研究简报

N,*N*′-二苄基-苯并咪唑四氯合铜(Ⅱ)化合物的合成、结构和性能研究

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Study on Synthesis, Structure and Properties of the *N*,*N*′-dibenzyl-benzimidazolium Tetrachlorocuprate(Ⅱ) Complex

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Abstract: A novel *N*,*N*′-dibenzyl-benzimidazolium tetrachlorocuprate(Ⅱ) complex, $[C_{21}H_{19}N_2]_2[CuCl_4]$, was synthesized and its crystal structure was determined by X-ray diffraction. It crystallizes in monoclinic system, space group *P*2/*c*, *a*=1.203 9(2) nm, *b*=0.975 0(2) nm, *c*=1.878 2(6) nm, *β*=114.12(2)°, *V*=2.012 2(8) nm^3. Its structure was identified by EA, IR and UV spectra and characterized by electrochemistry, thermal and magnetic property. The Cu(Ⅱ) atom of $[CuCl_4]^{2-}$ has distorted tetrahedral coordination geometry. In the crystal structure, there are strong extensive C–H···Cl hydrogen bonds and *π*-*π* stacking interactions, which stabilized the crystal structure. CCDC: 221570.

Key words: tetrachlorocuprate(Ⅱ) complex; benzimidazole derivation; TG-DSC; magnetic property

0 Introduction

Although biological systems efficiently organize simple units into aggregates with intricate and wonderful functions by non-covalent interactions, self-assembly of frameworks with specific topology, interesting properties and functions is still a challenge for chemists[1]. A number of hydrogen-bonded aggregates have been obtained by self-organization of organic or organic-inorganic components [2,3]. Hydrogen bonding between the organic cation and the metal layer is an important issue in understanding the organic-inorganic hybrid materials, which influences both the alignment and spacing of the nearest-neighbor metal sheets or chains. Liu et al. even reported that protonated 2,6-diaminopyridine and its derivations could crossed-link copper halide complexes through N–H···X (X=Cl, Br) and extensive C–H···X (X=Cl, Br) hydrogen bonding[4]. Hitchcock group also investigated the hydrogen-bond acceptor abilities of tetrachlorometalate(Ⅱ) complexes in ionic liquids. In their paper, the crystal structures of $[emim]_2[MCl_4]$ [emim=1-ethyl-3-methylimidaxolium,

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M=Co or Ni] demonstrate the involvement of all three ring protons in hydrogen bonds with the tetrachlorometalate(Ⅱ) anion[5]. Now, in this work, we report synthesis and crystal structure of the title compound, which is stabilized by not only ions electrostatic forces but also extensive C−H···Cl hydrogen bond and π-π stacking interaction. The IR and electronic reflectance spectra, electrochemistry property, the thermal stability and magnetic property of the title compound also have been studied.

1 Experimental

1.1 Materials and general methods

Elemental analyses were obtained with a Perkin-Elmer 1400C analyzer at the Analysis and Measurement Centre of Nanjing University. IR spectra were recorded on a Nicolet 170SX FT spectrophotometer with KBr pellets in the range from 4 000~500 cm^{-1}. Electronic reflectance spectra were recorded on a Shimadzu 240 spectrophotometer. The cyclic voltammogram was recorded on CHI 832 electrochemical analyzer in H_2O/EtOH mixture solution using a conventional three-electrode system, which consisted of a glassy carbon working electrode and Pt auxiliary electrode, an Ag/AgCl reference electrode, and a scan rate of 100 $mV \cdot s^{-1}$. A supporting electrolyte for measurement was 1.0×10^{-3} $mol \cdot L^{-1}$ KCl solution. The concentration of the title compound solution is 1.0×10^{-4} $mol \cdot L^{-1}$ and that of the DNA solution is 1.0×10^{-4} $mol \cdot L^{-1}$. TG and DSC curves were recorded on a NETZSCH-Geratebau GmbH thermoanalyser in flow of N_2, in the temperature range from 20 ℃ to 800 ℃, with a heating rate of 10 ℃·min^{-1}. Variable temperature magnetic susceptibilities were determined on a CAHN-2000 magnetic balance (75~300 K).

1.2 Synthesis of the title compound

All chemical reagents were obtained from a commercial source and used without further purification. Calf thymus DNA (CT-DNA) obtained from Sigma Company was also used as received.

