研究简报

含乳清酸配体的两个单核配合物的合成与晶体结构

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Syntheses and Crystal Structures of Two Mononuclear Complexes with Orotic Acid

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The two complexes $[Cu(C_5H_2N_2O_4)(H_2O)_3]\cdot 2H_2O$ (**1**) and $[Ni(C_5H_2N_2O_4)(H_2O)_4]\cdot H_2O$ (**2**) were synthesized by self-assembly reactions of $Cu(NO_3)_2\cdot 3H_2O$ or $Ni(CH_3COO)_2\cdot 4H_2O$ with orotic acid (2, 6-dioxo-1, 2, 3, 6-tetrahydro-4-pyrimidinecarboxylic acid), respectively. Their crystal structures were determined by single-crystal X-ray diffraction analyses. Crystallographic data for complex **1**: $C_5H_8N_2CuO_7\cdot 2H_2O$, $M_r = 307.7$, monoclinic $P2_1/n$, $a = 0.57710(1)$ nm, $b = 1.76863(6)$ nm, $c = 1.09955(4)$ nm, $\beta = 98.600(2)°$, $V = 1.109.63(6)$ nm^3, $Z = 4$, $D_c = 1.842$g·cm^{-3}, $\mu(Mo\,K\alpha) = 2.010$mm^{-1}, $F(000) = 628$, $R = 0.0436$, $wR = 0.1015$, And for complex **2**: $C_5H_{10}N_2NiO_8\cdot H_2O$, $M_r = 302.88$, orthorhombic $Pbcn$, $a = 2.0763(1)$nm, $b = 1.69355(9)$ nm, $c = 0.73478(4)$nm, $V = 2.5837(2)$nm^3, $Z = 8$, $D_c = 1.557$g·cm^{-3}, $\mu(Mo\,K\alpha) = 1.538$ mm^{-1}, $F(000) = 1248$, $R = 0.0545$, $wR = 0.1305$. The X-ray analyses revealed that the Cu(Ⅱ) and Ni(Ⅱ) atoms are both coordinated by carboxylic O atom and contiguous N atom of the pyrimidine ring. In complex **1** the Cu(Ⅱ) atom has a slightly distorted square pyramid coordination environment with additional three water molecules, while in complex **2** the Ni(Ⅱ) atom adopts a slightly distorted octahedral geometry with additional four water molecules. The three-dimensional frameworks of the two complexes are formed by intermolecular hydrogen bonding interactions. CCDC: **1**, 204881; **2**, 204882.

Keywords: synthesis crystal structure copper(Ⅱ) complex nickle(Ⅱ) complex orotic acid

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0 Introduction

In the past few years, the molecular-based magnetic properties of heteronuclear complexes simultaneously comprising lanthanide and transition metal ions have attracted increasing interest[1~6]. In our laboratory, we have synthesized such type of complexes with different carboxylic bridging ligands[7~10]. As an extension of this research area, our present work aims to synthesize novel complexes of rare earth and transition metal by using orotic acid as a bridging ligand. In the course of our investigation two new complexes of $[Cu(C_5H_2N_2O_4)(H_2O)_3]\cdot 2H_2O$ (**1**) and $[Ni(C_5H_2N_2O_4)(H_2O)_4]\cdot H_2O$ (**2**) were obtained. Since they contain one un-coordinated O atom of carboxyl group, two O atoms of the neutral carboxamide group, and one of the N atoms of the pyrimidine ring, they can be used as "metallic ligand" to bind lanthanide metal ions for the subsequent preparation of heteronuclear complexes. It is noted that the coordination chemistry of orotic acid has been studied widely for its complexes which play an important role in bioinorganic chemistry, pharmaceutics, material science and other aspects[11~13]. Complexes formulated as $[M(C_5H_2N_2O_4)(H_2O)_n]\cdot mH_2O$ ($n = 2 \sim 4$, $m = 1 \sim 2$ and M = Co, Ni, Zn, Cu, Mg, etc) have been reported[14~17, 11]. In this paper, we will report the syntheses and structures of two new complexes with orotic acid ligand.

