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研究简报

2-吡嗪羧酸铜配合物的合成及其结构表征

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关键词:2-吡嗪羧酸;铜;晶体结构;配位聚合物
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Synthesis and Structural Characterization of 2-Pyrazinecarboxylate Copper Compound $\{[Cu_2(Pyz)_2(H_2O)_4]\cdot SO_4\}_n$ (Pyz=2-pyrazinic acid)

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Abstract: Solvothermal reaction of 2-pyrazinic acid with $Cu(SO_4)_2\cdot 5H_2O$ yields the title complex $\{[Cu_2(Pyz)_2(H_2O)_4]\cdot SO_4\}_n$ (**1**), which was characterized by elemental analysis, IR and single crystal X-ray diffraction structural analysis. The complex **1** crystallizes in Monoclinic system, space group $P2_1/c$, with lattice parameters a=1.126 87(6) nm, b=0.073 511(4) nm, c=1.185 06(7) nm, β=95.070(2)°, and V=0.977 83(9) nm^3, Z=4, D_c=2.172 Mg·m^{-3}. CCDC: 692347.

Key words: 2-pyrazinic acid; copper; crystal structure; coordination polymer

The research on transition metal coordination complexes has been rapidly expending because of their fascinating structural diversity and useful properties such as catalytic behavior, micro-porosity, electrical conductivity, non-linear optical activity and cooperative magnetic behavior. In order to synthesize ideal coordination polymers the key step is the design and selection of bridging ligands. For instances, bridging ligands of polycarboxylate and polyamine or organic ligands containing nitrogen and oxygen hybrid atom were often used. Recently, several novel structural coordination polymers containing the derivative of pyrazine-2-carboxylate (pyz) have been obtained[1~13]. Our interest is to apply solvothermal reaction to construct a coordination polymeric complex having novel structural type using simple ligand. In this paper, we report the crystal structure of a novel coordination polymer, $\{[Cu_2(Pyz)_2(H_2O)_4]\cdot SO_4\}_n$ (**1**), which was synthesized by solvothermal reaction.

1 Experimental

1.1 Materials and methods

All reagents were commercially available and used without further purification. C, H and N analysis data were obtained using an American PE 2400 Ⅱ CHNS/O elemental analyzer. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system.

1.2 Synthesis of $\{[Cu_2(Pyz)_2(H_2O)_4]\cdot SO_4\}_n$ (1)

A mixture slurry composed of 0.249 7 g (1 mmol) of $Cu(SO_4)_2\cdot 5H_2O$ and 0.248 0 g (2 mmol) of 2-pyrazinic

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acid in 14 mL of mixed solvent (EtOH/H_2O, *V*/*V*, 1:1) was sealed into a 25 mL stainless-steel reactor with a teflon liner and heated at 120 ℃ for 72 hours under autogenous pressure. After the reactor was cooled, the blue block crystals of the title complex of **1** suitable to X-ray diffraction analysis were obtained. $C_5H_8CuN_2O_8S$ (319.73) Anal. Found(%): C 18.84, H 2.46 and N 8.76. Calcd(%): C 18.77, H 2.50 and N 8.76.

1.3 Crystal structure determination

The X-ray single crystal diffraction data collection for complex **1** was performed on a Bruker SMART APEX Ⅱ CCD diffractometer equipped with a graphite monochromatized Mo *Kα* radiation (λ=0.071 073 nm). Multi-scan absorption corrections were applied using the SADABS program[14]. The structure was solved by the direct method using the SHELXS-97 program[15]. Refinements on F^2 were performed using SHELXL-97[16] by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the ligand were generated geometrically, while the H atoms of the coordination water molecules were located from difference Fourier synthesis and refined with restraint parameters. A summary of crystallographic data and refinement parameters is given in Table 1.

CCDC: 692347.

Table 1 Crystal data and structure refinement parametes

Empirical formula	$C_5H_8CuN_2O_8S$	D_c / (Mg·m^{-3})	2.172
Formula weight	319.73	*F*(000)	644
Crystal system	Monoclinic	Temperature / K	296(2)
Space group	$P2_1/c$	Wavelength / nm	0.071 073
Crystal size / mm	0.30×0.28×0.24	*h*	$-13 \leqslant h \leqslant 13$
a / nm	1.126 87(6)	*k*	$-9 \leqslant k \leqslant 8$
b / nm	0.073 511(4)	*l*	$-13 \leqslant l \leqslant 14$
c / nm	1.185 06(7)	Completeness	98.7
β / (°)	95.070(2)	Final *R* indices [$I>2\sigma(I)$]	R_1=0.026 4, wR_2=0.072 0
V / nm^3	0.977 83(9)	*R* indices (all data)	R_1=0.028 6, wR_2=0.073 6
Z	4	Goodness-of-fit on F^2	1.089

