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From Metalloligand to Interpenetrating Channels: Synthesis, Characterization, and Properties of a 2p−3d−4f Heterometallic Coordination Polymer $\{[Na_5Cu_8Sm_4(NTA)_8(ClO_4)_8(H_2O)_{22}]\cdot ClO_4\cdot 8H_2O\}_n$

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A novel 3D heteropolymetallic coordination polymer, $\{[Na_5Cu_8Sm_4(NTA)_8(ClO_4)_8(H_2O)_{22}]\cdot ClO_4\cdot 8H_2O\}_n$ (H_3NTA = nitrilotriacetic acid), based on the metalloligand $[Cu(NTA)]^-$, has been prepared and characterized by X-ray crystal diffraction. The single-crystal structure shows that the complex forms a 3D framework with interpenetrating 1D channels along the *a* and *b* axes, respectively. These channels construct 2D "tube net" layers in the *ab* plane. The temperature-dependent magnetic properties have been studied and showed the presence of antiferromagnetic couplings between Cu^{II} ions. The investigation of ion exchange reveals that the uncoordinated perchlorate anions that filled in the channels can be exchanged by anions of tetrafluoroborate.

The design and synthesis of three-dimensional (3D) coordination polymers or open metal−organic frameworks (MOFs) based upon the principle of crystal engineering have been a field of rapid growth in supramolecular and metal chemistry not only because of their diverse and interesting structures but also because of their potential applications as functional materials in ion exchange, gas absorption, catalysis, nonlinear optical devices, and magnetism.[1−3] Up to now, a great many coordination polymers including a 3d−4f heterometallic series have been synthesized by the conventional self-assembly reactions.[4] However, the assembly of 3D heterometallic coordination polymers, especially ones containing more than two kinds of metals, is still less successful and is an arduous challenge for chemists.[5] Choosing appropriate polycarboxylic acids as structure-directing agents is a successful synthetic strategy for the construction of heterometallic coordination polymers and advanced frameworks.[4f,6] Nitrilotriacetic acid (H_3NTA) as a common polycarboxylic acid ligand is often used to prepare transition-metal complexes[7] and lanthanide complexes.[8] However, the reports

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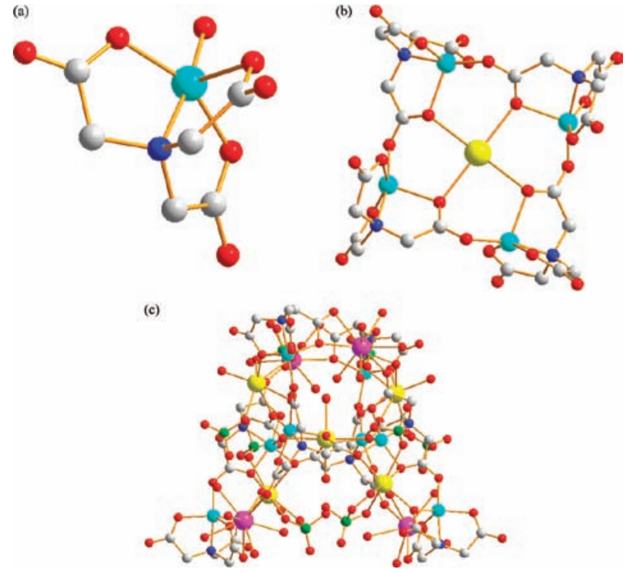

Figure 1. (a) Metalloligand; (b) the crown-ether-like unit; (c) the heptadecanuclear cluster as a SBU. (H atoms are omitted for clarity.) Color code: pink, Sm; turquoise, Cu; yellow, Na; green, Cl; gray, C; blue, N; red, O.

on 3d−4f coordination polymers with H_3NTA are rare.[9] Yet H_3NTA is a good candidate to construct heterometallic coordination polymers because of its flexible and various coordination donors. Its nitrilo N and carboxylate O atoms prefer to chelate a d-metal ion to form a “metalloligand”,[4c,9a,10] and noncoordinated carboxylate O atoms can act as potential donors for other metal ions. If these donors do ligate other metal (p-, d-, and f-metal) ions, an assembly process will occur that leads to the formation of a heterometallic coordination polymer.

In the context of this background, we synthesized a novel 3D 2p−3d−4f heterometallic coordination polymer, $\{[Na_5Cu_8Sm_4(NTA)_8(ClO_4)_8(H_2O)_{22}]\cdot ClO_4\cdot 8H_2O\}_n$ (**1**), based on a “metalloligand” (Supporting Information).[11,12] The complex were obtained stepwisely: (a) synthesis of a “metalloligand”, $[Cu(NTA)]^-$; (b) reaction of a “metalloligand”, $[Cu(NTA)]^-$ with $Sm(ClO_4)_3$. We failed to obtain the single crystals of the complex by a “one-pot” method, although we tried many times. Therefore, the stepwise method may be necessary to obtain single crystals of the complex, which offers an opportunity to link together these 2p, 3d, and 4f metals.

