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以吡啶基咪唑酮及联吡啶为配体的铜配位聚合物的合成、晶体结构及荧光性质

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摘要: 合成了 1 个铜配位聚合物{[Cu_2(Imazameth)$_2$(bipy)](ClO_4)·CH_2OH·H_2O}$_n$(**1**,Imazameth=(+/−2-(4-异丙基-4-甲基-5-氧-2-咪唑啉-2-基)-5-甲基烟酸,又称甲基咪草烟;bipy=4,4′-联吡啶)。并对其进行了元素分析,IR,荧光性质和 X 射线-单晶衍射表征。晶体结构表明:配合物 **1** 属于单斜晶系,$P2_1/c$ 空间群并且其不对称单元中包含水和乙醇分子。配合物 **1** 是由桥联配体 4,4′-联吡啶和甲基咪草烟连接成“瓦楞”形层状结构,并通过分子内 N−H···O 氢键和分子间 O−H···O 氢键拓展成三维超分子结构。配合物 **1** 有较强的荧光性质。

关键词: 甲基咪草烟; 晶体结构; 配位聚合物; 荧光性质
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Synthesis, Crystal Structure and Fluorescence Property of Cu(Ⅱ) Coordination Polymer with Pyridylimidazolidinone and Bipyridine

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Abstract: A metal-organic coordination polymer framework formulated as {[Cu_2(Imazameth)$_2$(bipy)](ClO_4)·CH_2OH·H_2O}$_n$ (**1**) (where Imazameth =(+/−)2-(4,5-Dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-5-methyl-3-pyridinecarboxylic acid, bipy =4,4′-bipyridine) has been prepared and characterized by spectral method (IR), elemental analysis, fluorescence properties and single crystal X-ray diffraction techniques. It crystallizes in the Monoclinic system, space group $P2_1/c$ and the asymmetric unit contains hydrogen-bonded water and alcohol molecules. The Cu atom is five-coordinated by three N atoms and two O atoms in distorted pyramid coordination geometry. In fact, it is a new two-dimensional copper complex with the peculiarity of having the 4,4′-bipyridine ligand and Imazameth ligand acting as bridge to form “corrugated” layered structure . Intramolecular N−H···O and intermolecular O−H···O hydrogen bonds result in the formation of a supermolecular crystal, in which they seem to be effective in the stabilization of the structure. The complex displays strong fluorescence property. CCDC: 756106.

Key words: imazameth; crystal structure; coordination polymer; fluorescence property

The design and synthesis of polynuclear coordination complexes by the self-assembly of transitional metal and flexible bridging ligands have been receiving intense interests because of the effects of their remarkable conformational diversity on the magnetic, optical, and biological properties[1-5] and their potential

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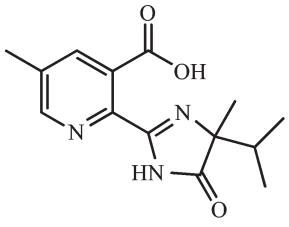
applications in catalysis, optical properties evolution, clathration, etc.[6-10]. Synthesis of one-, two- or three-dimensional polymeric network by suitable metal and ligand coordination is the main area of current research because both the network structure as well as properties of these coordination networks can be finely tuned via a systematic change of organic ligands[11]. In the specific case of coordination polymers, research activity has been motivated by the ability of metal-ligand coordination to provide a facile approach to the controlled assembly of extended networks[12].

Much effort has been devoted to the synthesis[13-14], crystal structure[15-16] and catalysis[17-18] of the compounds containing imidazolidinone during the last few years. One of them is (+/−)-2-(4,5-Dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-Imidazol-2-yl)-5-methyl-3-pyridinecarboxylic acid (Imazameth), which provides with efficient metal-chelating ability (Scheme 1). The Imazameth contains a pyridine carboxylic acid and an imidazole ring, which are well-known versatile ligands. The pyridine carboxylic acid and its anion have been extensively used in the design of coordination compounds, due to a variety of its bonding ability and exhibiting strong hydrogen bonds[19-22]. Imidazole ring, which is one of the polydentate amine ligands, generally coordinates to metal ions using the N atoms as donors. To the best of our knowledge, researches have been done into the transition-metal complexes, which are synthesized by the ligands with the similar structure to Imazameth and their respective properties such as asymmetric catalysis, second harmonic generation, piezoelectric and ferroelectric in the past few years[23]. As far as we know, the coordination chemistry of Imazameth to metal ions remains largely unexplored though it is a chiral compound, which can be used as a powerful building block to construct metal-organic frameworks (MOF).



