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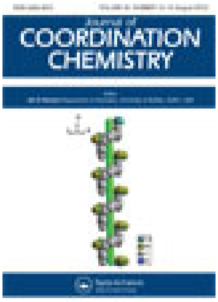

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Two binuclear tetracarboxylate-bridged complexes: syntheses, structures, and properties

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Two binuclear tetracarboxylate-bridged complexes: syntheses, structures, and properties

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$Cu_2(C_9N_5H_9)_2(C_6H_5CO_2)_4$ (**1**) and $Zn_2(C_9N_5H_9)_2(C_{10}H_7CH_2CO_2)_4$ (**2**) have been synthesized by hydrothermal methods with 2,4-diamine-6-phenyl-1,3,5-triazine (phdat) and aromatic carboxylic acid (benzoic acid (ba) or naphthylacetic acid (naa)) as ligands and characterized by single-crystal X-ray diffractions, elemental analyses, infrared spectra, magnetism, fluorescence spectra, and thermogravimetric analyses. In **1** and **2**, the two metals are bridged by four carboxylates in paddle-wheel-shaped binuclear $[M_2(CO_2)_4]$ units (M=Cu (**1**) and Zn (**2**)) and coordinated by one nitrogen from phdat, forming five-coordinate centers. The temperature-dependent magnetic susceptibility of **1** was obtained from 300 to 2 K, showing an anti-ferromagnetic interaction between Cu(II)'s. Compound **2** exhibits solid state fluorescence at 404 nm upon excitation at 304 nm.

Keywords: Binuclear; Anti-ferromagnetic; Fluorescence

1. Introduction

Attention has been focused on coordination compounds for diverse structural motifs and applications in gas storage [1], as magnetic [2] and optoelectronic materials [3]. The factor that influences structures and properties is the choice of ligands. Aromatic acids [4], nitrogen-containing ligands [5], or mixed aromatic acid/nitrogen-containing ligands [6] provide donors to coordinate metal ions and potential interaction sites to generate supramolecular contacts, such as hydrogen-bonding and π–π stacking interactions. Here, we choose aromatic acid (benzoic acid (ba) or naphthylacetic acid (naa)) and 2,4-diamine-6-phenyl-1,3,5-triazine (phdat) as ligands. The carboxylates of ba and naa may coordinate by diverse modes and are excellent H-bond acceptors. Phdat contains five nitrogen atoms, among them two amino nitrogen atoms are considered as perfect H-bond donors and three triazine-nitrogen atoms are able to coordinate to transition

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metals or be H-bond acceptors; aromatic rings from such ligands can provide potential π–π stacking interactions.

In this article, we present the syntheses and structural characterizations of $Cu_2(C_9N_5H_9)_2(C_6H_5CO_2)_4$ (**1**) and $Zn_2(C_9N_5H_9)_2(C_{10}H_7CH_2CO_2)_4$ (**2**). Complex **1** shows anti-ferromagnetic interactions, and the solid state fluorescence of **2** is observed at 404 nm upon excitation at 304 nm. Related compounds with Phdat are seldom reported [7].

2. Experimental

2.1. *Materials and methods*

$CuCl_2 \cdot 2H_2O$, $ZnCl_2$, ba, and naa are of A.R. grade and used as purchased. Phdat (99+%) is purchased from ACROS. Infrared (IR) spectra were recorded on a Nicolet 170 FT-IR spectrophotometer using KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses were performed *via* a Vario EL III Etro Elemental Analyzer. Magnetic measurements were carried out on a Quantum Design MPMS-XL SQUID magnetometer. Fluorescence data were collected on an F-7000 FL spectrophotometer. Thermogravimetric analyses (TGA) were performed with a heating rate of 10°C min^{-1} using a TGA/SDTA851e.

2.2. *Syntheses of the complexes*

Synthesis of 1: $CuCl_2 \cdot 2H_2O$ (2 mmol), phdat (1 mmol), ba (1 mmol), and H_2O (10 mL) were added to a Teflon-lined vessel, with stirring for 20 min. The mixture was sealed in a stainless-steel autoclave and heated to 120°C for 72 h, then cooled to room temperature. Green block crystals of **1** were obtained (0.112 g, yield 45.4% (based on ba). Anal. Calcd for $C_{46}H_{38}C_{10}Cu_2N_{10}O_8$ (%): C, 56.04; H, 3.88; N, 14.21. Found (%): C, 55.83; H, 3.67; N, 14.42. IR (KBr pellet, cm^{-1}): $\nu(NH_2)$ 3447, 3397, $\nu(O\cdots H)$ 3324, ν(CH) 3200, ν(C–O) 1628, 1407, ν(aromatic ring) 1543, 1267, 1128, 1076, 1025, 825, 779, 719, 686.

Synthesis of 2: Replacing $CuCl_2 \cdot 2H_2O$ (2 mmol) by $ZnCl_2$ (2 mmol) and ba by naa, colorless block crystals of **2** were obtained (0.132 g, yield 42.4% (based on naa). Anal. Calcd for $C_{66}H_{54}N_{10}O_8Zn_2$ (%): C, 63.62; H, 4.37; N, 11.24. Found (%): C, 63.43; H, 4.22; N, 11.52. IR (KBr pellet, cm^{-1}): $\nu(NH_2)$ 3500, 3418, $\nu(O\cdots H)$ 3315, ν(CH) 3192, ν(C–O) 1623, 1394, ν(aromatic ring) 1551, 1254, 1165, 825, 783, 698.