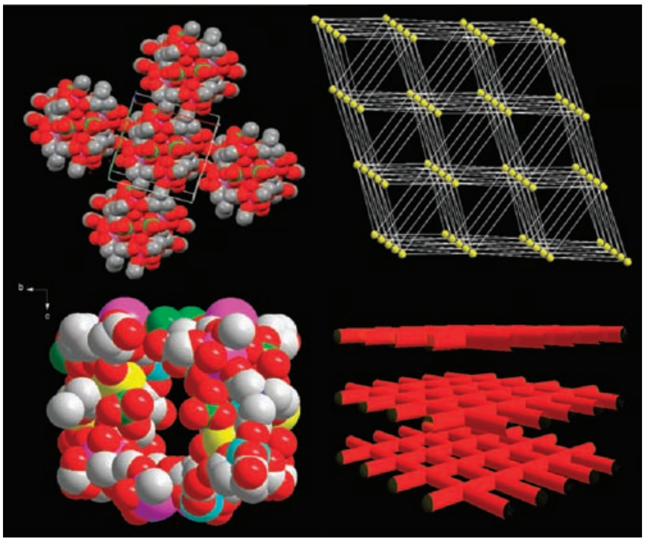

Figure 2. Upper (left to right): 2D layer constructed by SBUs in the *ab* plane and a simplified 3D network perspective view of compound **1**. Yellow balls represent SBUs. Lower: Packing view of compound **1** showing the “gourd-shaped” channels along the crystallographic *a* axis and “tube net” layers in the *ab* plane. (H atoms, uncoordinated perchlorate anions, and free water molecules are omitted for clarity.) Color code: pink, Sm; turquoise, Cu; yellow, Na; green, Cl; gray, C; blue, N; red, O.

The single-crystal analysis reveals that the complex crystallizes in the tetragonal system, space group $P\bar{4}2(1)c$, and is a quite unique 3D open MOF constructed via NTA^{3-}, Na^{I}, Cu^{II}, and Sm^{III}. As shown in Figure 1, the Cu^{II} ion is chelated by a NAT^{3-} ligand to form a metalloligand, which acts as a quinquedentate ligand. Also four metalloligands are linked together by carboxylate O atoms to form a crown-ether-like structural unit, in which a Na ion was chelated. From the viewpoint of synthetic chemistry, the Na ion should be considered as a cationic template to assist in the formation of the crown-ether-like units (Figure 1b). The crown-ether-like unit acting as a multidentate bridging ligand is connected with four other metalloligands, and also four Sm^{III} and four Na^{I} ions by carboxylate O atoms, leading to the formation of a heptadecanuclear cluster (SBU). To the best of our knowledge, this kind of heterometallic heptadecanuclear cluster has not been reported prior to this work. The coordination spheres of metal ions are completed by O atoms from water molecules, perchlorate anions, and other SBUs (Figure 1c and Figures S1−S4 in the Supporting Information). The SBU is bonded directly with four other SBUs by Sm−O bonds shoulder by shoulder in the *ab* plane, constructing 2D layers (Figure 2). Connection of the 2D layers through Sm−O bonds gives rise to an infinite 3D framework with highly ordered 1D “gourd-shaped” channels along the *a* and *b* direction, respectively (Figures 2 and S5 in the Supporting Information). These channels penetrate mutually in the *ab* plane and form 2D “tube net” layers (Figure 2), in which uncoordinated ClO_4^- and crystal water molecules are filled. The potential free volume of the complex is about 1713.4 $Å^3$, comprising 23.3% of the crystal volume, as calculated by the program *PLATON*[13] (guest water molecules are not included in the calculations). In addition, if the SBUs can be simplified

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[11] Crystal data for **1**: $C_{48}H_{108}N_8Cl_9Na_5Cu_8Sm_4O_{114}$, $M_r = 4165.26$, tetragonal, $P\bar{4}21c$, $a = b = 17.0410(14)$ Å, $c = 25.371(2)$ Å, $V = 7367.6(10)$ $Å^3$, $Z = 2$, $D_c = 1.878$ g cm^{-3}, $F(000) = 4104$, $S = 1.07$. R1 = 0.0461, wR2 = 0.1302 for all data. Direct methods were determined with *SHELXTL-97* and refinement on F^2 using *SHELXTL-97*.

[12] Elem anal. Calcd for **1**: C, 13.84; H, 2.61; N, 2.69. Found: C, 13.81; H, 2.65; N, 2.71.

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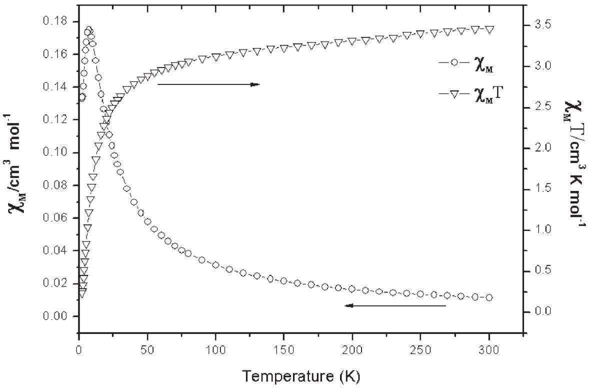

Figure 3. Thermal dependence of the $\chi_M T$ and χ_M curves.

as vertexes, the 3D framework can be represented as a (3, 12) net (Figure 2).

