配合物[Cu$_2$(C$_4$H$_2$O$_6$)(Phen)$_2$(H$_2$O)]·8H$_2$O 的合成、晶体结构和抗菌活性

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摘要：在 pH≈10 的乙醇-水溶液中以硫酸铜、酒石酸和邻菲咯啉反应合成了分子式为[Cu$_2$(C$_4$H$_2$O$_6$)(Phen)$_2$(H$_2$O)]·8H$_2$O 的配合物单晶。用 X-射线单晶衍射测定了晶体结构，并研究了配合物对大肠杆菌、金黄色葡萄球菌、枯草杆菌的抗菌活性。晶体属单斜晶系，空间群 $P2_1$。标题化合物为双核铜配合物，2 个铜原子配位数不同。Cu(1)是五配位的，具有扭曲的四方锥结构，5 个配位原子分别是酒石酸的去质子的羟基氧和羧基氧、邻菲咯啉的 2 个氮原子及 1 个水分子的氧原子。Cu(2)为四配位的，配位原子分别是酒石酸的去质子的羟基氧和羧基氧和邻菲咯啉的 2 个氮原子。分子中 Cu(1)···Cu(2)间的距离为 0.354 8 nm。存在分子内邻菲咯啉-邻菲咯啉的面—面 π-π 相互作用，面间距为 0.381 3 nm。配合物对大肠杆菌、金黄色葡萄球菌、枯草杆菌具有较强的抗菌活性。

关键词：铜配合物；酒石酸；邻菲咯啉；晶体结构；抗菌活性

Synthesis, Crystal Structure and Antibacterial Activity of Binuclear Copper(II) Complex [Cu$_2$(C$_4$H$_2$O$_6$)(Phen)$_2$(H$_2$O)]·8H$_2$O

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Abstract: The title complex [Cu$_2$(C$_4$H$_2$O$_6$)(Phen)$_2$(H$_2$O)]·8H$_2$O (where phen is 1,10-phenanthroline, C$_4$H$_6$O$_6$ is tartaric acid) has been synthesized and characterized by X-ray single-crystal diffraction. It crystallizes in the monoclinic system, space group $P2_1$ with a=0.716 52(6) nm, b=2.205 44(17) nm, c=1.067 83(11) nm, β=102.595(5)°, V=1.646 8(3) nm^3, Z=2, D_c=1.605 g·cm^{-3}, M_r=795.69, μ(Mo $K\alpha$)=1.369 mm^{-1}, F(000)=820, the final R=0.034 1 and wR=0.062 2 for 5 613 observed reflections[I>2σ(I)]. The complex is a binuclear copper compound, and the two Cu(II) atoms are in different coordination environments. The Cu(1) atom is five-coordinated with distorted square pyramid geometry, whereas the Cu(2) atom assumes the coordination geometry of a distorted square plane. The distance of Cu(1)···Cu(2) is 0.354 8 nm. In addition, there exist intramolecular π-π stacking interactions between two phen rings with the interplanar distance of 0.381 3 nm. The complex has a good effect against *E. Coli*, *S. Aureus* and *B. Subtilis*. CCDC: 634855.

Key words: copper(II) complex; tartaric acid; 1,10-phenanthroline; crystal structure; antibacterial activity

　　The binuclear complexes have been widely studied in many fields, such as catalysis, semi-conductor and bioinorganic chemistry because of their rich physical and chemical properties[1~4]. The complexes with carboxylic acids have already been reported[5~8]. Many *N*-con-taining ligands, such as 4,4-bipyridine, 2,2-bipyridine and 1,10-phenanthroline, have been widely applied in constructing coordination polymers as auxiliary ligands [9~11]. In present, hydrogen-bonding interactions and aromatic π-π stacking interactions are frequently exist-

ent, and they are very important non-covalent intermolecular force to form extended multi-dimensional structure from low-dimensional ones. In this paper, we describe the structure of a binuclear copper (Ⅱ) complex $[Cu_2(C_4H_2O_6)(Phen)_2(H_2O)] \cdot 8H_2O$, and weak interactions are also briefly discussed.