1 Experimental

1.1 Synthesis

Complex **1**: $Cu(NO_3)_2\cdot 3H_2O$ aqueous solution (3mL, 0.17mol · L^{-1}) was carefully dropped into orotic acid aqueous solution(10mL, 0.05mol · L^{-1}) and then tetramethylammonium hydroxide (25% solution) was added to adjust pH = 9. After the mixture solution was stirred thoroughly at room temperature for 5h, the resulting mixture was filtered and left undisturbedly at room temperature. The transparent blue needle crystals were yielded after a week. The yield is 42.4% (calculated by Cu).

Complex **2**: $Ni(CH_3COO)_2\cdot 4H_2O$ aqueous solution (3mL, 0.17mol · L^{-1}) was carefully dipped into orotic acid mixed solution of EtOH and water (1∶1, 10mL, 0.05mol · L^{-1}) and then tetramethylammonium hydroxide (25% solution) was added to adjust pH = 8. After the mixture solution was stirred thoroughly at room temperature for 5h, the resulting mixture was filtered and left undisturbedly at room temperature. The transparent green prism crystals were yielded after a week. The yield is 33.5% (calculated by Ni).

1.2 Crystal Structure Determination

A blue needle crystal with dimensions of 0.42mm × 0.34mm × 0.22mm of complex **1** and a green prism crystal with dimensions of 0.42mm × 0.28 mm × 0.15mm of complex **2** were selected for X-ray diffraction analyses. Data collections were performed on a Siemens SMART CCD diffractometer with graphite monochromatic Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm). Intensity data were collected in the range of $2.20° < \theta < 25.05°$ for complex **1** and $3.18° < \theta < 25.04°$ for complex **2** by ω scan technique at 293K, yielding 3373 and 7154 reflections, of which 1737 and 1399 observed reflections with $I > 2\sigma(I)$ were used to refine the structures, respectively. The SIEMENS SAINT software was used for data reduction. Empirical absorption correction SADABS was used. The structures were solved by direct methods, which revealed the positions of the metal atoms using SIEMENS SHELXTL Version 5.0 package of crystallographic software[18]. The remaining non-hydrogen atoms were located by successive different Fourier synthesis. Hydrogen atoms of pyrimidine rings in two complexes were added according to theoretical models. Hydrogen atoms of water molecules were located from the difference Fourier synthesis and refined isotropically with the O-H distances fixing on 0.095nm in the complex **1**. In the complex **2**, the hydrogen atoms (H1A, H2A. H3A, H4A) of coordinated water molecules were located from the difference Fourier synthesis and refined isotropically with the O-H distances fixing on 0.095nm, and the other hydrogen atoms of coordinated water molecules were generated in idealized positions with the O-H distances fixing on 0.095nm according to the hydrogen-bondings pattern, while the hydrogen atoms of

lattice water molecules (O5W, O6W) were not included. The structures were refined using full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. For complex **1**, the final $R = \sum | (|F_o| - |F_c|) | / \sum |F_o| = 0.0436$, $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.1015$ with 194 parameters, $w = 1/[\sigma(F_o^2) + (0.0657P)^2 + 5.2023P]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 1.090$, $(\Delta/\sigma)_{max} = 0.005$, $\Delta\rho_{max} = 459 e \cdot nm^{-3}$, $\Delta\rho_{min} = -514 e \cdot nm^{-3}$. For complex **2**, the final $R = 0.0545$, $wR = 0.1305$ with 191 parameters, $w = 1/[\sigma(F_o^2) + (0.0833P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 1.098$, $(\Delta/\sigma)_{max} = 0.009$, $\Delta\rho_{max} = 1055 e \cdot nm^{-3}$, $\Delta\rho_{min} = -636 e \cdot nm^{-3}$.

CCDC: **1**, 204881; **2**, 204882.

2 Results and Discussion

The selected bond lengths and bond angles are listed in Tables 1 and 2 for complex **1** and **2**, respectively.

