

(1,2-(1*H*-1,2,4-三唑))乙烷的一维双链 Cu(II)配合物合成与表征

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摘要: 利用高度柔性的双三唑配体(1,2-(1*H*-1,2,4-三唑))乙烷(L)和铜盐反应合成了 1 个新的具有一维双链结构的铜(II)配合物 $[\text{Cu}(\text{cis-L})_2\text{Br}]\text{Br}\cdot 2\text{H}_2\text{O}$ (**1**)。单晶结构表明:配合物 **1** 的晶体属于三斜晶系, $P\bar{1}$ 空间群。在配合物 **1** 中双三唑配体采用反式构型,桥联相邻的中心铜离子形成一维双链结构,晶格中游离的 Br 原子同配位水分子形成了四元环状的 $\text{Br}\cdots\text{O}$ 超分子环。测定了配合物 **1** 在 2~300 K 的变温磁化率,结果表明相邻铜离子间存在弱的反铁磁相互作用。

关键词: (1,2-(1*H*-1,2,4-三唑))乙烷; 铜配合物; 一维双链; 反铁磁

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Synthesis and Characterization of One Novel 1D Double-Chain Copper(II) Complex with 1,2-Bis(1,2,4-triazole-1-yl)ethane

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Abstract: Using the highly flexible bis-triazole ligand 1,2-bis(1,2,4-triazole-1-yl)ethane (L), one new complex $[\text{Cu}(\text{cis-L})_2\text{Br}]\text{Br}\cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized and characterized by elemental analysis, FTIR and single crystal X-ray diffraction analysis. It belongs to triclinic system with space group $P\bar{1}$, $a=0.757\ 0(2)$ nm, $b=0.877\ 2(3)$ nm, $c=1.641\ 5(5)$ nm, $\alpha=104.187(5)^\circ$, $\beta=90.905(5)^\circ$, $\gamma=98.589(5)^\circ$, $V=1.043\ 4(5)$ nm³, $Z=2$. In **1** two *cis*-L molecules bridge central copper(II) ions forming 1D double-chain structure, four-member $\text{Br}\cdots\text{O}$ supra-molecular cycles can also be observed. The varied temperature magnetic property of **1** has been investigated from 300 to 2 K indicating weak anti-ferromagnetic interactions between neighboring copper(II) ions. CCDC: 753647.

Key words: 1,2-bis(1,2,4-triazole-1-yl)ethane; copper complex; one-dimensional double-chain; anti-ferromagnetic

During the last two decades metal-organic coordination polymers have aroused great interest for chemists due to their extremely versatile coordination motifs and potential applications in many areas such as light-emitting diodes (LEDs), catalytic, magnetic properties and so on^[1-4]. Although a variety of metal coordination frameworks with beautiful topologies and interesting electronic, magnetic, optical properties have been synthesized, rational control in the construction of polymeric networks remains a great challenge.

Judicious selection of different flexible or rigid ligands can dramatically tune ultimate structural motifs of these coordination frameworks^[5].

1,2,4-triazole and, in particular, its derivatives are very interesting ligands for their important properties^[6]. For example, these triazole ligands strength is just in the region to give spin crossover compounds with iron(II) salts. Such systems are applicable for information storage and some other applications^[7]. Previously we reported a series of 3,5-substituted triazole-cadmium

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coordination polymers from zero- to three-dimensional tuned via different triazole ligands and anions^[8]. In this work the flexible 1,2-bis(1,2,4-triazole-1-yl)ethane (L) ligands was employed. L is highly flexible and can adopt variable *trans*- and *cis*- conformations. One new 1D $\{[\text{Cu}(\text{cis-L})_2\text{Br}]\text{Br} \cdot 2\text{H}_2\text{O}\}_n$ (**1**) compound can be isolated. In **1** two *cis*-L molecules bridge central copper (II) ions forming 1D double-chain structure, four-member $\text{Br} \cdots \text{O}$ supra-molecular cycles can also be observed. The varied temperature magnetic property of **1** from 300 to 2 K was also investigated.

1 Experimental

1.1 Materials and general methods

The bis-triazole ligand 1,2-bis(1,2,4-triazole-1-yl)ethane (L) was prepared according to the literature method^[9]. Other reagents were purchased commercially and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. FTIR spectrum (KBr pellets) was taken on an AVATAR-370 (Nicolet) spectrometer in the range 4 000 ~400 cm^{-1} region. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascals constants for all constituent atoms.

