

铜配合物 $[\text{CuL}_2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$ 的合成和晶体结构 ($\text{L}=3\text{-乙基-4-对甲氧苯基-5-(2-吡啶基)-1,2,4\text{-三氮唑}$)

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Synthesis and Crystal Structure of $[\text{CuL}_2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$ ($\text{L}=3\text{-Ethyl-4-(}p\text{-methoxyphenyl)-5-(2-pyridyl)-1,2,4\text{-triazole}$)

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Abstract: A new copper(II) complex, $[\text{CuL}_2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$, [$\text{L}=3\text{-ethyl-4-(}p\text{-methoxyphenyl)-5-(2-pyridyl)-1,2,4\text{-triazole}$], was synthesized and characterized by X-ray crystallography and infrared spectroscopy. The complex crystallizes in triclinic system with space group $P\bar{1}$, $a=0.843\ 9(7)\text{ nm}$, $b=0.965\ 5(8)\text{ nm}$, $c=1.093\ 6(8)\text{ nm}$, $\alpha=84.026(19)^\circ$, $\beta=82.33(2)^\circ$, $\gamma=89.167(19)^\circ$, $V=0.878\ 3(12)\text{ nm}^3$, $Z=1$ with final $R=0.033\ 8$. The copper atom lies in a distorted octahedral environment with two bidentate chelating ligands (L) in the equatorial plane and two Cl^- ions in the axial positions. The ligand L coordinates via one triazole nitrogen and one pyridine nitrogen atom. The molecules are stabilized by intermolecular hydrogen bonds in the crystal lattice. CCDC: 705817.

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

The design and synthesis of coordination compounds containing substituted 1,2,4-triazoles have been flourishing during the past decades^[1-3]. The reason for this is that 1,2,4-triazoles and their complexes have interesting structures^[4-5] and specific magnetic properties^[6-9], thus they are very popular in synthesis of compounds used in biochemistry^[10-12] and material sciences^[13-14]. The 1,2,4-triazole ligand can be functionalized with a number of substituents: amino groups at

positions 3 or 4^[15-17], alkyl/aryl groups at positions 3,5 and/or 4^[18-20], 2-pyridyl group at positions 3 and/or 5^[21-25]. 2-Pyridyl group is a rigid ring containing a donor atom, so 1,2,4-triazole ligand with 2-pyridyl group enhances the stability of the resulting complexes due to the chelate effects. Moreover the ligand also can provide more predictable coordination modes, therefore, it has been more frequently used to design and construct finite architectures with coordination to some metal

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ions. A wide range of such ligand systems have been synthesized and a large amount of mononuclear, oligonuclear and polynuclear complexes^[2] have been obtained from them, some of which show promising properties. Recently we have reported some complexes with 4-substituted-3,5-bis(2-pyridyl)-1,2,4-triazole^[18,21-25], 3-alkyl-4-aryl-5-(2-pyridyl)-1,2,4-triazole^[19-20]. All of these complexes show novel magnetic properties, spin crossover or order-disorder phenomena. As an extension of our research, we present here the synthesis and crystal structure of a new copper(II) complex with 3-ethyl-4-(*p*-methoxyphenyl)-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 synthesized according to the literature method^[19]. IR spectrum was recorded on a Nicolet 170SX FTIR instrument (KBr discs) in the 4 000~400 cm⁻¹ region. Elemental analyses were performed with a Perkin-Elmer 240 instrument.

1.2 Synthesis of [CuL₂Cl₂]·4H₂O

To a solution of 3-ethyl-4-(*p*-methoxyphenyl)-5-(2-pyridyl)-1,2,4-triazole (1.120 g, 4 mmol) in hot ethanol

(15 mL) was added dropwise a blue solution of CuCl₂·2H₂O (0.341 g, 2 mmol) in ethanol (5 mL) with stirring. Slow evaporation of the solvent at room temperature gave blue crystals suitable for X-ray data collection. Yield based on L: 1.26 g, 82.1%. Elemental analyses [Found(%): C 50.32, H 5.38, N 14.36. C₃₂H₄₀Cl₂CuN₈O₆ calcd.(%): C 50.10, H 5.26, N 14.61]. IR data (ν , cm⁻¹): ~3 406 (br, s); 2 939 (w); 1 611 (m); 1 516 (s); 1 303 (m); 1 261 (s); 1 175 (m); 1 027 (m); 847 (m); 794 (m); 613 (m).

1.3 Crystal structure determination

Summary of the crystallographic data is given in Table 1. Intensity data for crystal were collected using Mo *K* α (λ = 0.071 073 nm) radiation on a Bruker SMART APEX II CCD single crystal diffractometer at 293 K. The structure was solved by direct methods and was refined on F^2 by the full-matrix least-squares technique using the SHELXTL^[26] program package.

