

## 研究简报

[COH(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[Cu(pic)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]的合成与晶体结构郭光华<sup>1,2</sup> 郭国聪<sup>\*·1</sup> 周国伟<sup>1</sup> 王明盛<sup>1</sup> 蔡丽珍<sup>1</sup> 吴阿清<sup>1</sup> 黄锦顺<sup>\*·1</sup><sup>(1)</sup> 结构化学国家重点实验室, 中国科学院福建物质结构研究所, 福州 350002)<sup>(2)</sup> 中国科学院研究生院, 北京 100039)

关键词: 2-吡啶羧酸 过渡金属 4+2 拉长八面体 氢键 晶体结构

分类号: 0614.121

Synthesis and Structure of [COH(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[Cu(pic)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]GUO Guang-Hua<sup>1,2</sup> GUO Guo-Cong<sup>\*·1</sup> ZHOU Guo-Wei<sup>1</sup> WANG Ming-Sheng<sup>1</sup>CAI Li-Zhen<sup>1</sup> WU A-Qing<sup>1</sup> HUANG Jin-Shun<sup>\*·1</sup><sup>(1)</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,  
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The title compound was synthesized by reaction of Cu(ClO<sub>4</sub>)<sub>2</sub>, picolinic acid and carbamide in C<sub>2</sub>H<sub>5</sub>OH/CH<sub>3</sub>CN solution, and characterized by single-crystal X-ray diffraction. It crystallizes in the orthorhombic system, space group *Pbca* with  $a = 14.0481(8)$ ,  $b = 9.0130(5)$ ,  $c = 18.626(1)$  Å,  $V = 2358.3(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.771$  g · cm<sup>-3</sup>,  $\mu = 1.235$  mm<sup>-1</sup> and  $F(000) = 1276$ . The final R factor is 0.0440 for 1434 observed reflections. The X-ray analysis revealed that the copper (II) atom is coordinated by two picolinic ligands in the equatorial plane, while the two oxygen atoms of perchlorate occupy the axial positions of octahedron with lengthened Cu-O distances, resulting in a 4 + 2 elongated octahedral environment. In the compound, there also exist two protonated carbamide cations for charge balance. CCDC: 195354.

Keywords: picolinic acid transition metal 4 + 2 elongated octahedral hydrogen bond  
crystal structure

## 0 Introduction

In the past few years, the molecular-based magnetic properties of complexes simultaneously comprising lanthanide and transition metal ions have attracted in-

creasing interest. In our laboratory, we have synthesized such type of complexes with different bridging ligands<sup>[1-4]</sup>. As an extension of this research area, our present work is aim to synthesize novel structural compounds of rare earth and transition metal, by using pi-

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colinic acid (pic-H) as a chelating ligand. In the course of our investigation, we synthesize a new complex of  $[\text{COH}(\text{NH}_2)_2]_2[\text{Cu}(\text{pic})_2(\text{ClO}_4)_2]$ . Since it contains two non-coordinated oxygen of carboxyl group in picolinic ligand, it can be used as a "metallo ligand" to bind lanthanide metal ions for the preparation of compounds of rare earth and transition metal.

Before this work, complexes formulated as  $\text{M}(\text{pic})_2 \cdot n\text{H}_2\text{O}$  ( $n=0, 2$  or  $4$  and  $\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Mg}$  and  $\text{Pb}$ ) have been reported<sup>[5-10]</sup>, in which the environment of central metals were quadrangular coordination; however, the central metal of the title compound has a  $4+2$  elongated octahedral coordination environment. In this paper, we report the synthesis and crystal structure of the title complex  $[\text{COH}(\text{NH}_2)_2]_2[\text{Cu}(\text{pic})_2(\text{ClO}_4)_2]$ .

## 1 Experimental

### 1.1 Preparation of



The title compound was prepared by mixing 2 mL of an aqueous solution of  $\text{Cu}(\text{ClO}_4)_2$  (530 mg, 2 mmol) and picolinic acid (980 mg, 8 mol) in 30 mL  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CN}$  solution, and carbamide was added to adjust  $\text{pH}=5$ , and the solution was stirred thoroughly at room temperature. After a few minutes some blue precipitates were appeared, continued to stir for 4 h. The precipitates were filtered off and the filtrate allowed to stand at room temperature. Transparent blue crystals of the title complex were obtained in a few days, filtered, washed with a little amount of ethanol, air dried and kept in a sealed ampoule. Yield: 51.6% (calculated by Cu).

