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CRYSTAL STRUCTURE, ELECTROCHEMICAL AND MAGNETIC PROPERTIES OF A NEW BINUCLEAR COPPER(II) COMPLEX WITH BENZOIC ACID AS A LIGAND

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A new complex $[Cu_2(L)_4(DMF)_2]$ (**1**) with benzoic acid (HL) as a ligand is synthesized by the solid phase synthesis method. Crystal data for the complex are as follows: monoclinic, space group $P2_1/n$, $a = 10.593(2)$ Å, $b = 10.123(2)$ Å, $c = 16.336(3)$ Å, $\beta = 93.55(3)°$, $V = 1748.4(6)$ Å^3, $D_c = 1.439$ g/cm^{-3}, $Z = 4$, $F(000) = 780$, GOOF = 1.003, final discrepancy factors $R_1 = 0.0624$, $wR_2 = 0.1559$. In **1**, the Cu(II) ion is coordinated by six atoms to give a distorted octahedral coordination geometry. The electrochemical, fluorescent, and magnetic properties of **1** are studied. The results show that the electron transfer of **1** is quasi reversible in the electrode reaction corresponding to Cu(II)/Cu(I), and **1** exhibits three relatively strong fluorescent emission peaks at 403, 425, and 454 nm. In addition, complex **1** displays the antiferromagnetic property in a temperature range of 300 ~ 10 K.

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Introduction. In recent years, the rational design and assembly of coordination supramolecular complexes have attracted great interest due to their fascinating structural diversity as well as their potential applications in magnetism, photoluminescence, guest inclusion, gas adsorption, catalysis, and so on [1—10]. Basically, the construction of such metallosupramolecular assemblies mainly depends on the skillful selection of metal ions and organic ligands. Benzoic acid and its derivatives that commonly possess multiple coordination modes are excellent candidates for constructing supramolecular metal complexes through selective and directional noncovalent forces such as the hydrogen bonding, $\pi\cdots\pi$ and C—H$\cdots\pi$ interactions [11—18].

In order to obtain further information about the complex construction with the benzoic acid ligand, we selected benzoic acid as a ligand, obtained a new complex $[Cu_2(L)_4(DMF)_2]$, and determined its structure. In addition, we also reported our preliminary results of the electrochemical and magnetic properties of **1**.

Experimental. All materials were of analytic grade and used without further purification. Elemental analyses for C, H and N were carried out on a PerkinElmer elemental analyzer, model 2400II. The crystal structure determination was carried out on a Nonius CAD4 diffractometer. The cyclic voltammogram was measured on a CHI660D electrochemical workstation from Shanghai Hua Chen. The fluorescence spectrum was obtained at room temperature on an LS55 fluorescence spectrophotometer. PXRD was obtained on an Ultima IV X-Ray diffractometer. Magnetic measurements in the range of 10 ~ 300 K were performed on an MPMS-SQUID magnetometer with a field of 2 kOe on a crystalline sample in the temperature settle mode.

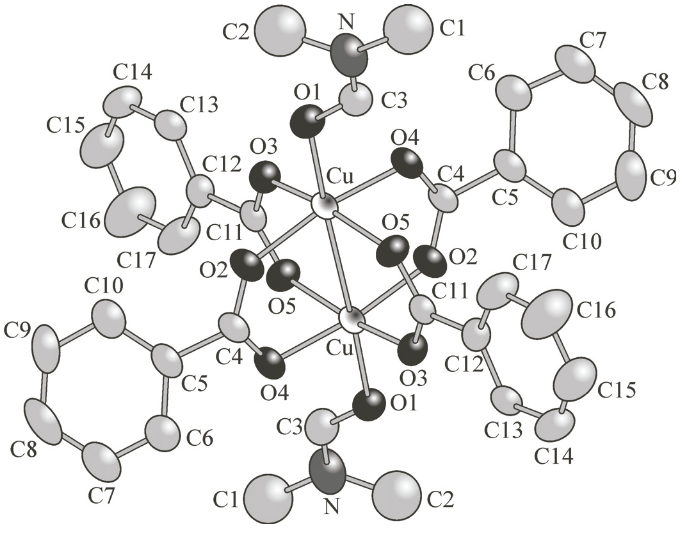

Fig. 1. Structure of **1** showing the coordination environment of the Cu(II) atom and coordination modes of the benzoic acid ligand and solvent molecules.
Hydrogen atoms are omitted for clarity. Symmetry codes: 1–*x*, –*y*, –*z*

