



研究简报

3-甲基-4-对甲苯基-5-(2-吡啶基)-1,2,4-三唑-铜(II)配合物

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Copper(II) Complex Based on 3-Methyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole

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Abstract: A copper(II) complex $[\text{CuL}(\text{H}_2\text{O})(\text{Sal})] \cdot 0.5\text{H}_2\text{O}$ was obtained by the reaction of copper(II) salicylate with 3-methyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) in ethanol-water solution at room temperature. The crystal belongs to triclinic system with space group $P\bar{1}$, and $a=0.913\ 6(4)\ \text{nm}$, $b=1.122\ 2(5)\ \text{nm}$, $c=1.263\ 3(7)\ \text{nm}$, $\alpha=67.10(2)^\circ$, $\beta=76.31(3)^\circ$, $\gamma=68.17(2)^\circ$, $V=1.101(1)\ \text{nm}^3$, $Z=2$. The final refinement gave $R_1=0.039\ 8$ and $wR_2=0.106\ 0$ for 3 453 reflections with $I>2\sigma(I)$. This complex is a good purple fluorescent material in solid state at room temperature. CCDC: 685713.

Key words: copper(II) complex; crystal structure; fluorescence

The design and synthesis of metal-organic complexes have been flourishing in recent years because of their intriguing architectures^[1] and potential application to gas storage, ion change, catalysis, and so on^[2]. Although a variety of metal coordination frameworks with beautiful topology and interesting properties have been synthesized to date, rational control in the construction of polymeric networks remains a great challenge in crystal engineering. The utilization of 1,2,4-triazole derivatives as bridging ligands in transition-metal complexes is currently of considerable interest because of the fact that it represents a hybrid of pyrazole and imidazole with regard to the arrangement of its heteroatoms, thus promising a rich and versatile

coordination chemistry^[3-5]. 1,2,4-triazole and, in particular, its derivatives can act as ligands to bridge metal ions by their potential bridging fashions ($\mu_{1,2}$, $\mu_{2,4}$, and $\mu_{1,2,4}$)^[6]. Many triazole based polynuclear compounds have been reported to date, including dinuclear, linear trinuclear, cyclic trinuclear, and hexanuclear ring complexes^[3-7]. Herein, we would like to report the synthesis and crystal structure of a neutral centrosymmetric monomeric copper(II) complex coordinated by 1,2,4-triazole derivative ligand and salicylate ligand together. $[\text{CuL}(\text{H}_2\text{O})(\text{Sal})] \cdot 0.5\text{H}_2\text{O}$ was obtained by the reaction of copper(II) salicylate with 3-methyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) in ethanol-water solution at room temperature. Blue block crystals suitable for X-

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ray diffraction were isolated by the solution evaporation method.

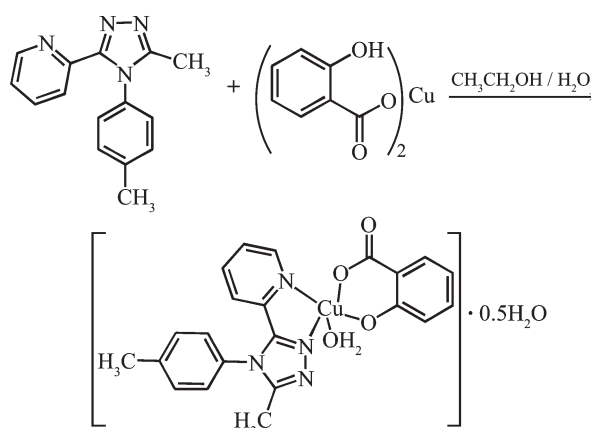
Diffraction data were collected with a Rigaku SCXmini diffractometer by the ω scan technique at room temperature with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). The lattice parameters were obtained by Crystal Clear^[8] with the θ range for data collection from 2.23° to 27.48° . The 9 108 reflections were collected, of which 3 854 were unique with $R_{\text{int}}=0.032\ 0$, $R_{\text{sigma}}=0.043\ 1$. The absorption correction was carried out by multi-scan method, and the structure was solved by direct methods with SHELXS-97^[9] and refined by full matrix least squares on F^2 with SHELXL-97^[9]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model and fixed isotropic thermal parameters. The crystal belongs to triclinic system with centro-symmetric space group $P\bar{1}$, and $a=0.913\ 6\ (4)\ \text{nm}$, $b=1.122\ 2\ (5)\ \text{nm}$, $c=1.263\ 3\ (7)\ \text{nm}$, $\alpha=67.10(2)^\circ$, $\beta=76.31(3)^\circ$, $\gamma=68.17(2)^\circ$, $V=1.101\ (1)\ \text{nm}^3$, $Z=2$, $S=1.081$, $R_1=0.039\ 8$ and $wR_2=0.106\ 0$ for 3 453 reflections with $I>2\sigma(I)$.

CCDC: 685713.

