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研究简报

3-甲基-4-对甲基苯基-5-(2-吡啶基)-1,2,4-三唑双核铜(Ⅱ)配合物的合成、晶体结构及磁性

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Synthesis, Crystal Structure and Magnetic Property of the Dinuclear Copper(Ⅱ) Complex with 3-Methyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole

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Abstract: A dinuclear Cu(Ⅱ) complex $[Cu_2(MMBPT)_2Cl_4(H_2O)_{2.5}]$ (I) [MMBPT=3-Methyl-4-(4-Methylphenyl)-5-(2-pyridyl)-1,2,4-triazole] was synthesized by reaction of MMBPT with $CuCl_2\cdot 2H_2O$ and its structure was determined by X-ray crystal structure analysis. The structure indicates that the complex crystallizes in monoclinic, space group $P2_1/c$ with a=1.273 4(3) nm, b=1.237 5(3) nm, c=2.403 2(5) nm, β=90.51(3)°. V=3.786 6(13) nm^3, Z=2, D_c=1.429 Mg·m^{-3}, μ=1.445 mm^{-1}, F(000)=1 660, and final R_1=0.055 5, wR_2=0.129 7. The crystal structure shows that the dinuclear Cu_2N_6 unit is almost planar in which each Cu(Ⅱ) ion was five-coordinated by one nitrogen atoms from MMBPT and two chlorine in the basal positions and two nitrogen atoms from two MMBPTs respectively in the axial one, to form a distorted trigonal bipyramidal geometry. Magnetic measurements reveal a relatively strong antiferromagentic interaction in the complex. CCDC: 720011.

Key words: 1,2,4-triazoles; crystal structure; dinuclear copper complex

1,2,4-Triazole and its derivatives represent an important class of heterocycles that find many useful applications as biological reagents: They are used as fungicides, insecticides, antimicrobe, herbicides and anti animal parasites[1]. Moreover, the coordination chemistry of substituted 1,2,4-triazoles has also received considerable attention in latest decade due to the fact that some of their complexes have spin-cross-over properties which can be used as molecular-based memory devices, dispays and switching materials[2~11]. Recently a few dinuclear transition metal complexes with 1,2,4-triazole ligands have been reported[12~16]. We have reported the syntheses, crystal structures and properties of one new cobalt(Ⅱ) complexes with 4-(*p*-methylphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole (MBPT)[17]. As a continuation of our investigation, we report here

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the synthesis, crystal structure and magnetic properties of a novel dinuclear copper(Ⅱ) complex with ligand MMBPT: $[Cu_2(MMBPT)_2Cl_4(H_2O)_{2.5}]$.

1 Experimental

1.1 General procedures

All chemicals were reagent grade and used as received. All solvents were of analytical grade and used directly. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 analyzer. Variable temperature magnetic susceptibilities of crystalline of the complex were measured on a Quantum Design MPMS SQUID-XL7 magnetometer in the temperature range of 1.8~300 K.Diamagnetic corrections were made with Pascalt′s constants for all the constituent atoms. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (400~4 000 cm^{-1}) with KBr pellets.

1.2 Syntheses of 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (MMBPT)[18]

N-propionyl-*N*′-(2-pyridoyl)hydrazine (5.0 g, 25 mmol) was added to the solution of di (*p*-methylphenyl) phosphazoanilide (6.9 g, 28.5 mmol) in *N*,*N*′-dimethylaniline (40 mL). The mixture was refluxing for 3 hours, and then the solvent was removed by vacuum distillation. To the residue concentrated chlorohydric acid (10 mL) was added and refluxing for 1 hour. After cooling, the solution was filtered, and the filtrate was neutralized to pH=8 with potassium carbonate, the white precipitate was formed and collected. The crude product recrystallized from water (4.3 g, yield 63.5%). m.p. 172~174 ℃. $C_{15}H_{14}N_4$ (%): Calcd. C 71.98, H 5.64, N 22.38; Found (%): C 71.73, H 5.81, N 22.26. IR(KBr): 3 056.7, 3 031.6, 2 925.5, 2 856.1, 1 589.1, 1 496.5, 1 450.2, 1 413.6, 1 373.1, 1 282.5, 1 152.2, 999.0, 827.3, 711.6. ^{1}H NMR ($DCCl_3$): 2.336 7 (3H, single), 2.425 2 (3H, Single), 7.061 8~7.268 2 (4H, symmetry), 7.159 4~8.042 0(4H, multiple, pyridine ring). ESI-MS: 251.28(M^+).