Graphics are generated using ORTEP^[27] and PLATON^[28]. All non-hydrogen atoms were refined anisotropically. Anion Cl⁻ was found to be disordered over two positions (Cl1A and Cl1B) and fixed at 0.5. Hydrogen atoms for C-H and O-H were placed in calculated positions and the contribution of these hydrogen atoms was included in the structure factor calculations.

CCDC: 705817.

Table 1 Summary of crystallographic data for the complex

Empirical formula	C ₃₂ H ₄₀ Cl ₂ CuN ₈ O ₆	<i>Z</i>	1
Formula weight	767.16	Density / (g·cm ⁻³)	1.45
Temperature / K	293(2)	<i>F</i> (000)	399
Wavelength / nm	0.071 073	Absorption coeff. / mm ⁻¹	0.829
Crystal size / mm	0.21×0.20×0.18	θ range / (°)	2.7~25
Crystal system	Triclinic	<i>h</i> / <i>k</i> / <i>l</i>	-10,10 / -11,11 / -12,13
Space group	$P\bar{1}$	Reflections collected	7169
<i>a</i> / nm	0.843 9(7)	Independent reflections (<i>R</i> _{int})	3 072 (0.025)
<i>b</i> / nm	0.965 5(8)	Observed reflections	2 879
<i>c</i> / nm	1.093 6(8)	Data / restraints / parameters	3 072 / 9 / 246
α / (°)	84.026(19)	Goodness-of-fit on F^2	1.057
β / (°)	82.33(2)	<i>R</i> , <i>wR</i> indices [$I > 2\sigma(I)$]	0.033 8, 0.094 0
γ / (°)	89.167(19)	<i>R</i> , <i>wR</i> indices (all data)	0.036 1, 0.096 2
<i>V</i> / nm ³	0.878 3(12)	Largest diff. peak and hole / (e ⁻ ·nm ⁻³)	-330, 260

2 Results and discussion

ORTEP diagram of the complex with atom

numbering scheme is shown in Fig.1. The complex crystallizes in the triclinic space group $P\bar{1}$ and there is an inversion centre at the copper(II) atom. The crystal

Table 2 Selected bond distances and bond angles for the complex

Cu1-Cl1A	0.275 73(18)	N2-C2	0.130 9(2)	C14-O1	0.142 6(3)
Cu1-N1	0.204 46(18)	N2-N3	0.138 2(19)	C15-C16	0.150 1(3)
Cu1-N2	0.200 43(18)	N3-C1	0.131 2(2)		
N1-C3	0.135 5(2)	N4-C2	0.136 1(2)		
N1-Cu1-Cl1A	91.71(6)	N2-Cu1-Cl1A	91.21(6)	Cl1A-Cu1-Cl1A ⁱ	180.00(1)
N1 ⁱ -Cu1-Cl1A	88.29(6)	N2-Cu1-N1 ⁱ	99.78(5)	C11-O1-C14	117.92(15)
N1 ⁱ -Cu1-N1	180.00	N2 ⁱ -Cu1-N2	180.00(6)		
N2-Cu1-N1	80.22(5)	N2 ⁱ -Cu1-Cl1A	88.79(6)		

Symmetry code: ⁱ $-x, 1-y, 1-z$.

structure consists of $[\text{CuL}_2\text{Cl}_2]$ and four water molecules, which is consistent with the elemental analysis result. Relevant interatomic distances and angles are given in Table 2.

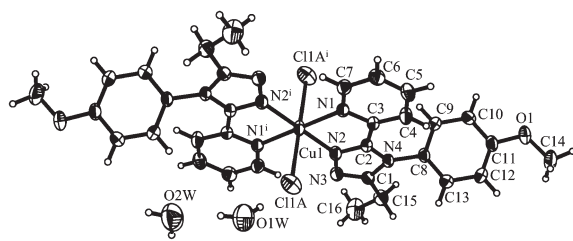
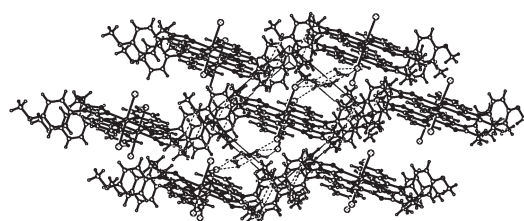
Symmetry code: ⁱ $-x, 1-y, 1-z$

Fig.1 ORTEP diagram of the complex with atom numbering scheme (30% probability level for the thermal ellipsoids)

