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Three-Dimensional 3d–4f Heterometallic Coordination Polymers: Synthesis, Structures, and Magnetic Properties

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Three new 3d–4f heterometallic coordination polymers, $[Ln_2(H_2O)_4M_2(H_2O)_2(QA)_5]\cdot nH_2O$ (H_2QA = quinolinic acid; Ln = Gd, M = Ni, $n = 7$ (**1**); Ln = Gd, M = Co, $n = 6.5$ (**2**); Ln = Dy, M = Co, $n = 6.5$ (**3**)), have been synthesized through hydrothermal pretreatment and cooling-down crystallization. These compounds possess the isostructural 3D frameworks with 1D chairlike channels along the *c* axis, which are occupied by noncoordinating water molecules. Crystal data: for **1**, $C_{35}H_{41}Gd_2Ni_2N_5O_{33}$, orthorhombic, space group $Pna2_1$, with $a = 28.567(6)$ Å, $b = 14.498(3)$ Å, $c = 12.250(2)$ Å, and $Z = 4$; for **2**, $C_{35}H_{40}Gd_2Co_2N_5O_{32.5}$, orthorhombic, space group $Pna2_1$, with $a = 28.843(3)$ Å, $b = 14.4325(13)$ Å, $c = 12.2275(9)$ Å, and $Z = 4$; for **3**, $C_{35}H_{40}Dy_2Co_2N_5O_{32.5}$, orthorhombic, space group $Pna2_1$, with $a = 28.8471(14)$ Å, $b = 14.4534(10)$ Å, $c = 12.2520(7)$ Å, and $Z = 4$. The magnetic behaviors for the three compounds have been investigated.

Introduction

The design and synthesis of heterometallic complexes, such as 3d−4f or 3d−5f metal systems, have attracted increasing attention.[1,2] The intense interest in this field is justified not only by the fascinating structural diversity of the complex architectures but also by the potential applications of these compounds as functional materials in magnetism,[3] molecular adsorption,[4] manufacture of light conversion devices[5] and bimetallic catalysis.[6] Although a number of 3d−4f heterometallic complexes with discrete structures were obtained by the conventional self-assembly reaction in solution,[7−22] the synthesis of polymeric compounds, especially three-dimensional open-framework 3d−4f heterome-

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tallic coordination polymers, is still less successful.[4,23] As has been well established, the lanthanide ions behave as hard acids and they prefer oxygen to nitrogen donors, while d-block metal ions are borderline acids, having a strong tendency to coordinate to N-donors as well as O-donors.[24] Therefore, a typical approach to construct 3d−4f heterometallic frameworks is self-assembly of mixed metal ions and proper ligands containing mixed-donor atoms, such as CN^-,[25] $N(CN)_2^-$,[26] carbonyl,[27] and pyridinecarboxylate ligands.[1,4,28] In this regard, elaborately designed ligands with N-donor and O-donor atoms were employed to generate 3d−4f heterometallic coordination polymers, most of which possess low-dimensional structures,[1,24,28−33] while ambidentate "extended reach" linear ligands have also been used for the formation of 3d−4f heterometallic complexes with sheet or mutually interpenetrating network structures.[34]

Hydrothermal techniques show great advantages over other methods for the syntheses of high-dimensional coordination compounds.[1,35] In a hydrothermal synthesis, even insoluble reagents which are not suitable for the conventional solution synthesis can be used, and thermally stable coordination compounds are usually able to form from a hydrothermal reaction system. In light of the advantages of hydrothermal techniques in combination with those of mixed-donor ligands, we chose quinolinic acid as the bridging ligand and prepared a series of 3d−4f heterometallic coordination polymers from a hydrothermal reaction system. The adjacent two carboxylate groups of quinolinate easily connect lanthanide ions, while the nitrogen atom as well as another oxygen atom of one carboxylate group coordinates to the 3d metal ions. In this paper, three novel 3d−4f heterometallic coordination polymers with a 3D open-framework structure, $[Ln_2(H_2O)_4M_2(H_2O)_2(QA)_5]\cdot nH_2O$ (H_2QA = quinolinic acid; Ln = Gd, M = Ni, $n = 7$ (**1**); Ln = Gd, M = Co, $n = 6.5$ (**2**); Ln = Dy, M = Co, $n = 6.5$ (**3**)), will be described and their thermal properties and temperature-dependent magnetic behavior will also be discussed.

