ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2016. Том 57, № 6 *Июль – август* *С. 1336 – 1340*

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:547.13:546.562

CRYSTAL STRUCTURE AND CATALYTIC PROPERTIES OF A TWO-DIMENSIONAL COPPER(II) COORDINATION POLYMER DERIVED FROM RIGID BIS(TRIAZOLE)

W.-L. Hou[1], **G.-Y. Dong**[2], **X. Zhang**[2]

[1]*Analysis and Test Center, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei, P. R. China*
E-mail: tscghua@126.com
[2]*College of Chemical Engineering, North China University of Science and Technology, Tangshan, Hebei, P. R. China*

Received April 14, 2015

A new Cu(II) coordination polymer, namely $\{[Cu_2(btb)_2(sip)(OH)]\cdot(H_2O)_{0.25}\}_n$ (btb = 4,4′-bis(1,2,4-triazolyl-1-yl)-biphenyl, H_3sip = 5-sulfoisophthalic acid), is hydrothermally synthesized and characterized by elemental analyses, infrared (IR) spectroscopy, and single crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$, $a = 14.9676(3)$ Å, $b = 14.3478(3)$ Å, $c = 21.2719(5)$ Å, $\beta = 125.325(2)°$, $V = 3727.11(14)$ Å^3, $Z = 4$, $C_{40}H_{28.50}Cu_2N_{12}O_{8.25}S$, $M_r = 968.39$, $D_c = 1.726$ g/cm^3, $\mu = 1.274$ mm^{-1}. The structural analyses reveal that the compound displays a 2D binodal rarely (4,5)-connected network with 4,5L50 topology. Moreover, the thermal and catalytic properties of the complex for the degradation of the congo red azo dye in a Fenton-like process are investigated.

DOI: 10.15372/JSC20160630

Keywords: bis(triazole), Cu(II) complex, crystal structure, catalytic property.

The design and synthesis of metal-organic coordination polymers (MOCPs) have been a subject of high attention for their potential applications in fields such as gas storage, chemical separation, catalysis, luminescence and their intriguing variety of topologies [1—3]. A variety of metal-organic architectures with diversified structures and interesting properties have been assembled through the judicious choice of organic ligands and metal ions. Isophthalic acid and its derivatives are one of the most successful multifunctional ligands because of their structural rigidity, chemical stability, and appropriate connectivity [4]. In particular, the 5-sulfoisophthalic acid(H_3sip) ligand has attracted intensive research attention [5, 6]. In contrast to the carboxylate group, the weak coordination nature of $—SO_3^-$ makes its coordination mode very flexible and sensitive to the chemical environment; besides, the sulfonate group has one more potentially coordinating oxygen atom.

Among various N-containing ligands, such as imidazole, pyridine, triazole and tetrazole, are frequently used to construct desirable MOCPs [7—9]. Bis(1,2,4-triazole) and its derivatives are versatile multidentate ligands which can provide abundant coordination modes and generate variable interesting structures and functional properties [10, 11]. However, when searching the Cambridge Structural Database (version 5.36, Feb 2015) [12] for MOCPs constructed from rigid the 4,4′- bis(1,2,4-triazolyl-1-yl)-biphenyl (btb) ligand, scarcely related structures were found. In recent work, we presented a 3D copper(II) MOCPs derived from btb, namely, $\{[Cu_3(btb)_3(nbta)_2]\cdot(H_2O)_2\}_n$ (H_3nbta = 5-nitro-1,2,3-benzenetricarboxylic acid), which represents a unique framework with 3,4,4T20 topology [13]. As part of our ongoing efforts to further investigate the effect of organic carboxylate ligands with the resulting coordination/supramolecular architectures based on the btb-containing mixed system, herein we report the synthesis, crystal structure, and catalytic properties of new coordination polymers $\{[Cu_2(btb)_2(sip)(OH)]\cdot(H_2O)_{0.25}\}_n$.

Materials and physical measurements. All commercially available solvents and starting materials bought from Alfa Aesar Company were used as received without further purification. The btb ligand was prepared as previously reported [14]. IR spectra were obtained with an Avatar 360 (Nicolet) spectrophotometer in the range 4000—400 cm^{-1} using KBr pellets. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C automatic analyzer. Thermal analyses were performed on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C under N_2 with a heating rate of 10 deg./min. The powder X-ray diffraction measurement was executed on a Rigaku D/Max 2500PC X-ray diffractometer using CuK_α radiation ($\lambda = 0.1542$ nm) from 2θ of 5—50° with a step size of 0.02° and a scanning rate of 10 deg./min. The absorptivity value of Congo red was recorded with a Shanghai Jingke 722N spectrophotometer at the maximum wavelength of 496 nm.

