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$\{[Nd_4(ox)_4(NO_3)_2(OH)_2(H_2O)_2]\cdot 5H_2O\}_n$: A Porous 3D Lanthanide-Based Coordination Polymer with a Special Luminescent Property

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Unique bridging modes of oxalates and nitrates have unexpectedly caused a porous 3D lanthanide-based coordination polymer, which has 1D channels and displays a special luminescent property.

Interest in porous metal-coordination polymers that are constructed by self-assembly processes has mushroomed recently[1] because of their versatile applications in the areas of redox catalysis, cathodic electrolysis, ion exchange, adsorption, separation, sensors, and molecular recognition.[2−5] However, much of the work has so far focused on coordination polymers containing transition metals,[2,6] while rare-earth metal compounds have received less attention.[7]

As a matter of fact, lanthanide ions are good choices to build multidimensional coordination polymers because of their tendency to adopt high coordination numbers, which can be employed for the construction of high-dimensional and high-connected frameworks; however, the variable and versatile coordination behavior of lanthanide ions frequently causes lattice interpenetration and, consequently, makes coordination polymers with no pores.[8] It is obvious that, compared with 3d metal porous polymers, the lanthanide-based polymers are more difficult to prepare.

Here, we report a porous 3D lanthanide-based coordination polymer, $\{[Nd_4(ox)_4(NO_3)_2(OH)_2\ (H_2O)_2]\cdot 5H_2O\}_n$, which was accidentally obtained in the process of designing and preparing 4f−3d heterometallic polymers. This compound has 1D channels and displays a special luminescent property.

The hydrothermal reaction of 2-pyrazinecarboxylic acid, Nd_2O_3, and $Fe(NO_3)_3$ in an aqueous solution at 165 °C for 6 days produced pink block crystals.[9] Single-crystal X-ray analysis[10] of the compound illustrated the presence of an oxalate (ox^{2-}) ligand and the absence of 2-pyrazinecarboxylic acid in the coordination environment of the Nd^{III} ion. Because no oxalate was directly introduced to the starting reaction mixture, the oxalate might be derived from the decomposition of 2-pyrazinecarboxylic acid. A similar situation also occurred in other systems.[11] In our attempts to synthesize the title compound starting directly from $Nd(NO_3)_3$ and oxalic acid, the same compound could not be obtained.

The polymer, crystallized as $\{[Nd_4(ox)_4(NO_3)_2(OH)_2\ (H_2O)_2]\cdot 5H_2O\}_n$, belongs to the triclinic system. Nd^{III} ions display two different coordination surroundings (Figure 1).

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(9) Synthesis of the compound: A mixture of 2-pyrazinecarboxylic acid (1.0 mmol, 0.134 g), Nd_2O_3 (0.1 mmol, 0.034 g), $Fe(NO_3)_3\cdot 9H_2O$ (0.3 mmol, 0.121 g), and H_2O (10 mL) in the molar ratio of 10:1:3:5552 was placed in a 25 mL stainless reactor with a Teflon liner and heated at 165 °C for 6 days. Pink rhombohedral crystals were obtained in approximately 63% yield (based on Nd_2O_3). Elem anal. Calcd for $C_8H_{16}N_2O_{31}Nd_4$: C, 7.92; H, 1.33; N, 2.31. Found: C, 7.84; H, 1.35; N, 2.28.

(10) Crystal data: $C_8H_{16}N_2O_{31}Nd_4$, $M_r = 1213.19$, triclinic, $P\bar{1}$, $a = 6.2672(10)$ Å, $b = 8.6204(14)$ Å, $c = 12.936(2)$ Å, $\alpha = 105.314(2)°$, $\beta = 90.439(2)°$, $\gamma = 105.081(2)°$, $V = 648.65(18)$ Å^3, $Z = 1$, $\rho_{calcd} = 3.106$ g cm^{-3}, $2\theta_{max} = 25.01°$ ($-6 \le h \le 7$, $-9 \le k \le 10$, $-10 \le l \le 15$), $T = 294(2)$ K, $F(000) = 566$. R1 (wR2) = 0.0276 (0.0693) [2200 observed ($I > 2\sigma(I)$)] for 2268 ($R_{int} = 0.0225$) independent reflections out of a total of 3324 reflections with 217 parameters. GOF = 1.032. CCDC no. 611110.

