

[Cu(PTA)(Phen)₂](*p*-MBA)(H₂O)配合物的合成、晶体结构及电化学分析

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Synthesis, Crystal Structure and Electrochemical Properties of Copper(II) Complex [Cu(PTA)(Phen)₂](*p*-MBA)(H₂O)

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Abstract: The crystal structure of the title complex with the stoichiometric formula [Cu(PTA)(Phen)₂](*p*-MBA)(H₂O) (Phen=1,10-phenanthroline, PTA=terephthalic acid, *p*-MBA=*p*-toluic acid) has been determined by single-crystal X-ray diffraction. The crystal (C₄₈H₄₀CuN₄O₁₀, *M_r*=896.38) belongs to the monoclinic space group *C*2/*c*, with the following crystallographic parameters: *a*=1.778 6(3) nm, *b*=1.912 5(3) nm, *c*=1.389 9(2) nm, *β*=114.686(2)°, *V*=4.295 7(12) nm³, *D_c*=1.386 g·cm⁻³, *Z*=4, *μ*(Mo *Kα*)=0.574 mm⁻¹, *F*(000)=1 860, final *GooF*=1.019, *R*=0.054 0, *wR*=0.148 3 for 2 644 observed reflections (*I*>2σ(*I*)). The crystal structure shows that the copper(II) ion is coordinated with two oxygen atoms from one terephthalic acid molecule and four nitrogen atoms from two 1,10-phenanthroline molecules, forming a distorted octahedral coordination geometry. The cyclic voltametric behavior of the complex is also reported. CCDC: 298809.

Key words: copper(II) complex; crystal structure; electrochemical property

0 Introduction

P-toluic acid is a very important chemical product, used extensively in the syntheses of pesticides, medicines, sensitive materials, organic pigments and plastics^[1]. Terephthalic acid is a frequently used polydentate ligand of bridging function, and it is used together with transition metals in the synthesis of binary complexes, which are reported as gas-storing materia-

ls^[2]. Since the recent discovery of the potential properties of carboxylic complexes in optics, magnetics, adsorptive separation, information storage and catalysis^[3], many terephthalic acid-bridged binuclear and polynuclear complexes with 1D, 2D or 3D structure have been synthesized^[4-6]. From the aspects of its synthesis method, structure and spectroscopic properties we report in this paper a mononuclear three-dimension copper(II) complex synthesized with the ligands tereph-

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thalic acid, *p*-toluic acid, and 1,10-phenanthroline.

1 Experimental

1.1 Materials and instrumentation

All materials were of analytical grade and used without further purification. IR spectra were measured with KBr pellets and a Shimadzu FTIR-8700 instrument in the range of 400~4 000 cm^{-1} . Elemental analysis of carbon, hydrogen, nitrogen was carried out with a Perkin-Elmer 2400 Analyzer. The electron transfer behavior of the complex was examined by means of cyclic voltammogram on a LK 98 electrochemical instrument. The melting point was determined with a not-previously-adjusted thermometer and a XT4 Microscopic Melting-point Detector.

1.2 Synthesis

$\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (2 mmol), *p*-toluic acid (2 mmol) and terephthalic acid (2.50 mmol) were dissolved in EtOH (50 mL), and then Phen (4 mmol) was added. The solution was set carefully to pH=6 with dilute aqueous solution of NaOH and the final mixture was refluxed for 8 hours. Subsequently, it was filtered and the filtrate was kept untouched and evaporated slowly at room temperature. Two weeks later, light green crystalline solid appeared and the title complex was obtained. Yield: 55%. Anal. calcd. (%) for $\text{C}_{48}\text{H}_{40}\text{CuN}_4\text{O}_{10}$: C, 64.31; H, 4.50; N, 6.25. Found (%): C, 64.26; H, 4.48; N, 6.23. Melting point: 238.5~239.0 $^{\circ}\text{C}$. IR (KBr, cm^{-1}): 3 446.0(s), 2 322.1(m), 1 868.9(m), 1 670.2(vs), 1 637.5(vs), 1 612.4(vs), 1 568.0(m), 1 544.9(m), 1 517.9(m), 1 508.2(m), 1 488.9(m), 1 454.2(s), 1 404.1(s), 1 319.2(m), 1 286.4(m), 1 184.2(m), 1 103.2(m), 850.5(m), 756.0(m), 744.5(m), 721.3(m), 590.2(w), 418.5(w).