Scheme 1 Structure of Imazameth

The reaction of Imazameth, 4,4′ -bipyridine with $Cu(ClO_4)_2$ was carried out under hydrothermal conditions to obtain **1**. In this work, we report its synthesis, crystal structure, spectral analysis (IR), elemental analysis and fluorescence properties. The title complex is the first planar network polymer derived from Imazameth and 4,4′-bipyridine with the spectral studies.

1 Experimental

1.1 Materials and instrumentation

The ligand, Imazameth, was synthesized from 2-amino-2,3-dimethylbutyronitrile, 5-methylpyridine-2,3-dicarboxylic acid and other chemicals and solvents[24-27]. All other chemicals were reagent grade and used without further purification. Elemental analysis for C, H, and N was carried out on a Perkin-Elmer 2400 Ⅱ elemental analyzer. The FTIR spectrum was obtained on a PE Spectrum One FTIR Spectrometer Fourier transform infrared spectroscopy in the 4 000~400 cm^{-1} regions, using KBr pellets. Fluorescence spectra were recorded on Perkin Elmer instruments LS55 Luminescence Spectrometer.

1.2 Synthesis of the complex 1

A solution of Imazameth (0.41 g, 1.5 mmol) in 10mL ethanol was added dropwise with stirring at room temperature to a solution of Cu $(ClO_4)_2$ (0.39 g, 1.5 mmol) in 5 mL water. The mixture was stirred at room temperature until it was homogeneous, and then added to a solution of 4,4′-bipyridine (0.16 g, 1 mmol) in 5 mL ethanol. Then, the mixture was sealed in a 25mL Teflon-lined stainless reactor, kept under autogenous pressure at 110 ℃ for 24 h, and then slowly cooled to room temperature at a rate of 5 ℃·h^{-1}. After 15 d, blue block crystals suitable for X-ray diffraction were separated and washed with water, which were stable in air and insoluble in water and common organic solvents. (Yield: 79% based on Cu). Calcd. For $C_{21}H_{30}N_4O_{10}ClCu$ (%): C 42.21, H 5.06, N 9.38; Found (%): C 42.19, H .04, and N 9.39.

1.3 X-ray data collection and structure refinement

Crystallographic data were collected on a Bruker

SMART APEX CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) at T=296(2) K. Absorption corrections were applied by using the SADABS program[28]. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares procedure against F^2 (SHELXL-97) [29-30]. Hydrogen atoms were located by geometric calculations. H atoms for H_2O molecules were located in different synthesis and refined isotropically (O-H 0.084 98~0.085 01 nm, U_{iso}(H)=1.2U_{eq} (carrier atoms of H_2O)). The remaining H atoms were positioned geometrically, with N-H 0.086 nm (for NH), O-H 0.082 nm (for OH), C-H 0.098 nm(for CH), C-H 0.097 nm (for CH_2), C-H 0.096 nm (for CH_3) and C-H 0.093 nm for aromatic H atoms, respectively. In addition, they were constrained to ride on their parent atoms with U_{iso}(H)=1.2U_{eq} (carrier atoms of CH, CH_2, OH, NH) and U_{iso}(H)=1.5U_{eq} (carrier atoms of CH_3).

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2　Results and discussion

2.1　FTIR spectrum

The most significant frequencies in the IR spectrum of complex **1** are given in Table 1. The strong and broad absorption bands at about 3 660~3 450 and 1 615 cm^{-1} are attributed to the symmetric O-H stretching modes and O-H bending modes of crystal water molecules in the crystal, respectively. Single crystal X-ray data support the presence of water in the complex. The shift to lower frequencies of these stretching modes and the shift to higher frequencies of the accompanying O-H bending modes may be attributed to hydrogen bonding. Other peculiar feature is observed, which exhibits a band at 1 369 cm^{-1}. An intense absorption of similar wavenumber was observed previously for a Co(Ⅲ) complex of Imazapyr coordinating through the deprotonated lactam group[15]. Compared with complex [Mn(Imz)$_2$][15], the title complex exhibit the similar wavenumber values for the carboxylate stretches. The COO groups of the title complex are ν_{as}(O-C-O) 1 610 cm^{-1}, ν_s(O-C-O) 1 481 cm^{-1}, $\Delta\nu$=129 cm^{-1} and the [Mn(Imz)$_2$] are 1 559 cm^{-1}, 1 416 cm^{-1}, $\Delta\nu$=143 cm^{-1}, respectively. While in complex [Co(Imz)$_3$]·3H_2O, the COO groups are ν_{as}(O-C-O) 1 628 cm^{-1}, ν_s(O-C-O) 1 401 cm^{-1}, $\Delta\nu$=227 cm^{-1}. The difference results form the O atoms of COO groups are engaged in the metal coordination in the Mn(Ⅱ) and Cu(Ⅱ) complex, except for the O···H–N hydrogen bonding, while there is only O···H–N hydrogen bonding in the Co(Ⅲ) complex. As regards the ν(C=N) modes, these are distinguished at 1 695 cm^{-1} in Imazameth and at 1 615 cm^{-1} in the Cu(Ⅱ) complex, which is consistent with the [Mn(Imz)$_2$] complex, 1 627 cm^{-1}. In comparison, the [Co(Imz)$_3$]·3H_2O derivative exhibits a high wavenumber value (1 661 cm^{-1}) consistent with the decreased length of the C=N bond (0.129 nm).