### 1.2 Crystal Structure Determination

A crystal of  $[\text{COH}(\text{NH}_2)_2]_2[\text{Cu}(\text{pic})_2(\text{ClO}_4)_2]$  with approximate dimensions of  $0.52 \times 0.24 \times 0.12$  mm<sup>3</sup> was mounted on a glass fiber. Data set were collected on a Siemens SMART CCD diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). A total of 6407 reflections were collected with 2070 unique reflections ( $R_{\text{int}}=0.041$ ) in the range of  $2.19^\circ < \theta < 25.06^\circ$  by  $\omega$  scan technique at

293 K. Siemens SAINT software was used for data reduction. Empirical absorption correction SADABS based on measurement of equivalent reflections were used. The structure was solved by direct methods using Siemens SHELXTL Version 5.0 package of crystallographic software<sup>[11]</sup>. The different Fourier maps based on these atomic positions yield all other non-hydrogen atoms. The structure was refined using a full-matrix least squares refinement on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models, except for H(1) atom which can be located based on the different Fourier maps. The final cycle of full-matrix least-squares refinement was based on 1434 observed reflections ( $I > 2\sigma(I)$ ) and 169 variable parameters and converged with un-weighted and weighted agreement factors of  $R_1 = \sum | |F_0| - |F_c| | / \sum |F_0|$ ,  $\omega R_2 = [ \sum \omega (F_0^2 - F_c^2)^2 / \sum \omega (F_0^2)^2 ]^{1/2}$ . The final  $R_1=0.0440$ ,  $\omega R_2=0.1060$ , ( $\omega=1/[ \sigma(F_0^2) + (0.073P)^2 + 5.1457P ]$  where  $P=(F_0^2 + 2F_c^2)/3$ ,  $S=1.235$ ,  $(\Delta/\sigma)_{\text{max}}=0.002$ . The maximum and minimum peaks on the final difference fourier map corresponded to  $0.331$  and  $-0.385 \text{ \AA}$ , respectively.

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## 2 Results and Discussion

The atomic coordinates and thermal parameters are given in Table 1. The selected bond lengths and angles are listed in Table 2. The copper (II) ion is situated on a crystallographic inversion center and has a  $4+2$  elongated octahedral coordination environment as shown in Fig. 1.  $\text{Cu}(\text{pic})_2$  moiety is nearly planar. The Cu (II) atom has centro-symmetric square-planar coordination with two nitrogen atoms (N(1), N(1A)) and two carboxyl oxygen atoms from two pyridine ligands. The axial positions are occupied by two perchlorate anions, each oxygen atom weakly coordinates to the Cu (II) atom which is nearly perpendicular to the equatorial plane. The distance of Cu-O(3) is  $2.523(3) \text{ \AA}$  which is longer than the normal coordination bond ( $1.8 \sim 2.0 \text{ \AA}$ )<sup>[12]</sup>, thus an octahedron elongation is observed along the O(3)-N-O(3A) axis due to the Jahn-Teller effect<sup>[13]</sup>.

It is worthy to note that there exist two  $\text{ClO}_4^-$  in the present compound, which differs from the previously reported complexes formulated as  $\text{M}(\text{pic})_2 \cdot$

Table 1 Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup>)

atom	x	y	z	U(eq)	atom	x	y	z	U(eq)
Cu(1)	0.5000	0.0000	0.5000	0.0372(1)	N(1)	0.5437(2)	0.1947(3)	0.5367(1)	0.0345(6)
O(1)	0.6213(1)	0.0026(2)	0.4496(1)	0.0373(5)	O(2)	0.7554(1)	0.1325(2)	0.4402(1)	0.0445(6)
C(1)	0.6342(2)	0.2225(3)	0.5171(1)	0.0336(7)	C(2)	0.6830(2)	0.3427(4)	0.5423(2)	0.0460(9)
C(3)	0.6373(2)	0.4416(4)	0.5876(2)	0.055(1)	C(4)	0.5434(2)	0.4150(4)	0.6059(2)	0.056(1)
C(5)	0.4989(2)	0.2900(4)	0.5797(2)	0.0447(9)	C(6)	0.6740(2)	0.1119(3)	0.4654(2)	0.0348(7)
Cl(1)	0.4196(5)	0.1232(9)	0.3272(4)	0.0441(2)	O(3)	0.4194(2)	0.1474(4)	0.4022(1)	0.088(1)
O(4)	0.4787(2)	0.0002(3)	0.3093(2)	0.0770(9)	O(5)	0.4553(2)	0.2521(3)	0.2915(2)	0.0861(9)
O(6)	0.3245(2)	0.0990(3)	0.3030(2)	0.0772(9)	N(3)	0.6884(2)	-0.1134(3)	0.3099(1)	0.0464(7)
N(2)	0.8257(2)	-0.2278(3)	0.2733(1)	0.0517(8)	O(7)	0.8315(1)	-0.0620(3)	0.3609(1)	0.0518(6)
C(7)	0.7808(2)	-0.1341(4)	0.3145(2)	0.0401(8)	H(1)	0.809(2)	-0.002(3)	0.391(1)	0.050(1)

