and two uncoupled Gd^{III} ions was applied to perform a quantitative analysis ($g_i = 2.04$, $J_i = -0.159$ cm^{-1}, $g_{ii} = 2.03$, $J_{ii} = 2.07$ cm^{-1}). The result indicates that the Gd^{III}–Gd^{III} interaction is weak antiferromagnetic, while the Gd^{III}–Cu^{II} interaction is ferromagnetic.[15]

In summary, by introducing mixed ligands with different donor atoms in different molar ratios, two novel heterometallic 3d–4f coordination frameworks were successfully synthesized. Compound **1** is the first structurally characterized 3D heterometallic framework containing multi encapsulated complex cations within a charged cage. Compound **2** has a 3D cavity framework containing complex cations. The quantitative analyses of the magnetic properties between **1** and **2** provide a comprehensive understanding of the nature of the Gd^{III}–Cu^{II} magnetic interaction.

Experimental Section

1: An aqueous mixture (10 mL) containing Gd_2O_3(36 mg, 0.10 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (48 mg, 0.20 mmol), H_2ip (17 mg, 0.10 mmol), and bpy(31 mg, 0.20 mmol) in a molar ratio of 1:2:1:2 was sealed and heated at 170°C for 4 days. After cooling at 6 $°C h^{-1}$ to room temperature, black prismatic crystals of **1** were collected by filtration and washed with distilled water (37% yield, based on Gd). Elemental analysis (%) calcd for **1** $C_{96}H_{64}N_8O_{30}Cu_2Gd_4$: C 44.94, H 2.51, N 4.37; found: C 44.82, H 2.37, N 4.24. IR (KBr pellet): $\nu = 650$(m), 706(m), 750(m), 1070(w), 1155(m), 1383(s), 1452(s), 1608(s), 3066(w) cm^{-1}.

2: Complex **2** was synthesized in a similar way to **1**, except the molar ratio being 1:2:1:1. Green prismatic crystals of **2** were collected in 42% yield (based on Gd). Elemental analysis (%) calcd for **2** $C_{58}H_{35}N_2O_{25}CuGd_3$: C 41.09, H 2.08, N 1.65; found: C 41.01, H 1.97, N 1.49. IR(KBr pellet): $\tilde{\nu} = 651$(m), 705(m), 756(m), 1074(w), 1156(m), 1380(s), 1456(s), 1610(s), 3105(w) cm^{-1}.

Variable-temperature magnetic susceptibilities were measured on a Quantum Design PPMS Model 6000 magnetometer in an applied field of 1000 Oe.

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[10] Crystal data for **1**: Crystal dimensions 0.15 × 0.10 × 0.05 mm, $M_r = 2565.64$, monoclinic, space group *C2/c*, $a = 26.359(2)$, $b = 14.3982(8)$, $c = 25.311(2)$ Å, $\beta = 113.016(2)°$. $V = 8841(1)$ $Å^3$, $Z = 4$, $\rho_{calcd} = 1.928$ $g cm^{-3}$. A total of 26837 reflections were collected in the range of $1.64 \leq \theta \leq 25.03°$, of which 7796 were unique reflections, $R(int) = 0.0476$, $\mu(Mo_{K\alpha}) = 3.522$ mm^{-1}, parameters = 632, $R1(F_0) = 0.0439$, $wR2(F_0^2) = 0.0735$, and GOF = 1.191 for reflections $I \geq 2\sigma(I)$. Crystal data for **2**: Crystal dimensions 0.16 × 0.14 × 0.10 mm, $M_r = 1695.17$, Triclinic, space group *P-1*, $a = 10.5295(1)$, $b = 12.4930(2)$, $c = 23.4994(1)$ Å, $\alpha = 95.800(1)°$, $\beta = 100.890(1)°$, $\chi = 111.740(1)°$, $V = 2769.62(5)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 2.033$ $g cm^{-3}$. A total of 14499 reflections were collected in the range of $0.90 \leq \theta \leq 25.08°$, of which 9719 were unique reflections, $R(int) = 0.0597$, $\mu(Mo_{K\alpha}) = 4.016$ mm^{-1}, parameters = 797, $R1(F_0) = 0.0692$, $wR2(F_0^2) = 0.1216$, and

GOF = 1.104 for reflections $I \geq 2\sigma(I)$. CCDC-236669 (**1**) and CCDC-236670 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[14] For **1**, the least-squares fitting of the experimental data gives the agreement factor $R = \Sigma(\chi_{\mathrm{obs}}T\text{-}\chi_{\mathrm{calcd}}T)^2/\Sigma(\chi_{\mathrm{obs}}T)^2 = 6.6\times10^{-3}$. For **2**, $R = 1.3\times10^{-3}$.

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