Table 1　IR spectral data of complex 1

(cm^{-1})

Assignments	{[Cu_2(Imazameth)$_2$(4,4′-bipyridine)]·(ClO_4)·CH_2OH·H_2O}$_n$
$\nu(OH)_{water}$	3 660~3 450bm
$\nu(CH_3)$	2 973~2 878m
$\nu(CH)_{pyridinering}$	3 070w
ν(C=O)	1 705vs
ν(C=N)	1 615vs
ν_s(O-C-O)	1 481s
ν_{as}(O-C-O)	1 610s

[a] Abbreviations: w, weak; m, medium; s, strong; vs, very strong; b, broad

2.2　Fluorescence properties

The fluorescence spectra of complex **1** and free ligand Imazameth in the solid state at room temperature are presented in Fig.1. The free ligand

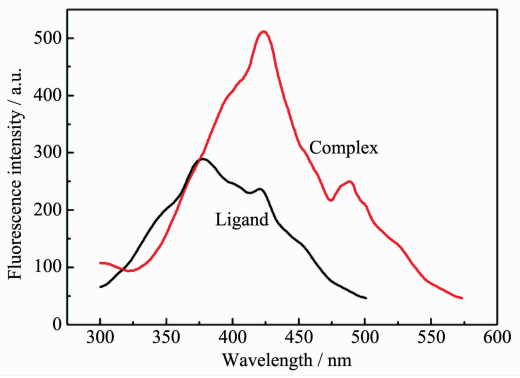


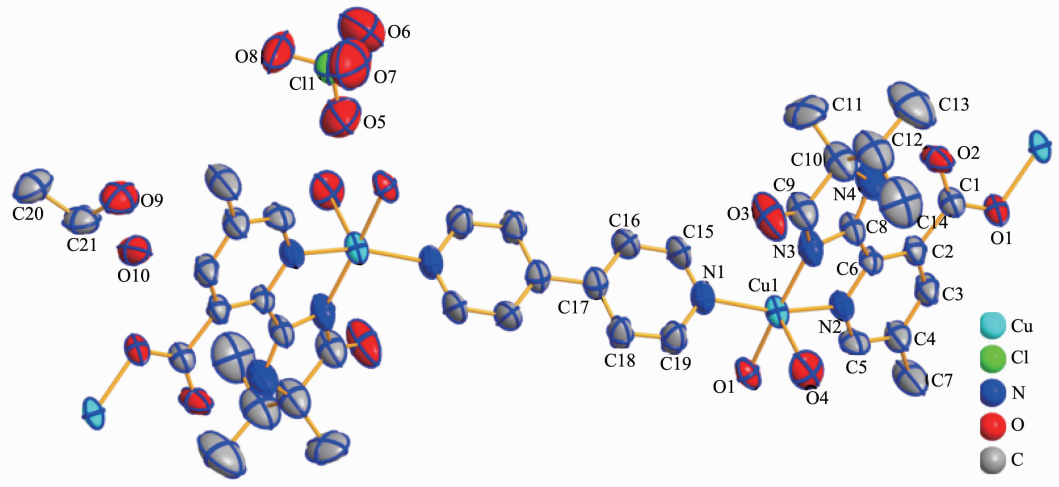
Fig.1　Fluorescence emission spectra of complex and free ligand

Imazameth shows intense emission bands at 377 and 420 nm when exited with light of 230 nm, which might be assigned to intraligand π-π* and n-π* charge transfer. On the contrary the copper complex shows very strong emission and red-shifted to 424 and 488 nm respectively, which is *ca.* 47 and *ca.* 68 nm red-shifted compared to the free ligand, could be assigned to the emission of ligand to metal charge transfer according o the previous literatures[27-28]. It is evident from some cases that complex formation sometimes increases the fluorescence inten-sity due to the reduction of symmetry of the ligand or charge transfer emission (MLCT or LMCT emission). In the present case sharp increase of fluorescence on complex formation may be due to charge transfer.

