Coordination Network

A 3D Coordination Framework Based on Linkages of Nanosized Hydroxo Lanthanide Clusters and Copper Centers by Isonicotinate Ligands**

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Nanoscale clusters are of great popularity due to the novel structural characteristics and rich electronic, magnetic, optical, and catalytic properties associated with their quantum-size effects.[1] Although the cluster chemistry of transition metals (TMs) is now well-established and many huge clusters

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of manganese,[2] copper,[3] nickel,[4] molybdenum,[5] and silver[6] have been synthesized successfully, the analogous chemistry of lanthanides is less developed[7] because the synthesis of nanosized high-nuclearity clusters is still a big challenge. At present, a common synthetic strategy for hydroxo lanthanide clusters is to control the hydrolysis of lanthanide salts in the presence of supporting ligands.[7,8] So far, most of the reported high-nuclearity hydroxo lanthanide clusters are discrete[7] because the presence of hydrophobic groups in the periphery of the cluster core prevents further aggregation. Recently, in an investigation on the nature of the magnetic exchange interactions between 3d and 4f metals in the solid state, some lanthanide–TM coordination polymers[9] and clusters[10] were reported. To date, except for four coordination polymers constructed from hydroxo lanthanide cluster cores of Dy_4,[11] Yb_6,[12] Ho_7, and Yb_7,[8] no systematic investigation on lanthanide–TM coordination polymers in which high-nuclearity hydroxo lanthanide clusters and TM ions are linked by organic ligands has been carried out.

We chose isonicotinic acid (HIN) as the multifunctional bridging ligand, based on the following considerations: 1) It is a rigid ligand with oxygen and nitrogen donors on opposite sides, enabling the IN ligand to act as a linear bridge. 2) The carboxy group may induce the oxophilic lanthanide ions to undergo hydroxo lanthanide cluster aggregation, the nitrogen atoms can coordinate to TM ions, and thus extended solids containing hydroxo lanthanide cluster cores and TM ions might be obtained. Here we report the systematic syntheses and structures of three coordination polymers by using lanthanide oxide, rather than lanthanide salts, as the source of lanthanides under hydrothermal conditions: $[Ln_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}(IN)_{22}Cu_6Cl_4(H_2O)_8]\cdot 6H_2O$ [Ln = Y (**1**), Gd (**2**), Dy (**3**)]. These structures contain the high-nuclearity hydroxo lanthanide cluster $[Ln_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}(H_2O)_8]^{20+}$, which acts as a building block that combines with copper ions through linear IN ligands to form a 3D framework.

Orange rectangular-prismatic crystals of **1**–**3** were obtained by hydrothermal reaction of Ln_2O_3, HIN, and $CuCl_2\cdot 2H_2O$ in water in the presence of $HClO_4$ (pH 2). The amount of $HClO_4$ used in the synthesis is a key point in the formation of **1**–**3**, because a chainlike Ln^{3+} polymer, which is isostructural with $[Tb(IN)_3(H_2O)_2]$,[13] formed under weakly acidic conditions.

X-ray crystal structure analyses revealed that **1**–**3** are isostructural and crystallize in the high-symmetry tetragonal space group $P4_2/mnm$. Therefore, only the structure of **2** is described in detail. The asymmetric unit of **2** contains four crystallographically unique Gd ions, two Cu cations, and four IN ligands (see Supporting Information). Gd1 and Gd4 are nine-coordinate: eight μ_3-OH and one μ_6-oxo for Gd1, and four μ_3-OH, one μ_6-oxo, three carboxylate oxygen (O_{COO^-}) atoms from three IN ligands, and one terminal water molecule for Gd4, while Gd2 and Gd3 are eight-coordinate: three μ_3-OH, one pyridyl nitrogen (N_{PY}), and four O_{COO^-} atoms from four IN for Gd2, and four μ_3-OH, one terminal water molecule, and three O_{COO^-} atoms from three IN for Gd3 (see Supporting Information). The Gd^{3+} ions are linked together through hydrophilic hydroxo and oxo bridges to give the novel tetradecanuclear $[Gd_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}]^{20+}$ cluster core, in which all μ_3-OH groups cap the triangular faces (Figure 1 and Supporting Information). In contrast to $[Ln_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}]^{24+}$,[7a,d] which contains an $[Ln_6(\mu_3\text{-}OH)_8]^{10+}$ octahedron and $[Ln_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4]^{10+}$ square

