КРАТКИЕ СООБЩЕНИЯ

CRYSTAL STRUCTURE, AND PHYSICAL PROPERTIES OF A ONE-DIMENSIONAL COORDINATION POLYMER BASED ON 2,2′-BIS(1H-1,2,4-TRIAZOLYL)ETHER

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A one-dimensional Cu(II) complex $[Cu(BTE)_2(ClO_4)_2]_n$ (**1**) (BTE = 2,2′-bis(1H-1,2,4-triazolyl)ether) is synthesized and characterized using single crystal X-ray diffraction, IR, and elemental analysis. Single crystal X-ray diffraction analysis reveals that complex **1** is a one-dimensional chain based on the rhomboid subunit $[Cu_2(BTE)_2]$ with a Cu…Cu separation of 9.0912(2) Å. There is no magnetic coupling between the Cu^{II} ions. Complex **1** displays a high photocatalytic degradation activity for methylene blue.

Coordination polymers have attracted great attention not only due to their intriguing structural diversity and new topologies but also owing to their potential applications in gas storage, chemical separations, microelectronics, nonlinear optics, heterogeneous catalysis, and so on [1—4]. It is well known that the construction of coordination polymers is influenced by several factors, such as the nature of organic ligands, solvents, metal ions, and so on [5, 6]. Among them the organic ligands play a key role in the construction of coordination polymers with interesting structures [7, 8]. Because of the excellent coordinating ability and large conjugated system, 1,2,4-triazoles have been widely used to build coordination polymers [9—12]. Unlike parent 1,2,4-triazole, 1,1′-(2,2′-oxybis(ethane-2,1-diyl))bis(1H-1,2,4-triazole)) (BTE) can adopt different conformations according to the geometric needs of a metal ion, on the basis of relative orientation of the $CH_2CH_2OCH_2CH_2$ groups [13—16]. Here we selected 1,1′-(2,2′-oxybis(ethane-2,1-diyl))bis(1H-1,2,4-triazole)) (BTE) and the perchlorate anion (ClO_4^-), generating a new one-dimensional Cu(II) complex $[Cu(BTE)_2(ClO_4)_2]_n$ (**1**) whose crystal structure, magnetic and photocatalytic properties we report in this paper.

Experimental. The 2,2′-bis(1H-1,2,4-triazolyl)ether (BTE) ligand was synthesized according to the literature [15]. All other reagents and solvents were commercially available and used without further purification. The IR spectrum (4000 ~ 400 cm^{-1}, KBr) was recorded on a VECTOR 22 spectrometer. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with CuK_α (λ = 1.5418 Å) radiation at room temperature. Magnetic measurements on a microcrystalline sample were carried out on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were applied for both sample holder as the background and compound, estimated from Pascal constants [17]. UV-vis spectrum was measured on a Perkin Elmer Lambda 25 spectrophotometer.

Crystal data and structure refinement for complex **1**

Parameter	**1**
Empirical formula	$C_{16}H_{24}Cl_2CuN_{12}O_{10}$
Formula weight	678.92
Crystal system	Triclinic
Space group	*P*-1
a, *b*, *c*, Å	8.6842(3), 9.0912(2), 10.4472(3)
α, β, γ, deg.	107.2520(10), 99.869(2), 116.3400(10)
V, Å^3	660.20(4)
D_{calc}, g/m^3	1.708
F(000)	347
Limits of data collection, deg.	$2.18 \leq \theta \leq 27.00$
Reflections collected / independent (R_{int})	4357 / 2884 (0.0475)
GOOF	1.027
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0402,\ wR_2 = 0.0627$
R indices (all data)	$R_1 = 0.0646,\ wR_2 = 0.0664$

$$R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|. \quad \omega R_2 = \Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]^{1/2}.$$

Synthesis of [Cu(BTE)₂(ClO₄)₂]ₙ. A 10 ml portion of $EtOH/H_2O$ (1:2, v/v) solution was carefully layered over an aqueous solution (10 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) in a test tube. Then 10 ml of an EtOH solution of BTE (0.5 mmol) was carefully layered above the $EtOH/H_2O$ solution. The resulting solutions stood for several days to give blue single crystals of complex **1** (yield 23 %, based on $Cu(ClO_4)_2 \cdot 6H_2O$). Elemental analysis for $C_{16}H_{24}Cl_2CuN_{12}O_{10}$ (*Mw* = 678.92): C 28.31, H 3.56, N 24.76 %. Found: C 28.37, H 3.57, N 24.83 %. IR data (cm^{-1}): 3457m, 2878w, 1528m, 1381s, 1211w, 1134s, 995s, 910w, 764w, 679m, 648m, 563w, 463m.

