

铜配合物 $[\text{CuL}_2(\text{ClO}_4)_2]$ 的合成、晶体结构及热稳定性 ($\text{L}=3\text{-对溴苯基-4-对甲苯基-5-(2-吡啶基)-1,2,4-三氮唑}$)

陈 浪 程慧敏 江静静 沈 旋 朱敦如*

(南京工业大学化学化工学院,材料化学工程国家重点实验室,南京 210009)

摘要:以 3-对溴苯基-4-对甲苯基-5-(2-吡啶基)-1,2,4-三氮唑(L)作为配体,合成了 1 个铜配合物 $\text{trans-}[\text{CuL}_2(\text{ClO}_4)_2]$,对其进行了红外、电喷雾质谱、热重分析和单晶结构表征,该配合物属于三斜晶系,空间群 $P\bar{1}$, $a=0.829\,29(15)\text{ nm}$, $b=0.854\,48(16)\text{ nm}$, $c=1.502\,7(3)\text{ nm}$, $\alpha=83.517(2)^\circ$, $\beta=89.200(2)^\circ$, $\gamma=73.064(2)^\circ$, $V=1.011\,9(3)\text{ nm}^3$, $Z=1$, $R_1=0.041\,2$ 。单晶结构表明,铜离子处于 1 个扭曲的八面体配位环境中,2 个高氯酸根离子呈反式配位,每个配体 L 通过三氮唑上的 1 个氮原子和吡啶氮原子参与配位。热重分析表明该配合物在 310 °C 开始发生分解。

关键词: 铜配合物; 晶体结构; 三氮唑

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Synthesis, Crystal Structure and Thermal Stability of $[\text{CuL}_2(\text{ClO}_4)_2]$ ($\text{L}=3\text{-(}p\text{-Bromophenyl)-4-(}p\text{-methylphenyl)-5-(2-pyridyl)-1,2,4\text{-triazole}$)

CHEN Lang CHENG Hui-Min JIANG Jing-Jing SHEN Xuan ZHU Dun-Ru*

(College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented

Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China)

Abstract: A copper(II) complex, $\text{trans-}[\text{CuL}_2(\text{ClO}_4)_2]$, ($\text{L}=3\text{-(}p\text{-bromophenyl)-4-(}p\text{-methylphenyl)-5-(2-pyridyl)-1,2,4\text{-triazole}$), was synthesized and characterized by FTIR, ESI-MS, TGA/DSC and X-ray crystallography. The complex crystallizes in triclinic system with space group $P\bar{1}$, $a=0.829\,29(15)\text{ nm}$, $b=0.854\,48(16)\text{ nm}$, $c=1.502\,7(3)\text{ nm}$, $\alpha=83.517(2)^\circ$, $\beta=89.200(2)^\circ$, $\gamma=73.064(2)^\circ$, $V=1.011\,9(3)\text{ nm}^3$, $Z=1$ and final $R=0.041\,2$. The copper atom lies in a distorted octahedral environment with two ClO_4^- ions in the trans positions. The ligand L coordinates via one triazole nitrogen and one pyridine nitrogen atom. The TG analysis shows that the complex is stable below 310 °C. CCDC: 843042.

Key words: Cu(II) complex; crystal structure; 1,2,4-triazole

0 Introduction

Over the past two decades, triaryltriazole ligands have gained considerable attention due to their versatile coordination chemistry^[1] and the intriguing magnetic properties of their resulting transition metal

complexes^[2-3]. Specially, some iron(II) complexes with triaryltriazole ligands show interesting spin-crossover properties which can be applied for molecular electronics, as information storage and switching materials^[4-5]. Recently, some 4-arylsubstituted 3,5-di(2-pyridyl)-1,2,4-triazoles and their metal complexes have

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*通讯联系人。E-mail:zhudr@njut.edu.cn;会员登记号:S060015982P。

been prepared by us and other groups^[6-12]. However, complexes with asymmetrically 3,4,5-triarylsubstituted 1,2,4-triazole have been little studied so far^[13]. As a continuation of our investigation of the asymmetrical substituted 1,2,4-triazoles^[14-19], we present here the synthesis, crystal structure, spectral characterization and thermal stability of a copper(II) complex with a new asymmetrical 3,4,5-trisubstituted triaryltriazole, 3-(*p*-bromophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole.