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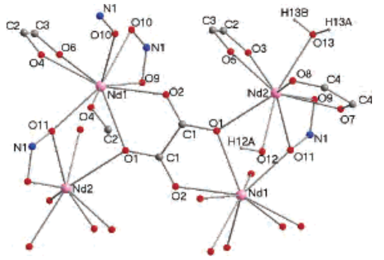

Figure 1. Diagram showing the building units with atom labels of the polymer.

$Nd1^{III}$ is coordinated with nine O atoms respectively from three oxalates and three nitrates, while the geometry of $Nd2^{III}$ is formed by nine O atoms respectively from three oxalates, a nitrate, a hydroxyl, and a water molecule. Each nitrate bridges a $Nd2^{III}$ ion and three $Nd1^{III}$ ions in the μ_4-η^2:η^2:η^2 fashion, thus resulting in a 1D structure like a double-sided sawtooth chain (Figure 2a). Adjacent sawtooth chains are connected by oxalates into 2D layers, which are further connected by oxalates into a 3D framework. To the best of our knowledge, the μ_4-η^2:η^2:η^2 bridging mode of nitrates has not been previously reported. Also deserving attention, the oxalates in the polymer simultaneously exhibit three kinds of bridging modes (mode a, μ_4; mode b, μ_3; mode c, μ_2; Figure 2b). This case has never been observed in other oxalate complexes.

Running to the *a* axis, the space-filling views of the polymer (Figure 3a) represent very highly ordered 1D channels with a diameter of about 10.5 Å [defined by the average separation between the diagonal Nd^{III} ions (Figure 3b)]. A cross section of a channel shows a 20-membered ring (20MR) comprising 6 Nd, 4 C, and 10 O atoms, of which the Nd atoms are connected by four oxalates and two nitrates, thus leading to an overall C_2 symmetry (Figure 3b). Six Nd atoms constitute the hexacyclic ring, which adopts the chair conformation (Figure 3c). The Nd···Nd distances of the Nd_6 ring are within the range from 4.062 to 6.446 Å (mean value 5.632 Å), while the Nd···Nd···Nd angles vary from 109.14 to 130.75°, with an average value of 117.51°. Similar Ln_6 rings also appear in the porous polymer $\{[Ln_2(C_2O_4)_3(H_2O)_6]\cdot 3H_2O\cdot 0.5HNO_3\}_n$ ($Ln = La^{III}$, Pr^{III}),[12] in which six Ln atoms are bridged by six oxalates.

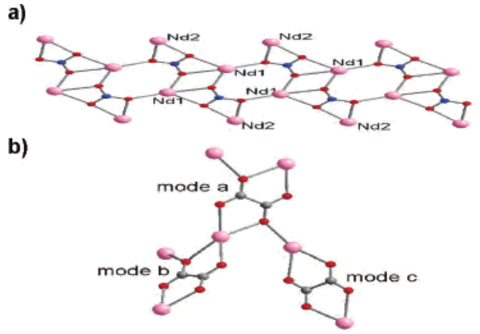

Figure 2. (a) 1D structure connected by NO_3^- in the polymer. (b) Three bridging modes of ox^{2-} in the polymer.