Synthesis of complex 1. A mixture of copper chloride (0.017 g, 0.1 mmol), benzoic acid (0.048 g, 0.4 mmol) was ground for half an hour in a mortar, then the mixture was dissolved in 10 ml of DMF, and filtrated. The filtrate was slowly evaporated at room temperature. Blue block single crystals suitable for the X-ray diffraction analysis were obtained in *ca.* 36 % yield after several days of standing at room temperature. Anal. Calcd. for $C_{17}H_{17}CuNO_5$: C 53.83, H 4.49, N 3.69. Found: C 53.80, H 3.82, N 4.45.

Crystallographic studies A crystal with dimensions of 0.20×0.10×0.10 mm was chosen to be measured on a Nonius CAD4 diffractometer equipped with graphite-monochromatic MoK_α radiation ($\lambda = 0.071073$ nm) in the ω—φ scan mode at 293(2) K. In total, 3380 reflections were collected within the range $2.23 \le \theta \le 25.40°$, of which 3200 were independent with $R_{\text{int}} = 0.0458$. 2215 were considered to be observed ($I > 2\sigma(I)$) and used in the subsequent refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [19—20]. Corrections for Lp factors and empirical absorption adjustment were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to $R_1 = 0.0624$, $wR_2 = 0.1559$; $w = 1/[\sigma^2(F_0)^2 + (0.1000P)^2 + 0.9000P]$, where $P = ((F_0)^2 + 2F_c^2)/3$, $(\Delta/\sigma)_{\max} = 0.001$, $S = 1.003$.

Crystal data and refinement parameters are: $C_{34}H_{34}Cu_2N_2O_{10}$ ($M = 757.72$), monoclinic, space group $P2_1/n$, $a = 10.593(2)$ Å, $b = 10.123(2)$ Å, $c = 16.336(3)$ Å, $\beta = 93.55(3)°$, $V = 1748.4(6)$ Å^3, $D_c = 1.439$ g/cm^{-3}, $Z = 4$, $F(000) = 780$. The final R indices are: $R = 0.0624$ and $wR_2 = 0.1559$ for 2215 observed reflections with intensities greater than 2σ (refinement on F^2), $R = 0.0952$ and $wR_2 = 0.1726$ for all 3200 reflections collected; GOOF = 1.003.

Results and discussion. Molecular and crystal structure. The crystal structure of **1** is revealed in Fig. 1. Selected bond lengths and bond angles are shown in Table 1. Complex **1** consists of two copper(II) ions, four benzoic acid anions, and two DMF molecules. The four benzoic acid anions have the same coordination mode: bidentate-bridging coordination. Owing to the bidentate-bridging coordination of two benzoic acid anions, two neighboring copper(II) ions are linked together and the whole molecule presents a binuclear structure where the Cu—Cu distance is 0.26350(12) nm. This distance is less than 0.3 nm, which shows that Cu—Cu has strong coupling actions [21]. The central copper(II)

Table 1

Selected bond lengths (Å) *and bond angles* (deg.) **1**

Cu—O(1)	2.159(4)	O(2)—Cu—O(5)	91.60(17)	O(4)—Cu—O(1)	97.08(15)
Cu—O(4)	1.970(4)	O(2)—Cu—O(3)	88.48(17)	O(5)—Cu—O(1)	90.05(15)
Cu—O(2)	1.962(4)	O(3)—Cu—O(4)	89.49(16)	O(3)—Cu—Cu	85.59(11)
Cu—O(5)	1.975(4)	O(4)—Cu—O(5)	88.04(16)	O(2)—Cu—Cu	81.91(12)
Cu—O(3)	1.949(4)	O(3)—Cu—O(1)	101.68(15)	O(4)—Cu—Cu	86.41(12)
Cu—Cu	2.6350(12)	O(2)—Cu—O(1)	94.67(16)	O(5)—Cu—Cu	82.46(11)

