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Three-Dimensional 3d–4f Polymers Containing Heterometallic Rings: Syntheses, Structures, and Magnetic Properties

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Two novel three-dimensional (3D) 3d–4f mixed complexes $[Ln(H_2O)_4][Ni_2TTHA(SCN)_2]\cdot H_3O^+$ [Ln = Pr (**1**), Ce (**2**); H_6TTHA = triethylenetetraaminehexaacetic acid], based on the building blocks of $[Ni_2TTHA(SCN)_2]^{4-}$, were synthesized and characterized by X-ray crystal diffraction and magnetic properties. The single-crystal structures show that these complexes form a 3D framework, comprised of an unusual infinite one-dimensional chain based on heterometallic Ln_2Ni_2 rings. The temperature-dependent magnetic susceptibilities were analyzed by an approximate model, leading to $g = 2.06$. $\Delta = 2.83$, $zJ' = -0.6$ cm^{-1} for complex **1** and $g = 2.07$, $\Delta = 1.00$, $zJ' = -0.5$ cm^{-1} for complex **2**.

In recent years, the construction of lanthanide (3d−4f) mixed-transition-metal supermolecular complexes has attracted increasing attention from chemists.[1,2] The intense interest in this field is justified not only by the attractive topologies but also by the exploitable properties such as magnetism, catalysis, molecular sensors, and so on.[3,4] Although a number of structures containing 3d−4f metals have been obtained by the conventional self-assembly reaction,[5−9] the assembly of extended structures of 3d−4f polymeric compounds, especially three-dimensional (3D) 3d−4f heterometallic coordination polymers, is still less successful and is a challenge for chemists.[10,11] Choosing appropriate poly(carboxylic acid)s as structure-directing agents is a successful synthetic strategy for the construction of diverse complexes and coordination polymers. Poly(aminecarboxylic acid)s and their derivatives [such as

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H_6TTHA (triethylenetetraaminehexaacetic acid), H_5DTPA, and H_4EDTA] are very important chelating ligands that can be used as structure-directing agents to form heteropolymetallic systems and advanced frameworks. However, previous reports on the metal complexes with H_6TTHA usually focused on the lanthanide complexes[12] and binuclear transition-metal complexes.[13] The 3d−4f coordination polymers are reported rarely, and those that are structurally and magnetically characterized are reported even more rarely. To date, reported H_6TTHA-derived 3d−4f mixed complexes have focused only on vanadium oxide−lanthanide heteronuclear complexes,[2a,b] while those formed by H_6TTHA and other transition-metal lanthanides have not been reported.

In this paper, two novel 3D complexes $[Ln(H_2O)_4][Ni_2TTHA(SCN)_2]\cdot H_3O^+$ (Ln = Pr, Ce) focused on Ni−Ln heteronuclear complexes were synthesized based on a binuclear building block of $[Ni_2(H_2O)_2(H_2TTHA)]$.[16] These complexes were obtained stepwise: (a) synthesis of binuclear unit $[Ni_2(H_2O)_2(H_2TTHA)]$; (b) reactions of binuclear complexes Ni_2TTHA and $LnCl_3$. This opens up the opportunity of linking together these 3d and 4f metals using a suitable ligand.

Single crystals for all complexes were obtained by the method described as follows: an aqueous solution (10 cm^3) of $NiCl_2\cdot 6H_2O$ (2 mmol, 238 mg) was added to the suspension of H_6TTHA (1 mmol, 496 mg) in 10 cm^3 water. The mixture turned blue. After 30 min, an aqueous solution (10 cm^3) of $LnCl_3\cdot 6H_2O$ (Ln = Pr, Ce) (1 mmol) and KSCN (2 mmol, 196 mg) was added to the solution. After constant stirring for about 1 h, the solution was transferred to an ethanol environment. Blue crystals were obtained after 1 week.[14,15] We tried to synthesize these complexes by a one-pot synthesis ($NiCl_2\cdot 6H_2O$, $LnCl_3\cdot 6H_2O$, and KSCN were added together to H_6TTHA). However, single crystals have not been obtained. Therefore, we think a stepwise method is necessary to get single crystals of target complexes.

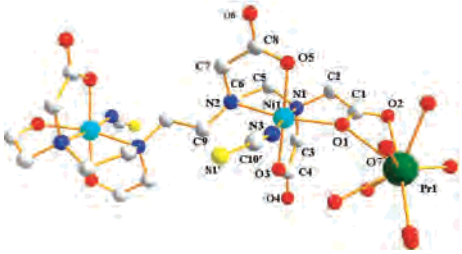

Figure 1. Perspective view of complex **1**. H atoms and lattice water molecules were omitted for clarity.

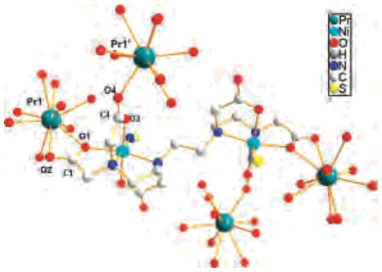

Figure 2. Two different coordination modes of the $[Ni_2TTHA(SCN)_2]^{4+}$ unit.