1.2 Synthesis of $\{[\text{Cu}(\text{cis-L})_2\text{Br}]\text{Br} \cdot 2\text{H}_2\text{O}\}_n$ (**1**)

Complex **1** was prepared by refluxing L ligand

(32.8 mg, 0.2 mmol) and $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ (25.9 mg, 0.1 mmol) in 15 mL aqueous solution for 1 h. The precipitate was filtrated and blue crystals were isolated from the filtrate within one week. Yield: 44% (based on Cu). Anal. Calc. for $\text{C}_{12}\text{H}_{20}\text{Br}_2\text{CuN}_{12}\text{O}_2$ (%): C, 24.52; H, 3.43; N, 28.60. Found(%): C, 24.12; H, 3.63; N, 28.80. IR (KBr, cm^{-1}): 3 400(br), 3 140(w), 3 126(m), 3 060(w), 1 555(s), 1 475(m), 1 446(s), 1 390(s), 1 362(w), 1 322(s), 1 189(s), 1 078(s), 985(s), 862(s), 835(s), 774(s), 680(m), 625(s), 407(w).

1.3 X-ray crystallography and structural refinement

Structure measurement of **1** was performed on a computer controlled Bruker SMART APEX-II CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation with radiation wavelength 0.071 073 nm by using a ω -scan technique. Semi-empirical absorption corrections using SADABS program were applied. The structure was solved by direct methods and refined with the full-matrix least-squares technique using the SHELX-97 programs^[10]. Hydrogen bond lengths and bond angles for **1** are listed in Table 3. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively.

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Table 1 Crystallographic data and structure refinement summary^a

Formula	$\text{C}_{12}\text{H}_{20}\text{Br}_2\text{CuN}_{12}\text{O}_2$	θ range / (°)	1.28 to 27.07
Formula weight	587.76	Limiting indices	$-9 \leq h \leq 9, -11 \leq k \leq 11, -20 \leq l \leq 20$
Crystal size / mm	0.47×0.30×0.18	D_c / ($\text{g} \cdot \text{cm}^{-3}$)	1.871
Crystal system	Triclinic	μ / mm^{-1}	4.913
Space group	$P\bar{1}$	Reflections collected / unique	8 992 / 4 498
a / nm	0.757 0(2)	R_{int}	0.019 8
b / nm	0.877 2(3)	Data / restraints / parameters	4 498 / 0 / 278
c / nm	1.641 5(5)	GoF	1.073
α / (°)	104.187(5)	$F(000)$	582
β / (°)	90.905(5)	R_1^a / wR_2^b ($I > 2\sigma(I)$)	0.027 2 / 0.060 4
γ / (°)	98.589(5)	R_1 / wR_2 (all data)	0.039 0 / 0.069 7
V / nm^3	1.043 4(5)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	532 and -433
Z	2		

^a $R = \sum (|F_o| - |F_c|) / \sum |F_o|$; ^b $wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)]^{1/2}$.

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

Cu1-N4	0.200 3(2)	Cu1-N7	0.200 9(2)	Cu1-N10	0.201 6(2)
Cu1-N1	0.202 0(2)	Cu1-Br1	0.271 03(7)		
N4-Cu1-N7	91.05(9)	N4-Cu1-N10	167.98(9)	N7-Cu1-N10	88.47(9)
N4-Cu1-N1	89.76(9)	N7-Cu1-N1	177.75(9)	N10-Cu1-N1	90.30(9)
N4-Cu1-Br1	96.18(7)	N7-Cu1-Br1	92.03(7)	N10-Cu1-Br1	95.85(7)

Table 3 Hydrogen bond lengths and bond angles for 1

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠D-H...A / (°)
O(1)-H(1A)···Br(2) ⁱ	0.077 9	0.251 1	0.328 5	172.10
O(1)-H(1B)···Br(2) ⁱⁱ	0.074 0	0.261 5	0.334 9	171.48
O(2)-H(2B)···O(1) ⁱ	0.085 6	0.196 8	0.282 1	174.11

Symmetry codes: ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $x+1, y, z+1$.