1 Experimental

1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand L was prepared according to a similar literature method^[17]. Elemental analyses (C, H, N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectrum was recorded on a Nicolet Avatar 380 FTIR instrument with KBr pellets in the range of 4 000~400 cm⁻¹. Electrospray ionization mass spectrum (ESI-MS) was recorded with an LCQ ADVANTAGE MAX mass spectrometer, with MeOH as the mobile phase; the flow rate of the mobile phase was 0.2 mL · min⁻¹. The spray voltage, the capillary voltage, and the capillary temperature were 4 kV, 40V, and 260 °C, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a simultaneous NETZSCH STA 449C thermal analyzer under flowing nitrogen from 35 to 400 °C at a

heating rate of 5 °C · min⁻¹.

1.2 Synthesis of *trans*-[CuL₂(ClO₄)₂]

A solution of Cu(NO₃)₂ · 3H₂O (0.15 mmol) in EtOH (2 mL) was added to a solution of L (0.3 mmol) in anhydrous EtOH (10 mL). The mixture was stirred for 15 min and then added a solution of NaClO₄ (0.3 mmol) in EtOH (3 mL). After refluxed for 6 h, a resulting light-blue product was filtered and washed with H₂O, and dried under vacuum to give 0.118 mmol (78.6%) of the complex. The light-blue single crystals suitable for X-ray diffraction were obtained by evaporation from an EtOH solution. Elemental analyses calcd. for C₄₀H₃₀Br₂Cl₂CuN₈O₈(%): C 45.98, H 2.89, N 10.72; found(%): C 45.89, H 2.97, N 10.87. IR data (ν , cm⁻¹): 3 083 (w); 2 924 (w); 1 595 (m); 1 511 (s); 1 464 (s); 1 304 (m); 1 097 (s); 1 056 (m); 929 (w); 832 (m); 753 (m); 733 (m); 623 (s). ESI-MS: m/z =945.52; 618.67; 423.04.

1.3 Crystal structure determination

The well-shaped single crystals of *trans*-[CuL₂(ClO₄)₂] were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 173(2) K on a Bruker SMART APEX CCD diffractometer using a graphite-monochromated Mo K α (λ =0.071 073 nm) radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL software^[20]. All non-hydrogen atoms were anisotropically refined. Crystallographic data are summarized in Table 1.

CCDC: 843042.

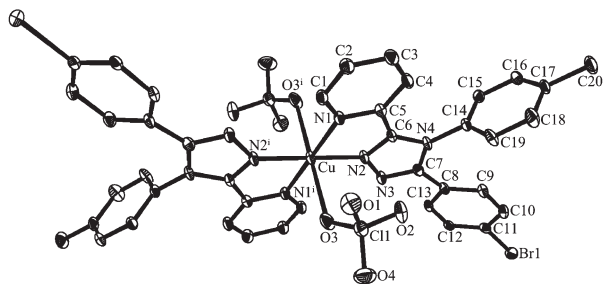
Table 1 Crystal data and structure refinement for the complex

Complex	[CuL ₂ (ClO ₄) ₂]	D_c / (g · cm ⁻³)	1.715
Empirical formula	C ₄₀ H ₃₀ Br ₂ Cl ₂ CuN ₈ O ₈	μ / mm ⁻¹	2.711
Formula weight	1 044.98	$F(000)$	523
Crystal system	Triclinic	Crystal size / mm	0.28×0.16×0.10
Space group	$P\bar{1}$	θ range / (°)	1.36~25.00
a / nm	0.829 29(15)	Reflections collected	7 133
b / nm	0.854 48(16)	Independent reflections (R_{int})	3 508 (0.035)
c / nm	1.502 7(3)	Reflections observed ($I > 2\sigma(I)$)	2 588
α / (°)	83.517(2)	Data / restraints / parameters	3508 / 0 / 277
β / (°)	89.200(2)	Goodness-of-fit on F^2	1.034
γ / (°)	73.064(2)	R/wR ($I > 2\sigma(I)$)	0.041 2/0.097 0
V / nm ³	1.011 9(3)	R/wR (all data)	0.063 1/0.116 3
Z	1	Max., Min. $\Delta\rho$ /(e · nm ⁻³)	585, -516

2 Results and discussion

2.1 Crystal structure

A projection of the structure of *trans*-[CuL₂(ClO₄)₂] is presented in Fig.1 together with the atomic labeling system. The complex crystallizes in the triclinic space group $P\bar{1}$ and there is an inversion centre at the Cu(II) atom. The crystal structure consists of a Cu(II) cation, two L ligands and two perchlorate anions, which is agreement with the elemental analysis result. Relevant interatomic distances and angles are given in Table 2.