X-ray crystallography. The crystal structure of complex **1** was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK_α radiation (λ = 0.71073 Å) at 291 K. Absorption correction was performed by using the SADABS program [18]. The structure was solved by a direct method using the SHELXL-97 program and refined by the full-matrix least squares technique on F^2 with SHELXL-97 [19]. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were refined isotropically, with the isotropic vibration parameters tied to the non-H atom to which they are bonded. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2. Hydrogen-bonding parameters are given in Table 3.

Results and discussion. Single crystal X-ray diffraction reveal that complex **1** crystallizes in a triclinic space group *P*-1, and the asymmetric unit contains a Cu^{2+} cation, one 2,2′-bis(1H-1,2,4-

Selected bond distances (Å) *and angles* (deg.) *for complex* **1**

Cu(1)—N(1)	2.010(2)	Cu(1)—N(1)^i	2.010(2)	N(1)—Cu(1)—N(6)^{ii}	89.52(9)
Cu(1)—N(6)^{ii}	2.017(2)	Cu(1)—N(6)^{iii}	2.017(2)	N(1)^i—Cu(1)—N(6)^{ii}	90.48(9)
Cu(1)—O(11)	2.459(1)	Cu(1)—O(11)^i	2.459(1)	N(1)—Cu(1)—N(6)^{iii}	90.48(9)
				N(1)^i—Cu(1)—N(6)^{iii}	89.52(9)

Symmetry transformations used to generate equivalent atoms: ^{i} –*x*+1, –*y*+1, –*z*+1; ^{ii} *x*, *y*–1, *z*; ^{iii} –*x*+1, –*y*+2, –*z*+1.

Table 3

Hydrogen bond lengths (Å) *and bond angles* (deg.) *in complex* **1**

D—H⋯A	d(D—H)	d(H⋯A)	d(D⋯A)	∠(DHA)
C(1)—H(1)⋯O(14)	0.93	2.31	3.225(5)	168
C(3)—H(3A)⋯O(14)[iv]	0.97	2.40	3.351(5)	168
C(7)—H(7)⋯O(13)[iv]	0.93	2.57	3.406(5)	149
C(7)—H(7)⋯O(13)[i]	0.93	2.51	3.252(4)	137
C(8)—H(8)⋯O(12)[v]	0.93	2.40	3.188(4)	143

Symmetry transformations used to generate equivalent atoms: [i] $-x+1$, $-y+1$, $-z+1$; [iv] x, $y+1$, z; [v] $x+1$, $y+2$, z.


Fig. 1. A view of the local coordination of the Cu^{2+} cations in **1**, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radii.
Symmetry codes: [i] $-x+1$, $-y+1$, $-z+1$; [ii] x, $y-1$, z; [iii] $-x+1$, $-y+2$, $-z+1$
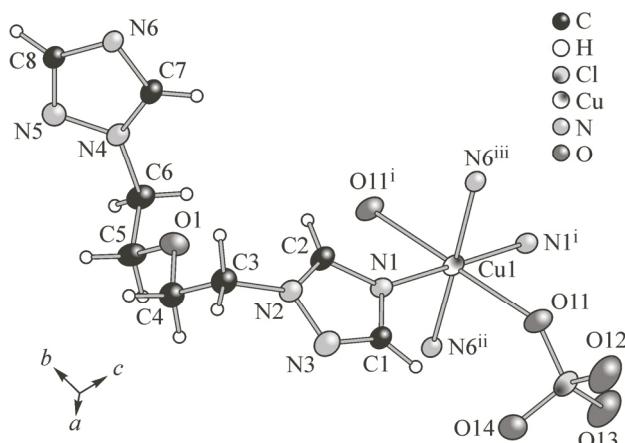
triazolyl)ether (BTE) ligand, and one perchlorate anion, as shown in Fig. 1. Each Cu(II) center is six-coordinated by four triazole nitrogen atoms (Cu1—N1 = 2.010(2), Cu1—N1^i = 2.010(2), Cu1—N6^{ii} = 2.017(2), Cu1—N6^{iii} = 2.017(2) Å) from four different BTE ligands, and two oxygen atoms from two perchlorate anions (Cu1—O11 = 2.459(1), Cu1—O11^i = 2.459(1) Å) (symmetry codes: [i] $-x+1$, $-y+1$, $-z+1$; [ii] x, $y-1$, z; [iii] $-x+1$, $-y+2$, $-z+1$). Averaged Cu—O and Cu—N distances are comparable to the reported values for other Cu based complexes [20—22].