Table 2 Bond Lengths(Å) and Angles(°)

Cu(1)-O(1)	1.947(2)	Cu(1)-O(3)	2.523(3)	Cu(1)-N(1)	1.981(2)
N(1)-C(5)	1.333(4)	N(1)-C(1)	1.346(3)	O(1)-C(6)	1.267(3)
O(2)-C(6)	1.250(3)	C(1)-C(2)	1.365(4)	C(1)-C(6)	1.494(4)
C(2)-C(3)	1.385(5)	C(3)-C(4)	1.384(5)	C(4)-C(5)	1.377(5)
Cl(1)-O(3)	1.413(2)	Cl(1)-O(4)	1.424(3)	Cl(1)-O(6)	1.427(2)
Cl(1)-O(5)	1.429(3)	N(3)-C(7)	1.315(4)	N(2)-C(7)	1.304(4)
O(7)-C(7)	1.294(4)				
O(1)-Cu(1)-O(1)#1	180.0	O(1)-Cu(1)-N(1)#1	96.64(9)	O(1)#1-Cu(1)-N(1)#1	83.36(9)
O(1)-Cu(1)-N(1)	83.36(9)	O(1)#1-Cu(1)-N(1)	96.64(9)	N(1)#1-Cu(1)-N(1)	180.0(1)
C(5)-N(1)-C(1)	119.3(3)	C(5)-N(1)-Cu(1)	129.2(2)	C(1)-N(1)-Cu(1)	111.3(2)
C(6)-O(1)-Cu(1)	114.1(2)	N(1)-C(1)-C(2)	121.9(3)	N(1)-C(1)-C(6)	113.8(2)
C(2)-C(1)-C(6)	124.2(2)	C(1)-C(2)-C(3)	119.1(3)	C(4)-C(3)-C(2)	118.8(3)
C(5)-C(4)-C(3)	119.1(3)	N(1)-C(5)-C(4)	121.7(3)	O(2)-C(6)-O(1)	124.1(3)
O(2)-C(6)-C(1)	119.1(3)	O(1)-C(6)-C(1)	116.8(2)	O(3)-Cl(1)-O(4)	110.7(2)
O(3)-Cl(1)-O(6)	109.5(2)	O(4)-Cl(1)-O(6)	110.6(2)	O(3)-Cl(1)-O(5)	109.6(2)
O(4)-Cl(1)-O(5)	108.7(2)	O(6)-Cl(1)-O(5)	107.8(2)	O(7)-C(7)-N(2)	117.0(3)
O(7)-C(7)-N(3)	121.1(3)	N(2)-C(7)-N(3)	122.0(3)		

Symmetry transformations used to generate equivalent atoms: #1:  $-x+1, -y, -z+1$ .