The copper(II) atom is surrounded by four nitrogen atoms from two ligands in the equatorial plane and two Cl^- ions in the axial positions to form a distorted octahedral geometry. The axial part of the octahedron is elongated with Cu1-Cl1A distance of 0.275 73(18) nm which is in the normal range (0.273~0.319 nm) for axial Cu-Cl bond^[29]. The equatorial coordination of the four nitrogen atoms is similar to $[\text{Cu}(\text{dpdapt})\text{Cl}_2]$ (dpdapt= N, N' -di (2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine). In $[\text{CuL}_2\text{Cl}_2]$, the Cu- N_{pyr} bond length [0.204 46(18) nm] is longer than Cu- N_{triaz} one [0.200 43(18) nm] by 0.004 03 nm. It is worthwhile to note that the sum of bond angles N2-Cu1-N1 [80.22(5)°] and N2-Cu1-N1ⁱ [99.78(5)°] is approximately to 180°, so the equatorial coordination of the four nitrogen atoms is a perfect square planar. The ligand L is nonplanar. The pyridyl ring makes an angle of 7.8(5)° with respect to the triazole ring, while the phenyl ring is inclined relative to the triazole ring by an

angle of 67.5(5)°.

The crystal structure is further stabilized by intermolecular hydrogen bonds as shown in Fig.2. These hydrogen bonds consist of a usual $\text{O}-\text{H}\cdots\text{O}$ contact, weak $\text{O}-\text{H}\cdots\text{Cl}$, $\text{C}-\text{H}\cdots\text{Cl}$, $\text{C}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{O}$ contacts (Table 3). There are two intermolecular hydrogen bonds between the water molecules, and the distances of $\text{O1W}\cdots\text{O2W}$ and $\text{O2W}\cdots\text{O2W}^i$ ($-x, 1-y, -z$) are 0.283 1(3) and 0.275 6(4) nm, respectively. Weak hydrogen-bond interactions between the water molecules and the chlorides are also observed, and the separations of $\text{O1W}\cdots\text{Cl1A}$ and $\text{O2W}\cdots\text{Cl1A}^i$ are 0.324 9(3) and 0.322 1(3) nm, respectively.



Broken lines show hydrogen bonding interactions

Fig.2 Packing diagram of the complex along the a -axis

In the IR spectrum of the complex, there are several broad, strong bands at $ca. 3406\text{ cm}^{-1}$, mainly attributed to H-O-H stretching vibrations, suggesting the existence of hydrogen bonding interactions^[30]. This result is in agreement with the X-ray analysis. The band at 1611 cm^{-1} (μm) can be assigned to one coordinated pyridine ring. In addition, two bands at $1261(\text{s})$ and 1027 cm^{-1} (μm) are due to Ar-O-CH₃ asymmetry and symmetry stretching vibrations, respectively. The C-H out of plane absorption of the *para*-substituted phenyl is located around $847(\text{m})$ and 794 cm^{-1} (μm). The triazole

Table 3 Hydrogen bonding interactions in the complex

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (D...A) / nm	∠D-H...A / (°)
O1W-H1WA...Cl1A	0.087	0.324 9(3)	165
O1W-H1WA...Cl1B	0.087	0.332 8(3)	163
O1W-H1WB...O2W	0.086	0.283 1(3)	170
O2W-H2WA...O2W ⁱ	0.092	0.275 6(4)	101
O2W-H2WB...Cl1A ⁱ	0.089	0.322 1(3)	121
O2W-H2WB...Cl1B ⁱ	0.089	0.320 5(3)	124
C6-H6A...Cl1A ⁱⁱ	0.093	0.349 0(3)	129
C7-H7A...N3 ⁱⁱⁱ	0.093	0.319 6(3)	145
C15-H15B...O1 ^{iv}	0.097	0.331 2(3)	154

Symmetry codes: ⁱ -*x*, 1-*y*, -*z*; ⁱⁱ 1-*x*, 1-*y*, 1-*z*; ⁱⁱⁱ -*x*, 1-*y*, 1-*z*; ^{iv} -*x*, 2-*y*, 2-*z*.

out-of-plane ring absorption is observed at 613 cm⁻¹ (m).

3 Conclusions

A new copper(II) complex with 3-ethyl-4-(*p*-methoxyphenyl)-5-(2-pyridyl)-1,2,4-triazole has been synthesized. The copper atom is in a distorted octahedral environment. Two *trans*-oriented chloride anions coordinate to the copper atom in axial positions. Each ligand coordinates via one triazole nitrogen atom and one pyridine nitrogen atom.

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