

КРАТКИЕ СООБЩЕНИЯ

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A NOVEL DINUCLEAR Cu^{II} COMPLEX BASED ON FLEXIBLE BIS(TRIAZOLE):
SYNTHESIS, STRUCTURE AND PHYSICAL PROPERTIES

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New dinuclear copper(II) complex [Cu₂(BTE)₂(N₃)₄] (**1**) (BTE = 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-1,2,4-triazole)) is synthesized and characterized using single crystal X-ray diffraction, IR spectroscopy, and elemental analysis. Single crystal X-ray diffraction reveals that complex **1** is a centrosymmetric dinuclear Cu(II) cluster unit with a Cu—Cu separation of 3.267(6) Å. In addition, complex **1** exhibits a high photocatalytic degradation activity for the degradation of rhodamine B.

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Coordination polymers have recently attracted great attention because of their potential applications as functional materials in the fields of nonlinear optics, magnetism, gas storage, ion exchange, catalysis, etc. [1–3]. In the self-assembly process, several factors influence the final structures of coordination polymers, such as pH, template, reaction temperature, solvent system, metal ions, organic ligand, and so on [4, 5]. Among them, the choice of organic ligands is one of the most important aspects that affect the construction of coordination polymers with interesting structures. Generally, multi-pyridine ligands feature prominently in the construction of coordination polymers, and the reported coordination polymers are mostly constructed by multi-pyridine ligands [6–8]. Due to the excellent coordinating ability and large conjugated system, 1,2,4-triazole and its derivatives have been widely used to build coordination polymers [9–11]. Comparing to the corresponding 1,2,4-triazole ligand, 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 different metal ions based on the relative orientation of CH₂CH₂OCH₂CH₂ groups [12–14]. Here, we chose 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-1,2,4-triazole) (BTE) and azide (NO₃⁻), generating new dinuclear copper(II) complex, [Cu₂(BTE)₂(N₃)₄] (**1**) whose crystal structure we now report. In addition, the photocatalytic activity of complex **1** has been investigated.

Experimental. The 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-1,2,4-triazole) ligands were synthesized according to the literature method [12]. All other reagents and solvents were commercially available and used without further purification. The IR spectra were obtained in the range 4000–400 cm⁻¹ as KBr disks on a VECTOR 22 spectrometer. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. The UV-vis spectrum was measured using a Perkin Elmer Lambda 25 spectrophotometer.

Synthesis of [Cu₂(BTE)₂(N₃)₄]. To a solution of Cu(NO₃)₂·6H₂O (59.1 mg, 0.2 mmol) and BTE (41.6 mg, 0.2 mmol) in CH₃CN (5 ml) a NaN₃ solution (26.1 mg, 0.4 mmol) in H₂O (5 ml) was added

Table 1

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

Empirical formula	C ₁₆ H ₂₄ Cu ₂ N ₂₄ O ₂
Formula weight	711.69
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	15.326(3), 11.928(2), 15.467(3)
<i>V</i> , Å ³	2827.5(9)
<i>D</i> _{calc} , g/m ⁻³	1.569
<i>F</i> (000)	1448
Limits of data collection, deg.	2.16 ≤ θ ≤ 26.00
Collected / Independent reflections (<i>R</i> _{int})	13089 / 2778 (0.0597)
Goodness-of-fit	1.032
<i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0394, <i>wR</i> ₂ = 0.1014
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0587, <i>wR</i> ₂ = 0.1083

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

dropwise with gentle stirring. After several weeks, blue block single crystals suitable for the X-ray analysis were obtained. (yield 54.1 %, based on Cu(NO₃)₂·6H₂O). Anal. calcd (%) for C₁₆H₂₄Cu₂N₂₄O₂ (*M*_w = 711.69): C 27.00, H 3.40, N 47.24. Found (%): C 27.07, H 3.41, N 47.37. Selected IR (KBr, cm⁻¹): 1237 (m), 1572 (s), 2096 (s), 2141 (s), 3332(m).

X-ray crystallography. The crystal structure was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK_α radiation (λ = 0.71073 Å) at 296 K. Absorption correction was applied using the SADABS program [15]. The structure was solved by a direct method using the SHELXL-97 program [16] and refined by the full-matrix least-squares technique on *F*² with SHELXL-97. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. The crystallographic data are summarized in Table 1.

Results and discussion. The structure of complex **1** features a centrosymmetric dinuclear Cu(II) cluster unit. Single crystal X-ray diffraction reveals that complex **1** crystallizes in the orthorhombic space group *Pbcn* with an asymmetric unit consisting of a divalent copper atom, a BTE ligand, a μ_{1,1}-N3 bridging group (N1—N3), and a monodentate N₃ ligand (N4—N6). Copper atom Cu1 possesses a distorted square pyramidal (τ = 0.146) {CuN₅} coordination environment in which the basal plane contains two nitrogen atoms from a BTE ligand with Cu—N distances of 2.006(2) and 2.009(2) Å, a nitrogen atoms of one μ_{1,1}-N3 bridging group with a Cu—N distance of 1.998(3) Å, and a nitrogen atom of one monodentate N₃ ligand with a Cu—N distance of 1.994(3) Å. The apical position is occupied by a nitrogen atom of another μ_{1,1}-N3 bridging group with a Cu—N distance of 2.339(3) Å.

Two crystallographically equivalent Cu^{II} cations are bridged by two μ_{1,1}-N3 bridging groups to form a Cu₂N₂ rhomboid subunit with a Cu···Cu separation of 3.267(6) Å and a Cu—N_{azide}—Cu angle of 82.56(11)°. As shown in Fig. 1, in the Cu₂N₂ rhomboid subunit two Cu^{II} cations are bridged by two BTE ligands adopting the *cis* conformation and two monodentate N₃ ligands to form a binuclear copper(II) cluster.