1 Experimental

1.1 Preparation of $[Cu_2(C_4H_2O_6)(Phen)_2(H_2O)] \cdot 8H_2O$

$CuSO_4 \cdot 5H_2O$ (2 mmol) and tartaric acid (2 mmol) dissolved respectively in 10 mL water solvent and o-phen (2 mmol) dissolved in ethanol-water (95%) solvent were mixed and stirred for 2 h. The pH value of the resulting solution was adjusted to 10.0 with NaOH solution (10%). The blue single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation at room temperature.

1.2 Crystal structure determination

A blue single crystal (0.60 mm × 0.30 mm × 0.03 mm) of the complex was selected for the X-ray diffraction structural analysis. All measurements were performed on a Siemens SMART CCD X-ray diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K. A total of 12 933 reflections were collected, of which 6 568 (R_{int}=0.036 2) were independent and 5 613 with $I>2\sigma(I)$ were considered as observed. The data set was collected in the range of $2.16° \leqslant \theta \leqslant 27.48°$ with h=−9~9, k=−21~28 and l=−13~13 by using ψ-ω scan

techniques and corrected for Lp effects. The empirical adsorption corrections based on the measurements of equivalent reflections were applied with SADABS[12]. The unit cell parameters were determined and refined using SMART software[13], and raw frame data were reduced with SAINT program[14]. The structure was solved by direct methods with SHELXS-97 program[15]. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined using full-matrix least-squares techniques with SHELXL-97 to the final R=0.034 1 and wR=0.062 2 $\{w=1/[\sigma^2(F_o^2) + (0.012 5P)^2 + 0.000 0P]$, where $P = (F_o^2 + 2F_c^2)/3)\}$ for 5 613 observed reflections with $I>2\sigma(I)$. $(\Delta/\sigma)_{max}$=0.000 and S=1.002. The hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms and treated as riding atoms. In the final difference Fourier map, the residual maximum and minimum peaks are 401 e·nm^{-3} and −291 e·nm^{-3}, respectively.

CCDC: 634855.

2 Results and discussion

2.1 Description of the structure

Crystal data and structure refinement details are listed in Table 1, the selected bond distances and bond angles in Table 2, and the hydrogen bonding in Table 3. The structure of the complex is depicted in Fig.1, and packing of the complex in a unit cell is shown in Fig.2.

The molecule of the complex is a binuclear

Table 1 Crystal data and structure refinement

Empirical formula	$C_{28}H_{36}Cu_2N_4O_{15}$	Absorption coefficient / mm^{-1}	1.369
Formula weight	795.69	F(000)	820
Temperature / K	293(2)	Crystal size / mm	0.60 × 0.30 × 0.03
Wavelength / nm	0.071073	θ range for data collection / (°)	2.16 to 27.48
Crystal system	Monoclinic	Limiting indices	$-9 \leqslant h \leqslant 9, -21 \leqslant k \leqslant 28, -13 \leqslant l \leqslant 13$
Space group	$P2_1$	Reflections collected / unique	12 933 / 6 568 (R_{int}=0.036 2)
a / nm	0.7165 2(6)	Completeness to θ=27.48°	99.9%
b / nm	2.205 44(17)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.067 83(11)	Data / restraints / parameters	6 568 / 23 / 496
β / (°)	102.595(5)	Goodness-of-fit on F^2	1.002
Volume / nm^3	1.646 8(3)	Final R indices [$I>2\sigma(I)$]	R_1=0.034 1, wR_2=0.062 2
Z	2	R indices (all data)	R_1=0.042 7, wR_2=0.065 7
Calculated density / (g·cm^{-3})	1.605	Largest diff. peak and hole/ (e·nm^{-3})	401, −291

Table 2　Selected bond lengths (nm) and angles (°)