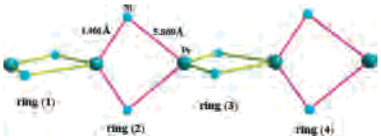

Figure 3. 1D chain based on Pr_2Ni_2.

X-ray crystallography reveals that two complexes are isomorphous. Here, we choose complex **1** to represent the detailed structure. As shown in Figure 1, complex **1** crystallizes in the orthorhombic system, space group *Pccn*. Two Ni^{2+} ions are chelated by the TTHA ligand to form a metalloligand, with six uncoordinated oxygen atoms coordinating to four Pr^{3+} ions (Figure 2). The coordination geometry around the Ni^{2+} center is a pseudo-octahedron, in which three oxygen atoms [Ni1−O1 2.098(4) Å, Ni1−O3 2.041(4) Å, and Ni1−O5 2.046(5) Å] and one N atom [Ni1−N2 2.123(5) Å] from the TTHA anion are in the equatorial plane. N3 from SCN^- and N1 from TTHA occupy the axial positions [Ni1−N 1.954(5) Å and Ni1−N1 2.076(5) Å]. The Ni^{2+} ion is 0.165(5) Å from the equatorial plane. Every Pr^{3+} ion lies in a distorted bicapped-square antiprismatic prism, with six oxygen atoms of the C−O−O′ group from TTHA bridging to four Ni^{2+} ions and four coordinated water molecules. The average Pr−O bond length is 2.567 Å. For the metalloligand, two carboxylate groups take the bidentate chelating coordinated fashion, while others linked Pr^{3+} ions with an oxygen monodentate coordination mode ((Figure 2). The Ni−Pr distances are 5.869(1) and 4.466(4) Å, respectively.

It is interesting to note that the Pr and Ni centers are alternately arrayed and linked by carboxyl groups to construct a novel heterometallic ring Pr_2Ni_2 with dimensions of 5.869 × 4.466 Å [5.656(4) × 4.327(3) Å for Ce_2Ni_2]. This ring composed of 3d and 4f metals assembles into an infinite one-dimensional (1D) chain (Figure 3). The dihedral angle between adjacent rings (rings 1 and 2) is 74.72°. The alternate rings (rings 1 and 3) are coplanar. These rings are further linked into a 3D framework in the *ab* plane through Ni−NCCN−Ni bridges with a Ni−Ni distance of 7.393(9) Å [7.183(9) Å for complex **2**; Figure 4).

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(14) Crystal data for **1**: $C_{20}H_{38}N_6Ni_2O_{18.50}PrS_2$, $M = 981.01$, orthorhombic, *Pccn*, $Z = 4$, $a = 15.532(3)$ Å, $b = 16.645(3)$ Å, $c = 14.127(3)$ Å, $V = 3652.3(13)$ Å^3, $D_x = 1.784$ Mg/m^3, $F(000) = 1980$, R1 = 0.0461, wR2 = 0.1153. Crystal data for **2**: $C_{20}H_{38}N_6Ni_2O_{18.50}CeS_2$, $M = 980.22$, orthorhombic, *Pccn*, $Z = 4$, $a = 15.030(16)$ Å, $b = 16.193(18)$ Å, $c = 13.563(15)$ Å, $V = 3301(6)$ Å^3, $D_x = 1.972$ Mg/m^3, $F(000) = 1976$, R1 = 0.0492, wR2 = 0.1263. Direct methods were determined with *SHELXS-97* and refinement on F^2 using *SHELXL-97*.

(15) Elem anal. Calcd for $C_{20}H_{38}N_6Ni_2O_{18.50}PrS_2$ (**1**): C, 24.49; H, 3.90; N, 8.57. Found: C, 24.45; H, 3.92; N, 8.52. Calcd for $C_{20}H_{38}N_6Ni_2O_{18.50}CeS_2$ (**2**): C, 24.51; H, 3.91; N, 8.57. Found: C, 24.47; H, 3.95; N, 8.51.

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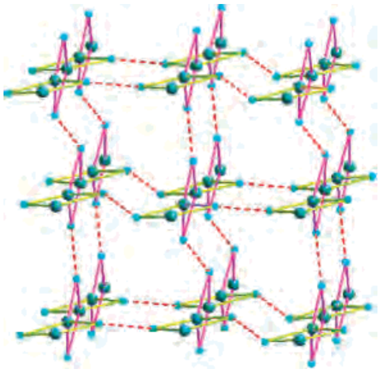

Figure 4. 3D topology of complex **1**. Thick lines: carboxyl bridges. Dashed lines: −NCCN− bridges. Green: Pr. Blue: Ni.

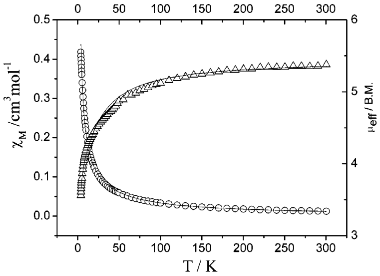

Figure 5. χ_M (○) vs T and μ_{eff} (△) vs T plots for complex **1**. The solid lines represent the theoretical values based on the equations.