Table 2

Hydrogen bonds of **1**

D—H···A	*d*(D—H), Å	*d*(H···A), Å	*d*(D···A), Å	∠DHA, deg.
C(7)—H(7A)[a]…O(1)	0.9300(1)	2.6687(6)	3.3413(6)	129.798(12)
C(14)—H(14A)[b]…O(4)	0.9300(1)	2.6749(5)	3.5855(6)	166.410(15)

Symmetry transformations used to generate equivalent atoms: [a] $-0.5+x$, $-1.5-y$, $-0.5+z$, [b] $-0.5-x$, $-1.5+y$, $-0.5-z$.

Table 3

Comparison of φ *bend angles and magnetic data for dinuclear* Cu(II) *carboxylates*

Complexes	φ bend, deg.	$-2J$, cm^{-1}	Ref.
$[Cu(DMB)_2(H_2O)_2]$[a]	12.0(2)	250	25
$[Cu_2(3,3'\text{-dimethoxy-}H_2BPDC)(DMF)_2]\cdot 6H_2O$[b]	8.8(2)	286	26
$[Cu_2L_4(DMF)_2]$	4.55(5)	310	this work
$[Cu_2(mEP)_2(H_2O)_2]^2$ [c]	1.66(2)	315	27
$[Cu_2(5\text{-msbdc})_2(H_2O)_2]\cdot 3DMF$[d]	1.56(2)	317	28

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[a] HDMB=2,6-dimethoxybenzoic acid.

[b] 4,4′-biphenyldicarboxylic acid.

[c] mEP = 1,2-benzenedicarboyxlate monoethyl ester.

[d] 5-msbdc = 5-methylsulfanylmethyl-1,3-benzenedicarboxylic acid.

ion is coordinated with four oxygen atoms from four benzoic acid anions, one oxygen atom from a DMF molecule, and another copper ion to give a distorted octahedral coordination geometry where O(2), O(3), O(4), and O(5) are located on the equatorial plane; O(1) and another copper ion occupy the axial positions. The O(2)—Cu—O(5), O(2)—Cu—O(3), O(3)—Cu—O(4), and O(4)—Cu—O(5) bond angles are 91.58, 88.49, 89.49, and 88.05°, respectively, and 357.61° in total. The plane equation of Cu, O (2), O (3), O (4), and O(5) is $0.8632x + 0.4818y - 0.1512z = 5.8703$; the atoms from the least squares plane values are 0.0173, –0.1860, –0.1828, –0.1809, –0.1831; the average deviation is 0.15002, suggesting that O(2), O(3), O(4), O(5), and Cu are almost coplanar. In **1**, Cu—O (1), Cu—O (2), Cu—O (3), Cu—O (4) and Cu—O (5) bond distances are 2.159(4), 1.962(4), 1.949(4), 1.970(4), and 1.975(4) Å (Table 2) respectively. The Cu—O (1) bond distance is much longer than the latter, which could be attributed to the special position of O (1) on the axial plane. Assembled by C(14)—H(14A)…O(4) hydrogen bonds (2.6754(41) Å, Table 3) and Cu—O metal coordination, **1** forms a one-dimensional chain. The crystal structure of **1** is further stabilized by interchain hydrogen bonds (2.6680(34) Å, Table 2), which assemble the molecules into a two-dimensional network structure (Fig. 2).