Synthesis of $\{[Cu_2(btb)_2(sip)(OH)]\cdot(H_2O)_{0.25}\}_n$. A mixture of $CuCl_2\cdot2H_2O$ (51 mg, 0.3 mmol), btb (29 mg, 0.1 mmol), H_3sip (21.8 mg, 0.1 mmol), NaOH (12.0 mg, 0.3 mmol), H_2O (15 ml) were sealed in a 25-ml Teflon-lined stainless vessel and heated to 160 °C for 3 days under autogenous pressure, and then cooled down to room temperature with a rate of 5 deg./h. Blue block crystals of the complex suitable for X-ray diffraction were obtained in a 62.1 % yield based on $CuCl_2\cdot2H_2O$. Anal. Calc. for $C_{40}H_{28.5}Cu_2N_{12}O_{8.25}S$ ($M_r = 968.39$) (%): C 49.6, H 3.0, N 17.4. Found: C 49.9, H 2.8, N 17.6. IR (KBr, cm^{-1}): 3418m, 3096m, 1598s, 1465w, 1280s, 1210m, 1148m, 1055w, 975s, 827s, 785m, 753s, 673w, 653w, 536w, 481m.

X-ray crystallography. A single crystal with dimensions of 0.26×0.18×0.09 mm was selected for X-ray diffraction. The crystallographic data for the complex were collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) and ω-2θ scan mode at 296(2) K. A semi-empirical absorption correction was applied using the SADABS program [15]. The structure was solved by direct methods with the SHELXS-97 program [16] and refined

Table 1

Crystal data and structure refinements for the complex

Empirical formula	$C_{40}H_{28.50}Cu_2N_{12}O_{8.25}S$
M, g/mol	968.39
T, K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
a, b, c, Å	14.9676(3), 14.3478(3), 21.2719(5)
Space group	$P2_1/c$
Volume, Å^3	3727.11(14)
Z	4
Calculated density, g/cm^3	1.726
Absorption coefficient, mm^{-1}	1.274
$F(000)$	1970
Crystal size, mm	0.26×0.18×0.09
θ_{min}—θ_{max}, deg.	2.74—27.10
Limiting indices	$-19 \le h \le 19$, $-19 \le k \le 17$, $-27 \le l \le 26$
Reflections collected / unique [R_{int}]	40869 / 8171 [0.0551]
Data / restraints / parameters	8171 / 4 / 586
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0381$, $wR_2 = 0.0870$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.0944$

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for the complex*

Parameter	Value	Parameter	Value	Parameter	Value
Cu1—O8	1.935(2)	O8—Cu1—O3A	176.33(8)	O8—Cu1—N3B	90.26(8)
Cu1—N3B	1.993(2)	O3A—Cu1—N3B	93.11(8)	O8—Cu1—N6	91.52(8)
Cu1—O6	2.343(2)	O3A—Cu1—N6	84.96(8)	N3B—Cu1—N6	172.42(9)
Cu2—O2C	1.965(2)	O8—Cu1—O6	94.56(7)	O3A—Cu1—O6	86.71(7)
Cu2—N9	2.015(2)	N3B—Cu1—O6	93.25(8)	N6—Cu1—O6	93.96(8)
Cu1—O3A	1.954(2)	O8—Cu2—O2C	176.40(7)	O8—Cu2—N12B	89.05(8)
Cu1—N6	2.008(2)	O2C—Cu2—N12B	94.33(8)	O8—Cu2—N9	90.35(8)
Cu2—O8	1.938(2)	O2C—Cu2—N9	86.23(8)	N12B—Cu2—N9	177.72(9)
Cu2—N12B	1.986(2)	O8—Cu2—O7	94.46(7)	O2C—Cu2—O7	84.20(7)
Cu2—O7	2.325(2)	N12B—Cu2—O7	91.67(8)	N9—Cu2—O7	86.18(8)

