

## Lanthanide(III)–Cobalt(II) Heterometallic Coordination Polymers with Radical Adsorption Properties

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Two new coordination polymers  $\{[\text{Ln}_2(\text{PDA})_6\text{Co}_3(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}\}_n$  [ $\text{Ln} = \text{Nd}$ ,  $x = 7$  (**1**);  $\text{Ln} = \text{Gd}$ ,  $x = 3.25$  (**2**);  $\text{H}_2\text{PDA} = \text{pyridine-2,6-dicarboxylic acid}$ ] have been prepared under hydrothermal conditions with  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoO}$ , and  $\text{H}_2\text{PDA}$  in a molar ratio of 2:3:6. X-ray crystallographic analyses reveal that they crystallize in the hexagonal group  $P6/mcc$  and exhibit a nanotubular 3D framework. The adsorption experiment shows that **1** and **2** can adsorb radicals, which is proven by electron paramagnetic resonance spectra with the characteristic bands of the radicals at  $g = 2.006$  and  $2.005$ , respectively.

In recent years, open metal–organic frameworks (MOFs) have been widely studied and have received much attention for many practical applications ranging from ion exchange, catalysis, adsorption, separation, and sensor to optoelectronics.<sup>1</sup> Consequently, many chemical researchers attempt to use various methods to obtain MOFs, and then the synthetic method of MOFs is rapidly being advanced from the accidental to rational stage,<sup>2</sup> gaining directed frameworks such as porous frameworks. Up to now, a great many porous coordination polymers have been synthesized and character-

ized, including some 4f–3d heterometallic series.<sup>3–6</sup> However, porous coordination polymers containing both lanthanide (4f) and transition (3d) metals are mostly focused on the lanthanide–copper (Ln–Cu) system,<sup>4</sup> while those with lanthanide–cobalt (Ln–Co) metals are rare.<sup>5</sup>

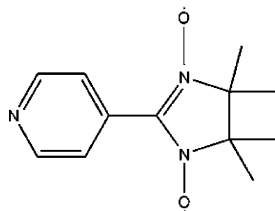
In particular, based on their porous size and high surface area, porous coordination polymers may adsorb some molecules in the pores. Porous materials such as Werner complexes,<sup>7</sup> Prussian blue compounds,<sup>8</sup> and Hofmann clathrates and their derivatives<sup>9</sup> that can adsorb small molecules are widely known. In the past decade, there are many examples of porous coordination polymers that absorb small molecules, such as  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CO}_2$ .<sup>10</sup> The research works with adsorption of larger molecules also have some reports, such as butane, toluene, styrene, and the dyes Astrazon Orange R, Nile Red, and Reichardt's dye.<sup>11</sup> However, to the best of our knowledge, there is no report of porous coordination polymers to adsorb radical molecules.

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Scheme 1 Molecular Structure of NIT4Py



In previous work, our group have reported a series of Ln–Mn, Ln–Cr, and Ln–VO mixed-metal coordination polymers with 1D, 2D, and 3D frameworks.<sup>6,12</sup> In this contribution, two new Ln<sup>III</sup>–Co<sup>II</sup> porous coordination polymers ( $\{[\text{Ln}_2(\text{PDA})_6\text{Co}_3(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}\}_n$  [Ln = Nd,  $x = 7$  (**1**); Ln = Gd,  $x = 3.25$  (**2**)] were obtained by hydrothermal synthesis that were structurally characterized by single-crystal X-ray diffraction (XRD).<sup>13</sup> The adsorption properties of **1** and **2** are investigated and indicate that they adsorb radical NIT4Py [NIT4Py = 2-(4'-pyridyl)-4,4',5,5'-tetramethylimidazole-1-oxyl-3-oxide; Scheme 1] proven by electron paramagnetic resonance (EPR) spectra.

The X-ray crystallography reveals that **1** and **2** are isomorphous and crystallize in the hexagonal group  $P6/mcc$ . The molecular motifs of two compounds show extreme similarity with a slight difference in the number of lattice water molecules. Both **1** and **2** possess a nanoporous 3D structure with columnar channels.