Table 1　Selected Bond Lengths(nm) and Bond Angles(°) for Complex 1

Cu(1)-O(11)	0.1982(2)
Cu(1)-N(1)	0.2011(2)
Cu(1)-O(1W)	0.2000(3)
Cu(1)-O(2W)	0.1982(2)
Cu(1)-O(3W)	0.2403(2)
C(11)-O(12)	0.1239(3)
C(11)-O(11)	0.1271(3)
O(11)-Cu(1)-O(2W)	171.1(1)
O(11)-Cu(1)-O(1W)	89.2(1)
O(2W)-Cu(1)-O(1W)	90.4(1)
O(11)-Cu(1)-N(1)	81.91(8)
O(2W)-Cu(1)-N(1)	98.2(1)
O(1W)-Cu(1)-N(1)	171.0(1)
O(11)-Cu(1)-O(3W)	98.41(9)
O(2W)-Cu(1)-O(3W)	90.5(1)
O(1W)-Cu(1)-O(3W)	90.4(1)
N(1)-Cu(1)-O(3W)	92.10(9)

Complex **1**: The X-ray diffraction result shows that the Cu atom is five-coordinate, which can be described as a slightly distorted tetragonal pyramid (Fig. 1(a)). The Cu atom is nearly situated at the center of the basal plane defined by the carboxylate O atom (Cu-O11: 0.1982(2) nm), the deprotonated adjacent N atom of the pyrimidine ring (Cu-N1: 0.2011(2)nm), and two water molecules (Cu-O(1W): 0.2000(3), Cu-O(2W): 0.1982(2)nm). Meanwhile the apical position is occupied by another water molecule with Cu-O(3W) distance of 0.2403(2) nm. The distortion of tetragonal pyramid is also reflected in the angles with the range of 89.2(1)°~98.41(9)° for *cis*-angles deviated from 90°, and 171.0(1)° and 171.1(1)° for *trans*-angles deviated from 180°, respectively. The distances of Cu-O(1W) and Cu-O(2W) are much shorter than that

Table 2　Selected Bond Lengths(nm) and Bond Angles(°) for Complex 2

Ni(1)-O(11)	0.2037(3)
Ni(1)-N(11)	0.2052(3)
Ni(1)-O(4W)	0.2052(3)
Ni(1)-O(1W)	0.2061(4)
Ni(1)-O(3W)	0.2078(3)
Ni(1)-O(2W)	0.2083(3)
O(12)-C(11)	0.1239(5)
O(11)-C(11)	0.1254(5)
C(11)-C(12)	0.1531(6)
O(11)-Ni(1)-N(11)	79.9(1)
O(11)-Ni(1)-O(4W)	95.2(2)
N(11)-Ni(1)-O(4W)	174.9(2)
O(11)-Ni(1)-O(1W)	90.4(2)
N(11)-Ni(1)-O(1W)	89.5(1)
O(4W)-Ni(1)-O(1W)	89.1(2)
O(11)-Ni(1)-O(3W)	89.5(1)
N(11)-Ni(1)-O(3W)	93.6(1)
O(4W)-Ni(1)-O(3W)	87.9(1)
O(1W)-Ni(1)-O(3W)	176.9(1)
O(11)-Ni(1)-O(2W)	174.0(1)
N(11)-Ni(1)-O(2W)	94.3(1)
O(4W)-Ni(1)-O(2W)	90.6(2)
O(1W)-Ni(1)-O(2W)	91.1(1)
O(3W)-Ni(1)-O(2W)	89.3(1)

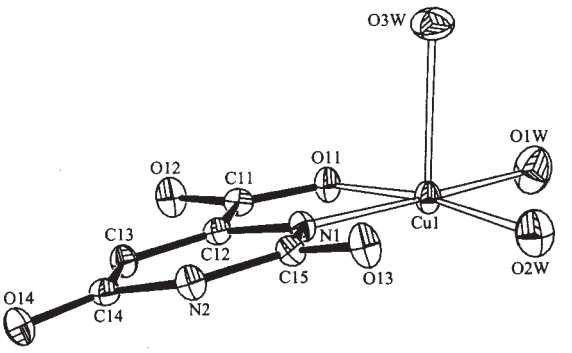

Fig. 1(a)　Molecular structure of complex **1** with thermal ellipse at the 30% probability level