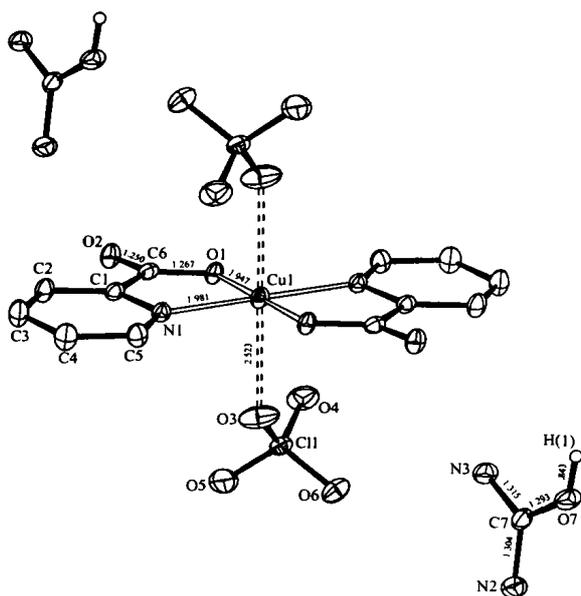


Fig. 1 An ORTEP drawing of the title compound

$n\text{H}_2\text{O}$ ,  $n = 0, 2$  or  $4$ <sup>[5-10]</sup>. In order to charge balance of the compound, there must exist two positive charges in the complex. The bond distances of Cu-O(1) and Cu-N(1) are 1.947(2) Å and 1.981(2) Å, respectively. The C-O bond distances of carboxyl group in the present compound, in which the C-O bond distance with the oxygen bonded to copper (II) atom is longer than that with the non-coordinated oxygen atom, is similar to the case found in the compounds formulated as  $\text{M}(\text{pic})_2 \cdot n\text{H}_2\text{O}$  and  $\text{Cu}(\text{pic})_2[\text{SC}(\text{NH}_2)_2]$ <sup>[14]</sup>, in which the picolinic acid functions as a anion ligand. Contrary, the C-O bond distances of carboxyl group with the oxygen atom bonded to transition metal atom in a neutral picolinic acid ligand is shorter than that with the non-coordinated oxygen atom, as found in  $[\text{Zn}(\text{pic})(\text{pic}-\text{H})\text{Cl}]$ <sup>[15]</sup> (C-OH, 1.281 Å; C-O, 1.161 Å) and in  $\text{Ag}(\text{C}_5\text{H}_4\text{NCO}_2\text{H}_{1/2}) \cdot \text{H}_2\text{O}$ <sup>[16]</sup> (C-OH, 1.275

Å; C-O, 1.216 Å). These observations suggest obviously that the picolinic acid functions as an anion ligand in the title compound. The bond lengths of C(7)-O(7) (1.294(4) Å), C(7)-N(2) (1.304(4) Å), C(7)-N(3) (1.315(4) Å) and angles O(7)-C(7)-N(2) (117.0(3)°), N(2)-C(7)-N(3) (122.0(3)°) of carbamide in the present compound are in full agreement with those found in  $[\text{C}_{12}\text{H}_{24}\text{O}_6] (\text{COH}(\text{N}_2\text{H}_2)_2\text{NO}_3)^{17}$  (C-O, 1.297 Å; C-N1, 1.306 Å; C-N2, 1.316 Å; O-C-N1, 115.8°; N1-C-N2, 121.9°), in which carbamide behaves as a  $[\text{COH}(\text{NH}_2)_2]^+$  cation. The presence of hydrogen makes the bond distance of C=O in  $[\text{COH}(\text{NH}_2)_2]^+$  cation slightly longer than that of neutral  $[\text{CO}(\text{N}_2\text{H}_4)]$  molecule, as found in  $\text{C}_6\text{H}_{12}\text{Br}_2(\text{CO}(\text{N}_2\text{H}_4))^{18}$  (C=O, 1.262 Å) and in  $\text{CO}(\text{N}_2\text{H}_4)^{19}$  (C=O, 1.258 Å). These observations indicate that the carbamide in the present compound can be considered as a  $[\text{COH}(\text{NH}_2)_2]^+$  cation for charge balance. Therefore, the title compound can be formulated as  $[\text{COH}(\text{NH}_2)_2]_2[\text{Cu}(\text{pic})_2(\text{ClO}_4)_2]$ .

Crystal structure of the title compound represents that the monomeric  $[\text{Cu}(\text{pic})_2(\text{ClO}_4)]^{2-}$  moieties are bridged by protonated carbamide cations via two types of hydrogen bonds to form a three-dimensional supra-molecular architecture, as shown in Fig. 2. One of the two type of hydrogen bonds is composed of the oxygen atoms of perchlorate anions and the amido groups of carbamide cations with an average  $\text{N}\cdots\text{O}$  distance of 3.016 Å, the other one consists of protonated oxygen

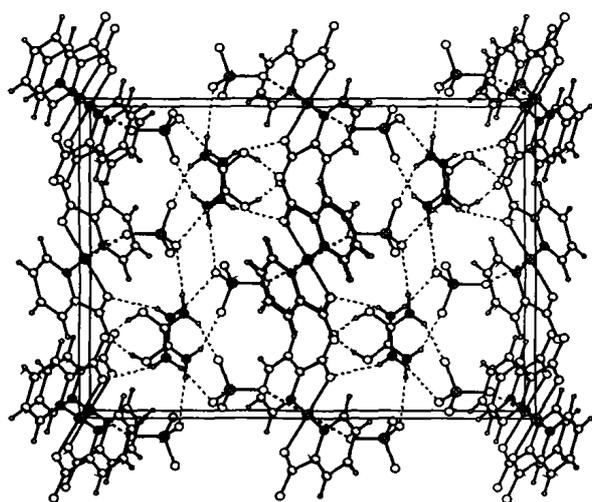


Fig. 2 Crystal structure of the title compound  
Single broken lines show the H-bonds

atoms of carbamide cations and the non-coordinated oxygen atoms of carboxyl of picolinate anions with  $\text{O}\cdots\text{O}$  distance of 2.529 Å.

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