1.3 Preparation of the complexes of $[Cu_2(MMBPT)_2Cl_4(H_2O)_{2.5}]$

To the warm solution of 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (0.500 g , 2.0 mmol) in 10 mL ethanol, copper chloride ($CuCl_2\cdot 2H_2O$, 0.682 g, 4.0 mmol) in distilled water (10 mL) was added. The mixture turned green immediately and filtered. The filtrate was left to stand at room temperature for several days. Green solid product formed and collected (0.71 g, yield 60%). Single crystals suitable for X-ray diffraction were selected. Anal. Calcd. for $C_{30}H_{33}Cl_4Cu_2N_8O_{2.5}$(%): C 44.24, H 4.08, N 13.76; found (%): C 44.43, H 4.15, N 13.58.

1.4 Crystal structure determination

A single crystal with dimensions of 0.14 mm×0.13 mm×0.12 mm was selected for X-ray structure analysis. The data were collected on a Rigaku SCX Mini CCD diffractometer using a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K. A total of 33 704 reflections were collected in the range of 3.20° $\leqslant\theta\leqslant$26.00° by using an ω-2θ scan mode, of which 7 382 were unique with R_{int}=0.062 7 and 5 286 observed reflections with $I>2\sigma(I)$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 program[19,20]. Positional parameters of all the H atoms were calculated geometrically and were allowed to to ride on their respective parent atoms, with $U_{iso}(H)=1.2U_{eq}(C)$ or $U_{iso}(H)=1.5U_{eq}(O)$. All of the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least-squares method. Structure solution and refinement based on independent reflections with and observed reflections with $I>2\sigma(I)$. Crystal data and structure refinement parameters for the title complex are listed in Table 1.

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Table 1 Crysta data and structure refinement parameters for the title complex

Empirical formula	$C_{60}H_{66}C_{18}Cu_4N_{16}O_5$	F(000)	1 660
Formula weight	1 629.09	Crystal size / mm	0.14×0.13×0.12
T / K	293(2)	θ range for data collection / (°)	3.20~26.00
Crystal system	Monoclinic	Index ranges	$-15\leqslant h\leqslant 15, -15\leqslant k\leqslant 15, -29\leqslant l\leqslant 29$
Space group	$P2_1/c$	Reflections collected / unique (R_{int})	33 704 / 7 382 (0.062 7)

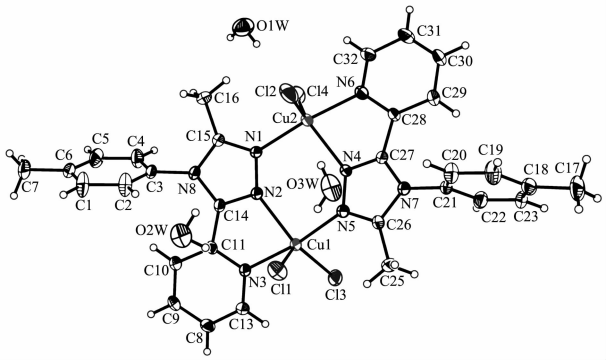
Continued Table 1

a / nm	1.273 4(3)	Absorption correction	Multi-scan
b / nm	1.2375(3)	Refinement method	Full-matrix least-squares on F^2
c / nm	2.4032(5)	Data / restraints / parameters	7 382 / 0 / 425
β / (°)	90.51(3)	Goodness-of-fit on F^2	1.069
Z	2	R_1, wR_2 (all data)	0.084 6, 0.144 4
D_c / (g·cm^{-3})	1.429	R_1, wR_2 [$I>2\sigma(I)$]	0.055 5, 0.129 7
μ / mm^{-1}	1.445	Largest diff. peak and hole / (e·nm^{-3})	1 118 and −313

2 Results and discussion

2.1 Crystal structure

The ORTEP drawing of the structure with atomic numbering are shown in Fig.1. X-ray crystal structure analysis of complex **1** reveals that the crystallographic unit of the title complex is composed of two Cu(II) ions, four chlorine anions, two 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazoles(MMBPT) and two and half lattice water molecules. The selected bond lengths and angles of this compound are listed in Table 2. The dinuclear $[Cu_2N_6]$ unit in the complex is almost planar and Rms deviation is 0.018 84 nm. Two Cu(Ⅱ) Centers are equivalently bridged by the MMBPT ligands with the intramolecular Cu⋯Cu separation of 0.417 7 nm. The Cu(Ⅱ) ion is pentacoordinated by two triazole N atoms and one pyridine N atom from MMBPT and two Cl atoms. The two five-membered chelate rings are formed by atoms Cu1-N3-C11-C14-N2 and Cu2-N4-C27-C28-N6 which are nearly planar respectively. These two chelate rings make a dihedral angle of 14.11(0.07)° each other.