Cu(1)-O(3)	0.189 6(3)	Cu(1)-N(2)	0.203 5(2)	Cu(2)-O(5)	0.194 8(3)
Cu(1)-O(1)	0.194 5(2)	Cu(1)-O(11)	0.224 6(2)	Cu(2)-N(4)	0.199 3(2)
Cu(1)-N(1)	0.201 5(3)	Cu(2)-O(4)	0.189 90(19)	Cu(2)-N(3)	0.200 8(3)
O(3)-Cu(1)-O(1)	86.29(10)	N(1)-Cu(1)-O(11)	96.23(11)	C(11)-N(1)-Cu(1)	130.1(3)
O(3)-Cu(1)-N(1)	164.54(10)	N(2)-Cu(1)-O(11)	95.85(9)	C(22)-N(1)-Cu(1)	112.2(2)
O(1)-Cu(1)-N(1)	94.87(11)	O(4)-Cu(2)-O(5)	84.77(11)	C(20)-N(2)-Cu(1)	128.8(3)
O(3)-Cu(1)-N(2)	93.26(12)	O(4)-Cu(2)-N(4)	168.70(10)	C(21)-N(2)-Cu(1)	111.9(3)
O(1)-Cu(1)-N(2)	166.80(10)	O(5)-Cu(2)-N(4)	94.38(13)	C(31)-N(3)-Cu(2)	130.8(3)
N(1)-Cu(1)-N(2)	82.11(14)	O(4)-Cu(2)-N(3)	98.59(12)	C(42)-N(3)-Cu(2)	111.6(2)
O(3)-Cu(1)-O(11)	98.92(10)	O(5)-Cu(2)-N(3)	176.33(10)	C(40)-N(4)-Cu(2)	128.3(3)
O(1)-Cu(1)-O(11)	97.26(9)	N(4)-Cu(2)-N(3)	82.63(13)	C(41)-N(4)-Cu(2)	112.5(3)

Table 3　Bond lengths and bond angles of hydrogen bonds

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠(DHA) / (°)
O(11)–H(1)⋯O(4)#1	0.091 3(18)	0.178 7(19)	0.269 4(3)	172(3)
O(24)–H(18)⋯O(6)#2	0.097 5(18)	0.172 1(19)	0.269 0(4)	172(5)
O(26)–H(22)⋯O(2)#3	0.093(2)	0.192(2)	0.2828(5)	163(5)
O(27)–H(24)⋯O(5)#2	0.095 0(19)	0.207(2)	0.298 6(4)	162(4)
O(28)–H(25)⋯O(4)#1	0.091 8(19)	0.190(2)	0.281 3(4)	171(4)
O(28)–H(26)⋯O(3)	0.093 0(19)	0.174 5(19)	0.267 4(3)	178(4)

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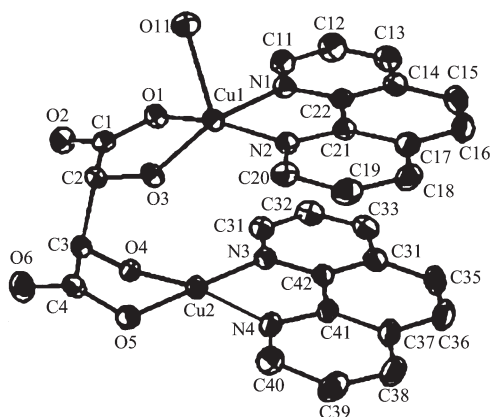