The Fourier transform IR spectra of complexes **1** and **2** are similar. For complex **1**, all spectra show a broad band at ca. 2900−3700 cm^{-1}, mainly due to $\nu(H_2O)$ centered at about 3416 cm^{-1}. A very strong band appears at 1591 cm^{-1} due to the antisymmetric stretching of carboxyl groups, and the symmetrical carboxyl stretching band appears at 1385 cm^{-1}. Another strong band at 2105 cm^{-1} is attributed to ν(SCN) stretching.

Variable-temperature magnetic susceptibility data (1.8−300 K) at a magnetic field strength of 5 kG were collected for complexes **1** (Figure 5) and **2** (Figure 6 in the Supporting Information). These complexes show similar magnetic properties. For complex **1**, the μ_{eff} value at room temperature was 5.38 μ_B, a value close to 5.37 μ_B for an isolated Pr^{III} ion in the $^3H_4$ ground state ($g = {}^4/_5$) and two isolated Ni^{II} ions. Upon cooling, the μ_{eff} value decreases slowly, where the μ_{eff} value is 4.87 μ_B at 50 K. Below 50 K, the μ_{eff} value falls sharply to 2.85 μ_B at 2 K.

Obviously, a strictly theoretical treatment of magnetic properties for such a complicated 3D system cannot be carried out because of this topology and the large anisotropy of the Pr^{III} ion. However, to obtain a rough quantitative estimate of the magnetic interaction parameters between paramagnetic species, we assume that the total magnetic susceptibility χ_{tot} is given by the sum of the isolated Ni^{II} (eq 1) and Pr^{III} ions:

$$X_{tot} = \chi_{Pr} + 2\chi_{Ni}$$

$$\chi_{Ni} = \frac{Ng^2\beta^2}{3KT}S(S+1) \tag{1}$$

The Pr^{3+} ion has a $^3H_4$ ground term ($J = 4$). In a axial crystal field, the Pr^{3+} ion may exhibit a splitting of the m_J energy levels ($\hat{H} = \Delta\hat{J}_z^2$).[17−19] Thus, χ_{Pr} can be described by the expression (eq 2) previously derived by Oconnor and co-workers.[17] In the expression, Δ is the zero-field-splitting

$$\begin{aligned}\chi_{Pr} = \frac{Ng^2\beta^2}{KT}&[2\exp(-\Delta/4KT) + 8\exp(-4\Delta/KT) + \\ &18\exp(-9\Delta/KT) + 32\exp(-16\Delta/KT)]/ \\ &[1 + 2\exp(-\Delta/4KT) + 2\exp(-4\Delta/KT) + \\ &2\exp(-9\Delta/KT) + 2\exp(-16\Delta/KT)]\end{aligned} \tag{2}$$

parameter. Then the zJ' parameter based on the molecular field approximation is introduced (eq 3) to roughly simulate the magnetic interactions between the paramagnetic species.[20]

$$\chi_{pot} = \chi_{tot}/[1 - zJ'\chi_{tot}/Ng^2\beta^2] \tag{3}$$

The parameters obtained by the simulation of the experimental data using the above expression are $g = 2.06$. $\Delta = 2.83$, and $zJ' = -0.6$ cm^{-1}. The agreement factor R defined here as $\sum_i(X_i^{obs})^{-1}(X_i^{obs} - X_i^{calc})^2$ is equal to 7.51 × 10^{-4}.

For complex **2**, the magnetic susceptibility expression for Ce^{III} based on $\hat{H} = \Delta\hat{J}_z^2$) is as follows:

$$\chi_{Ce} = \frac{Ng^2\beta^2}{KT} \times \left[\frac{\frac{50}{4}\exp(-25\Delta/4KT) + \frac{18}{4}\exp(-9\Delta/4KT) + \frac{1}{2}\exp(-\Delta/4KT)}{2\exp(-25\Delta/4KT) + 2\exp(-9\Delta/4KT) + 2\exp(-\Delta/4KT)}\right]$$

The parameters obtained by the simulation of the experimental data using the above expression are $g = 2.07$, $\Delta = 1.00$, and $zJ' = -0.5$ cm^{-1}. The agreement factor R defined here as $\sum_i(X_i^{obs})^{-1}(X_i^{obs} - X_i^{calc})^2$ is equal to 4.51 × 10^{-4}.

In conclusion, we report two novel 3d−4f mixed complexes based on a binuclear unit [Ni$_2$TTHA(SCN)$_2$]$^{4-}$. The results show that these complexes form a 3D framework, comprised of an unusual infinite 1D chain based on heterometallic Ln$_2$Ni$_2$ rings. Two points are worth mentioning: First, this report provides an available way of constructing 3d−4f complexes through diffusion of the synthesis. Second, H$_6$TTHA as a suitable ligand can be used as a structure-directing agent to form other 3d−4f mixed complexes. The systematic and detailed investigation of 3d−4f coordination polymers associated with H$_6$TTHA is currently underway.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2**, additional figures (Figure 6), and magnetic susceptibility data. This material is available free of charge via the Internet at http://pubs.acs.org.

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