Benzimidazole (0.24 g, 2.0 mmol) was reacted with benzyl chloride (0.52 g, 4.0 mmol) in 20 mL pyridine. After refluxing for 2 h, solid of anhydrous $CuCl_2$ (0.14 g, 1.0 mmol) was added. The reaction mixture was kept refluxing for 4 h, and the light yellow precipitate was formed, and then cooled to room temperature. The products were collected and the brown-yellow crystals were obtained by recrystallization from EtOH. (Anal. calc. for $C_{42}H_{38}N_4Cl_4Cu$: C, 62.73; H, 4.76; N, 7.00%. found: C, 62.69; H, 4.72; N, 6.95%). m.p. 49~51 ℃. Yield: 80%.

1.3 Determination of crystal structure

In the determination of the structure of the single crystal, X-ray intensities data were recorded by Rigaku Raxis-Ⅳ diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). In the range of $1.85°<\theta<24.56°$, 3 331 independent reflections were obtained. Intensities were corrected for Lorentz and polarization effects and empirical absorption.

The structure was solved by direct methods using SHELXS-97[6] program. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. The hydrogen atoms were located from the difference Fourier map. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave R= 0.037 0, wR=0.065 2 for 2 015 reflections with $I>2\sigma(I)$; the weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.030\ 4P)^2]$, where $P=(F_o^2+2F_c^2)/3$. The max and min difference peaks and holes are 282 and −240 $e \cdot nm^{-3}$, respectively. S=0.898.

CCDC: 221570.

2 Results and discussion

2.1 Crystal and molecular structure of the title compound

Fig.1 shows the molecular structure of the compound. Selected bond distances and angles are listed in Table 2. Fig.2 shows a perspective view of the crystal packing in the unit cell for the title compound. The structure consists of a tetrahedral $CuCl_4^{2-}$ anion linked by two *N*,*N*′-dibenzyl-benzimidazolium cations through not only ions electrostatic forces but also extensive C−H···Cl hydrogen bonds. The Cu-Cl lengths are in the range from 0.223 16(9) to 0.225 64(9) nm and the Cl-Cu-Cl angles vary within the range from 98.16(5) to 133.96(4)°. These bond distances and angles are in good agreement with those of the Cu^{2+} ion in the distorted tetrahedral coordination[7]. In the title compound, the large range for the Cl-Cu-Cl angles in $CuCl_4^{2-}$ ion is attributed to the fact that it has an orbital degenerate state $^2T_2$ and is subjected to a rather

Table 1　Crystal data and structure refinement for the title complex

Empirical formula	$C_{21}H_{19}Cl_2Cu_{0.5}N_2$
Formula weight	804.10
Crystal system	Monoclinic
Space group	*P*2/*c*
a / nm	1.203 9(2)
b / nm	0.975 0(2)
c / nm	1.878 2(6)
β / (°)	114.12(2)
Volume / nm^3	2.012 2(8)
Z	4
Calculated density / ($Mg·m^{-3}$)	1.327
Absorption coefficient / mm^{-1}	0.843
F(000)	830
Limiting indices	$0 \leqslant h \leqslant 15$, $-12 \leqslant k \leqslant 11$, $-23 \leqslant l \leqslant 21$
Reflections collected / unique	5 218 / 3 331 [R_{int}=0.029 5]
Data / restraints / parameters	3 331 / 0 / 231
Goodness-of-fit on F^2	0.898
Final *R* indices [$I>2\sigma(I)$]	R_1=0.037 0, wR_2=0.065 2
R indices (all data)	R_1=0.103 4, wR_2=0.073 6
Largest diff. peak and hole / ($e·nm^{-3}$)	282 and −240

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

Cu(1)-Cl(2)	0.223 16(9)	Cu(1)-Cl(4)	0.223 16(9)
Cu(1)-Cl(1)	0.225 64(9)	Cu(1)-Cl(3)	0.225 64(9)
Cl(4)-Cu(1)-Cl(2)	98.99(5)	Cl(4)-Cu(1)-Cl(1)	99.02(3)
Cl(2)-Cu(1)-Cl(1)	133.96(4)	Cl(4)-Cu(1)-Cl(3)	133.96(4)
Cl(2)-Cu(1)-Cl(3)	99.02(3)	Cl(1)-Cu(1)-Cl(3)	98.16(5)