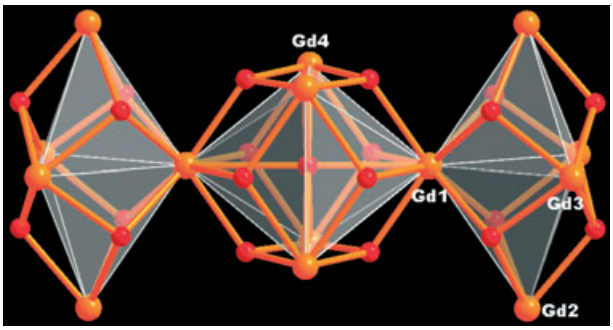


Figure 1. Polyhedral representation of the structure of the $[Gd_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}]^{20+}$ core, in which one octahedral $[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ unit shares two opposing apexes (Gd1 atoms) with two trigonal-bipyramidal $[Gd_5(\mu_3\text{-}OH)_6]^{4+}$ units. In the octahedral Gd_6 unit: Gd1—Gd4 3.907(1), Gd4—Gd4 3.895(1)–4.033(1) Å; in the trigonal-bipyramidal Gd_5 units: Gd1—Gd2 3.894(1), Gd1—Gd3 3.802(1), Gd2—Gd3 3.888(1), Gd3—Gd3 3.859(1), and Gd2—Gd2 6.407(1) Å. Gd: orange; O: red.

pyramids, the Gd_{14} core in **2** consists of one octahedral $[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$[7g,h] unit that shares two opposing Gd1 apexes with two novel $[Gd_5(\mu_3\text{-}OH)_6]^{4+}$ trigonal bipyramids, which is a rare geometry in the reported cores of $[Ln_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4]^{10+}$,[7a,d] $[Ln_5(\mu_4\text{-}O)(\mu_3\text{-}OH)_4]^{9+}$,[14] and $[Ln_5(\mu_5\text{-}O)(\mu_3\text{-}O\mathit{i}Pr)_4]^{9+}$.[15]

In the structure of **2**, two Cu centers are four-coordinate, but they have different coordination environments ($Cu(1)Cl_2N_2$ and $Cu(2)N_4$). Although Cu^{2+} ions were used as starting materials, the Cu1 and Cu2 centers both have an oxidation state of +1, attributed to a reduction reaction involving the IN ligand. This observation is consistent with a tetrahedral geometry, which is common for the Cu^+ ion,[16] and was confirmed by magnetic measurements (see below). Whereas the Cu2 centers are bonded to four IN ligands through N_{PY} atoms, two Cu1 centers are bridged by Cl^- to form a Cu_2Cl_2 dimer with Cu···Cu distance of 2.662(4) Å and are coordinated to four N_{PY} atoms from IN ligands (see Supporting Information).

The linkages between the Gd_{14} cores and two different types of copper centers through IN ligands give rise to an unusual coordination polymer with extremely complex 3D framework (Figure 2 and Supporting Information). Twenty-six IN ligands coordinate to the Gd_{14} cores through the N_{PY} or the O_{COO^-} atoms (see Supporting Information). Scheme 1 illustrates the four coordination modes of the IN ligands. Two IN ligands of mode I are terminal and only coordinate to the Gd_{14} core through the O_{COO^-} atoms (see Supporting Information). The others correspond to modes II–IV, each of which is exhibited by eight bridging IN ligands. In mode II, each IN ligand connects two Gd_{14} cores with perpendicular orientations through the N_{PY} and O_{COO^-} atoms. The coordination of the ligands is such that the pyridyl (or carboxylate) donors form a *trans* arrangement across the Gd_{14} core (see Supporting Information). In modes III and IV, the IN ligands