The copper(II) ion in $[\text{CuL}(\text{H}_2\text{O})(\text{Sal})]\cdot 0.5\text{H}_2\text{O}$ has d^9 electron configuration and $S=1/2$ with strong spin-orbit coupling, two g values of 2.249 3 and 2.059 9 are obtained from low-temperature ESR measurement. Owned to the LMCT (ligand-to-metal charge transfer) transition, $[\text{CuL}(\text{H}_2\text{O})(\text{Sal})]\cdot 0.5\text{H}_2\text{O}$ exhibit strong absorption bands at the range of 200~400 nm, and it exhibits purple fluorescence in solid state at room temperature.

Compound $[\text{CuL}(\text{H}_2\text{O})(\text{Sal})]\cdot 0.5\text{H}_2\text{O}$ is a neutral

monomeric copper(II) complex. As Fig.1 shows, Cu(II) ion has a distorted tetragonal pyramid coordination environment, it is five-coordinated by two oxygen atoms of salicylate dianion with bond lengths of Cu1-O3 0.189 3(2) nm and Cu1-O4 0.187 1(2) nm, two nitrogen atoms of 3-methyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole ligand with bond distance Cu1-N4 0.202 9(2) and Cu1-N2 0.205 0(3) nm, these two N atoms and two O atoms are seated almost at one plane, and one oxygen atom of water sits at the peak of the tetragonal pyramid with bond length Cu1-O2 0.230 2(2) nm (Fig.1). With the existence of coordinated and



Scheme 1

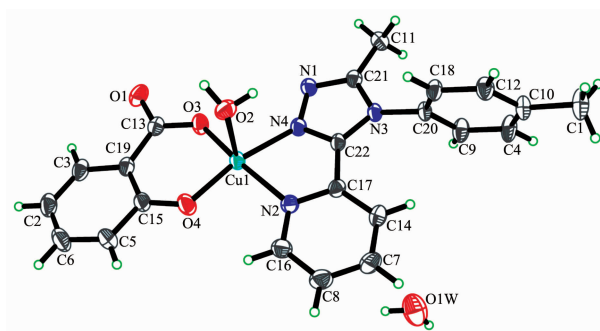


Fig.1 Asymmetric unit of $[\text{CuL}(\text{H}_2\text{O})(\text{Sal})]\cdot 0.5\text{H}_2\text{O}$

Table 1 Selected bond lengths (nm) and angles ($^\circ$) for the complex

Cu1-O2	0.230 2(2)	Cu1-O3	0.189 3(2)	Cu1-O4	0.187 1(2)
Cu1-N2	0.205 0(3)	Cu1-N4	0.202 9(2)		
O2-Cu1-O3	97.03(9)	O2-Cu1-O4	94.94(10)	O2-Cu1-N2	93.29(9)
O2-Cu1-N4	93.72(8)	O3-Cu1-O4	94.93(10)	O3-Cu1-N2	167.04(11)
O3-Cu1-N4	92.46(9)	O4-Cu1-N2	91.96(10)	O4-Cu1-N4	167.84(11)
N2-Cu1-N4	79.03(10)	Cu1-O3-C13	129.8(2)	Cu1-O4-C15	125.5(2)
Cu1-N2-C16	125.7(2)	Cu1-N2-C17	115.86(19)	Cu1-N4-N1	136.40(17)
Cu1-N4-C22	113.61(19)				

uncoordinated water, the crystal packing involves many types of typical O—H \cdots O, O—H \cdots N and weak C—H \cdots O hydrogen bonds generating a three-dimension structure (Table 2, Fig.2). The structure is stabilized by weak C—H \cdots π interactions of C1—H1C \cdots Cg6 (Cg6 is centroid of the methylphenyl ring C4, C9, C20, C18, C12, C10 with symmetry operation $1-x, 2-y, -z$) of 0.388 1(5) nm, O2—H2A \cdots Cg1 (Cg1 is the centroid of the five-member ring formed by coordination of copper ion and the triazole, Cu1, N2, C17, C22, N4, with symmetry operation x, y, z) of 0.294 6(3) nm, C11—H11B \cdots Cg1 with symmetry operation $1-x, 2-y, 1-z$ of 0.360 0(4) nm, C11—H11C \cdots Cg5 (Cg5 is the centroid of the phenyl ring of the salicylate C2, C3, C19, C15, C5, C6, with symmetry operation $2-x, 2-y, 1-z$) of 0.361 5(4) nm, C12—H12A \cdots Cg5 with symmetry operation $x, y, -1+z$ of 0.370 8(4) nm (Table 3), and $\pi\cdots\pi$ interactions of Cg2 \cdots Cg2 (Cg2 is the centroid of the five-member triazole ring N1, N4, C22, N3, C21, with symmetry operation $1-x, 2-y, 1-z$) of 0.357 1(3) nm, Cg4 \cdots Cg4 (Cg4 is the centroid of the six-member pyridyl ring N2,

C16, C8, C7, C14, C17, with symmetry operation $2-x, 1-y, 1-z$) of 0.363 7(3) nm as well. The crystallized water can be removed completely at *ca.* 140 °C.