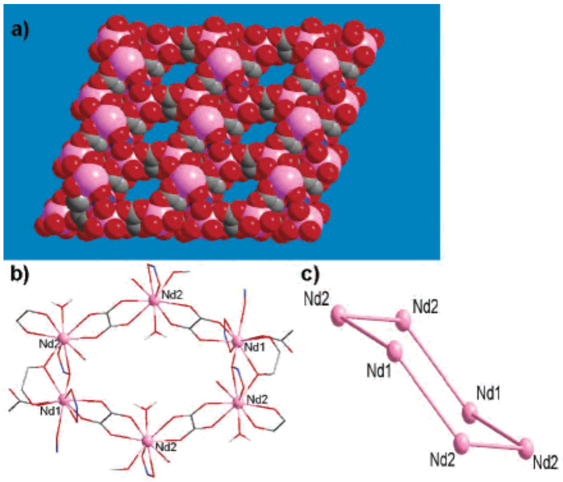

Figure 3. (a) Space-filling plots of the porous structure running to the *a* axis. Color code: pink, Nd; blue, N; red, O; gray, C. H atoms are omitted for clarity. (b) Cross section of the nanotube for the polymer, which shows 20MR and C_2 symmetry. (c) Hexacyclic ring made up of six Nd atoms, which adopts the chair conformation.

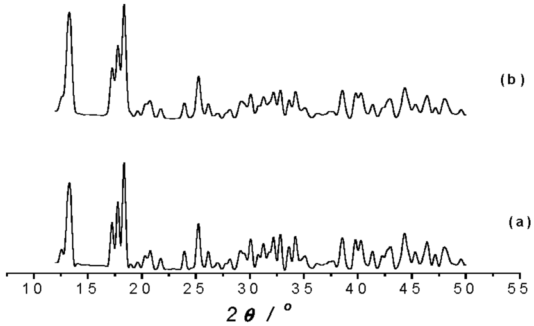

Figure 4. XRD patterns for the compound (a) at room temperature and (b) after heating to 120 °C for 24 h.

To examine the thermal stability of the polymer, thermal gravimetric analysis (TGA) was carried out. TGA was performed on crystalline samples of the compound in the range of 20−600 °C. The weight loss of 7.30%, between 20 and 120 °C, corresponds to the loss of all uncoordinated water molecules (calcd 7.42% for $5H_2O$), which was consistent with the elemental analyses (EA) of $[Nd_4(ox)_4(NO_3)_2(OH)_2(H_2O)_2]\cdot 5H_2O$. The compound lost coordinated water molecules between 120 and 230 °C but did not decompose until 340 °C. To explore whether the framework would break down upon removal of guest water molecules (uncoordinated and adsorbed water molecules) with the powder X-ray diffraction (XRD) technique, the compound was heated at 120 °C for 24 h, and the XRD patterns of the dehydrated solid showed the main reflections remaining nearly identical with the pristine samples, which supported the notion that the crystal lattice of the compound would remain intact after removal of the guest water molecules (Figure 4). A further investigation was conducted to determine whether the compound would adsorb other small molecules such as methanol. $\{[Nd_4(ox)_4(NO_3)_2(OH)_2(H_2O)_2]\cdot 2CH_3OH\}_n$ was obtained by removal of the uncoordinated and adsorbed water in the compound and immersion of the resultant sample in methanol for 12 h. This was demonstrated by TGA and EA. The results presented here suggest that the compound might be a porous metal−organic framework.

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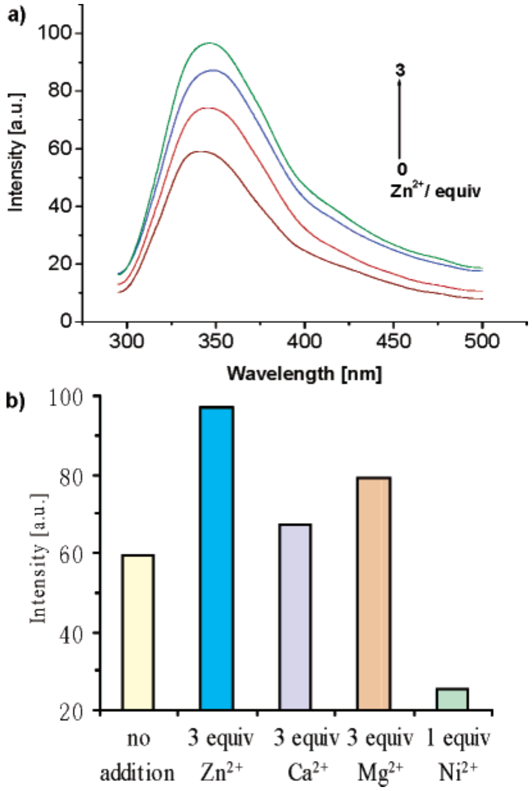