2.2 Description of crystal structure

A perspective view of the molecular structure of the complex **1** along with the atom-numbering scheme is depicted in Fig.2. The crystallographic data are listed in Table 2, and selected bond lengths and angles and hydrogen-bond geometry are given in Table 3 and 4, respectively.

The X-ray crystal structure determination of complex **1** reveals that the local coordination environment around the Cu ion can be best described as a slightly distorted pyramid (5-coordinated) with three N atoms (two N atoms from pyridyl rings and the oxo-imidazole rings of Imazethapyr ions, respectively, and one N atom from 4,4′-bipyridine) and two O atoms (one O atom from a carboxylate group, and the other



All the hydrogen atoms are omitted for clarity

Fig.2 Coordination environments of Cu atoms with 50% thermal ellipsoids of the complex

Table 2 Crystallographic data for complex 1

Empirical formula	$C_{21}H_{30}N_4O_{10}ClCu$	Absorption coefficient / mm^{-1}	0.917
Color / shape	Blue / block	$F(000)$	1 240
Formula weight	597.48	Crystal size	0.41×0.39×0.38
Temperature / K	296(2)	θ range for data collection / (°)	1.88~25.02
Wavelength / nm	0.071 073	Reflections collected	16 279
Crystal system	Monoclinic	Unique reflections (R_{int})	5 018 (0.059 3)
Space group	$P2_1/c$	Completeness to θ=25.00° / %	99.90
a / nm	1.063 45(12)	Absorption correction	Semi-empirical
b / nm	2.116 1(2)	Max. and min. transmission	0.722 0 and 0.705 0
c / nm	1.35798(14)	Data / restraints / parameters	5 018 / 0 / 362
β / (°)	111.400(5)	Goodness-of-fit on F^2	1.042
Volume / nm^3	2.845 2(5)	R indices ($I>2\sigma(I)$)	R_1=0.069 1, wR_2=0.197 8
Z	4	R indices (all data)	R_1=0.108 9, wR_2=0.228 2
D_c / ($g\cdot cm^{-3}$)	1.395		

Table 3　Selected bond lengths (nm) and angles (°)

Cu(1)-N(1)	0.201 8(4)	O(1)-Cu(1)[b]	0.195 0(4)	N(3)-C(8)	0.134 9(7)
Cu(1)-N(2)	0.204 5(4)	N(1)-C(15)	0.128 6(8)	N(3)-C(9)	0.139 1(8)
Cu(1)-N(3)	0.194 6(5)	N(1)-C(19)	0.134 3(7)	O(1)-C(1)	0.125 8(6)
Cu(1)-O(1)[a]	0.195 0(4)	N(2)-C(5)	0.134 0(7)	O(2)-C(1)	0.124 0(6)
Cu(1)-O(4)	0.223 2(4)	N(2)-C(6)	0.135 1(6)		
N(3)-Cu(1)-O(1)[a]	172.45(17)	N(1)-Cu(1)-O(4)	99.93(19)	O(1)a-Cu(1)-O(4)	86.73(17)
O(1)a-Cu(1)-N(1)	88.33(18)	N(3)-Cu(1)-N(1)	96.98(19)	N(2)-Cu(1)-O(4)	101.66(19)
O(1)a-Cu(1)-N(2)	92.94(16)	N(3)-Cu(1)-N(2)	80.15(18)		
N(3)-Cu(1)-O(4)	97.6(2)	N(1)-Cu(1)-N(2)	158.41(19)		

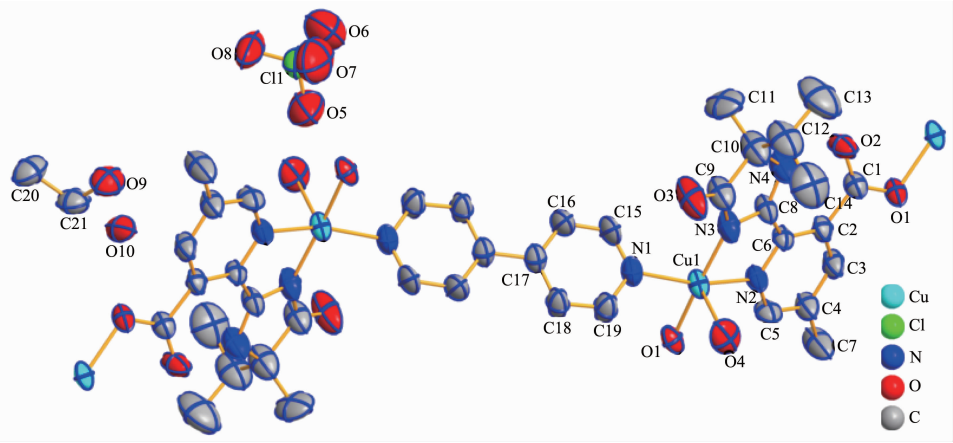
Symmetry transformations used to generate equivalent atoms: [a] x, $-y+1/2$, $z+1/2$; [b] x, $-y+1/2$, $z-1/2$.