The crystal structures are constructed by two building blocks, LnN<sub>3</sub>O<sub>6</sub> and CoO<sub>6</sub> (Figure S1 in the Supporting Information). Each Ln<sup>III</sup> ion is nine-coordinated by three PDA anions, and each PDA anion coordinates to a Ln<sup>III</sup> ion through one N atom and two individual carboxylate O atoms. The coordination geometry of a Ln<sup>III</sup> ion conforms closely to a tricapped trigonal prism. The other carboxylate O atoms coordinate to Co<sup>II</sup> ions. Each Co<sup>II</sup> ion is six-coordinated by

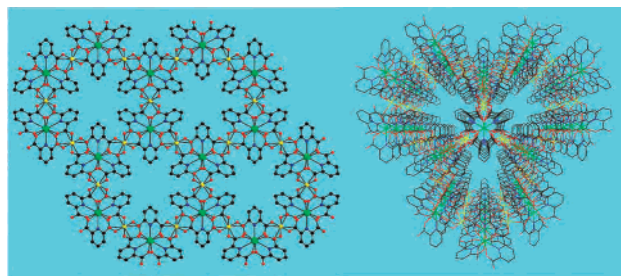


Figure 1. Left: View of a [001] projection of the Ln–Co series accentuating the column channels. Right: 3D framework with nanosized channels. Color code: green, Ln; yellow, Co; red, O; blue, N; black, C.

four carboxylate O atoms at the equatorial plane and two water molecules at the apical sites, which form an elongated octahedral geometry. The fact that each carboxylate group has one O atom coordinated to Co<sup>II</sup> ions means that each Ln<sup>III</sup> ion is surrounded by six Co<sup>II</sup> ions in its vicinity, while each Co<sup>II</sup> ion has four Ln<sup>III</sup> ions as nearest neighbors, which confirms the Ln–Co (2:3) molar relationship. As a result of this connectivity pattern, a 2D planar honeycomb structure parallel to (001) is formed with Ln polyhedra. The layers are connected via Co<sup>II</sup> ions, each of which bonds to four carboxylate O atoms (two from above and two from below), and then the 2D structure further develops into a 3D framework structure with columnar channels (Figure 1). The cross section of the channel is formed by six LnO<sub>6</sub>N<sub>3</sub> polyhedra and six CoO<sub>6</sub> polyhedra in which the Ln<sup>III</sup> and Co<sup>II</sup> ions are arrayed alternately and connected through O–C–O bridges (Figure S2 in the Supporting Information). The diameters of the hexagonal channels (defined as the distance between Ln1A and Ln1D; Figure S3 in the Supporting Information) are 17.82 and 17.57 Å for **1** and **2**, respectively.

The results from thermogravimetric analysis (TGA) of **1** show two steps of weight loss, while those of **2** show three steps of weight loss (Figure S4 in the Supporting Information). The first weight loss of the two compounds from 30 to 150 °C corresponds to the loss of nine uncoordinated water molecules, which indicates that each molecule absorbs some water molecules to achieve saturation because of the presence of large pores. The absorption of water molecules was also confirmed by elemental analyses. The powder XRD (PXRD) spectra indicate that the framework remains intact after removal of the uncoordinated water molecules trapped in the nanotube (Figure S5 in the Supporting Information). The second weight loss of **1** from 150 to 300 °C corresponds to six coordinated water molecules. However, the six coordinated water molecules of **2** were divided into two steps to lose. The TGA results show that those compounds are highly stable and do not decompose until 400 °C.

For the large pores of these coordination polymers, we investigated the absorption ability of **1**. The powder of **1a** (**1** adsorbed NIT4Py) was washed by distilled water many times to remove NIT4Py molecules adsorbed on the surface.

The X-band EPR powder spectra of **1** and **1a** (**1** adsorbed NIT4Py) were recorded at room temperature, as shown in Figure 2A,B. The spectrum of **1** shows a hyperfine splitting pattern, which may have resulted from the coupling of Nd<sup>III</sup>

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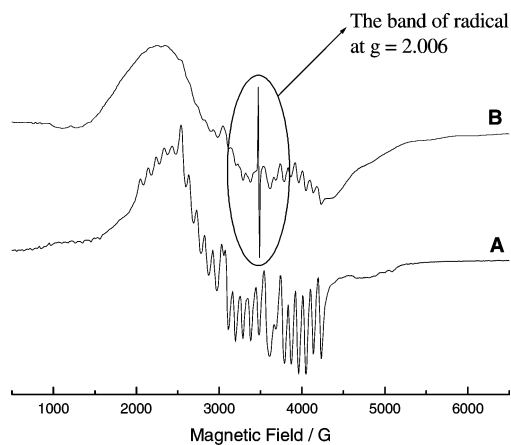


Figure 2. EPR spectra of **1** (A) and **1a** (B).