Hydrogen atoms are omitted for clarity; Symmetry code: ⁱ 1-x, 1-y, -z

Fig.1 Projection of structure of the complex with 30% thermal ellipsoids probability

The Cu(II) atom is coordinated by four nitrogen atoms from two L ligands in the equatorial plane and

two oxygen atoms from two perchlorate anions in the axial position to form a distorted octahedron. Each L ligand coordinates to Cu(II) atom through N atom of the pyridyl ring and one N atom of the triazole, which is similar to the coordination modes in a related Cu(II) complex^[18]. The Cu-O distance is 0.243 2(3) nm, showing the involvement of two ClO₄⁻ ions in the coordination, which is similar to that found in a homologous Cu(II) complex, [CuL'₂(ClO₄)₂]^[21] (L'=4-(p-methylphenyl)-3,5-di(2-pyridyl)-1,2,4-triazole). The Cu-N bond lengths are within the normal ranges observed for an octahedral Cu(II) complex^[18]. However, the Cu-N bond to the triazole nitrogen is 0.006 1 nm shorter than that to the pyridyl nitrogen. The same feature has been observed in the similar Cu(II) complexes^[15,18,21]. The ligand L in the complex is non-planar. The triazole ring makes dihedral angles of 12.4(2)°, 19.2(2)° and 77.5(2)° with the pyridyl ring, the *p*-bromophenyl ring and *p*-methylphenyl ring, respectively. The crystal structure is further stabilized by weak intermolecular C-H...N, C-H...O hydrogen bonds and C-H...C_g1 interactions (Fig. 2 and Table 3, C_g1 is the centroid of the *p*-methylphenyl ring).

Table 2 Selected bond distances (nm) and bond angles (°) for the complex

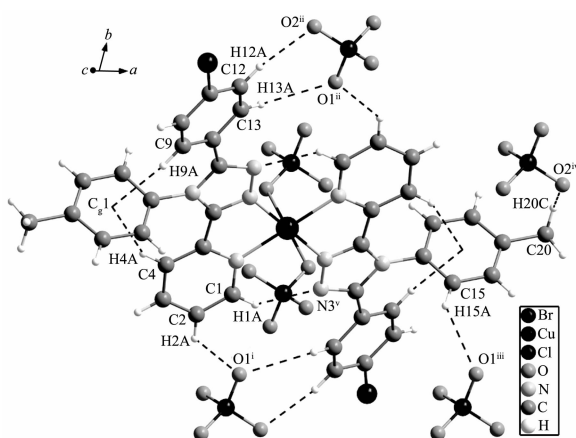
Cu-N1	0.204 4(3)	N2-N3	0.137 0(5)	C17-C20	0.151 4(6)
Cu-N2	0.198 3(3)	Br1-C11	0.189 4(4)		
Cu-O3	0.243 2(3)	N4-C14	0.144 5(5)		
O3-Cu-N1	93.66(13)	N1-Cu-O3 ⁱ	86.34(13)	N2-Cu-N2 ⁱ	180.00
O3-Cu-N2	90.44(13)	O3-Cu-O3 ⁱ	180.00		
N1-Cu-N2	80.30(13)	N1-Cu-N1 ⁱ	180.00		

Symmetry code: ⁱ 1-x, 1-y, -z.

Table 3 Hydrogen bonding interactions in the complex

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠DHA / (°)
C2-H2A...O1 ⁱ	0.095 0	0.249 5	0.324 3	135.56
C13-H13A...O1 ⁱⁱ	0.095 0	0.260 9	0.340 4	141.44
C15-H15A...O1 ⁱⁱⁱ	0.095 0	0.263 8	0.343 1	141.22
C12-H12A...O2 ^{iv}	0.095 0	0.245 1	0.328 6	146.58
C20-H20C...O2 ^v	0.098 0	0.270 6	0.340 2	128.35
C1-H1A...N3 ^v	0.095 1	0.233 9	0.314 9	142.77
C4-H4A...Cg1	0.095 0	0.289 2	0.372 9	147.52
C9-H9A...Cg1	0.095 0	0.282 0	0.333 9	149.35

Symmetry codes: ⁱ 1-x, -y, -z; ⁱⁱ x, 1+y, z; ⁱⁱⁱ x-1, 1+y, z; ^{iv} x-1, y, z; ^v -x, 1-y, -z.