Table 4　Hydrogen-bond geometry

D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠D–H···A / (°)
O(4)–H(4A)···O(10)[a]	0.085	0.233	0.297 2(9)	132.8
O(4)–H(4B)···O(7)[b]	0.085	0.205	0.289 0(19)	170.9
O(4)–H(4B)···O(8′)[b]	0.085	0.213	0.284(4)	139.6
O(9)–H(9)···O(7′)b	0.082	0.220	0.290(5)	143.1
O(10)–H(10C)···O(9)	0.085	0.195	0.280(3)	176.5
O(10)–H(10D)···O(3)[c]	0.085	0.228	0.312 8(11)	175.5

Symmetry codes: [a] x, $-y+1/2$, $z+1/2$; [b] x, $-y+1/2$, $z-1/2$; [c] $-x+1$, $y+1/2$, $-z+1/2$.

from H_2O) to complete such a 5-coordinate mode. Thus, each Imazethapyr ion links two Cu ions through one of the two O atoms of the carboxylate moiety and two N atoms of pyridyl and oxo-imdazole rings to complex each Cu ion with a stable planar five-membered chelating ring (1Cu2N2C, as shown in Fig.2). A comparison of the bond lengths in the chelated ring reveals that the pyridine N (2)-Cu bond is significantly longer than the imidazole N(3)-Cu bond. Most probably, this is a consequence of the different basicity of the N(2) and N(3) donors. As usual in such systems, the N-Cu-N angle of the chelated ring (80.15°) is significantly contracted relative to that for the regular pyramid geometry. The rings A (Cu1/N2/N3/C6/C8), B (N3/C8/N4/C10/C9), and C (C2/C3/C4/C5/C6/N2) are, of course, planar and the dihedral angles between them are A/B 5.71(5)°, A/C 5.06(9)°, and B/C 4.70(9)°, thus they are also nearly co-planar. In fact, complex **1** is a new one-dimensional copper complex with the peculiarity of having the Imazethapyr ligand very unusually acting as



All the hydrogen atoms are omitted for clarity

Fig.2　Coordination environments of Cu atoms with 50% thermal ellipsoids of the complex

bridges, which form polymeric chains along the crystallographic *c* axis (Fig.3a). Furthermore, each 4,4′-bipyridine ligand links two different Cu atoms from contiguous chains, which forms a two-dimensional condensed framework as depicted in Fig.3b. The dihedral angles between ring B and 4,4′-bipyridine is 54.62°, which results from stereochemical effect. In addition, the intramolecular N–H···O and intermolecular O–H···O hydrogen bonds seem to be effective in the stabilization of the structure, resulting in the formation of a supramolecular structure.

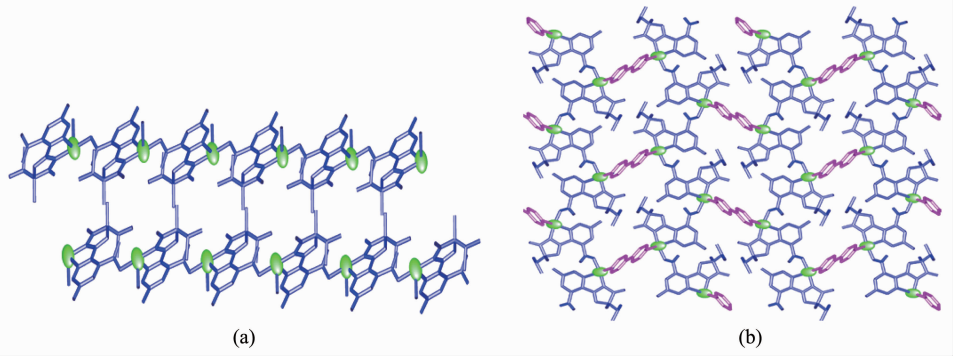


Fig.3 (a) 1D; (b) 2D view of the complex with H atoms are omitted for clarity

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