Experimental Section

Materials. $GdCl_3\cdot 6H_2O$ and $DyCl_3\cdot 6H_2O$ were prepared by dissolving Gd_2O_3 and Dy_2O_3, respectively, in hydrochloric acid followed by drying and crystallization. The H_2QA and other reagents of analytical grade were obtained from commercial sources and used without further purification.

Synthesis of $[Gd_2(H_2O)_4Ni_2(H_2O)_2(QA)_5]\cdot 7H_2O$, 1. A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (0.087 g, 0.3 mmol), $GdCl_3\cdot 6H_2O$ (0.111 g, 0.3 mmol), and H_2QA (0.100 g, 0.6 mmol) was dissolved into a mixed solution of absolute ethanol (2 mL) and distilled water (10 mL), followed by addition of 2-propanolamine (0.1 mL) until the pH value of the system was adjusted to about 6.5. The resulting solution was stirred for about 1 h at room temperature, sealed in a 23-mL Teflon-lined stainless steel autoclave, and heated at 150 °C for 3 days under autogenous pressure. Afterward, the reaction system was gradually cooled to room temperature at a rate of 15 °C/h. Blue crystals of **1** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 45% based on Gd. Anal. Calcd for **1**: C, 28.16; H, 2.75; N, 4.69. Found: C, 26.93; H, 2.57; N, 4.69. IR spectrum (cm^{-1}): 3385 (s), 1578 (s), 1465 (m), 1378 (s), 1266 (m), 1159 (w), 1110 (s), 885 (m), 847 (m), 785 (w), 710 (m), 673 (w), 616 (w), 541 (w), 460 (m).

Synthesis of $[Gd_2(H_2O)_4Co_2(H_2O)_2(QA)_5]\cdot 6.5H_2O$, 2. Compound **2** was prepared in the same way as for **1**, using $Co(NO_3)_2\cdot 6H_2O$ (0.087 g, 0.3 mmol) instead of $Ni(NO_3)_2\cdot 6H_2O$ as the 3d metal source. Rose-colored crystals were obtained in a 43% yield based on Gd. Anal. Calcd for **2**: C, 28.32; H, 2.70; N, 4.72. Found: C, 27.61; H, 2.65; N, 4.84. IR spectrum (cm^{-1}): 3383 (s), 1568 (s), 1465 (m), 1391 (s), 1266 (m), 1159 (w), 1110 (s), 885 (m), 847 (m), 785 (w), 710 (m), 666 (w), 616 (w), 541 (w), 467 (m).

Synthesis of $[Dy_2(H_2O)_4Co_2(H_2O)_2(QA)_5]\cdot 6.5H_2O$, 3. Compound **3** was prepared similarly, using $Co(NO_3)_2\cdot 6H_2O$ (0.087 g, 0.3 mmol) and $DyCl_3\cdot 6H_2O$ (0.113 g, 0.3 mmol) instead of $Ni(NO_3)_2\cdot 6H_2O$ and $GdCl_3\cdot 6H_2O$ as the metal sources, respectively. Rose-colored crystals were obtained in a 40% yield based on Dy. Anal. Calcd for **3**: C, 28.12; H, 2.68; N, 4.69. Found: C, 28.10; H, 2.69; N, 4.79. IR spectrum (cm^{-1}): 3371 (s), 1578 (s), 1465 (m), 1384 (s), 1266 (m), 1153 (w), 1110 (s), 878 (m), 847 (m), 785 (w), 710 (m), 673 (w), 613 (w), 541 (w), 460 (m).