2 Results and discussion

2.1 Structure of $\{[Cu_2(Pyz)_2(H_2O)_4]\cdot SO_4\}_n$ (1)

Selected bond distances (nm) and bond angles (°) for compounds **1** is listed in Table 2. The ORTEP drawing of **1** is shown in Fig.1. The title complex **1** crystallizes in the Monoclinic system, with space group $P2_1/c$. It indicates that Cu(1) is coordinated by O(3), O(4), O(3A), O(4A), N(2) and N(2A) atoms; O(3), O(4), O(3A) and O(4A) are from four coordinated water molecules and N(2) and N(2A) from two bridging pyrazies, respectively. The bond lengths and associated angles

Table 2 Selected bond distances (nm) and bond angles (°) for compound 1

Cu(1)-O(3)	0.197 11(18)	Cu(1)-N(2)	0.203 50(19)	Cu(1)-O(4)	0.236 5(2)
Cu(2)-O(1)	0.196 33(18)	Cu(2)-N(1)	0.197 94(19)	Cu(2)-O(5)	0.244 70(17)
O(5)-S(1)	0.147 57(18)	O(6)-S(1)	0.145 7(2)	O(7)-S(1)	0.148 38(18)
O(8)-S(1)	0.148 2(2)	O(2)-C(1)	0.131 5(3)	O(1)-C(1)	0.125 8(3)
O(3)#1-Cu(1)-N(2)	90.72(8)	O(3)-Cu(1)-N(2)	89.28(8)	O(3)#1-Cu(1)-N(2)#1	89.28(8)
O(3)-Cu(1)-N(2)#1	90.72(8)	O(3)#1-Cu(1)-O(4)	91.06(8)	O(3)-Cu(1)-O(4)	88.94(8)
N(2)-Cu(1)-O(4)	90.20(8)	N(2)#1-Cu(1)-O(4)	89.80(8)	O(3)#1-Cu(1)-O(4)#1	88.94(8)
O(3)-Cu(1)-O(4)#1	91.06(8)	N(2)-Cu(1)-O(4)#1	89.80(8)	N(2)#1-Cu(1)-O(4)#1	90.20(8)
O(1)#2-Cu(2)-N(1)	97.53(8)	O(1)-Cu(2)-N(1)	82.47(8)	O(1)#2-Cu(2)-N(1)#2	82.47(8)
O(1)-Cu(2)-N(1)#2	97.53(8)				

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y, -z+1$; #2: $-x+2, -y+1, -z+1$.

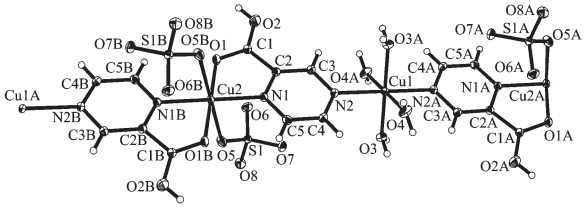
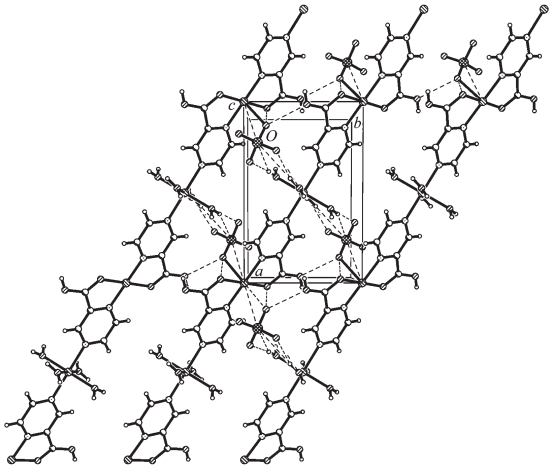