Fig.1　Structure of the complex
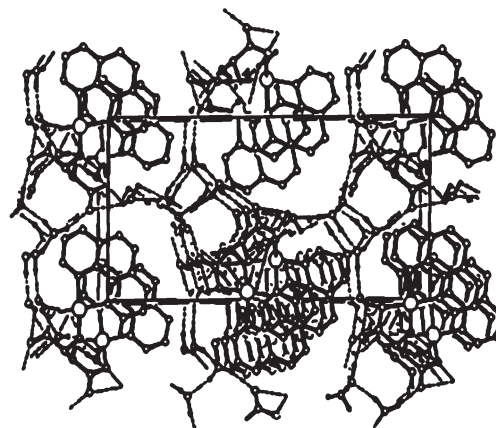

Fig.2　Packing of the complex in a unit cell

molecule with bridged tartrate, in which the two crystallographically independent Cu(Ⅱ) are in different coordination environments. Fig.1 shows a perspective view of the binuclear molecule structure with atoms labeled. The Cu(1) atom is five-coordinated by N(1), N(2) of one phen ligand, O(1), O(3) of tartrate ligand and O (11) of water, assuming a distorted square pyramidal environment. The bond angle of O(1)-Cu(1)-N(1) is 94.87°, O(3)-Cu(1)-O(1)86.29°, O(3)-Cu(1)-N(2) 93.26° and N(1)-Cu(1)-N(2) 82.11°, with the sum

of 356.53°. Therefore the plane consisting of Cu, N(1), N(2), O(1) and O(3) is uncoplanar. The bond angles of O(1)-Cu(1)-O(11), O(3)-Cu(1)-O(11), N(2)-Cu(1)-O(11) and N(1)-Cu(1)-O(11) are 97.26°, 98.92°, 95.85° and 96.23°, respectively, indicating atom O (11) is at the top of the pyramid and N(1), O(1), N(2), O(3) at the bottom. The distances of Cu (1) and O (10) to the bottom are 0.024 27 nm and 0.248 80 nm, respectively. The Cu (2) atom is surrounded by two nitrogen atoms N (3) and N (4) from the other phen ligand, and two

oxygen atoms O(4) and O(5) from tartrate ligand, giving a distorted square-planar geometry. Four coordinated oxygen atoms from hydroxyl and carboxyl group of tartaric acid are all deprotonated. The basal bond angles around Cu(2) is 360.37°, showing that the Cu(2) atom is essentially in the mean plane of the basal donors. The distance between the two copper atoms Cu(1)···Cu(2) is 0.354 8 nm.

In addition, there exist intramolecular π-π stacking interactions between two phen rings with the interplanar distance of 0.381 3 nm. The crystal water molecules form hydrogen bonding with the coordinated oxygen atoms and other crystal water molecules to generate a 3-dimensional structure.

2.2　Antibacterial activity[16]

Medium consisted of beef extract and peptone, apparatuses involved in the experiment and Φ 6 mm filter papers were placed at 121 ℃ for 30 min. The medium was cooled down to 50 ℃ and divided into three groups of culture dishes to form solid plates into which *E. Coli*, *S. Aureus* and *B. Subtilis* were inoculated respectively.

Table 4　Diameter of antibacterial active ring (mm) of complex

Concentration/ (g·L⁻¹)	15	10	7.5	5	2.5
E. Coli	29.5	28	27	26	23
S. Aureus	35	34	32.5	31	27.5
B. Subtilis	28	27	27	27	26

Table 5　Diameter of antibacterial active ring (mm) of CuSO₄

Concentration / (g·L⁻¹)	15	10	7.5	5	2.5
E. Coli	12	11	7.5	—	—
S. Aureus	10.5	9	8.5	7.5	7
B. Subtilis	7.5	7.5	7.5	7	—

The inoculated mediums covered by the filter papers immerged into the complex solution were incubated at constant temperature 37 ± 1 ℃. After 24 h diameter of antibacterial active ring was assayed.

The complex has a good effect against *E. Coli*, *S. Aureus* and *B. Subtilis*. It is to say that the complex owns a wide bacteriostatic spectrum. The activity of the complex increases as the concentration increases because it is a well known fact that concentration

plays a vital role in increasing the degree of inhibition. The results indicate that the complexes exhibit greater antimicrobial activity compared to that of CuSO₄ under identical experimental conditions. This would suggest that the chelation could facilitate the ability of the complex to cross a cell membrane[17]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with donor groups and possible electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane.

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