Physical Measurements. The infrared spectra were recorded within the 400−4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The C, H, N elemental analyses were conducted on a Perkin-Elmer 240C element analyzer, whereas

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Table 1. Crystal and Structure Refinement Data for **1**−**3**

param	**1**	**2**	**3**
empirical formula	$C_{35}H_{41}Gd_2Ni_2N_5O_{33}$	$C_{35}H_{40}Gd_2Co_2N_5O_{32.5}$	$C_{35}H_{40}Dy_2Co_2N_5O_{32.5}$
fw	1491.65	1483.08	1493.58
wavelength/Å	0.710 73	0.710 73	0.710 73
temp/K	293(2)	293(2)	293(2)
cryst system	orthorhombic	orthorhombic	orthorhombic
space group (No.)	$Pna2_1$ (33)	$Pna2_1$ (33)	$Pna2_1$ (33)
a/Å	28.567(6)	28.843(3)	28.8471(14)
b/Å	14.498(3)	14.4325(13)	14.4534(10)
c/Å	12.250(2)	12.2275(9)	12.2520(7)
V/Å^3	5073.5(17)	5090.1(8)	5108.3(5)
Z	4	4	4
D_{calcd}/Mg/m^3	1.953	1.935	1.942
μ/mm^{-1}	3.417	3.316	3.633
F(000)	2936	2908	2924
reflcns collcd/unique	45 551/11 441	35 928/12 440	35 823/12 586
R_{int}	0.0568	0.1215	0.1350
cryst size/mm	0.120 × 0.045 × 0.010	0.20 × 0.16 × 0.09	0.16 × 0.13 × 0.09
data/restraints/params	11 441/25/712	12 440/13/712	12 586/13/712
goodness-of-fit on F^2	0.849	0.804	0.839
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0338 wR2 = 0.0663	R1 = 0.0528 wR2 = 0.0818	R1 = 0.0580 wR2 = 0.1039
R indices (all data)	R1 = 0.0527 wR2 = 0.0739	R1 = 0.1276 wR2 = 0.0971	R1 = 0.1441 wR2 = 0.1255
largest diff peak and hole/e·Å^{-3}	1.308 and −0.746	1.040 and −0.982	1.185 and −0.987

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{1/2}$.

the differential thermal (DT) and thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermogravimetric analyzer under an atmospheric environment at a heating rate of 20 °C/min. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP spectrometer. The powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å), and the recording speed was 0.3°/min over the 2θ range of 4−40° at room temperature. Temperature-dependent magnetic susceptibility data for polycrystalline compounds **1**−**3** were recorded on a Quantum Design MPMS-XL SQUID magnetometer under an applied field of 5000 Oe over the temperature range 4−300 K.

Crystallographic Analyses. Crystallographic data for compound **1** were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å) at a temperature of 20 ± 2 °C. The data processing was accomplished with the PROCESS-AUTO processing program. Crystallographic data for **2** and **3** were recorded at room temperature on a Bruker-AXS Smart CCD diffractometer equipped with a normal-focus, 2.4 kW X-ray source (graphite-monochromated Mo Kα radiation with $\lambda = 0.710\,73$ Å) operating at 50 kV and 40 mA with increasing ω (width of 0.3° and exposure time 30 s/frame). All the structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-97 crystallographic software package. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. Pertinent crystallographic data and structure refinement parameters for **1**−**3** are summarized in Table 1.

Results and Discussion

Syntheses. Obviously, compounds **1**−**3** are crystallized during the cooling-down process of the hydrothermally pretreated reaction systems, and it seems that the careful control of the crystallization rate favors the formation of large single crystals. For the preparation of high-quality single crystals of compounds **1**−**3**, we employed two synthetic strategies. The first is to use a mixture solution of H_2O and EtOH as the reaction medium, and the second is to cool the reaction system slowly from 150 °C to room temperature at a rate of 15 °C/h. In the absence of EtOH or if the reaction mixture was directly cooled in air at ambient temperature, powder forms of compounds **1**−**3** were obtained. Slow cooling of the hydrothermally pretreated reaction system leads the crystallization to proceed in a controlled manner, but the role played by the presence of EtOH is not very clear yet. EtOH may hinder the diffusion of crystallization nutrients in the reaction system and makes the crystal growth slower and more homogeneous. Sodium hydroxide or triethylamine instead of 2-propanolamine was also used to adjust the pH value under otherwise the same synthetic conditions, but only very small polycrystals were obtained, suggesting that 2-propanolamine also plays a role in the crystal growth process. Furthermore, the formation of single crystals of compounds **1**−**3** is very sensitive to the pH value of the reaction mixture. In our experiments, only at pH = 6.5 can the reaction mixtures produce compounds **1**−**3**, and at pH values 5, 6, and 7, compounds **1**−**3** all fail to crystallize properly. The three compounds are stable in air and are insoluble in common solvents such as ethanol, benzene, acetone, acetonitrile, and chlorobenzene. Phase purity of the compounds is sustained by their powder X-ray diffraction patterns, which are consistent with the ones simulated on the basis of the X-ray single-crystal structural data.