1.3 X-ray structure determination

A light green single crystal with dimensions of 0.22 mm \times 0.20 mm \times 0.12 mm was used for structural determination at 294(2) K with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) on a Bruker SMART 1000 CCD diffractometer. A total of 12 003 reflections were collected in the 2θ range from 1.65 $^{\circ}$ to 26.40 $^{\circ}$, of which 4 396 ($R_{\text{int}}=0.039\,0$) were independent and 2 644 with $I>2\sigma(I)$ were considered as ob-

served. The structure was solved by the direct method and successive difference Fourier syntheses, and the refinement on F^2 was performed by virtue of full-matrix least-squares. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated position. All calculations were performed on a computer with SHELX-97 program package^[7]. The final $R=0.054\,0$ and $wR=0.148\,3$ ($w=1/[\sigma^2(F_o^2)+(0.099\,6P)^2+2.095\,1P]$, where $P=(F_o^2+2F_c^2)/3$). (Δ/σ)_{max}=0.003, $S=1.019$, ($\Delta\rho$)_{max}=647 and ($\Delta\rho$)_{min}=-402 $\text{e}\cdot\text{nm}^{-3}$. Crystallographic data for the title complex are shown in Table 1.

CCDC: 298809.

Table 1 Crystallographic data for the title complex

Empirical formula	$\text{C}_{48}\text{H}_{40}\text{CuN}_4\text{O}_{10}$
Formula weight	896.38
Color / habit	Green / octahedral
Size / mm	0.22 \times 0.20 \times 0.12
θ range for data collection / ($^{\circ}$)	1.65 to 26.40
Crystal system	Monoclinic
Space group	$C2/c$
a / nm	1.778 6(3)
b / nm	1.912 5(3)
c / nm	1.389 9(2)
β / ($^{\circ}$)	114.686(2)
V / nm^3	4.295 7(12)
D / ($\text{g}\cdot\text{cm}^{-3}$)	1.386
Z	4
$F(000)$	1 860
$\mu(\text{Mo } K\alpha)$ / mm	0.574
Reflections collected	12 003
Independent reflections	4 396 ($R_{\text{int}}=0.039\,0$)
Final GOF	1.019
R_1, wR_2 [$I>2\sigma(I)$]	0.054 0, 0.148 3
R_1, wR_2 (all data)	0.103 6, 0.180 2
Largest difference peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	647, -402

2 Results and discussion

2.1 Infrared absorption spectrum

The strong and broad band at 3 446.0 cm^{-1} occurs in the IR spectrum of the complex, which is most probably ascribed to the stretching vibration of uncoordinated water molecule. Compared with the carboxylic stretches (1 678.0 cm^{-1} , 1 423.4 cm^{-1}) of the

free terephthalic acid, the strong band at 1 670.2 cm⁻¹ is the absorption peak of its uncoordinated carboxyl and $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ of its coordinated carboxyl shift to 1 637.5 cm⁻¹ and 1 454.2 cm⁻¹ respectively. The $\Delta\nu[\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-)=183.3 \text{ cm}^{-1}]$ between the two bands of the coordinated carboxyl is less than 200 cm⁻¹, which indicates that in the complex the coordinated carboxyl is bidentate^[8]. These are consistent with the results of crystal structure analysis. In addition to those mentioned above, it was also found that the absorption bands due to $\delta_{\text{C}=\text{C}}$, $\delta_{\text{C}-\text{H}}$ of phen red-shift from 854 cm⁻¹, 740 cm⁻¹ to 850.5 cm⁻¹, 721.3 cm⁻¹, respectively. This indicates that phen molecules take part in the coordination with the central copper(II) ion^[9].

2.2 Crystal structure

Fig.1 is an ortep view of the complex molecular structure and Fig.2 a packing diagram of the complex with hydrogen bonds. Selected bond distances and angles are collected in Table 2. Selected hydrogen bond distances and angles are given in Table 3.

The complex structure consists of [Cu(PTA)(Phen)₂], *p*-MBA and H₂O. The copper(II) ion is surrounded by two Phen molecules and one terephthalic acid. Two oxygen atoms from the terephthalic acid and four nitrogen atoms of two 1,10-phenanthroline molecules

coordinate with the copper(II) ion. The donor atoms are arranged in an octahedral configuration with N(1), N

