A Novel Lanthanide–Transition Metal Complex Constructed by Orotic Acid

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Hydrothermal reaction of $Cu(CH_3COO)_2{\cdot}5H_2O$ and $NdCl_3{\cdot}6H_2O$ with orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, H_3dtpc) in water gave rise to a novel polymeric complex, $[Nd_2Cu_3(Hdtpc)_6(H_2O)_4]_n$, with two-dimensional layer structure. Nd(III) atom is nine-coordinated by nitrogen and oxygen atoms of Hdtpc ligands and water molecules and Cu(II) atom is four-coordinated by two chelated Hdtpc in a square planar geometry. The hydrogen bond interactions among layers lead to the formation of three-dimensional network structure.

Owing to the fascinating coordination behavior and the significance in biosynthesis of pyrimidine nucleotides of DNA[1] and antitumor activity for some of its metal complexes,[2,3] orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, H_3dtpc) has attracted much attention in the past ten years.[1] Many novel complexes constructed by orotic acid have been reported in recent years.[4,5] The most interesting characters of orotic acid ligand are as follows: 1) it has multiple coordination sites that may form higher dimensional structures; 2) it possesses an asymmetric geometry that may lead to acentric crystal structure; 3) it contains potential hydrogen-bond acceptor, hydrogen-bond donor, hydrogen-bond acceptor (ADA) array.[1] Hence, orotic acid ligand may coordinate to different metal ions to form diversity structures. Moreover, the notable coordination characters also make the ligand to become very good choice for the construction of polymeric and supramolecular structures. However, in previous works, orotic acid was often used as bidentate dianionic ligand to chelate to one metal ion, after deprotonating the carboxylic group and its adjacent nitrogen atom.[1] Although Nepveu reported several polynuclear manganese(II) complexes using orotic acid as μ_3-bridging ligand,[5] up to date, there are no systematic studies on the complexes with bridging orotic ligands, especially for the polymeric complexes owing to the weak coordination ability of the carbonylic oxygen and the difficulty for single crystal growth. Herein we report the hydrothermal synthesis and crystal structure of a novel Nd(III)–Cu(II) coordination polymer containing three types of μ_3-bridging orotate ligand, $[Nd_2Cu_3(Hdtpc)_6(H_2O)_4]_n$ (**1**).

The reaction of $Cu(OAc)_2{\cdot}6H_2O$, $NdCl_3{\cdot}6H_2O$, orotic acid (H_3dtpc) and water at 160 °C in a molar ratio of 2:1:2:3500 yielded crystals of **1** suitable for X-ray diffraction analysis.[6] The crystallographic analyses[7] reveal that the complex is a two-dimensional layer polymer consisting of $[Nd_2Cu_3(Hdtpc)_6(H_2O)_4]$ building units, as shown in Figure 1.

The carboxylic group and its adjacent nitrogen atom of H_3dtpc are deprotonated during the hydrothermal reaction. Each Cu(II) atom is chelated by two $Hdtpc^{2-}$ ligands through one carboxylic O and the deprotonated N atoms in a square planar geometry, with the average Cu–O and Cu–N distances being 1.917 and 2.015 Å, respectively. Every Nd(III) atom is nine-coordination by four carboxylic and three carbonyl oxygen atoms from three ligands and two coordinated water molecules, with the average Nd–O distance being 2.523 Å. Three kinds of μ_3-bridging Hdtpc ligands are present in the molecule: a) the carboxylic group acts as chelating–bridging ligand, chelating a lanthanide atom and bridging a copper atom, the carbonylic oxygen at the *para* position of the deprotonated nitrogen atom attaches to another lanthanide atom (Scheme 1a); b) one of the carboxylic oxygen atom links a copper and a lanthanide atom, simultaneously, the carbonyl oxygen at the *ortho* position of the deprotonated nitrogen atom attaches to a lanthanide atom (Scheme 1b); c) the carboxylic group acts as bridging ligand, linking a lanthanide and a copper atom, the carbonyl oxygen at the *ortho* position of the deprotonated nitrogen atom attaches to another lanthanide atom (Scheme 1c). Thus, the $[Nd_2Cu_3(Hdtpc)_6(H_2O)_4]$ units are connected by Nd–O bonds from the carboxylic and carbonyl oxygens to form a one-dimensional chain structure, with average Nd–Cu distance being 4.240 Å, illustrating the lack of any direct interaction between Nd and Cu.