Fig.1　Coordination environment of the Cu(Ⅱ) ion in **1**

indicate that Cu(1) is located in a distorted octahedral environment. The bond lengths for Cu(1)-Ow range from 0.197 11(18) to 0.236 5(2) nm, the bond lengths for Cu(1)-N is 0.203 50(19) nm. The bond angles of O-Cu(1)-O, O-Cu(1)-N and N-Cu(1)-O vary from 88.94(8)° to 91.06(8)°; these values differ from those expected for a regular octahedron. Cu(2) is chelated by two 2-Pyrazinecarboxylate ligands leading to the formation of two five-membered rings (ring 1: N1/C2/C1/O1/Cu2, ring 2: N1A/C2A/C1A/O1A/Cu2). The Cu(2) possesses distorted octahedral coordination environment and is surrounded by two pyz O atoms [O(1), O(1B)], two pyz N atoms [N(1), N(1B)] and two O atoms [O(5), O(5B)] from two SO_4^{2-}. The bond distances for Cu(2)-O (1), Cu (2)-N(1) and Cu(2)-O(5) are 0.196 33(18), 0.197 94(19) and 0.244 70(17) nm, respectively. The bond length of O(1)-C(1) [0.125 8(3) nm] is significantly shorter than that of O(2)-C(1) [0.131 5(3) nm], which indicates the -COOH group of 2-pyrazinic acid is not disassociated. The bond angles of O(1)-Cu(2)-N(1) and O(1)-Cu(2)-N(1B) are 82.47(8)° and 97.53(8)°, respectively, which deviate from 90° for a ideal octahedral geometry. The one-dimensional chain is constructed through coordination of Cu (Ⅱ) ion with bridging ligand pyz. The chain structure is similar to that of complexes [CuCl(pyz)$(H_2O)]_n$ and $[Cu(N_3)(pyz)(H_2O)]_n$[17], but the chains of the latter two complexes appear as straight lines. Hydrogen bonding exists in the inter-chains consisting of coordinated H_2O molecules, the coordinated -COOH groups, the sulfur atoms and oxygen atoms of SO_4^{2-} (Table 3). Through the hydrogen bonding the two dimensional sheet is formed in the *ab* plane and the sheets pile up along the c direction to construct a three-dimensional structure (Fig.2).



Hydrogen bonds are shown in dotted line

Fig.2　3D network of **1** viewed along *c*-axis

Table 3　Hydrogen bonds for 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠(DHA) / (°)
O(3)–H(3B)···S(1)#6	0.084 7(10)	0.291 5(14)	0.371 5(2)	158(3)
O(3)–H(3B)···O(8)#6	0.084 7(10)	0.184 3(12)	0.267 9(3)	169(4)
O(3)–H(3A)...S(1)#5	0.084 6(10)	0.282 3(16)	0.361 96(19)	158(3)
O(3)–H(3A)...O(7)#5	0.084 6(10)	0.183 5(11)	0.267 8(3)	174(3)
O(4)–H(4A)···S(1)#5	0.084 9(10)	0.291 5(14)	0.371 5(2)	158(3)
O(4)–H(4A)···O(8)#5	0.084 9(10)	0.198 4(15)	0.280 8(3)	163(4)
O(4)–H(4B)···S(1)#4	0.085 0(10)	0.278(2)	0.347 0(2)	139(3)
O(4)–H(4B)···O(7)#4	0.085 0(10)	0.199 5(12)	0.283 2(3)	168(4)
O(2)–H(2)···O(6)#3	0.82	2.05	2.85 7(3)	169.0
O(2)–H(2)···S(1)#3	0.82	2.91	3.70 7(2)	163.3

Symmetry transformations used to generate equivalent atoms: #3: $-x+2$, $y-1/2$, $-z+1/2$; #4: x, $-y+1/2$, $z+1/2$; #5: $-x+1$, $-y+1$, $-z+1$; #6: $-x+1$, $y-1/2$, $-z+1/2$.

2.2　IR spectroscopy

The IR spectra of complex **1** exhibit a strong broad band around 3 363 cm^{-1} due to H-bonds of the type O–H···O and O–H···S between H_2O molecules and SO_4^{2-}

groups. The H-bonds of the types N–H···O and O–H···N or O–H···O in free pyrazinic acid are replaced by O–H···O and O–H···S bonds since both nitrogen atoms of the pyrazinato ligand are involved in coordination to copper. Complex **1** show a substantial decrease of the ν(C=O) to about 1 629 cm^{-1}, compared to that of free ligand (1 712 cm^{-1}), which indicate the C=O of 2-pyrazinic acid is coordinated to Cu^{2+}. The peaks of 1 586(s), 1 548(m), 1 498(m) and 1 459(m) cm^{-1} belong to pyrazine ring vibration.

3 Conclusion

In summary, assembling hybrid ligands of Pyz, SO_4^{2-} and H_2O, a novel one-dimensional coordination polymer has been synthesized by solvothermal process. Through hydrogen bonding a three-dimensional supramolecular structure is constructed.

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