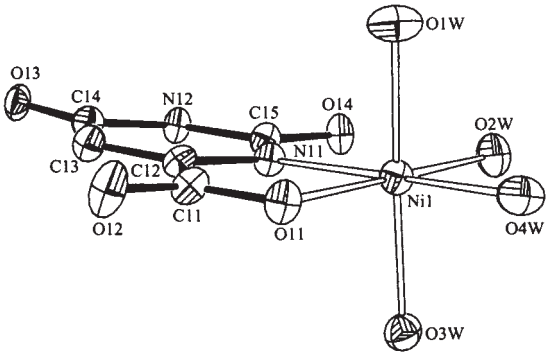

Fig. 1(b) Molecular structure of complex **2** with thermal ellipse at the 30% probability level

of Cu-O(3W) due to the Jahn-Tellller effects[19]. The structure of **1** is similar to that of complex $[Cu(NH_3)_2(C_5HN_3O_6)(H_2O)]$ in which two NH_3 molecules locate on the basal plane instead of two water molecules in **1**[20], and The bond distances around the Cu atom also have no significant differences in two complexes.

The two species of Cu complexes in **1** are linked to form a dimer by the hydrogen bonds of N2⋯O13 (0.2843(5) nm), and the dimers are linked by O3W⋯O14 hydrogen bonds with distance of 0.2771(5) nm to form a chain along the *a* axis, as shown in Fig. 2(a). Then hydrogen bonding interactions of O2W⋯O14 (0.3087(3)nm) and O1W⋯O14 (0.3093(3) nm) make the chains into a three-dimension framework along the [0 1 1] and [0 1 −1] directions with channels in which the lattice water molecules are located (Fig. 2(b)). The lattice water molecules form hydrogen bond each other (O4W⋯O5W: 0.2886(3)

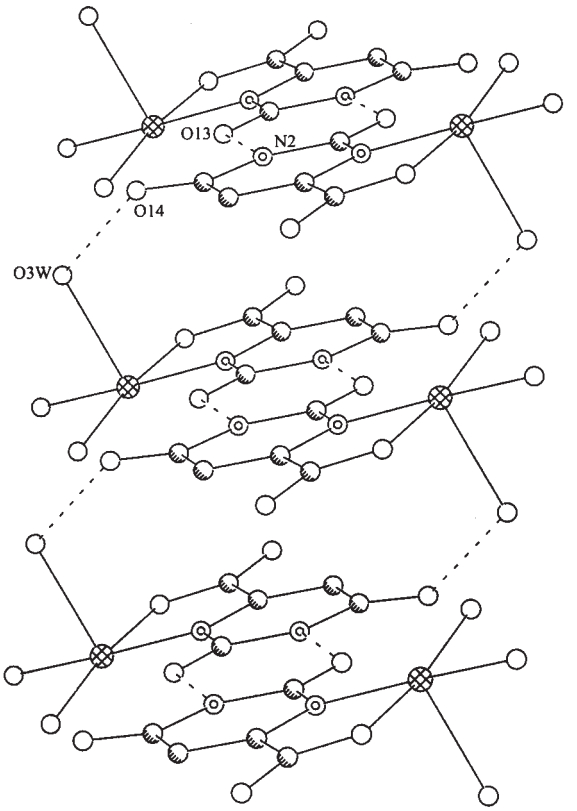

Fig. 2(a) Chain of complex **1** connected by hydrogen bonds extended along [100] direction.

nm), and they also form hydrogen bonds with coordinated water (O3W⋯O5W: 0.2793(3) nm) and carboxylate oxygen atom (O4W⋯O11: 0.3080(3) nm) simultaneously. The distances and angles of hydrogen bonds for complex **1** are listed in Table 3.