Rhodamine B (RhB) was selected as a model pollutant in aqueous media to evaluate the photocatalytic effectiveness of complex **1**. The photodegradation processes of RhB without complex **1** have also been studied for comparison under the same conditions. From Fig. 2, it was found that 95.72 % RhB was successfully photodegraded in the presence of complex **1** under tungsten lamp irradiation in

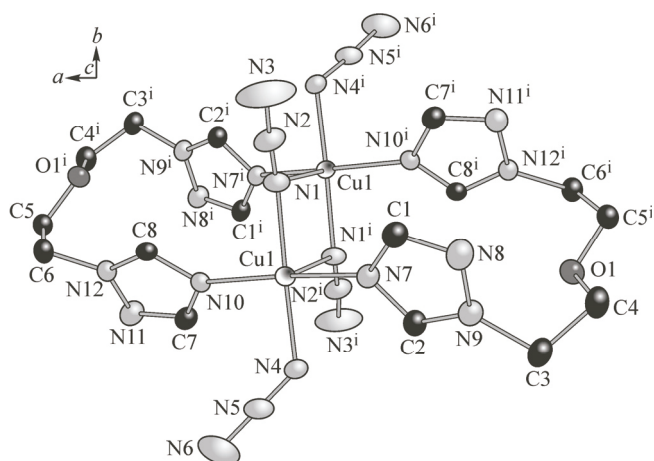


Fig. 1. The binuclear structure of complex **1**, all hydrogen atoms are omitted for clarity. Symmetry codes: $i -x, -y+2, -z+1$

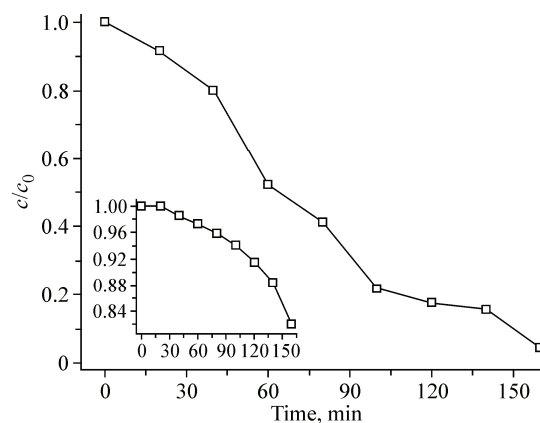


Fig. 2. Plots of concentration versus irradiation time for RhB under irradiation with a 500 W tungsten lamp in the presence of complex **1** (inset: the dark adsorption equilibrium for RhB of complex **1**)

160 min. However, when the research was conducted in the blank experiment, the degradation efficiency of the RhB reaction reduced to 18.10 % in 160 min as illustrated in the inset of Fig. 2, which indicates that complex **1** is more active for the decomposition of RhB.

In summary, we have presented the synthesis and crystal structure of new dinuclear copper(II) complex $[\text{Cu}_2(\text{BTE})_2(\text{N}_3)_4]$ (**1**). The single crystal X-ray diffraction analysis revealed that complex **1** was a centrosymmetric dinuclear Cu(II) cluster unit with a Cu—Cu separation of 3.267(6) Å. In addition, complex **1** exhibits a high photocatalytic degradation activity for the degradation of rhodamine B.

Crystallographic data for the structural analysis of complex **1** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1436690. 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).

REFERENCES

1. Stock N., Biswas S. // Chem. Rev. – 2012. – **112**. – P. 933 – 969.
2. Li J.R., Kuppler R.J., Zhou H. // Chem. Soc. Rev. – 2009. – **38**. – P. 1477 – 1504.
3. Wang X.Z., Zhu D.R., Xu Y. et al. // Cryst. Growth Des. – 2010. – **10**. – P. 887 – 894.
4. Lin J.G., Zang S.Q., Tian Z.F. et al. // CrystEngComm. – 2007. – **9**. – P. 915 – 921.
5. Yang Y., Du P., Ma J.F. et al. // Cryst. Growth Des. – 2011. – **11**. – P. 5540 – 5553.
6. Gabriel C., Vangelis A.A., Raptopoulou C.P. et al. // Cryst. Growth Des. – 2015. – **15**. – P. 5310 – 5326.
7. Wu X.-S., Liang J., Hu X.-L. et al. // Cryst. Growth Des. – 2015. – **15**. – P. 4311 – 4317.
8. Yao P.-F., Tao Y., Li H.-Y. et al. // Cryst. Growth Des. – 2015. – **15**. – P. 4394 – 4405.
9. Groeneveld L.R., Vos G., Verschoor G.C. et al. // J. Chem. Soc., Chem. Commun. – 1982. – P. 620 – 621.
10. Ding J.-G., Zhu X., Cu Y.-F. et al. // CrystEngComm. – 2014. – **16**. – P. 1632 – 1644.
11. Peng Y.-F., Zhao S., Li K. et al. // CrystEngComm. – 2015. – **17**. – P. 2544 – 2552.
12. Gao J.-Z., Yang J., Liu Y.-Y. et al. // CrystEngComm. – 2012. – **14**. – P. 8173 – 8185.
13. Yang Y., Du P., Yang J. et al. // CrystEngComm. – 2013. – **15**. – P. 4357 – 4371.
14. Du P., Yang Y., Yang J. et al. // Dalton Trans. – 2013. – **42**. – P. 1567 – 1580.
15. Sheldrick G.M. SADABS, An empirical absorption correction program, Madison, WI, Bruker Analytical X-ray Systems, 1996.
16. Sheldrick G.M. SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.