The dihedral angle between the two triazole rings is 77.7°, and the bond angle C4O1C5 is 113.7(3)°. Two crystallographically equivalent copper atoms are bridged by two BTE ligands to form a rhomboid subunit [Cu$_2$(BTE)$_2$] with a Cu…Cu separation of 9.0912(2) Å. Neighboring [Cu$_2$(BTE)$_2$] subunits are interconnected to form infinite coordination polymer ribbons arranged parallel to the *b* direction (Fig. 2). There are also extensive inter- and intramolecular C—H⋯O hydrogen bonds (Table 3). Two adjacent 1D chains are linked by π—π interaction between the triazole rings
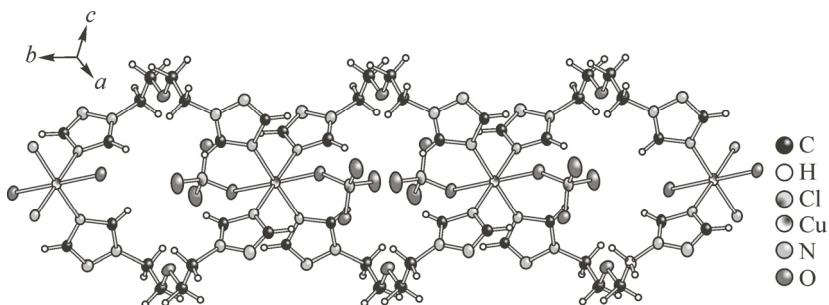

Fig. 2. View of 1D framework of **1**
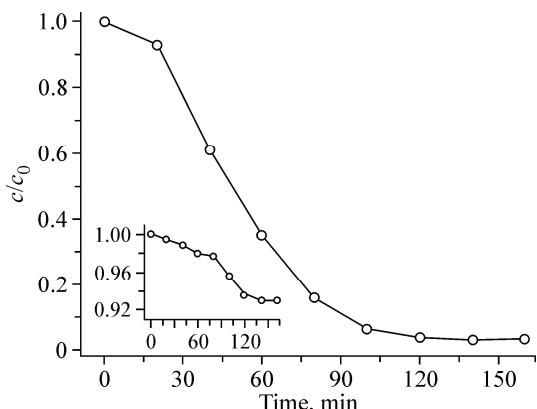
Fig. 3. Plots of concentration versus irradiation time for MB under irradiation with 500 W tungsten lamp in the presence of complex **1** (**inset:** the dark adsorption equilibrium for the MB of complex **1**)

($Cg1 \cdots Cg1 = 3.828(2)$ Å; $Cg1$ is the centroid of the N4—N5—N6—C7—C8 ring) to form a two-dimensional layer parallel to the (0 0 1) crystal planes.

Magnetic measurements were performed on polycrystalline samples of complex **1** in the range of 1.8—300 K. The $\chi_M T$ product was 0.381 cm^3·K·mol^{-1}, somewhat higher than expected for an isolated $S = 1/2$ Cu^{2+} ion (0.375 cm^3·K·mol^{-1}) at room temperature. The $\chi_M T$ products are almost a constant (0.375—0.385 emu·K·mol^{-1}) from room temperature down to 1.8 K, indicating no magnetic coupling between adjacent Cu^{2+} ions.

Methylene blue (MB) was selected as model pollutant in aqueous media to evaluate the photocatalytic efficiency of complex **1**. The photo-degradation processes of methylene blue (MB) in a blanc test have also been studied for comparison under the same conditions. It was found that 96.9 % MB was successfully photodegraded in the presence of complex **1** under tungsten lamp irradiation after 200 min (Fig. 3). However, in the blank experiment the degradation efficiency was reduced to 7.00 % in 160 min as illustrated in the inset of Fig. 3, which indicates that complex **1** is more active for the decomposition of MB.

In summary, we have prepared a one-dimensional polymer based on the rhomboid subunit [Cu$_2$(BTE)$_2$] with a Cu…Cu separation of 9.0912(2) Å. It displays high photocatalytic activity for methylene blue degradation. There is no magnetic coupling between adjacent Cu^{2+} ions.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 1431842. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EQ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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