Symmetry transformations used to generate equivalent atoms: A = –*x*+1, –*y*, –*z*+1; B = *x*–1, *y*, *z*–1; C = –*x*+1, –*y*+1, –*z*+1.

with SHELXL-97 by the full-matrix least-squares fitting on F^2 [17]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of all water molecules and the hydroxyl group could be located from a difference Fourier map, while the other hydrogen atoms were placed in calculated positions. The summary of the crystallographic data and structure analysis are given in Table 1. The selected bond lengths and bong angles are listed in Table 2. CCDC 1055347 contains the supplementary crystallographic data for the complex. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Results and discussion. Crystal structure of $\{[Cu_2(btb)_2(sip)(OH)]\cdot(H_2O)_{0.25}\}_n$. The single crystal X-ray diffraction analysis reveals that the complex crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of the compound contains two copper ions (Cu1, Cu2), a sip^{3-} anion, a hydroxyl anion, two btb neutral ligands, and a quarter of free water molecules. The Cu—O/N bond lengths are in the normal range of 1.935(2)—2.343(2) Å [18]; each of the copper center possesses a $\{CuN_2O_3\}$ square pyramidal geometry in which the equatorial sites are taken up by one sulfonate oxygen atom, two nitrogen atoms from two individual btb ligands, and the apical positions are occupied by one carboxylate oxygen atom and a single hydroxyl oxygen atom (Fig. 1); deviations from the idealized square pyramidal geometry differ from Cu1 and Cu2, with τ factors being 0.02 and 0.07,

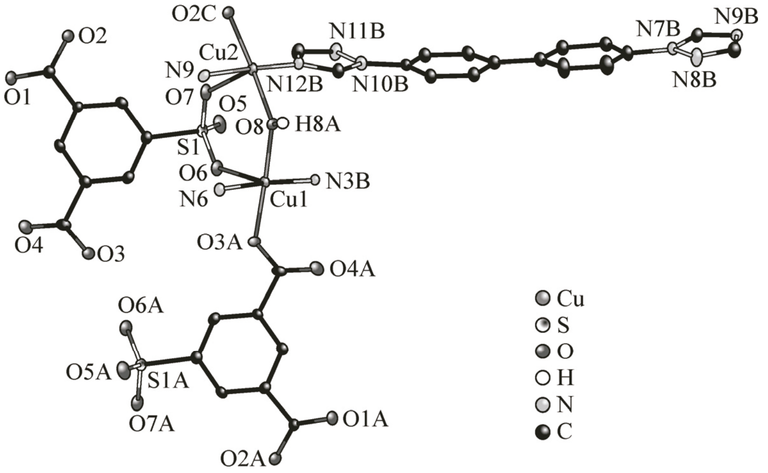

Fig. 1. Coordination environment of the Cu(II) ion in the complex (at a 30 % ellipsoid probability level; all the hydrogen atoms are omitted for clarity except for the hydroxyl group).
Symmetry codes: A = –*x*+1, –*y*, –*z*+1; B = *x*–1, *y*, *z*–1; C = –*x*+1, –*y*+1, –*z*+1