Electrochemical property. Fig. 3 shows the cyclic voltammogram (CV) of **1** with the scan rate 0.1 V/s^{-1}. In the CV measurement of **1**, we employed a conventional three-electrode system where a silver electrode as the reference electrode and two platinum electrodes were chosen as the working electrode and the counter electrode, respectively. **1** was dissolved and diluted to 1×10^{-3} mol/l^{-1} with DMF, and the supporting electrolyte is a 6-fluorine 4-butyl amine phosphate solution of 0.1 mol/l^{-1}. The scanning range is –1.5 ~ 1.5 V. As revealed by Fig. 3, there is a pair of redox peaks in every CV curve, $E_{pc} = -0.234$ V, $E_{pa} = 0.846$ V. The $\Delta E = 1.08$ V, $i_{pc}/i_{pa} = 1.22$. Thus, the n value is about 1, indicating that one electron is involved in the oxidation of **1**, and the electrode reaction corresponds to Cu(II)/Cu(1).

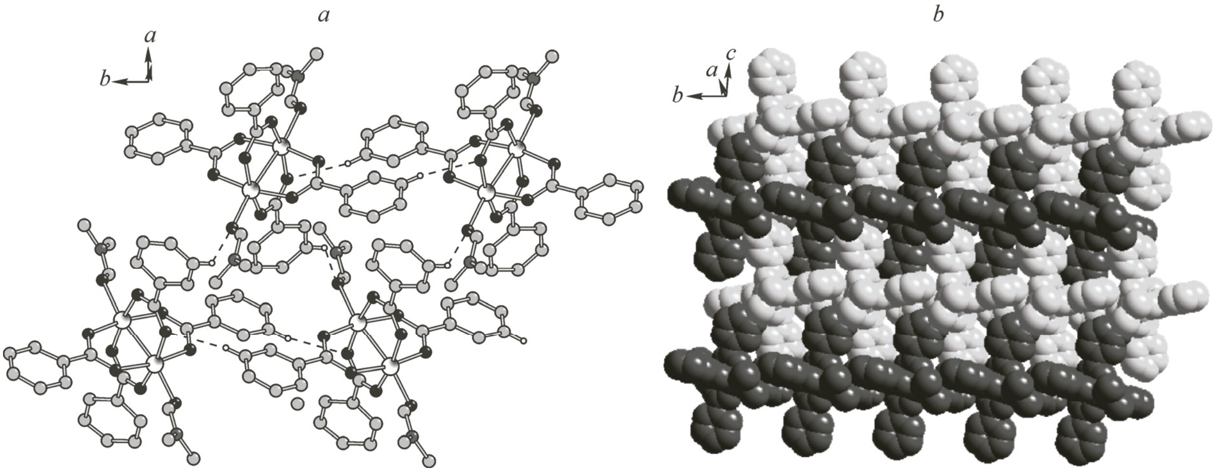

Fig. 2. Simplified 2D hydrogen bonding diagram of complex **1** viewed along the *b* direction. All hydrogen atoms are excluded for clarity (*a*). 2D network structure of **1** formed via hydrogen bonds along the *b* axis (*b*)

Magnetic properties. The temperature dependence of the magnetic susceptibility in the range of 10—300 K for **1** was measured at an applied field of 2 kOe, and the $\chi_M T$ value versus T plot is shown in Fig. 4 (χ_M is the molar magnetic susceptibility per Cu(II) ion). At 300 K, the $\chi_M T$ value is 0.3288 $cm^3/mol^{-1}/K$, which is below the spin-only value for two noninteracting Cu(II) ions (0.75 $cm^3/mol^{-1}/K$ at RT). Then the $\chi_M T$ value decreases sharply to a value of 0.0165 $cm^3/mol^{-1}/K$ at 75 K and then gradually to 0.0091 $cm^3/mol^{-1}/K$ at 46 K. This magnetic behavior agrees with strong antiferromagnetic couplings between the Cu(II) centers. The magnetic susceptibility data were best fitted to modified Bleaney—Bowers equation (1) for $S = 1/2$ dimers under the spin Hamiltonian $H = -JS_1S_2$

$$\chi_M = \frac{2Ng^2\,|\beta^2}{KT}\frac{1}{3+e^{-2J/KT}}(1-\rho)+\rho\frac{Ng^2\beta^2}{2KT}, \qquad (1)$$

in which *N*, *g*, β, and *K* have their usual meanings [22]. The *F* parameter denotes the fraction of a paramagnetic impurity in the sample. The best least-squares fitting parameters give $g = 1.791$, $-2J = 310\ cm^{-1}$, $F = 1.87\ \%$ with the agreement factor $R = \sum[(\chi_M T)_{obsd} - (\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{obsd}]^2 = 4.82\times10^{-6}$.