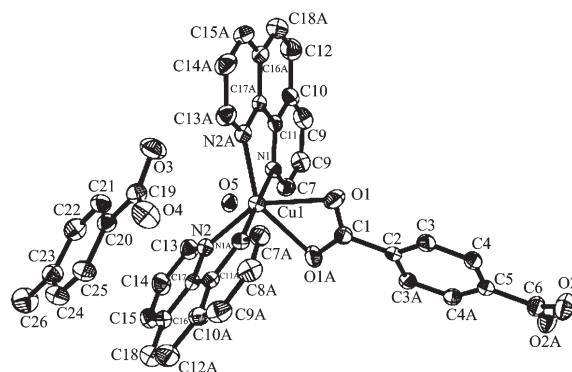


Fig.1 Molecular structure of the title complex

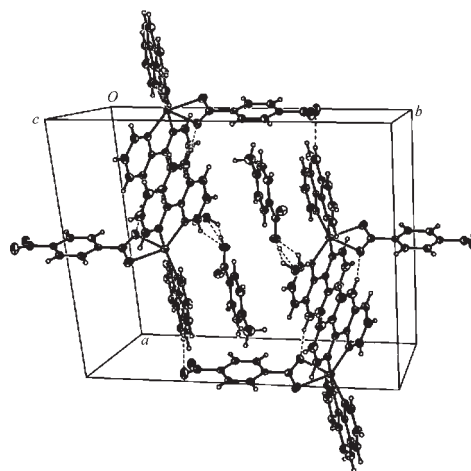


Fig.2 Packing diagram of the title complex in a cell

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

Cu(1)-N(1A)	0.199 9(3)	Cu(1)-N(2A)	0.210 6(3)	O(1)-C(1)	0.124 4(4)
Cu(1)-N(1)	0.199 9(3)	Cu(1)-O(1)	0.230 0(3)	C(1)-O(1A)	0.124 4(4)
Cu(1)-N(2)	0.210 6(3)	Cu(1)-O(1A)	0.230 0(3)	C(1)-C(2)	0.150 7(8)
N(1A)-Cu(1)-N(1)	179.00(16)	N(2)-Cu(1)-N(2A)	123.01(16)	N(1A)-Cu(1)-O(1)	91.41(11)
N(1A)-Cu(1)-N(2)	80.59(11)	N(1A)-Cu(1)-O(1)	87.71(11)	N(1)-Cu(1)-O(1A)	87.71(11)
N(1)-Cu(1)-N(2)	99.89(11)	N(1)-Cu(1)-O(1)	91.41(11)	N(2)-Cu(1)-O(1A)	90.93(11)
N(1A)-Cu(1)-N(2A)	99.90(11)	N(2)-Cu(1)-O(1)	145.42(11)	N(2A)-Cu(1)-O(1A)	145.42(11)
N(1)-Cu(1)-N(2A)	80.58(12)	N(2A)-Cu(1)-O(1)	90.93(11)	O(1)-Cu(1)-O(1A)	56.74(15)

Table 3 Hydrogen bond lengths and angles

D-H...A	Symmetry operation	D-H / nm	H-A / nm	D...A / nm	∠DHA / (°)
O(3)-H(3A)···O(5)	$x, y, 1+z$	0.085 03	0.177 51	0.260 2(4)	163.76
O(5)-H(5A)···O(2)	$1-x, -y, 1-z$	0.084 44	0.186 17	0.270 3(4)	174.07
O(5)-H(5B)···O(3)	$x, y, -1+z$	0.087 53	0.220 37	0.260 2(4)	107.34
C(12)-H(12)···O(2)	$1/2+x, 1/2+y, z$	0.092 84	0.252 88	0.344 2(7)	167.79
C(13)-H(13)···O(3)	$1-x, y, 3/2-z$	0.092 98	0.248 83	0.330 5(6)	146.73
C(18)-H(18)···O(1)	$-1/2+x, 1/2-y, -1/2+z$	0.092 94	0.249 61	0.328 9(6)	143.33