The temperature dependence of the magnetic susceptibility of **1** has been performed on a Quantum Design MPMS SQUID magnetometer at a 2000 Oe field in 1.8−300 K. The diamagnetic correction was evaluated by using Pascal's constants. As shown in Figure 3, the observed $\chi_M T$ value for **1** at 300 K is 3.46 cm^3 K mol^{-1}, close to the calculated value of 3.36 cm^3 K mol^{-1} for four Sm^{III} ions with a free-ion ground state ($J = 6$, $g = {}^2/_7$)[14] and eight spin-only Cu^{II} ions. Upon cooling, $\chi_M T$ of **1** decreases slowly from 300 to 60 K and then drops very rapidly to reach 0.24 cm^3 K mol^{-1} at 1.8 K. Because Na^I ions are diamagnetic, such magnetic behaviors should be a combined effect of the crystal-field splitting of Sm^{III} ions, thermal depopulation of the free-ion excited states, and exchange-coupled interaction between the metal ions.[5c] From χ_M vs T curve, χ_M reaches a maximum at around 7 K, which indicates the existence of antiferromagnetic couplings within the paramagnetic centers.[6c] The magnetic susceptibility above 7 K obeys the Curie−Weiss law with a Curie constant of 3.55 cm^3 K mol^{-1} and a Weiss constant θ of −11.82 K suggests antiferromagnetic interactions and spin-coupling effects of Sm^{III} ions. According to the literature,[10c,15] the contribution of Sm^{III} to $\chi_M T$ is feeble and the Sm^{III}−Cu^{II} exchange interaction is very weak. Therefore, the Cu^{II}−Cu^{II} antiferromagnetic couplings play a predominate role in the magnetic behavior of **1**.

As revealed by the crystal structure, the uncoordinated perchlorate anions were loosely bound to the framework, which indicates that they might be replaced by other anions under appropriate conditions. To investigate the ion-exchange properties, a well-ground sample of the compound was suspended in a $NaBF_4$ solution of MeOH/H_2O with stirring to allow anion exchange (see the Supporting Information). The IR spectrum of the exchanged product (Figure S6 in the Supporting Information) showed the disappearance of intense bands (1200−1050 cm^{-1}), which originated from uncoordinated ClO_4^- and the appearance of BF_4^- peaks at 1114, 1087, and 1025 cm^{-1}, indicating that the sample had undergone an ion-exchange process[16] and the structure of compound **1** had changed, which had been validated by powder X-ray diffraction (PXRD) (Figure 4). When the ion-exchanged compound was repeated, with the process of ion exchange with $NaClO_4$ instead of $NaBF_4$ at 60 °C, the characteristic BF_4^- peaks disappeared and ClO_4^- bands appeared again in the range of 1200−1050 cm^{-1} and the structure of compound was reestablished (Figures 4 and S6 in the Supporting Information).

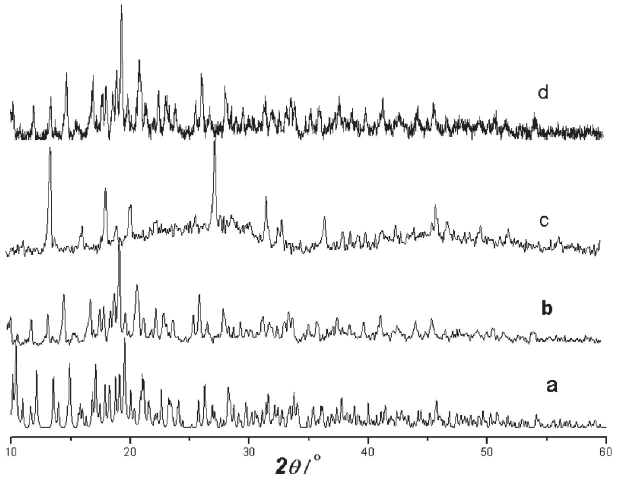

Figure 4. PXRD patterns of the ion-exchange process: (a) the simulated PXRD pattern of **1** calculated from the single-crystal structure; (b) as-synthesized **1**; (c) the ion-exchanged compound; (d) the ion-exchanged compound exchanged with $NaClO_4$.

In summary, we report a novel 3D 2p−3d−4f heterometallic coordination polymer with 2D "tube net" layers based on a metalloligand $[Cu(NTA)]^-$. The magnetism properties are investigated, together with the interesting ion-exchanged properties. The results presented herein indicate that the method of metalloligand provides an applicable way of constructing heterometallic MOFs, and H_3NTA can be used as a structure-directing agent to form heteropolymetallic complexes. The systematic and detailed investigation of 2p−3d−4f coordination polymers associated with H_3NTA is currently underway.

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Supporting Information Available: X-ray crystallographic file in CIF format for **1**, additional figures (Figures S1−S6), and an ion-exchange reaction section. This material is available free of charge via the Internet at http://pubs.acs.org.

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