Symmetry code: (A) $-x$, $1-y$, $-z$

Fig.1 A view of the title compound, displacement ellipsoids are drawn at the 30% probability level

The geometry around central copper atom can be viewed in terms of distorted trigonal bipyramidal geometry with τ=0.68 for Cu1 and τ=0.71 for Cu2 respectively (for a square pyramid τ=0 and for a trigonal bipyramid τ=1; structural parameter, $\tau=(\beta-\alpha)/60$; where α and β are the two largest angles around the central atom[21]). The atoms N2, Cl1 and Cl3 act as the equatorial plane of the trigonal bipyramid, while the axial positions are occupied by the atoms N3 and N5. In the axial direction, the N3-Cu1-N5 angle of the bipyramid is 171.84(13)° and greatly deviates from linearity. Similarly, The atoms N4, Cl2 and Cl4 act as the equatorial plane of the trigonal bipyramid, while the

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

Cu1-N5	0.201 6(3)	Cu1-Cl1	0.241 07(14)	Cu2-Cl4	0.230 86(14)
Cu1-N3	0.206 1(3)	Cu2-N1	0.201 4(3)	Cu2-Cl2	0.243 11(16)
Cu1-N2	0.218 0(3)	Cu2-N6	0.203 5(3)	N1-N2	0.138 9(4)
Cu1-Cl3	0.229 85(13)	Cu2-N4	0.216 7(3)	N4-N5	0.1387(5)
N4-Cu2-Cl4	126.42(11)	N1-Cu2-Cl4	92.04(11)	N2-Cu1-Cl1	104.67(10)
N5-Cu1-N3	171.84(13)	N3-Cu1-Cl3	92.81(10)	Cl3-Cu1-Cl1	123.40(5)
N5-Cu1-N2	94.53(13)	N2-Cu1-Cl3	130.88(10)	N1-Cu2-N6	174.10(13)
N3-Cu1-N2	77.36(13)	N5-Cu1-Cl1	93.92(11)	N6-Cu2-N4	78.48(13)
N5-Cu1-Cl3	91.86(11)	N3-Cu1-Cl1	89.09(10)	Cl4-Cu2-Cl2	131.38(6)

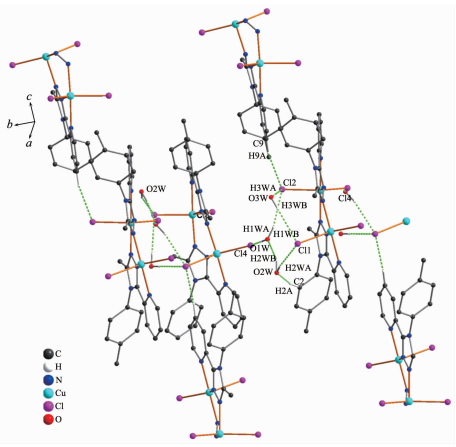
axial positions are occupied by the atoms N1 and N6. In the axial direction, the N1-Cu2-N6 angle of the bipyramid is 174.10(13)° and greatly deviates from linearity. These bond geometries well agree with those in complex[22]. The Cu1-N3 [0.206 1(3) nm], Cu1-N5 [0.201 6(3) nm], Cu2-N1 [0.201 4(3) nm] and Cu2-N6 [0.203 5(3) nm] bond distances in the axial direction are slightly shorter than Cu1-N2 [0.218 0(3) nm] and Cu2-N4 [0.216 7(3) nm] bond in the equatorial plane. In addition, the basal Cu1-Cl3 bond lengths are nearly the same with the basal Cu2-Cl4 [0.229 85(13) and 0.230 86(14) nm respectively] which are slightly shorter than other basal Cu1-Cl1 and Cu2-Cl2 bond lengths [0.241 07(14) and 0.243 11(16) nm respectively].