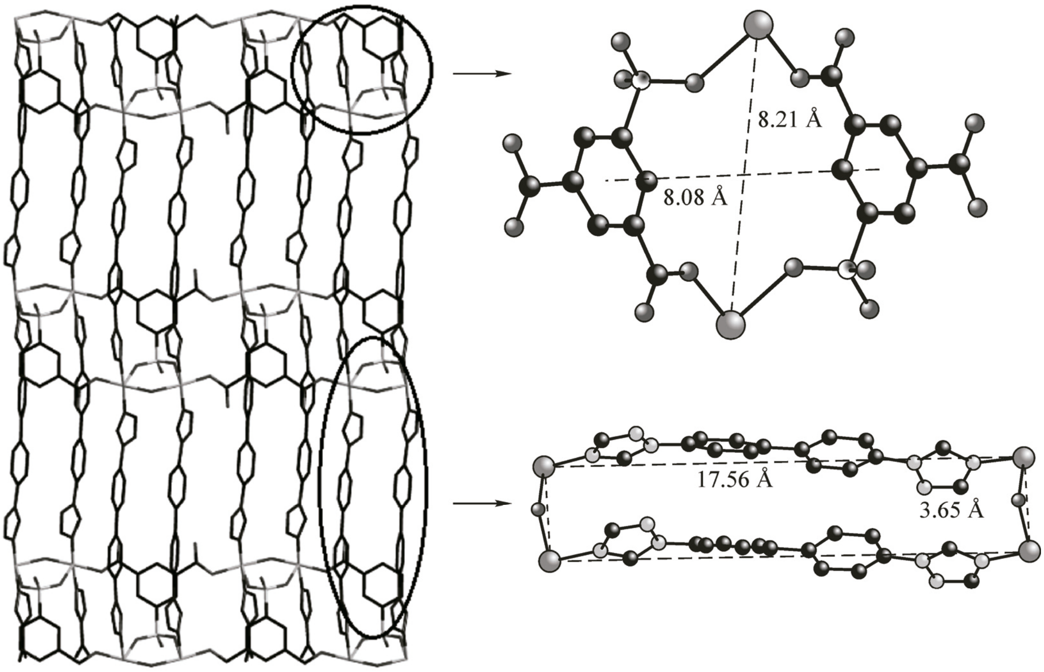

Fig. 2. View of the 2D layer structure

respectively [19]. The sip^{3-} ligand employs the μ_4:η^1:η^1:η^1:η^1 bridging mode to connect copper atoms to construct a 1D ladder-like chain along the *b* axis. In addition, the btb ligands adopt a bis(monodentate) bridge linking the adjacent metal ions to generate another 1D linear chain. Such two types of chains are assembled into a 2D layer structure (Fig. 2), where two kinds of multinuclear units exist. One of them is constituted by two btb ligands, four Cu(II) ions, and a couple of hydroxyl groups with the dimensions of 17.56×3.65 Å. Another binuclear cycle is formed by a pair of sip^{3-} anions and two metal ions, where the through-space Cu···Cu and centroid-centroid distances are 8.21 Å and 8.08 Å, respectively. Topologically, the sip^{3-} anions and the central Cu(II) ions can be reduced severally as four- and five-connected nodes. Therefore, the 2D framework of this MOCP can be abstracted as a rarely (4,5)-connected network with a $\{3.4^2.5^2.6\}\{3.4^3.5^3.6^3\}2$ topology by TOPOS 4.0 [20].

Thermal analysis. To investigate the thermal stability of the complex, thermogravimetric analyses were carried out. As shown in Fig. 3, the complex remains stable up to 300 °C and exhibits a mass loss of 29.6 % (calcd: 27.3%) between 300 °C and 427 °C, which can correspond to the release of H_2O

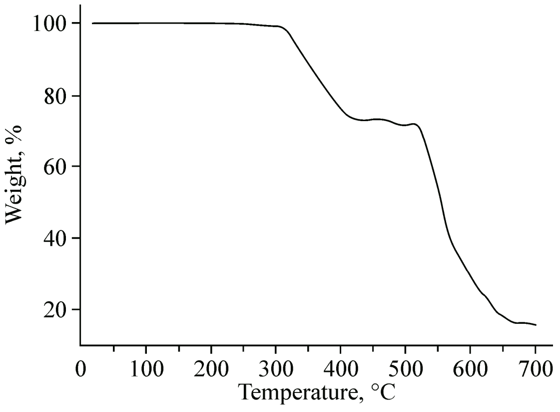

Fig. 3. TGA curve of the complex

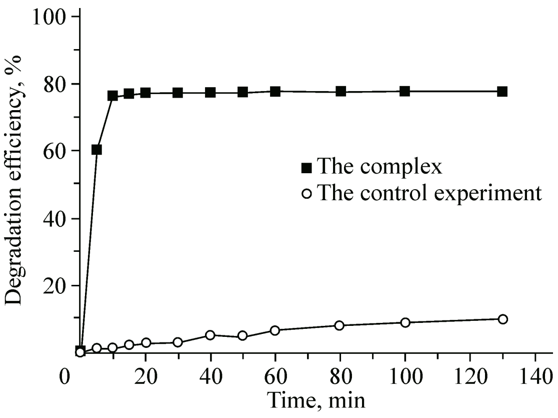

Fig. 4. Experimental results of the catalytic degradation of the Congo red azo dye

and sip^{3-}. A further loss of 58.2 % between 427°C and 514°C belongs to the departure of the btb ligand (calcd.56.3 %). The residual weight is 16.2 % (calcd: 16.4 %), corresponding to CuO as the final product.