Crystal Structure of $[Gd_2(H_2O)_4Ni_2(H_2O)_2(QA)_5]\cdot 7H_2O$, 1. Selected bond distances and angles for compound **1** are listed in Table S1 (see Supporting Information). An ORTEP view of compound **1** is shown in Figure 1. In the asymmetric unit of **1** there exist two crystallographically distinct Gd(III) ions, two Ni(II) ions, five QA anions, and six coordinating

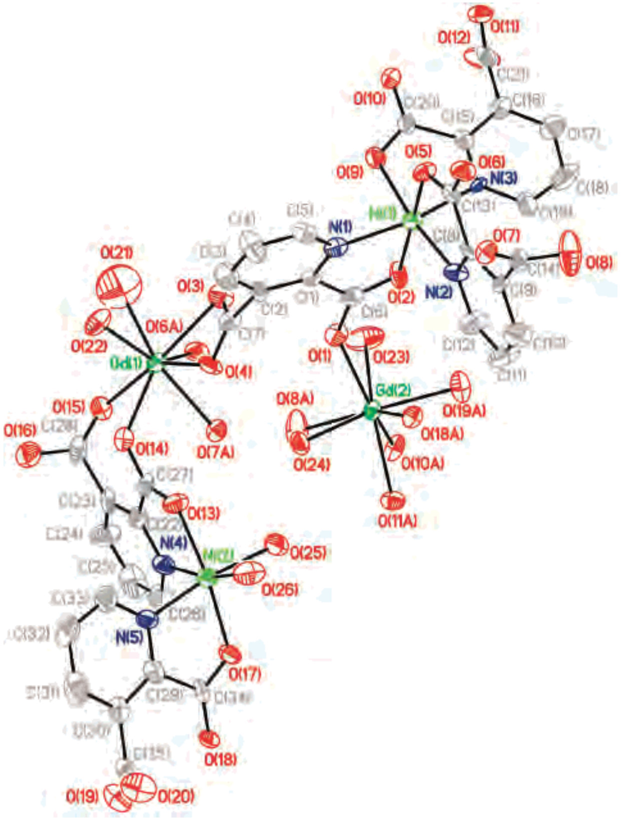
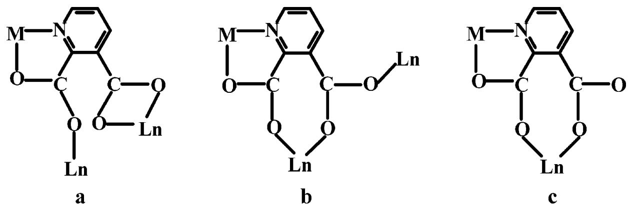


Figure 1. ORTEP view of compound **1** with 50% thermal ellipsoids. All hydrogen atoms and the noncoordinating water molecules are omitted for clarity.

and seven noncoordinating water molecules. The Gd1 center is coordinated by eight oxygen atoms from three QA anions and two coordinating water molecules, and the Gd2 ion is eight-coordinated as well, surrounded by six oxygen atoms from four QA anions and two oxygen atoms from two coordinating water molecules. The distances of Gd−O bonds range from 2.300(5) to 2.530(4) Å, all of which are within the range of those observed for other related Gd(III) complexes.[23] The O−Gd−O bond angles fall in the range of 52.02(16)−160.94(18)°. The coordination geometry of Ni(II) ions can be described as a distorted octahedron. The Ni1 center is chelated by three QA ions through three nitrogen atoms (N1, N2, N3) and three oxygen atoms (O2, O5, O9). The O2, O5, O9, and N2 atoms constituted the basal plane of the octahedron, whereas the N1 and N3 atoms are at the axial positions. The dihedral angles between the pyridine rings of the three QA anions coordinate to Ni1 are ca. 63.2, 73.4, and 67.6°, respectively. The Ni2 ion is coordinated by two nitrogen atoms from two QA anions and four oxygen atoms from two coordinating water molecules and two QA anions. N5, O17, and O13 from QA anions and O25 from a coordinating water molecule make up the basal plane, while the axial positions are occupied by one nitrogen atom from a QA anion (N4) and one oxygen atom from a coordinating water (O26) with the N4−Ni−O26 angle being 167.891(2)°. The Ni−N and Ni−O distances in **1** range from 2.035(6) to 2.101(6) Å and from 2.034(5) to 2.139(5) Å, respectively, which are similar to those found in the related Ni(II) complexes.[7c,24]