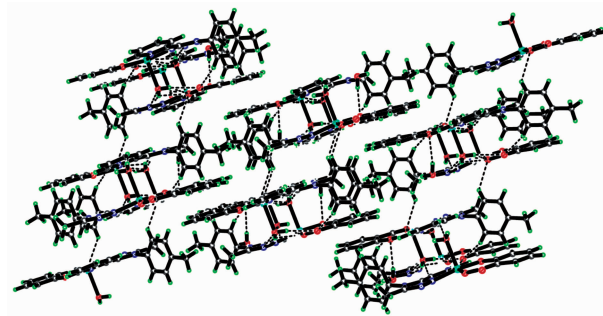


Fig.2 Hydrogen bonding interaction view of the complex (along *b* axis)

The fluorescent study shows the compound exhibits one intense emission band at *ca.* 390 nm with the exciting radiation set at 352 nm, shows purple fluorescent emission at room temperature in solid state (Fig.3). The enhanced luminescence efficiency is therefore attributed to the coordination of the ligands to Cu(II) that effectively increases the rigidity of the ligand and reduces the loss of energy through radiation-less

Table 2 Hydrogen bonds for the complex

D—H \cdots A	<i>d</i> (D—H) / nm	<i>d</i> (H \cdots A) / nm	<i>d</i> (D \cdots A) / nm	\angle DHA / (°)
O2—H2C \cdots N1 ⁱ	0.085	0.216	0.295 8(3)	156.2
O2—H2A \cdots O1 ⁱ	0.082 4(10)	0.227(1)	0.309 0(4)	172(3)
O2—H2A \cdots O3 ⁱ	0.082 4(10)	0.232(3)	0.281 2(3)	118(2)
O2—H2A \cdots O3 ⁱ	0.082 4(10)	0.232(3)	0.281 2(3)	118(2)
C18—H18A \cdots O1 ⁱ	0.093	0.247	0.332 9(3)	153.7
C3—H3A \cdots O1	0.093	0.245	0.277 4(4)	100.4
C16—H16A \cdots O4	0.093	0.249	0.299 7(4)	114.1
O1W—H1WA \cdots O4 ⁱⁱ	0.085	0.254	0.315 7(6)	129.8
C8—H8A \cdots O1 ⁱⁱⁱ	0.093	0.255	0.342 3(4)	155.5
C9—H9A \cdots O3 ^{iv}	0.093	0.249	0.323 6(4)	137.5
C7—H7A \cdots O2 ^v	0.093	0.243	0.317 8(4)	137.5

Symmetry transformations used to generate equivalent atoms: ⁱ $-x+2, -y+2, -z+1$; ⁱⁱ $x-1, y, z$; ⁱⁱⁱ $x, y-1, z$; ^{iv} $-x+1, -y+2, -z+1$;

^v $-x+2, -y+1, -z+1$.

Table 3 X—H \cdots Cg(Pi-Ring) Interactions (H \cdots Cg<0.34 nm, $-\Gamma < 30.0^\circ$)

X—H \cdots Cg	<i>d</i> (X \cdots H) / nm	<i>d</i> (H \cdots Cg) / nm	<i>d</i> (X \cdots Cg) / nm	\angle DHA / (°)
C1—H1C \cdots Cg6 ^{vi}	0.096	0.302 99	0.388 1(5)	148.45
O2—H2A \cdots Cg1 ^{vii}	0.082 4(10)	0.281(5)	0.294 6(3)	91(3)
C11—H11B \cdots Cg1 ^{viii}	0.096	0.291 21	0.360 0(4)	129.51
C11—H11C \cdots Cg5 ^{ix}	0.096	0.292 80	0.361 5(4)	129.52
C12—H12A \cdots Cg5 ^x	0.096	0.279 98	0.370 8(4)	165.75

Symmetry codes: ^{vi} $1-x, 2-y, -z$; ^{vii} x, y, z ; ^{viii} $1-x, 2-y, 1-z$; ^{ix} $2-x, 2-y, 1-z$; ^x $x, y, -1+z$.

decay of the intra-ligand emission excited state.

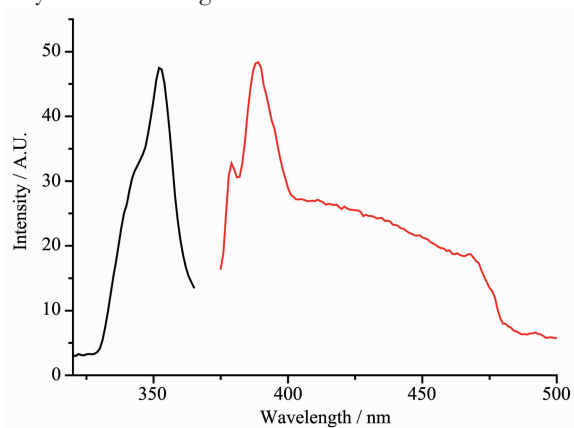


Fig.3 Fluorescent spectra of the complex in the solid state at room temperature

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