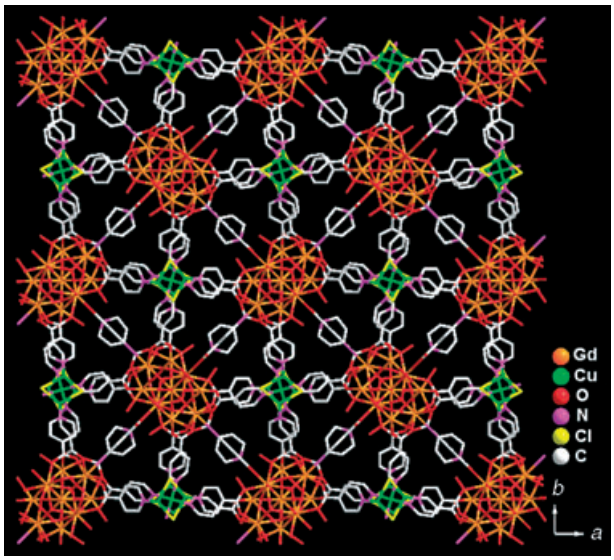
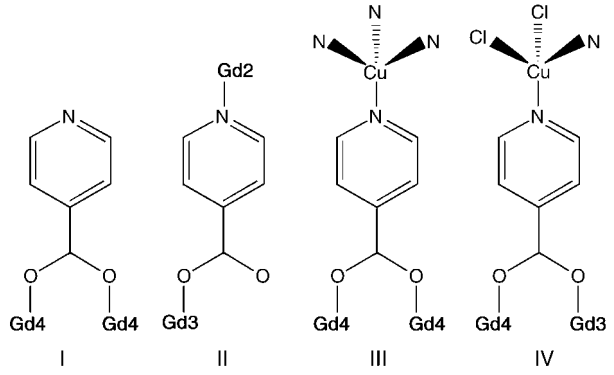


Figure 2. The overall 3D structure of **2** showing the unusual framework along the *c* axis. The lattice water molecules are omitted for clarity.



Scheme 1. Coordination modes of the IN ligands in the structure of **2**. All oxygen atoms coordinate to Gd atoms in monodentate mode.

coordinate to the Gd_{14} core through the O_{COO^-} atoms, leaving their N_{PY} atoms to bond to Cu2 ions and Cu1 atoms of Cu_2Cl_2 dimers, respectively (see Supporting Information). Thus, The structure can be understood such that the strictly alternating Gd_{14} cores, Cu_2Cl_2 dimers, and Cu ions are bridged by IN ligands of modes III and IV to form a 3D framework having 1D channels with dimensions of about 7×7.5 Å along the *c* axis (see Supporting Information). The channels are occupied by lattice water, coordinated water, and terminal IN ligands of mode I (see Supporting Information). Furthermore, the IN ligands belonging to mode II are also located in the channels and connect two Gd_{14} cores to result in an overall 3D network (Figure 2 and Supporting Information).

Temperature-dependent molar susceptibility measurements on powdered samples of **1–3** were carried out at an applied field of 0.5 T in the temperature range 5–300 K. The molar magnetic susceptibility of **1** (measured on 40.2 mg) is negative and temperature-independent in the range 50–300 K, consistent with the assigned structure containing diamagnetic Cu^+ and Y^{3+} ions. For **2**, the μ_{eff} value per molecule is 29.5 μ_B at room temperature, close to the expected value of 29.7 μ_B for fourteen noninteracting Gd^{3+} ions[17] ($S = 7/2$, $g = 2.0$) and remains almost constant down to about 50 K, then drops rapidly below 50 K to 25.0 μ_B at 5 K. The Curie–Weiss equation with $\theta = -2.1$ K fits well to the data in the range between 5 and 300 K, which suggests weak antiferromagnetic interaction between Gd^{3+} ions. Compound **3** exhibits similar temperature dependence to **2**; the μ_{eff} value of 40.3 μ_B at room temperature is in agreement with that expected for fourteen isolated Dy^{3+} ions (39.8 μ_B, $^6H_{15/2}$ ground state with $g_{15/2} = 4/3$),[17] the abrupt decrease of μ_{eff} at low temperature is mainly attributed to the splitting of the ligand field of the Dy^{3+} ion because of strong spin-orbital coupling, and some contributions from the possible antiferromagnetic interactions between the Dy^{3+} ions.[11]

In summary, we have successfully constructed three novel 3D coordination polymers containing distinct nanosized Ln_{14} clusters and copper centers by using lanthanide oxides as the source of lanthanides under hydrothermal conditions. The key points of the synthetic procedures have been well established.[18] The linkages between novel nanosized Ln_{14} cores and two different types of copper centers through IN ligands result in an unprecedented 3D network topology. These results provide a perspective towards 4f–3d mixed-metal functional materials and confirm the potential for developing new structural classes of solid-state materials by using nanosized hydroxo lanthanide clusters as building blocks.