2 Results and discussion

As is shown in Fig.1, **1** is a 1D chain structure bridged by two L molecules. The central copper(II) ion is five-coordinated by four nitrogen atoms of four *cis*-L ligands and one bromide anion. The central copper(II) ion also has weak interaction with lattice bromide anion (0.338 6 nm). The Cu(1)-N distances (from 0.200 3(19) to 0.2007 2(17) nm) are comparable with those of other Cu(II)-triazole complexes^[11]. Neighboring copper(II) ions are linked by two *cis*-L ligands to form 1D double-chain structure. The Cu...Cu separation across bridging ligands is 0.877 2(3) nm. It is interesting that bromide anions and lattice water molecules O(1) have weak interaction to generate intermolecular hydrogen bonds. Thus four-membered Br₂O₂ cycle clusters constructed via hydrogen bonding can be found in the supra-molecular structure (Fig.2). The four-member cycle clusters link two neighboring chains to form ladder

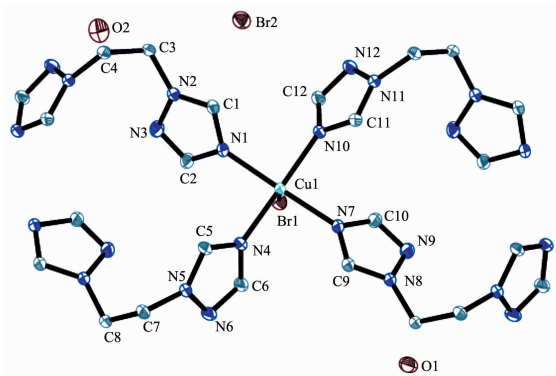
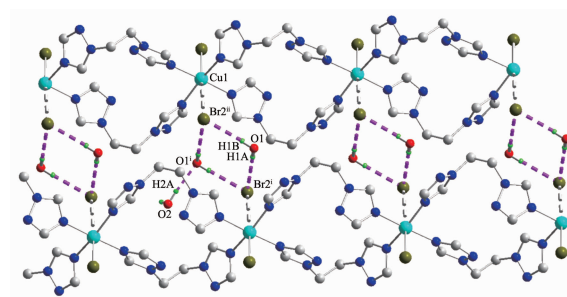


Fig.1 An ORTEP drawing of **1** showing the coordination environment of five-coordinated Cu^{II} ions



Symmetry codes: ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $x+1, y, z+1$

Fig.2 Four-membered Br₂O₂ cycles link two neighboring chains to form 1D ladder structures

structure. Furthermore, the lattice water O(2) also has the hydrogen-bonding interaction with O(1)ⁱ, which help to stabilize the supra-molecular structure.

2.1 Magnetic properties of 1

The complex **1** was studied by magnetic susceptibility measurements in the 2~300 K regions. The magnetic behaviour of **1** is shown in the form of a $\chi_M T$ versus T plot (Fig.3). A magnetic moment of 1.87

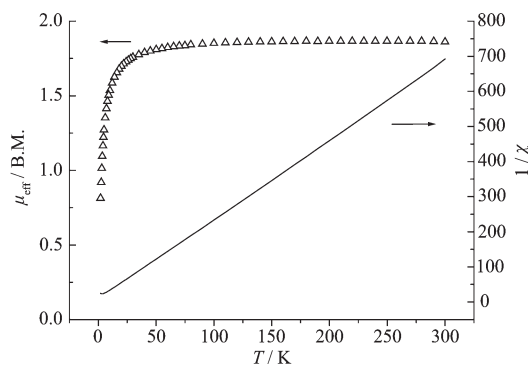


Fig.3 μ_{eff} versus T and $1/\chi_M$ versus T plot for **1** indicating the existence of weak anti-ferromagnetic interactions

B.M./Cu²⁺ is observed, a value typical μ_{eff} value for a Cu(II) atom with d^9 configuration^[12]. The magnetic behaviour of **1** can be interpreted by the Curie-Weiss law with Curie value and Weiss constant of 0.44 (5) cm³·K·mol⁻¹ and -5.02(5) K, which also reveal the existence of weak anti-ferromagnetic interaction in **1**. The result should be ascribed that the long L ligands can not effectively transmit the magnetic interactions between neighbouring copper(II) ions.

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