As can be seen in Table 2 for the title compound, the interior N2-Cu1-N5 angle of the bridging arrangement is 94.53(13)° while the N1-Cu2-N4 bridge-angle being 94.26(6)°. The pyridine ring[N3, C13, C8, C9, C10, C11] makes an angle of 6.38(0.08)° with respect to the triazole ring [N1, N2, C14, N8, C15], and they are are approximately coplanar. While the pendant substituted phenyl rings [C1, C2, C3, C4, C5,C6] are twisted away from coplanarity with the adjacent triazole unit [N1, N2, C14, N8, C15] and forms dihedral angles of 71.78(0.19)°. Similarly, The triazole ring [N4, N5, C26, N7, C27] make dihedral angle 10.41 (0.19)°and 84.17(0.17)° with the pyridine ring[N6, C28, C29, C30, C31, C32] and the phenyl ring [C18, C19, C20, C21, C22, C23]. The C-C and C-N bond lengths within the aromatic rings are normal (C-C distances range from 0.136 4(8) to 0.143 1(7) nm and C-N distances from 0.132 2(5) to 0.138 4(5) nm). These bond lengths are similar to those observed for other 1,2,4-triazole complexes[23,24]. The three chloro ligands [Cl1, Cl2 and Cl4] are also involved in hydrogen bonding with H2WA, H3WB, H3WA and H1WA. The crystal structure is further stabilized by intramolecular and intermolecular hydrogen bonds building up a three dimensional framework (Table 3 and Fig.2).

Table 3　Hydrogen-bond geometry

D–H···A	D-H / nm	H···A / nm	D···A / nm	D–H···A / (°)
O2W–H2WB···O1W^{i}	0.085	0.208	0. 2863(6)	153.4
O1W–H1WB···Cl2^{ii}	0.085	0.245	0.328 4(4)	166.4
O1W–H1WA···Cl4	0.085	0.238	0.321 9(4)	170.7
O2W–H2WA···Cl1	0.085	0.242	0.324 9(5)	163.7
O3W–H3WA···Cl2	0.085	0.282	0.367 1(9)	179.8
O3W–H3WB···Cl1	0.085	0.262	0.347 5(8)	179.5

Symmetry codes: ^{i} $-x+1$, $y+1/2$, $-z+1/2$; ^{ii} $-x+1$, $y-1/2$, $-z+1/2$.



Symmetry codes: (A) $-x+1$, $y+1/2$, $-z+1/2$, (B) $-x+1$, $y-1/2$, $-z+1/2$

Fig.2　Three-dimensional framework structure of the title compound, dashed line indicates hydrogen bond

2.2　Magnetic property

The magnetic susceptibility of $[Cu_2(\mu\text{-L})_2Cl_4]\cdot 2.5H_2O$ was measured in the temperature range of 1.8~300 K, and the data are shown in Fig.3 as plot of $\chi_m T$ versus temperature (T). A strong antiferromagnetic interaction was observed. The $\chi_m T$ data is fitted to Bleaney-Bowers[25] equation (**2**). According to the isotopic Heisenberg exchange Hamiltonian $H=2JS_1\cdot S_2$, the $S_1=S_2=1/2$ for Cu(Ⅱ) ions. N is the Avogadro′s number, μ_B is Bohr magneton, g is the Landé gvalue, J is the exchange integral, and k is the Boltzmann′s constant. A good fit was obtained using the parameters $J=-31.327\,92$ cm^{-1} and $g=2.125\,41$.

$$\chi_M=\frac{2Ng^2\beta^2/(kT)}{3+\exp[-2J/(kT)]} \quad (1)$$

$$\chi_M T=\frac{2Ng^2\beta^2/k}{3+\exp[-2J/(kT)]} \quad (2)$$

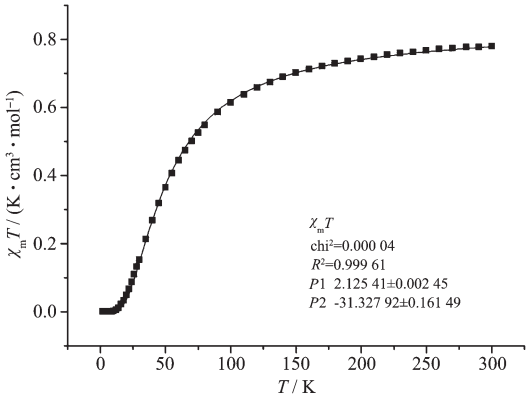


Fig.3 Plot of $\chi_m T$ vs T for $[Cu_2(\mu\text{-}L)_2Cl_4]\cdot 2.5H_2O$

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