The $-2J$ value (310 cm^{-1}) of **1** is in the normal range (250—330 cm^{-1}) for the binuclear copper(II) carboxylate complexes [23]. It is well-known that for the exchange interaction in these molecules,

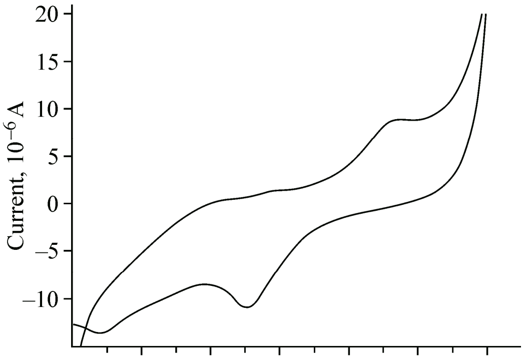

Fig. 3. Cyclic voltammograms of **1**

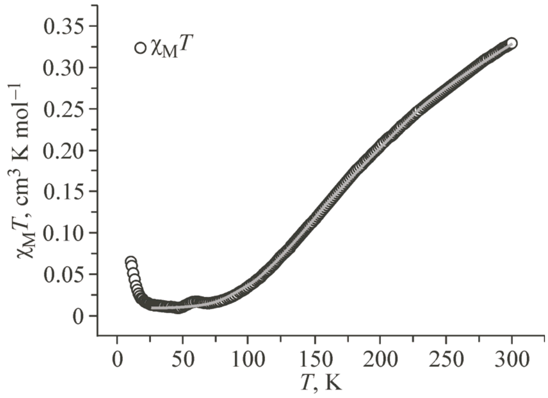

Fig. 4. Temperature dependence of the molar magnetic susceptibility of **1** in the form of $\chi_M T$ versus *T*. Solid line represents the best fitting curves

a superexchange mechanism consists in a direct metal—metal interaction in which the electronic structure of the bridging O—C—O moiety determines the magnitude of the antiferromagnetic interaction. Very important here is the bending of the Cu—O—C—O—Cu bridge (φ_{bend}, the dihedral angle between Cu—O—O—Cu and the carboxyl moiety). It is noteworthy that larger φ_{bend} would lead to a larger decrease in $-2J$ because of a reduced overlap of the Cu $d_{x^2-y^2}$ orbital with the $2p_x$ carboxylate oxygen orbital in the symmetric HOMO [24]. In the case of **1**, φ_{bend} is 4.55(5)°, which is smaller than that in [Cu(DMB)$_2$(H$_2$O)$_2$] [25], and larger than those observed for space-filling agents and/or the coordination center may present new opportunities in the design and synthesis of more robust MOFs with tunable properties.

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Supplementary material. CCDC 101607 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-_request/cif.[or from the Cambridge Crystallographic Data

Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

REFERENCES

1. *Leong W.L., Vittal J.J.* // Chem. Rev. – 2011. – **111**. – P. 688 – 764.
2. *Li C.-P., Du M.* // Chem. Commun. – 2011. – **47**. – P. 5958 – 5972.
3. *Guo Z.-Y., Wu H., Srinivas G.* // Angew. Chem. Int. Ed. – 2011. – **50**. – P. 3178 – 3181.
4. *Zhao D., Tan W., Yuan Q.* // Adv. Mater. – 2011. – **23**. – P. 90 – 93.
5. *Sun D.-F., Cao R., Liang Y.-C.* // Dalton. Trans. – 2001. – P. 2335 – 2340.
6. *Kobel W., Hanack M.* // Inorg. Chem. – 1986. – **25**. – P. 103 – 107.
7. *Eddaoudi M., Kim J., Rosi N.* // Science. – 2002. – **295**. – P. 469 – 472.
8. *Noro S.-I., Kitagawa S., Kondo M.* // Angew. Chem. Int. Ed. – 2000. – **39**. – P. 2081 – 2084.
9. *Chen B.-L., Eddaoudi M., Hyde S.-T.* // Science. – 2001. – **291**. – P. 1021 – 1023.
10. *Seo J.-S., Whang D., Lee H.* // Nature. – 2000. – **404**. – P. 982 – 986.
11. *Ayyasimi K., Krishnan S., Selvaraj B., Munirathinam N., Subbaiah G.* // Transition Met. Chem. – 2012. – **37**. – P. 393 – 397.
12. *Pallab B., Shouvik C., Ashutosh G.* // Inorg. Chim. Acta. – 2013. – **396**. – P. 66 – 71.
13. *Felix K., Alexander S.-M., Florian M., Edwin W.* // J. Mol. Struct. – 2014. – **1064**. – P. 122 – 129.
14. *Jiang X.-R., Yuan H.-Y., Feng Y.-L.* // J. Solid. State Chem. – 2012. – **191**. – P. 181 – 190.
15. *Xiong P.-P., Li J., Bu H.-Y., Zhang R.-L., Chen S.-P.* // J . Solid State Chem. – 2014. – **215**. – P. 292 – 299.
16. *Xu J.-K., Yan X.-C., Sun X.-C., Sun G.-L., Bi C.-F.* // Z. Anorg. Allg. Chem. – 2014. – **640**. – P. 398 – 404.
17. *Peng X., Cui G.-H., Li D.-J., Liu T.-F.* // J. Mol.Struct. – 2010. – **967**. – P. 54 – 60.
18. *Ramya A.-R., Reddy L.-P., Cowley A.-H., Kalyan, Vasudevan V.* // Inorg. Chem. – 2010. – **49**. – P. 2407 – 2415.
19. *Sheldrick G.-M.* SHELXS/L-97, Programs for Crystal Structure Determination. – University of Göttingen, Germany, 1997.
20. *Sheldrick G.-M.* SHELXS/L-97, Programs for Crystal Structure Refinement. – University of Göttingen, Germany, 1997.
21. *Wang Y.-Y., Shi C.-C., Shi Q.* // Chinese J. Inorg. Chem. – 2000. – **16**. – P. 321 – 328.
22. *Kahn O.* Molecular Magnetism VCH: Weinheim, Germany, 1993.
23. *Wang J.-J., Gou L., Hu H.-M., Han Z.-X., Li D.-S., Xue G.-L., Yang M.-L., Shi Q.-Z.* // Cryst. Growth. Des. – 2007. – **7**. – P. 1514 – 1521.
24. *Kawata T., Uekusa H., Ohba S., Furukawa T., Tokii T., Muto Y., Kato M.* // Acta Crystallogr., Sect. B. – 1992. – **48**. – P. 253 – 261.
25. *Erre L.-S., Micera G., Piu P., Cariati F., Ciani G.* // Inorg. Chem. – 1985. – **24**. – P. 2297 – 2300.
26. *Wang X.-Z., Zhu D.-R., Xu Y., Yang J., Shen X., Zhou J., Fei N., Ke X.-K., Peng L.-M.* // Cryst. Growth. Des. – 2010. – **10**. – P. 887 – 894.
27. *Jia L.-H., Liu Z.-L., Liu W., Gu Y.-F., Yao K.-L.* // Chinese J. Inorg. Chem. – 2008. – **24**. – P. 285 – 289.
28. *Burrows A.-D., Frost C.-G., Mahon M.-F., Winsper M., Richardson C., Attfield J.-P., Rodgers J.A.* // Dalton. Trans. – 2008. – **47**. – P. 6788 – 6795.