Chart 1. Coordination Modes of the QA Anions in Compound **1**



The five QA anions in the asymmetric unit of **1** adopt three coordination modes as depicted in Chart 1. All carboxyl groups of H_2QA ligand are deprotonated, in agreement with the IR data in which no strong absorption peaks around 1700 cm^{-1} for −COOH are observed. The IR spectrum of compound **1** also shows characteristic bands of carboxyl groups at near 1578 cm^{-1} for the antisymmetric stretching and at near 1467 and 1396 cm^{-1} for the symmetric stretching.[36] The very strong broad bond at around 3400 cm^{-1} is assigned to the vibrations of coordinating and noncoordinating water molecules in **1**.[37] For convenience, the QA anions containing the nitrogen atoms labeled N1−N5 are designated QA1−QA5, respectively. In coordination mode a, the nitrogen and one of the 2-carboxylate oxygen atoms of QA1 chelate one Ni1 ion and the other 2-carboxylate oxygen atom adopts a monodentate coordination, connecting one Gd2 ion; the 3-carboxylate group chelate one Gd1 ion through its two oxygen atoms. In mode b, the nitrogen and one of the 2-carboxylate oxygen atoms of QA2 chelate one Ni1 ion and the other of the 2-carboxylate oxygen atoms and one of the 3-carboxylate oxygen atoms coordinate to one Gd1 ion in a chelating fashion, whereas the other of the 3-carboxylate oxygen atoms is bonded to one Gd2 ion. Further, in mode c, the nitrogen and one of the 2-carboxylate oxygen atoms of QA3−QA5 chelate one nickel ion and the other 2-carboxylate oxygen atom and one of the 3-carboxylate oxygen atoms link one Gd(III) ion, leaving the remaining 3-carboxylate oxygen atom alone.

As shown in Figure 2, the Gd1, Gd2, and Ni1 ions are connected together via QA1 and QA2 ions to generate a 1D undulating Gd−O−Ni chain along the *c* axis. The two neighboring Gd−O−Ni chains are further bridged by the QA4−Ni2−QA5 building units, giving rise to a 1D chairlike "Gd_4Ni_4-metal-ring" channel along the *c* axis (Figure 2) which measures ca. 14.8 × 7.4 Å in diameter (defined by the separation between two nonadjacent Ni atoms). Moreover, four adjacent "Gd_4Ni_4-metal-ring" channels are bridged by four QA3 ions, resulting in the formation of the chairlike "Gd_4Ni_6-metal-ring" channel measuring of ca. 20.7 × 8.4 Å in diameter (based on $d_{Gd\cdots Gd}$), again along the *c* axis (Figure 3a). When van der Waals radii of the atoms are taken into account, the effective dimensions of the channels are about 10.6 × 3.2 and 15.9 × 3.6 Å for the "Gd_4Ni_4-metal-ring" and "Gd_4Ni_6-metal-ring" channels, respectively, which are occupied by noncoordinating water molecules. When the