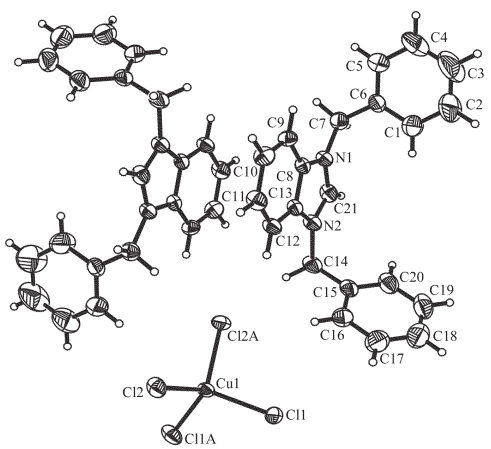

Fig.1　Molecular structure with the atomic numbering scheme for $[C_{21}H_{19}N_2]_2[CuCl_4]$

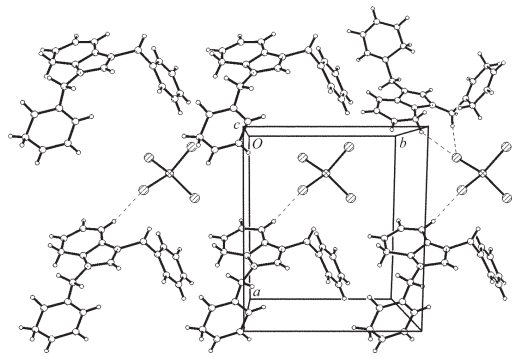

Fig.2　A perspective view of the crystal packing in the unit cell for $[C_{21}H_{19}N_2]_2[CuCl_4]$

large Jahn-Teller force that leads to a compressed tetrahedron. Bond distances and angles in the two *N*,*N*′-dibenzyl-benzimidazolium cations fall within the normal rang, with average distance of C-N in benzimidazole ring 0.132 6(3) nm. The benzimidazole ring with conjunction C(14), C(7) atoms are fairly planar, the largest deviation from the plane is 0.002 2 nm. The dihedral angles of this plane and two conjunction phenyl rings are 69.05 and 84.65°, respectively. The two phenyl rings form a dihedral angle of 70.97°.

The important feature of the structure is the existence of hydrogen-bonds (See Table 3). In a survey of neutron diffraction data, Taylor and Kennard[8] have demonstrated, using the values of 0.12 and 0.175 nm for the van der Waals radii of hydrogen and chlorine atoms respectively, that a contact shorter than 0.295 nm reliably indicates the presence of a C–H⋯Cl hydrogen bond. In the title compound, the shortest contact H(21A)⋯Cl(1) [0.260 82 nm] indicates that a strong, discrete hydrogen bond is formed between the H_2 proton of the *N*,*N*′-dibenzyl-benzimidazolium cations and a chlorine atom of the anion. The existences of these hydrogen bonds demonstrate that the salt cannot be described as a simple collection of ion pairs. In addition, there are three types of strong *π*-*π* stacking interactions; imidazole ring (*X*, *Y*, *Z*)-phenyl ring (1−*X*, 2−*Y*, −*Z*), phenyl ring (*X*, *Y*, *Z*)-imidazole ring (1−*X*, 2−*Y*, −*Z*) and phenyl ring (*X*, *Y*, *Z*)-phenyl ring (1−*X*, 2−*Y*, −*Z*). The center-to-center distances are 0.375 8, 0.375 8 and 0.374 2 nm, respectively. The shortest interplanar distances above are 0.357 9, 0.355 3 and 0.357 8 nm, respectively. In the solid state, all above extensive hydrogen bonds and *π*-*π* stacking interactions stabilize the crystal structure.

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

D–H···A	Symmetry code	D-H	H···A	D···A	D–H···A
C(7)–H(7A)···Cl(2)	x, 1+y, z	0.097 00	0.276 63	0.370 55	163.19
C(12)–H(12A)···Cl(2)	1–x, 1–y, –z	0.093 00	0.281 28	0.365 18	150.61
C(21)–H(21A)···Cl(1)		0.093 00	0.260 82	0.347 83	155.97

In IR, two absorption bands at 3 429 and 3 033 cm^{-1} are assigned to the C-H stretching vibration of the benzimidazole ring. The title compound also exhibits characteristic strong bands at 1 561(C=C), 1 618 (C-N for $\nu_{C\text{-}N^{+}\text{-}R}$), 1 454, 1 374 (C=N), 744 ($\nu_{C\text{-}H}$ benzene ring) and 705 cm^{-1} ($\nu_{C\text{-}H}$ imidazole ring) for the substuituted benzimidazole ring [9]. For the title compound, the band at 1 454 and 1 374 cm^{-1} are attributed to the stretching vibration of C=N, which are shifted from their positions for the free benzimidazole ligand (1 454 and 1 383 cm^{-1})[10], indicating nitrogen substitution.