Symmetry codes: ⁱ 1-x, 1-y, -z; ⁱⁱ x, 1+y, z; ⁱⁱⁱ x-1, 1+y, z; ^{iv} x-1, y, z; ^v -x, 1-y, -z

Fig.2 Hydrogen bonding interactions in the complex

2.2 Spectral characterization

In the IR spectrum of the complex, there are three bands at 1097 (s), 929 (w) and 624 cm^{-1} (s), attributable to the IR-allowed ν mode, IR-forbidden ν mode and the nondegenerate ClO_3 symmetrical bending frequency of the ClO_4^- anions, respectively^[15]. A band at 1595 cm^{-1} (m) can be assigned to the coordinated pyridine ring. In addition, the asymmetrical stretching frequency of Ph-Br is at 1056 cm^{-1} (m)^[14]. These features are in agreement with the results of X-ray analysis.

The structure of $\text{trans}[\text{CuL}_2(\text{ClO}_4)_2]$ in solution was also studied by electrospray ionization mass spectrometry (ESI-MS)^[22-23]. Fig.3 displays a positive ion ESI mass spectrum of the complex in the methanol solution. Three main peaks were observed. The base peak at m/z 945.52 is $[\text{CuL}_2(\text{ClO}_4)]^+$ ion. The peaks at m/z 618.67,

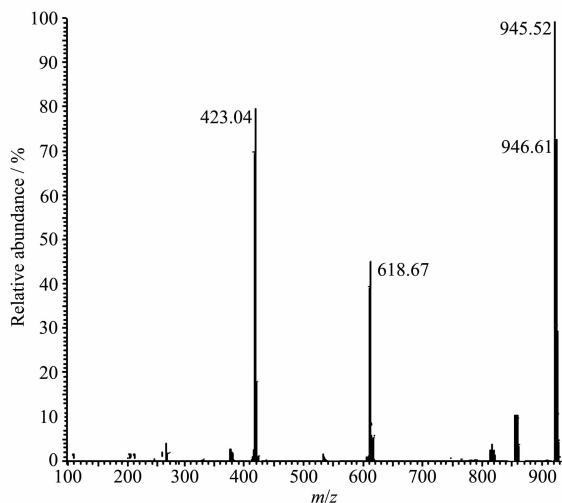


Fig.3 ESI-MS spectra of the complex

423.04 are $[\text{CuL}_3]^{2+}$ and $[\text{CuL}_2]^{2+}$ ion, respectively.

2.3 Thermal stability

Due to lack of any guest molecules in $\text{trans}[\text{CuL}_2(\text{ClO}_4)_2]$, TGA (Fig.4) shows a high thermal stability of the complex. Practically no weight loss was observed up to 310 $^\circ\text{C}$. An abrupt weight loss is only observed above 310 $^\circ\text{C}$ as a result of the explosion of the complex or rapid combustion of the ligands because of the existence of ClO_4^- anions, associated with an exothermic peak at 327 $^\circ\text{C}$ in the DSC curve of $\text{trans}[\text{CuL}_2(\text{ClO}_4)_2]$. The remaining weight of 7.28% after heating to 350 $^\circ\text{C}$ is due to the final residue of CuO, in agreement with the calculated value of 7.66%. The thermal decomposition feature of the complex is also in good agreement with its crystal structure.

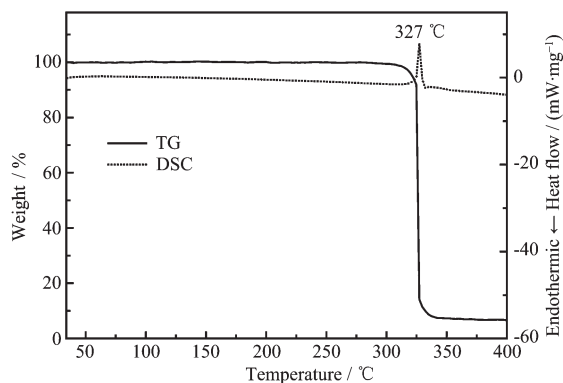


Fig.4 TGA/DSC curves of the complex

3 Conclusions

A new Cu(II) complex with 3-(*p*-bromophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole has been synthesized and characterized by elemental analyses, IR, TGA/DSC, ESI-MS spectra and X-ray crystal structure analysis. The copper atom is in a distorted octahedral environment and coordinated by two trans-oriented ClO_4^- anions. Each ligand coordinates via one triazole nitrogen atom and pyridine nitrogen atom. The TG analysis shows that the complex is stable below 310 $^\circ\text{C}$.

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