(2), N(1A), O(1) being at the quadrilateral positions and N(2A), O(1A) being at axial positions. The bond angles of N(1)-Cu(1)-N(2), N(1A)-Cu(1)-N(2), N(1A)-Cu(1)-O(1), N(1)-Cu(1)-O(1) are $99.89(11)^\circ$, $80.59(11)^\circ$, $87.71(11)^\circ$ and $91.41(11)^\circ$, respectively. The total of these bond angles is 359.6° , which shows that the four atoms N(1), N(2), N(1A), and O(1) are almost coplanar. The least-square plane equation is $8.1613x + 13.1252y + 11.0264z = 10.7469$. N(1) and N(1A) are above the plane and their deviations from the plane are 0.02645 nm and 0.0337 nm, respectively. N(2) and O(1) are below the plane and their deviations from the plane are -0.03145 nm and -0.02837 nm, respectively. The deviation from the plane for Cu(1) is 0.03110 nm. The deviation distances for axial atoms N(2A) and O(1A) are 0.23159 nm and -0.18716 nm, respectively. The coordination bond distances between the copper(II) ion and the nitrogen atoms of the 1,10-phenanthroline ligand are: Cu(1)-N(2), 0.2106(3) nm; Cu(1)-N(2A), 0.2106(3) nm; Cu(1)-N(1), 0.1999(3) nm; Cu(1)-N(1A), 0.1999(3) nm. The bond lengths of Cu(1)-N(2) and Cu(1)-N(2A) are slightly longer than those of Cu(1)-N(1), Cu(1)-N(1A), which indicates that N(1) and N(1A) are more strongly coordinated to the copper(II) ion than N(2) and N(2A). The mean bond distance of Cu-N is 0.20525(3) nm, which is shorter than that of Cu-N observed in the complex Cu(Phen)₂(dca)₂ [av. 0.2150(4) nm]^[10]. In addition, the bond length of Cu(1)-O(1) [0.2300(3) nm] is equal to that of Cu-O(1A); C(1)-O(1) and C(1)-O(1A) bond lengths of one carboxyl are obviously equivalent to 0.1244(4) nm, which indicates that the carboxylic oxygen atom O(1) and O(1A) are coordinated to the copper(II) ion and the terephthalic acid is a bidentate ligand. On the basis of these results, the copper(II) ion in the complex is distortedly octa-coordinated.

It is worthy to note that the crystal is stabilized by extensive hydrogen bonds. With the uncoordinated water molecule being the bridge, the *p*-toluic acid molecule is connected with the [Cu(PTA)(Phen)₂] molecule by hydrogen bonds. H(3A) in the uncoordinated *p*-toluic acid molecule is attached to O(5) in the uncoordinated water molecule to form bond O(3)-H(3A)⋯O(5)

[0.2602(4)nm, 163.76°]. H(5B) in the uncoordinated water molecule is connected with O(3) in the nearby uncoordinated *p*-toluic acid molecule and they form a strong bond O(5)-H(5B)⋯O(3) [0.2602(4) nm, 107.34°]. H(5A) in the same uncoordinated water molecule is bonded with O(2) of the uncoordinated carboxyl from the terephthalic acid to form bond O(5)-H(5A)⋯O(2) [0.2703(4) nm, 174.07°]. In addition, the 1,10-phenanthroline is connected with the uncoordinated *p*-toluic acid molecule and the coordinated terephthalic acid by weak hydrogen bonds C(13)-H(13)⋯O(3) [0.3305(6) nm, 146.73°], C(12)-H(12)⋯O(2) [0.3442(7) nm, 167.79°], and C(18)-H(18)⋯O(1) [0.3289(6) nm, 143.33°]. In a word, Cu(PTA)(Phen)₂, *p*-MBA, and H₂O are bonded with each other to form a stabilized structure through strong and weak hydrogen bonds.

2.3 Cyclic voltammogram

Fig.3 is a cyclic voltammogram of the title complex. In the mixed solution of water and methanol, the electrochemical experiment of the title complex ($4.46 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) was carried out with a glass carbon (GC) working electrode, a Pt plate auxiliary electrode and a saturated calomel (SCE) reference electrode. All the potentials are reported against SCE. The scanning rate was $50 \text{ mV} \cdot \text{s}^{-1}$. The cyclic voltammogram of the title complex shows there is only one pair of redox peaks, which probably corresponds to the redox couple of copper(II)/copper(I). $E_{\text{pa}}=0.173 \text{ V}$, $E_{\text{pc}}=-0.300 \text{ V}$. The average formal potential [$E_{1/2}=(E_{\text{pa}}+E_{\text{pc}})/2$] is -0.0635 V . The peak-to-peak separation is 0.473 V, exhibiting a quasi-reversible electrode process.

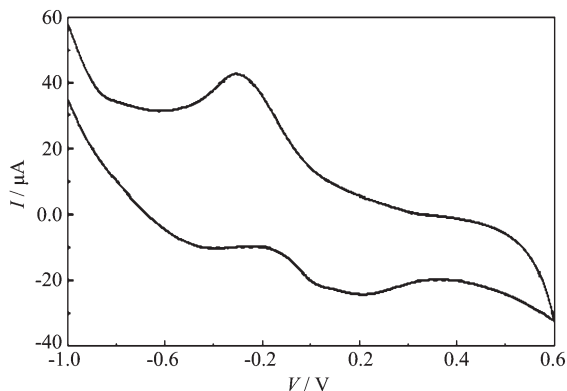


Fig.3 Cyclic voltammogram of the title complex

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