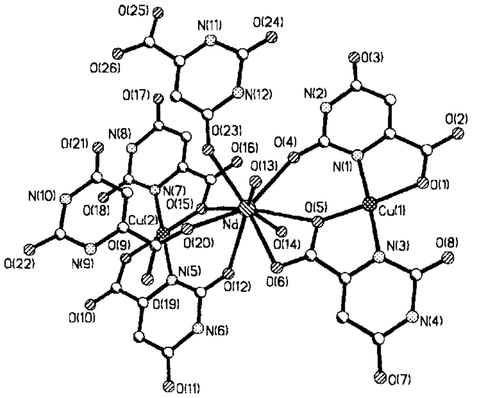
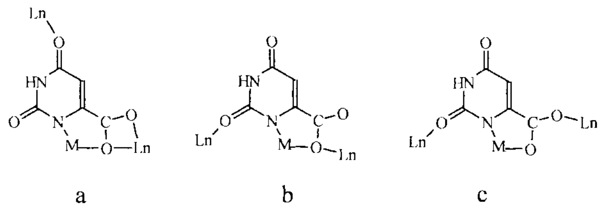


Figure 1. Local coordination environment around metal ions. Selected bond lengths(Å) and angles(°): Nd-O(4), 2.492(9); Nd-O(5), 2.627(11); Nd-O(6), 2.645(11); Nd-O(12), 2.593(11); Nd-O(13), 2.422(12); Nd-O(14), 2.399(12); Nd-O(15), 2.591(10); Nd-O(20), 2.455(9); Nd-O(23), 2.485(13); O(14)-Nd-O(4), 78.1; O(13)-Nd-O(4), 78.4; O(13)-Nd-O(14), 141.6; O(20)-Nd-O(4), 147.8; O(14)-Nd-O(12), 64.2; Cu(1)-O(1), 1.896(10); Cu(1)-O(5), 1.939(10); Cu(1)-N(1), 2.008(13); Cu(1)-N(3), 2.022(13); Cu(2)-O(9), 1.890(10); Cu(2)-O(15), 1.890(10); Cu(2)-N(5), 1.988(13); Cu(2)-N(7), 1.988(13); O(5)-Cu(1)-O(1), 176.9(5); O(5)-Cu(1)-N(1), 93.4(5); O(1)-Cu(1)-N(1), 83.9(5); O(1)-Cu(1)-N(3), 99.6(5); N(1)-Cu(1)-N(3), 176.0(5); O(9)-Cu(2)-O(15), 180.00(2); O(9)-Cu(2)-N(5), 84.8(5); O(9)-Cu(2)-N(15), 95.2(5).



Scheme 1

The structure can be viewed as copper building block, [Cu(Hdtpc)$_2$], connected by Nd(III) linker, each Nd(III) linker connects four [Cu(Hdtpc)$_2$] blocks, and each [Cu(Hdtpc)$_2$] to two Nd(III) linkers, forming the two dimensional structure. In other words, the structure can also be viewed as consisting of Nd–Cu ladders, in which the side pieces are formed by Nd chains and the rungs by [Cu(Hdtpc)$_2$] blocks, each two neighboring ladders are linked through Nd–O bonds, forming the final structure (Figure 2).

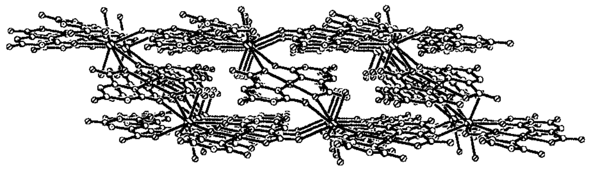


Figure 2. The two-dimensional layer structure along *a* axis.

Because Hdtpc ligand contains potential hydrogen-bond acceptor and hydrogen-bond donor, each two adjacent layers are further linked by the hydrogen-bond interactions of coordinated water molecules and oxygen atoms of the ligands, leading to a three-dimensional network structure with the hydrogen bond distances of O···O ranging from 2.814 to 2.937 Å.

Detail studies, such as other complexes along with magnetic properties, are underway and will be reported in a full paper.

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References and Notes

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6 Synthesis of compound **1**: A mixture of $Cu(CH_3COO)_2 \cdot 5H_2O$ (0.1 g, 0.5 mmol), $NdCl_3 \cdot 6H_2O$ (0.09 g, 0.25 mmol) and H_3dtpc (0.08 g, 0.5 mmol) in 16 mL H_2O was placed in a stainless steel vessel and heated to 160 °C for 60 h, then cooled to room temperature during 5 h, the blue-black block crystals were obtained and collected by filtration and washed with water. Yield: 45%. Anal. Calcd: C, 24.42; H, 1.37; O, 30.36%. Found: C, 24.45; H, 1.42; O, 30.34%.

7 Crystallographic data for **1**: Crystal dimensions 0.20 × 0.25 × 0.45 mm, Formula: $C_{30}H_{20}N_{12}Cu_3Nd_2O_{28}$, fw = 1475.68, triclinic, space group $P1$, a =9.9104(4), b = 9.9563(4), c = 11.3623(5) Å, α = 101.345(2), β = 109.658(2), γ = 106.442(2)°, V = 958.26(7) Å^3, Z = 1, T=293 K, D_c = 2.557 g/cm^3, 358 variable parameters, R = 0.0749 and R_w = 0.1782 for 3399 independent reflections with $F \geq 2.0 \sigma(F_o)$. The intensity data of **1** were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. The structure was solved by directed methods and the positions of H atoms were generated from difference Fourier maps. All of the calculations were performed on a Legand computer by using the SHELXTL-93 program package. Detail crystallographic data of **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC-162620).