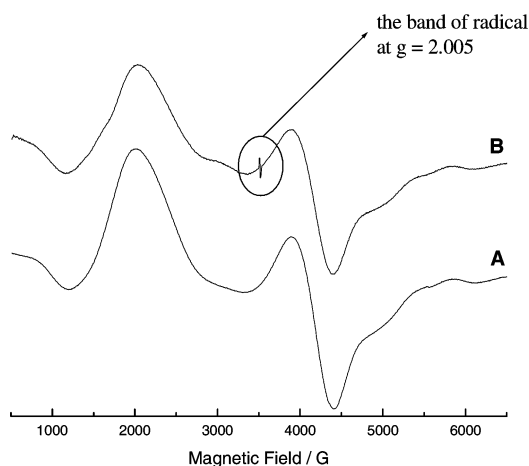


Figure 3. EPR spectra of **2** (A) and **2a** (B).

and  $\text{Co}^{\text{II}}$  ions (Figure 2A). The orbital angular momentums of  $\text{Nd}^{\text{III}}$  and  $\text{Co}^{\text{II}}$  ions are complex and prevent a simple and explicit analysis. The difference of two spectra is that there is a band in Figure 2B at  $g = 2.006$  that is the characteristic band of the radical, indicative of **1** adsorbing NIT4Py.

For confirmation of the adsorption property observed in **1**, we also further investigate the adsorption of **2**. For a magnetically uncoupled  $\text{Gd}^{\text{III}}$  ion ( $4f^7$ ,  $S = 7/2$ ), a central line with  $g \sim 2$  (transition  $+1/2 \leftrightarrow -1/2$ ) and three lateral lines at both sides of the central line (transition  $\pm 7/2 \leftrightarrow \pm 5/2$ ,  $\pm 5/2 \leftrightarrow \pm 3/2$ ,  $\pm 3/2 \leftrightarrow \pm 1/2$ ) are expected.<sup>14</sup> However, it is obvious that the EPR spectrum of **2** does not arise from the  $\text{Gd}^{\text{III}}$  ion, as shown in some papers associated with the  $\text{Gd}^{\text{III}}$  ion, which is always centered at  $g \sim 2$ .<sup>15</sup> Additionally, the EPR spectrum of the  $\text{Co}^{\text{II}}$  ion is difficult to observe at room temperature. The EPR spectrum of **2** may result from the coupling of  $\text{Gd}^{\text{III}}$  and  $\text{Co}^{\text{II}}$  ions. Compared with that of **1**, the hyperfine splitting pattern is not observed in that of **2**, which is due to the quenching orbital angular momentum of the  $\text{Gd}^{\text{III}}$  ion ( $4f^7$ ,  $L = 0$ ). Figure 3A shows the EPR spectrum

of **2**. The EPR spectrum of **2a** (**2** adsorbed NIT4Py) is displayed in Figure 3B, and the characteristic band of the radical is at  $g = 2.005$ . It is certain that **1** and **2** could adsorb NIT4Py as proven by EPR spectra. The characteristic band of the free radical is at  $g = 2.008$  (Figure S6 in the Supporting Information) and has no significant difference from that of **1a** and **2a**.

In a comparison with adsorption of other (nonradical) organic compounds, we choose methanol as the guest molecules to do the adsorption experiment. The TGA (Figure S7 in the Supporting Information) and elemental analysis reveal that compound **1** adsorbed five methanol molecules after the loss of all of the uncoordinated water molecules per  $\text{Nd}_2\text{Co}_3$  unit. We tried to determine the amount of NIT4Py adsorbed, but the elemental analysis, mass spectrometry, and TGA measurements did not give satisfactory results, which implied that the adsorbed amount of NIT4Py was very small.

The magnetic susceptibilities as a function of temperature were measured for **1** and **2** in the range of 2–300 K (Figure S8 in the Supporting Information). The  $\chi_{\text{m}}T$  values are equal to 12.64 and 24.58  $\text{cm}^3 \text{K mol}^{-1}$  at room temperature, respectively, which are higher than the theoretical values [8.84 (**1**) and 21.32 (**2**)  $\text{cm}^3 \text{K mol}^{-1}$ ] for three spin-only isolated  $\text{Co}^{\text{II}}$  ions and two  $\text{Ln}^{\text{III}}$  ions in the ground state for **1** ( $^4I_{9/2}$ ,  $g = 8/11$ ) and **2** ( $^8S_{7/2}$ ,  $g = 2$ ), indicating a typical contribution of the orbital momentum for the  $^4T_{1g}$  ground state of  $\text{Co}^{\text{II}}$  ions.<sup>16</sup> The coupling interactions between Nd and Co, and between Gd and Co, are not explicitly characterized because of the strong spin–orbit coupling of Nd and Co ions.

In summary, two new 4f–3d porous coordination polymers with columnar channels have been synthesized. TGA shows that these coordination polymers do not decompose until 400 °C and the crystal lattice remains intact after the guest water molecules are removed, which is further confirmed by PXRD. Most importantly, **1** and **2** can adsorb radical NIT4Py, and EPR spectra exhibit the characteristic band of the radical. The novel adsorption properties of these polymers indicate the promising applications in storage and adsorption for large molecules.

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**Supporting Information Available:** X-ray crystallographic files of **1** and **2** in CIF format and experimental details and additional figures (Figures S1–S8) in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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