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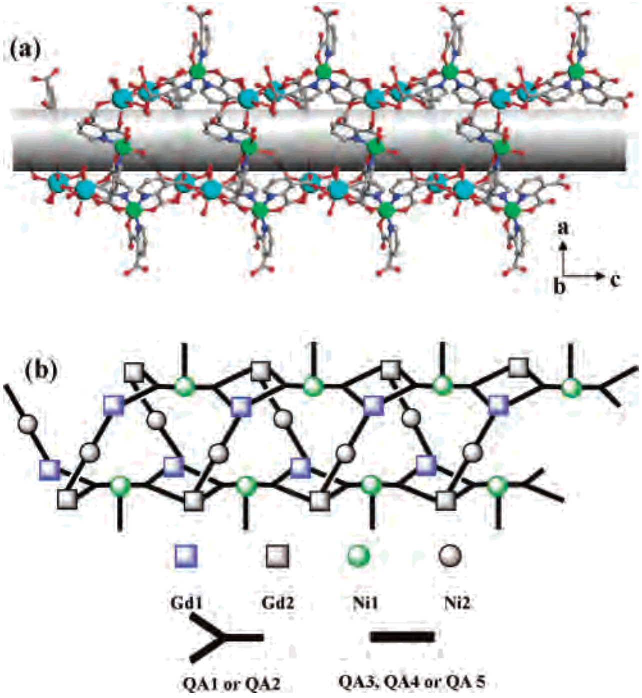

Figure 2. (a) 1D chairlike "Gd_4Ni_4-metal-ring" channel in **1** represented by the gray-colored cylinder. Key: Gd, cyan; Ni, green; C, gray; N, blue; O, red. All hydrogen atoms are omitted for clarity. (b) Schematic illustration of the connections of two neighboring Gd−O−Ni chains that leads to the 1D chairlike "Gd_4Ni_4-metal-ring" channel in **1**.

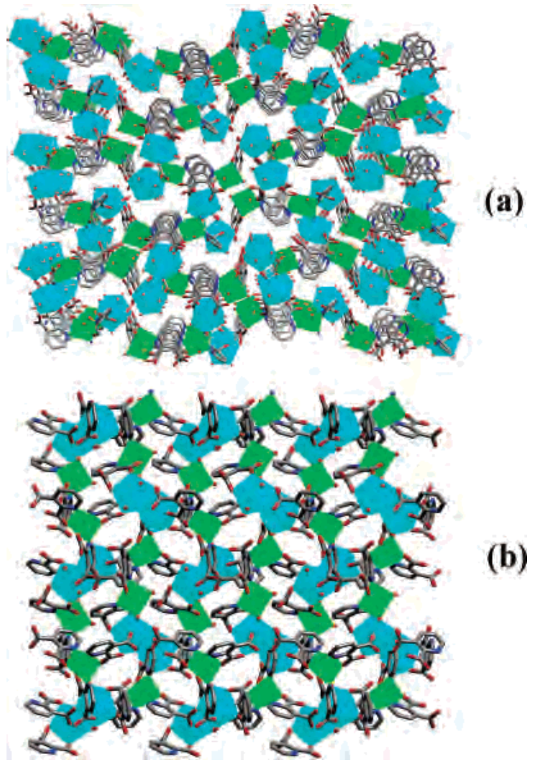

Figure 3. 3D framework structure of **1** viewed (a) along the *c* axis showing the 1D chairlike "Gd_4Ni_4-metal-ring" and "Gd_4Ni_6-metal-ring" channels and (b) along the *b* axis showing the smaller channels. The noncoordinating water molecules occluded in the channels and all hydrogen atoms are omitted for clarity.

structure of **1** is viewed along the *b* axis, channels (Figure 3b) which are smaller but more regular than those in the *c* axis can also be seen.

Compounds **2** and **3** are isostructural with **1**. Nevertheless, small difference exists for these three compounds. The amounts of noncoordinating water molecules/formula unit of **2** and **3** are less than that of **1**. As shown in Tables S2 and S3 (Supporting Information), the metal−oxygen and metal−nitrogen bond distances and angles for compounds **2** and **3** are observed to vary from compound to compound because the radii of Co(III) and Gd(III) ions are slightly larger than those of Ni(III) and Dy(III) ions. All the M(II)−ligand bonds in **2** and **3** are slightly longer than the corresponding bonds in **1**, whereas all of the Ln(III)−O bonds in **3** are slightly shorter than the corresponding ones in **1** and **2.** As a result, the cell volume for the three compounds is in the order **1** < **2** < **3**.