Catalytic properties. Azo dyes are an important source of environmental contamination, and most of them are toxic, non-biodegradable, and potentially carcinogenic in nature. Therefore, it is necessary to find an effective way to remove this pollutant from waste water. Advanced oxidation technologies such as the Fenton-like method have drawn increasing attention to degrade dye waste water. To date, some researches have proved that the transition metal coordination compounds exhibit promising activities in a Fenton-like process [21—23]. The degradation of the Congo red by hydrogen peroxide, activated with the title complexes, was investigated according to the literature [18].

As shown in Fig. 4, when H_2O_2 was added into the Congo red solution as the control experiment, there was no evident removal of color with degradation efficiency of the Congo red only 9.7 % after 130 min, indicating that this dye cannot be effectively oxidized by hydrogen peroxide solely. However, when the complex is added into the system, the color of the methyl orange was visibly removed and the degradation efficiency was up to 77.3 % after 130 min. Clearly, under the same conditions, the complex has a prominent effect for the degradation of the Congo red in the Fenton-like system.

REFERENCES

1. *Lin Z.J., Lu J., Hong M., Cao R.* // Chem. Soc. Rev. – 2014. – **43**. – P. 5867.
2. *Du M., Li C.P., Liu C.S., Fang S.M.* // Coord. Chem. Rev. – 2013. – **257**. – P. 1282.
3. *Cook T.R., Zheng Y.R., Stang P.J.* // Chem. Rev. – 2013. – **113**. – P. 734.
4. *Gandolfo C.M., LaDuca R.L.* // Cryst. Growth Des. – 2011. – **11**. – P. 1328.
5. *Lü J., Li F., Yuan D.Q., Cao R.* // Polyhedron. – 2007. – **26**. – P. 2979.
6. *Yang E.C., Liu Z.Y., Zhang C.H., Yang Y.L., Zhao X.J.* // Dalton Trans. – 2013. – **42**. – P. 1581.
7. *Li S., Ma H., Pang H., Zhang L.* // Cryst. Growth Des. – 2014. – **14**. – P. 4450.
8. *Cao L.H., Wei Y.L., Yang Y., Xu H., Zang S.Q., Hou H.W.* // Cryst. Growth Des. – 2014. – **14**. – P. 1827.
9. *Li M., Zhao S., Peng Y.F., Li B.L., Li H.Y.* // Dalton Trans. – 2013. – **42**. – P. 9771.
10. *Nijesh K., Rojisha V.C., De S., Parameswaran P.* // Dalton Trans. – 2015. – **44**. – P. 4693.
11. *Rezende M.P., Andrade A.F., Freitas M.P.* // J. Mol. Struct. – 2015. – **8**. – P. 1093.
12. *Allen F.H.* // Acta Crystallogr. – 2002. – **B58**. – P. 380.
13. *Wang X.X., Li Z.X., Yu B.Y., Hecke K.V., Cui G.H.* // Inorg. Chem. Commun. – 2015. – **54**. – P. 9.
14. *Cristau H.J., Cellier P.P., Spindler J.F., Taillefer M.* // Chem. Eur. J. – 2004. – **10**. – P. 5607.
15. *Sheldrick G.M.* SADABS. – Göttingen, Germany: University of Göttingen, 1996.
16. *Sheldrick G.M.* SHELXS-97. – Göttingen, Germany: University of Göttingen, 1997.
17. *Sheldrick G.M.* SHELXL-97. – Göttingen, Germany: University of Göttingen, 1997.
18. *Cui G.H., He C.H., Jiao C.H., Geng J.C., Blatov V.A.* // CrystEngComm. – 2012. – **14**. – P. 4210.
19. *Yang L., Powell D.R., Houser R.P.* // Dalton Trans. – 2007. – P. 955.
20. *Blatov V.A.* // Struct. Chem. – 2012. – **23**. – P. 955.
21. *Yang S., Wang P., Yang X., Shan L., Zhang W., Shao X., Niu R.* // J. Hazard. Mater. – 2010. – **179**. – P. 552.
22. *Saien J., Soleymani A.R., Sun J.H.* // Desalination. – 2011. – **279**. – P. 298.
23. *Qin L., Gu Y., Li G.Y., Xiao S.L., Cui G.H.* // Transition Met. Chem. – 2013. – **38**. – P. 407.