The solid reflectance electronic spectrum of the title compound shows two broad bands around 290 and 500 nm. The former can be to intra-ligand, probably $\pi \rightarrow \pi^{*}$, transition of the benzimidazole group, and the latter to a *d-d* transitions of the Cu(Ⅱ) moiety, which may be taken as evidence for tetrahedral Cu(Ⅱ) spin-allowed transition $^{2}T_{2}(D) \rightarrow {}^{2}E_{2}(D)$.

The cyclic voltammogram of the title compound (curve 1) was measured in H_2O/EtOH solution in the range 1.2 to –0.6 V. The title compound is electrochemically active and displays a clearly quasi-reversible redox process at E_{pa}=0.625 V and E_{pc}=0.225 V, which is assigned to a one-electron redox that is $Cu^{Ⅱ}/Cu^{Ⅰ}$ (Fig.3). In curve 2, when DNA solution was added in, it could be seen that the redox potentials and the oxidation peak current did not change while the reduction peak decreased apparently, which suggested that there exist a strong interaction between the title compound and the DNA. So the title compound could be used as probe to investigate the interaction between transition metal compounds with DNA. The further study is in progress.

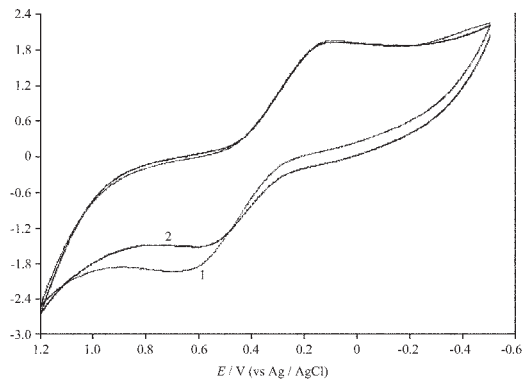

Fig.3 Cyclic voltammogram (1) the title compound (2) the title compound + DNA

2.2 Thermal analysis

The title compound has no weight loss at above 49 ℃ and has a small absorption peak, which is attributed to the phase-changing of the title compound. The compound began to loss at about 100~200 ℃ corresponding to one benzyl group (calc. 11.31%), which is assigned to the second endothermal peak. Then the compound continued to decompose, and, at 500 ℃, the residue is $CuCl_2$ (lose weight: Calc.: 83.21%, Found: 83.22%).

2.3 Magnetic property

The magnetic susceptibility of a powdered sample was measured from 75 to 300 K. The magnetic susceptibility as a function of temperature is shown in Fig.4 in terms of χ_m vs T (left) and $1/\chi_m$ vs T (right),

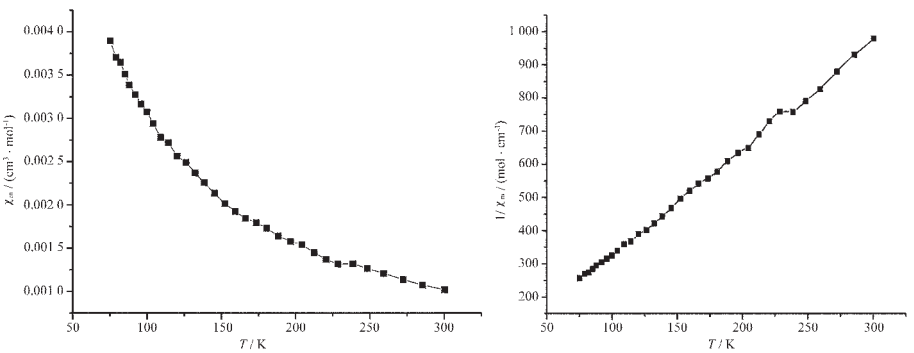

Fig.4 Temperature dependence of χ_m (left), $1/\chi_m$ (right) for the title compound

where χ_m is the molar magnetic susceptibility per copper atom and T the temperature. The complex obeys the Curie-Weiss law $\chi_m=C/(T-\theta)$, with C=0.311 $cm^3 \cdot K \cdot mol^{-1}$ and θ=−4.67 K, respectively. This behaviour suggests that a very weak antiferromagnetic interaction operate in the title compound. The decrease of the effective magnetic moment from 1.55 B.M. per Cu(Ⅱ) at 300 K to 1.48 B.M. per Cu(Ⅱ) at 75 K. The effective magnetic moment per copper atom at room temperature is 1.58 B.M., which is smaller than the spin only value for independent Cu ions of 1.73 B.M.

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