Thermal Analysis. Thermogravimetric curves have been obtained in air for crystalline samples of the three complexes in the temperature range 35−800 °C. It is seen from the TGA curve of **1** (Figure S4) that the first weight loss of 8.55% from 35 to 165 °C corresponds to removal of the seven free water molecules in each formula unit (calcd: 8.45%). On the other hand, the fact that some characteristic X-ray powder diffraction peaks disappear after heating to 165 °C suggests that the framework partially collapses upon removal of the free water molecules. The second weight loss of 7.20% between 165 and 355 °C is attributable to the loss of all coordinating water molecules in each formula unit (calcd: 7.24%), whereas the weight loss of about 45.15% in the range from 355 to 600 °C is ascribed to the removal of the organic component (calcd: 48.87%). The TG analysis results of **1**−**3** are almost identical, indicating that the thermal behaviors of the three compounds are very similar because of isto-structuralism.

Magnetic Properties. The temperature dependence of the magnetic susceptibility is recorded for polycrystalline samples of **1**−**3** at an applied magnetic field of 5000 Oe over the temperature range 4−300 K. The results are shown as plots of $\chi_M T$ and χ_M^{-1} versus T for **1**−**3** in Figure 4 a−c, respectively. For **1**, the $\chi_M T$ value is 18.60 $cm^3 \cdot K \cdot mol^{-1}$/formula unit at room temperature, close to the spin-only value (calculated 17.75 $cm^3 \cdot K \cdot mol^{-1}$) of 2 uncoupled $S_{Ni} = 1$ spins of Ni(II) atoms and 2 uncoupled $S_{Gd} = 7/2$ spins of Gd(III) atoms assuming both ions having a g value of 2.0. As the temperature is lowered, the $\chi_M T$ value remains essentially constant from 300 to about 12 K, below which it decreases sharply to 17.16 $cm^3 \cdot K \cdot mol^{-1}$ at 4 K. The rapid drop of $\chi_M T$ at low temperatures probably results from the zero-field splitting of the Ni(II) centers primarily with some contribution from the overall weak antiferromagetic coupling among the metal ions.[24] Curie−Weiss fitting of the magnetic data over the whole temperature range 4−300 K results in a Curie constant $C = 18.64$ $cm^3 \cdot K \cdot mol^{-1}$ and a Weiss constant $\Theta = -0.22$ K, characteristic of a weak overall antiferromagnetic interaction by taking into account the fact that the orbital momentum of the Gd(III) ion is completely quenched in the ground state.[38] For **2**, there is a continuous decrease in the value of $\chi_M T$ as the temperature is lowered from room

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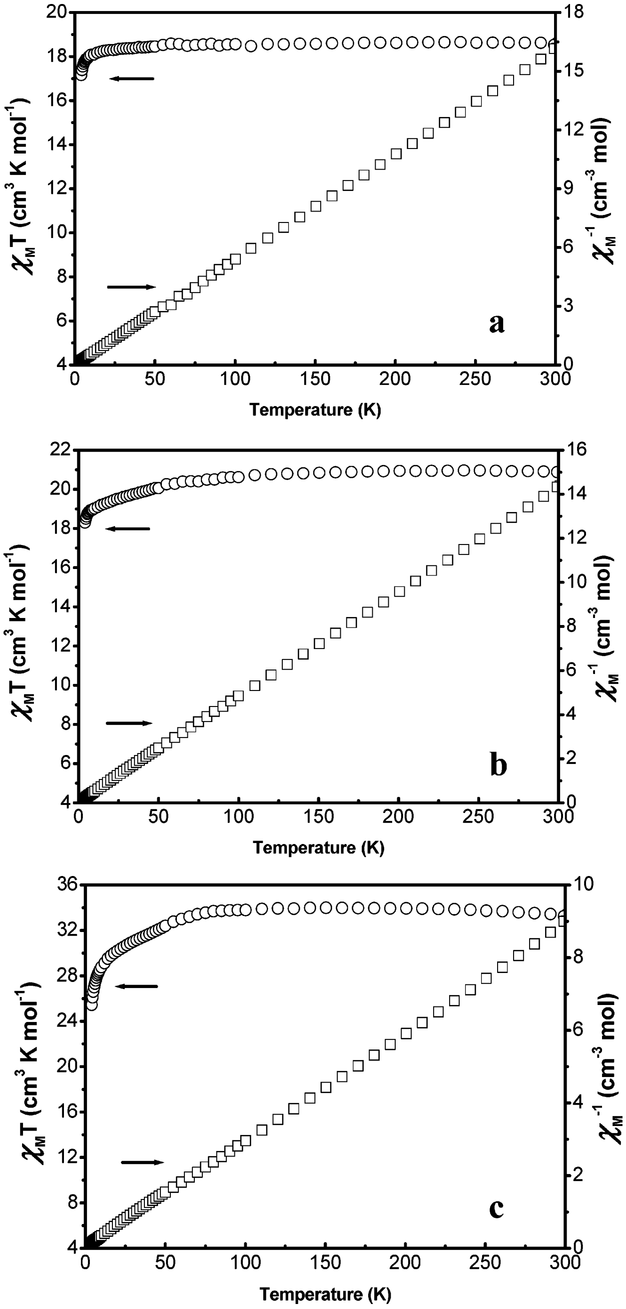