Experimental Section

Synthesis of **1–3**: A mixture of Ln_2O_3 (Y_2O_3, 0.5 mmol, 0.113 g; Gd_2O_3, Dy_2O_3, 0.181 g; 0.187 g), HIN (0.246 g, 2 mmol), $CuCl_2 \cdot 2H_2O$ (0.034 g, 0.2 mmol), H_2O (8 mL), and $HClO_4$ (0.385 mmol) in a molar ratio of about 2.5:10:1:2222:1.9 was sealed in a 30 mL acid digestion bomb and heated at 170 °C for 6 d. Orange rectangular prism crystals of **1–3** were collected after washing with water.

Crystal data of **1**: $C_{132}H_{136}Cl_4Cu_6N_{22}O_{79}Y_{14}$, $M_r = 5062.41$, tetragonal, $P4_2/mnm$, $a = b = 20.284(10)$, $c = 21.344(14)$ Å, $V = 8782(8)$ Å^3, $Z = 2$, $\rho = 1.914$ g cm^{-3}, $F(000) = 5004$, $\mu(Mo_{K\alpha}) = 5.434$ mm^{-1}, $2\theta_{max} = 50.06°$, $(-24 \le h \le 11, \ -24 \le k \le 24, \ -22 \le l \le 24)$, $T = 293$ K, 39645 measured reflections, 4018 independent reflections. $R1$ ($wR2$) = 0.0968 (0.2110) for 3732 reflections ($I > 2\sigma(I)$) and 321 parameters. GOF = 1.126. Crystal dimensions: $0.26 \times 0.18 \times 0.12$ mm^3.

Crystal data of **2**: $C_{132}H_{136}Cl_4Cu_6Gd_{14}N_{22}O_{79}$, $M_r = 6019.17$, tetragonal, $P4_2/mnm$, $a = b = 20.620(3)$, $c = 21.807(4)$ Å, $V = 9272(3)$ Å^3, $Z = 2$, $\rho = 2.156$ g cm^{-3}, $F(000) = 5704$, $\mu(Mo_{K\alpha}) = 5.750$ mm^{-1}, $2\theta_{max} = 50.04°$, $(-24 \le h \le 24, \ -12 \le k \le 24, \ -25 \le l \le 22)$, $T = 293$ K, 43928 measured reflections, 4348 independent reflections. $R1$ ($wR2$) = 0.0480 (0.1064) for 4231 reflections ($I > 2\sigma(I)$) and 329 parameters. GOF = 1.161. Crystal dimensions: $0.30 \times 0.15 \times 0.12$ mm^3.

Crystal data of **3**: $C_{132}H_{136}Cl_4Cu_6Dy_{14}N_{22}O_{79}$, $M_r = 6092.67$, tetragonal, $P4_2/mnm$, $a = b = 20.540(3)$, $c = 21.650(4)$ Å, $V = 9134(3)$ Å^3, $Z = 2$, $\rho = 2.215$ g cm^{-3}, $F(000) = 5760$, $\mu(Mo_{K\alpha}) = 6.481$ mm^{-1}, $2\theta_{max} = 50.04°$, $(-21 \le h \le 24, \ -24 \le k \le 24, \ -18 \le l \le 25)$, $T = 293$ K, 45652 measured reflections, 4276 independent reflections. $R1$ ($wR2$) = 0.0515 (0.1065) for 4192 reflections ($I > 2\sigma(I)$) and 329 parameters. GOF = 1.191. Crystal dimensions: $0.25 \times 0.13 \times 0.10$ mm^3.

Data were collected on a SMART-CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. The structures of **1–3** were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package. All non-hydrogen atoms (except O1, C19, C20, OW3, OW4 in **1–3**) were refined anisotropically. The

positions of H atoms were generated geometrically and allowed to ride on their parent carbon atoms.

CCDC-244785–244787 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] During preparation of this communication, other phase-pure lanthanide–TM coordination polymers, such as $[Ln_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}(IN)_{22}Cu_6X_4(H_2O)_8]\cdot 6H_2O$ (Ln = Er, Tb, $X = Cl^-$; Ln = Er, Gd, Y, $X = Br^-$), were obtained as single crystals. Single-crystal X-ray diffraction showed that these compounds are analogous to the present compounds. Further investigation on the fluorescent and magnetic properties of these compounds is in progress.