Figure 5. (a) Emission spectra of the compound in DMSO (10^{-3} M) at room temperature (excited at 285 nm) upon the addition of ~0−3 equiv of the Zn^{2+} ions, respectively: brown, no addition; red, 1 equiv; blue, 2 equiv; green, 3 equiv. (b) Luminescent intensity of the compound at 345 nm in DMSO at room temperature upon the addition of Zn^{2+}, Ca^{2+}, Mg^{2+}, or Ni^{2+} ions (excited at 285 nm). Cations were added as $ZnCl_2$, $CaCl_2$, $MgCl_2$, or $NiCl_2$.

The emission spectrum of the compound (Figure 5a) at room temperature in a dimethyl sulfoxide (DMSO) solution excited at 285 nm exhibited an intense band at about 345 nm. As is well-known, the characteristic luminescence of Nd^{3+} should lie at ~1060 nm in the near-IR region, which corresponds to the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$;[13] as a result, the observed emission at 345 nm could not be assigned to the f−f transition of Nd^{3+} but could be connected with the oxide-to-Nd^{III} absorption band (charge-transfer spin transition). Interestingly, the emission intensity of the compound increased gradually upon the addition of 1−3 equiv of Zn^{2+}. To make a further understanding of this phenomenon, the same experiments were performed for the introduction of Ca^{2+} and Mg^{2+} into the system. The presence of 3 equiv of Ca^{2+} or Mg^{2+} in a DMSO solution of the compound also increased the luminescent intensities like the presence of the Zn^{2+} ion did, but the effect of either Ca^{2+} or Mg^{2+} was not as good as that of Zn^{2+} ion (Figure 5b). Upon the addition of 1−3 equiv of transition metals such as Ni^{2+}, Co^{2+}, Mn^{2+}, and Fe^{2+} to the solution of the compound, the luminescent intensities decreased or quenched. According to the above results, the polymer may be used as a luminescent probe to distinguish and select some metal ions. When main-group metals Zn^{2+}, Ca^{2+}, and Mg^{2+} were added in the compound respectively, the luminescent intensities all increased, which was distinct from the case in other complexes, $[LnL_1]$ [L_1 = (diethylenetriaminepentaacetic acid)bisamide; Ln = Eu^{III}, Tb^{III}][14] and $\{[Ln(PDA)_3Mn_{1.5}(H_2O)_3]\cdot 3.25H_2O\}_\infty$ (PDA = pyridine-2,6-dicarboxylic acid; Ln = Eu^{III}, Tb^{III}),[15] in which the presence of Ca^{2+} or Mg^{2+} had no effect on the luminescent intensities. This may be caused by the different luminescent mechanism (charge-transfer spin transition versus f−f transition). In this Communication, enhancement of the luminescent intensity may result from more effective intramolecular energy transfer from the oxalate or nitrate ligands to the Nd^{3+} ions.

In summary, we have synthesized a novel porous lanthanide-based polymer under hydrothermal reaction conditions, which contains hexacyclic Nd^{III} rings adopting the chair conformation. The most simplest and hackneyed ligands, oxalates and nitrates, have unexpectedly caused an unusual product, because of daedal and multiform bridging modes of oxalates and nitrates. The result provides a new route to synthesizing porous 3D polymers based on the lanthanide assembly. The porous and luminescent properties have been studied, and we expect that this coordination polymer will find applications such as in adsorption and as a luminescent probe.

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Supporting Information Available: X-ray crystallographic file in CIF format, complementary drawings, TGA, and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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