Figure 4. Plots of the temperature dependence of $\chi_M T$ (open circles) and χ_M^{-1} (open squares) for complexes **1** (a), **2** (b), and **3** (c).

temperature to 4 K, at which the $\chi_M T$ value is 18.30 cm^3·K·mol^{-1}. The $\chi_M T$ value/formula unit is 20.92 cm^3·K·mol^{-1} at room temperature, slightly higher than the expected one of 19.50 cm^3·K·mol^{-1} for noninteracting Gd(III) and Co(II) ions assuming both ions having a *g* value of 2.0. This phenomenon is attributed to the fact that the orbital angular momentum of Co(II) is not completely quenched in the crystal field. In the 4−300 K temperature range, the magnetic susceptibility data of **2** can be described by a Curie−Weiss fitting with $C = 21.05$ cm^3·K·mol^{-1} and $\Theta = -1.62$ K. The negative Θ value also indicates the presence of weak antiferromagnetic interactions[3c] among the metal centers. For compound **3**, the observed value of $\chi_M T$ is 33.38 cm^3·K·mol^{-1}/formula unit at room temperature, which is, again, slightly larger than the spin-only value of 32.09 cm^3·K·mol^{-1} expected for isolated two Dy(III) ($S_{Dy} = 15/2$) and two Co(II) ($S_{Co} = 3/2$) ions (assuming $g_{Dy} = 4/3$ and $g_{Co} = 2.0$), indicative of the presence of the large unquenched orbital angular momentum of Dy(III) and Co(II) ions in the crystal field.[38] When the temperature is lowered, the $\chi_M T$ value for **3** remains almost constant from room temperature to about 80 K where the value starts to decrease, reaching its minimum of 25.44 cm^3·K·mol^{-1} at 4 K. The Curie−Weiss fitting of the magnetic data in the full measured temperature range 4−300 K for **3** gives rise to $C = 33.93$ cm^3·K·mol^{-1} and $\Theta = -1.68$ K. Despite the decrease of $\chi_M T$ value on cooling and the presence of negative Θ value, the nature of the magnetic interaction between Dy(III) and Co(II) ions cannot be unambiguously interpreted as antiferromagnetic because of the strong spin−orbit coupling of the Dy(III) ion.[30,39]

Conclusions

Three isostructural 3d−4f heterometallic compounds **1**−**3** crystallize from a hydrothermally pretreated reaction system containing appropriate ligands with mixed-donor atoms. These compounds show an interesting 3D open-framework topology with different channels. Most of the previously reported open-framework metal-coordination polymer compounds are composed of either d-block metals or rare-earth metals with suitable ligands, while 3d−4f heterometallic compounds with porous network structures are less common in the literature. The successful preparation of the three coordination polymers **1**−**3** provides valuable information for further construction of other 3D 3d−4f frameworks. Clearly, the use of ligands with mixed-donor atoms is a key strategy in the crystallization of 3d−4f frameworks.

Acknowledgment. This work was supported by the National Natural Science Foundation of China and the Education Ministry of China.

Supporting Information Available: Selected bond lengths and angles, three crystallographic tables, X-ray crystallographic files (CIF), FTIR spectra, and DTA-TG curves for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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