Complex **2**: The complex **2** is polymorphism to that $[Ni(C_5H_4N_2O_4)(H_2O)_4]\cdot H_2O$ reported by Karipides et al[14,16], whose space group is $P\bar{1}$. The Ni atom

Table 3 Hydrogen Bond Distances and Bond Angles of Complex 1

atom involve	distance/nm			angle/(°)
	O(N)-H	H⋯O	O(N)⋯O	O(N) − H⋯O
O4W − H4B⋯O12	0.0946(9)	0.189(1)	0.2829(3)	174(4)
O1W − H1B⋯O14[a]	0.0955(9)	0.2180(2)	0.3093(3)	160(4)
O2W − H2A⋯O14[b]	0.0953(9)	0.255(4)	0.3087(3)	116(3)
O3W − H3A⋯O14[c]	0.0944(9)	0.183(1)	0.2768(3)	173(2)
O3W − H3B⋯O5W[d]	0.0944(9)	0.187(1)	0.2793(3)	167(2)
O4W − H4A⋯O11[e]	0.095(1)	0.232(2)	0.3080(3)	137.1(2)
N2 − H11A⋯O13[f]	0.086	0.198	0.2841(3)	179.3
O5W − H5B⋯O4W[g]	0.0944(9)	0.198(1)	0.2886(3)	159.9(2)

Symmetry transformations used to generate equivalent atoms: (a) 0.5 − *x*, 0.5 + *y*, 0.5 − *z*; (b) −0.5 − *x*, 0.5 + *y*, 0.5 − *z*; (c) − *x*, − *y*, − *z*; (d) −0.5 + *x*, 0.5 − *y*, −0.5 + *z*; (e) 1 − *x*, − *y*, 1 − *z*; (f) −1 − *x*, − *y*, − *z*; (g) 2 − *x*, − *y*, 1 − *z*.

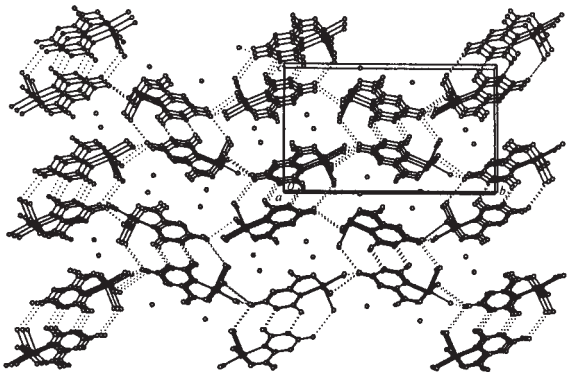

Fig. 2(b)　Three-dimensional framework of complex **1** formed through hydrogen bond interactions, the hydrogen bonds around the lattice water molecules are omitted for clarity
The hydrogen bonds are represented by dotted lines.

in **2** has slightly distorted octahedral coordination geometry, which is the same as its polymorphism[14, 16], as shown in Fig. 1(b) and the coordination modes of orotic anion is similar to that of **1**. The bond lengths related to the Ni atom in **2** are Ni-O(11): 0.2037(3) nm, Ni-N(11): 0.2052(3) nm, Ni-O(1W): 0.2061(4) nm, Ni-O(2W): 0.2083(3) nm, Ni-O(3W): 0.2078(3) nm, Ni-O(4W): 0.2053(3) nm, which are in good agreement with those found in its polymorphism.

The three-dimensional framework of **2** is constructed through the intermolecular hydrogen bonding interactions as illustrated in Fig. 3, which can be classified as six types: (i) O(coordinated water molecule) – H···O(oxygen atoms of carboxamide); (ii) O(coordinated water molecule) – H ··· O(coordinated water molecule); (iii) O(coordinated water molecule) – H···O(carboxylate oxygen atom); (iv) O(coordinated water molecule) – H···O(lattice water molecule); (v) O(lattice water molecule) -H ··· O(lattice water molecule); (vi) N···H – O(oxygen atoms of carboxamide). Two species of the molecule in **2** are connected by hydrogen bonds of type (i) (O1W···O13: 0.2715(5)nm, O3W···O13: 0.2724(5)nm) to form a dimer, and two dimers constituted simultaneously a bis-dimer by hydrogen bonds of type (ii) (O2W···O3W: 0.3005(4) nm) and type (vi) (N12···O14:

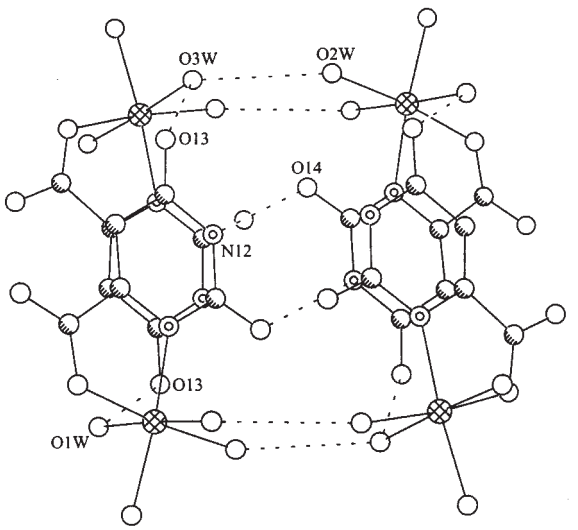

Fig. 3(a)　Bis-dimmer of complex **2** connected by hydrogen bonds

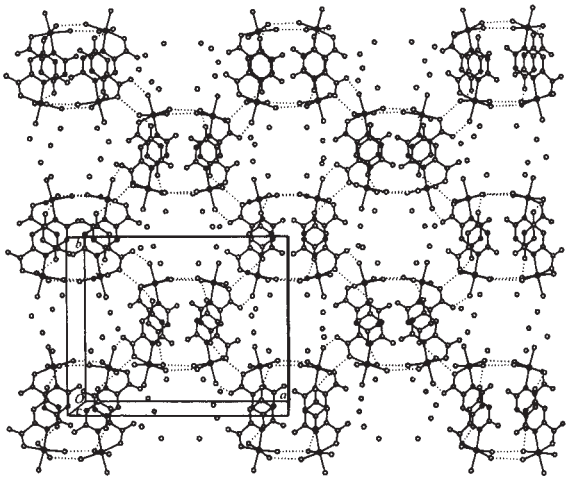

Fig. 3(b)　Three-dimensional framework of complex **2**, the short contacts around the lattice water molecules are omitted for clarity
The hydrogen bonds are represented by dotted lines.

0.2806(4) nm), as shown in Fig. 3(a). Then hydrogen bonding interactions of type (i) (O1W···O13: 0.2715(5)nm, O3W···O13: 0.2724(5)nm) and type (iii) (O1W ··· O11: 0.2707(4) nm) make the bis-dimmers into columniations along the *c* axis, which are linked by hydrogen bonds of type (iv) along the [1 1 0] and [1 –1 0] directions to form a three-dimension framework with channels in which the lattice water molecules are located. The hydrogen bonds for complex **2** are listed in Table 4.

Table 4 Hydrogen Bond Distances and Bond Angles of Complex 2

atom involve	distance/nm			angle/(°)
	O(N)-H	H···O	O(N)···O	O(N) – H···O
O1W – H1A···O11[a]	0.095(1)	0.179(2)	0.2707(4)	161(6)
O1W – H1B···O13[b]	0.095(1)	0.191(5)	0.2715(5)	141(6)
O2W – H2A···O3W[c]	0.095(1)	0.241(2)	0.3005(4)	120(1)
O2W – H2B···O5W[d]	0.095(1)	0.197(2)	0.2810(8)	146(3)
O3W – H3B···O2W[e]	0.0946(9)	0.238(1)	0.3005(4)	124(1)
O3W – H3B···O5W	0.0946(9)	0.240(1)	0.2987(8)	120(1)
O3W – H3A···O13[e]	0.095(1)	0.179(1)	0.2724(5)	170(3)
O4W – H4A···O12[f]	0.095(1)	0.185(2)	0.2719(5)	151(3)
O4W – H4B···O6W	0.095(1)	0.183(2)	0.2716(8)	153(4)
N12 – H12A···O14[g]	0.086	0.196	0.2806(4)	169.8
O5W···O6W			0.297(1)	
O6W···O12[h]			0.2778(7)	

Symmetry transformations used to generate equivalent atoms: (a) 0.5 – x, 1.5 – y, 0.5 + z; (b) x, 1 – y, 0.5 + z; (c) 1 – x, y, 0.5 – z; (d) x, y, z + 1; (e) x, 1 – y, – 0.5 + z; (f) 0.5 – x, 1.5 – y, 0.5 + z; (g) 1 – x, 1 – y, 1 – z; (h) 0.5 – x, 0.5 + y, z.

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