2.3. *X-ray crystallography*

Compounds **1** and **2** were selected for X-ray diffraction analyses, with dimensions of 0.42 mm × 0.41 mm × 0.30 mm and 0.48 mm × 0.35 mm × 0.26 mm. X-ray single-crystal data were collected at 296(2) K on a Bruker Apex-II CCD area detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reduction and absorption corrections were made using empirical methods. These structures were solved by direct methods using SHELXS-97 [8] and refined by full-matrix least-squares methods using SHELXL-97 [9]. Anisotropic displacement parameters were refined for all non-hydrogen atoms and all

Table 1. Crystal data and refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{46}H_{38}C_{10}Cu_2N_{10}O_8$	$C_{66}H_{54}N_{10}O_8Zn_2$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	10.2948(5)	13.0558(7)
b	10.9668(6)	20.1077(11)
c	12.1652(10)	12.0573(6)
α	109.7910(10)	90
β	96.9770(10)	109.2140(10)
γ	113.0470(10)	90
Volume (Å^3), Z	1136.86(13), 1	2989.0(3), 2
Formula weight	985.94	1245.93
Calculated density (Mg m^{-3})	1.440	1.384
F(000)	506	1288
Absorption coefficient (mm^{-1})	1.000	0.868
Reflections measured	5837	15,151
Independent reflections	3973 [R(int) = 0.0130]	5264 [R(int) = 0.0130]
Goodness-of-fit on F^2	1.057	1.044
R indices (all data)[a,b] Rw	$R_1 = 0.0315$, $wR_2 = 0.0791$	$R_1 = 0.0346$, $wR_2 = 0.0918$
Largest and mean delta/sigma	0.000/0.000	0.001/0.000
Largest difference peak and hole (e Å^{-3})	0.290 and −0.257	0.398 and −0.352

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3]$. **1**, $a = 0.0353$, $b = 0.5901$; **2**, $a = 0.0437$, $b = 1.6025$.

hydrogen atoms were added in the riding model without refinement. Crystal data and refinement details are presented in table 1.

3. Results and discussion

3.1. *Structures of 1 and 2*

Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with a 3-D network consisting of binuclear units, hydrogen-bonding, and $\pi\cdots\pi$ packing interactions. As shown in figure 1, each Cu has a square pyramidal geometry, coordinated by four oxygen atoms of four carboxylates, and one nitrogen atom from one Phdat with basal Cu–O lengths of about 1.9647(16)–1.9684(16) Å and the axial Cu–N distance of about 2.2348(17) Å (table 2). The Cu(1) and four basal oxygen atoms (O(1), O(2), O(3), and O(4)) present an almost planar geometry with a mean deviation from planarity of 0.0694 Å. The Cu(1) and Cu(1 A) (A = $-x, -y, -z$) are bridged by four *syn*,*syn*-μ_2:η^1:η^1carboxylates from four ba's, forming a paddle-wheel-shaped binuclear $Cu_2(CO_2)_4$. The Cu$\cdots$Cu distance is 2.6667(5) Å, showing a weak interaction between Cu's, which is comparable with those of [Cu_2(μ-HCO_2)$_4$(Mepyrz)$_2$] and [Cu_2(μ-AcO)$_4$(pydz)$_2$] [10], but longer than those of other paddle-wheel $Cu_2(CO_2)_4$ compounds containing axial solvents [11]. In phdat, the triazine and phenyl rings are not coplanar with interplanar angles of about 34.5°.

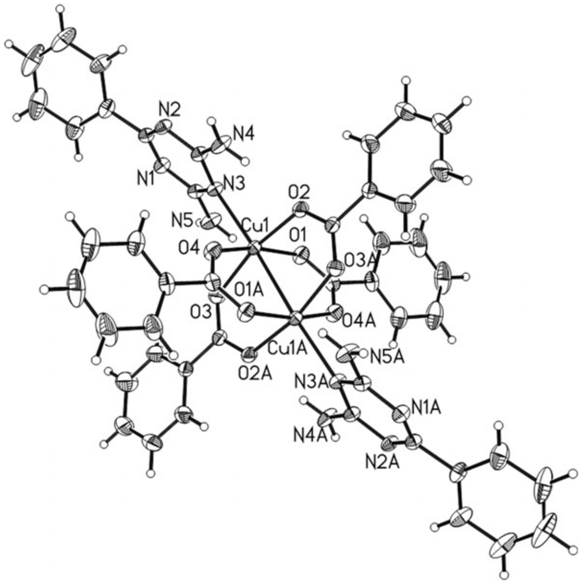

Figure 1. The coordination diagram of **1**. For clarity, all carbon and hydrogen atoms are not labeled. Symmetry code: A: $-x$, $-y$, $-z$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cu(1)–O(4)	1.9647(16)	Cu(1)–O(1)	1.9669(16)
Cu(1)–O(3)	1.9669(16)	Cu(1)–O(2)	1.9684(16)
Cu(1)–N(3)	2.2348(17)	Cu(1)–Cu(1)#1	2.6667(5)
O(4)–Cu(1)–O(1)	167.38(7)	O(4)–Cu(1)–O(3)	88.05(8)
O(1)–Cu(1)–O(3)	91.13(7)	O(4)–Cu(1)–O(2)	90.71(7)
O(1)–Cu(1)–O(2)	87.32(7)	O(3)–Cu(1)–O(2)	167.28(6)
O(4)–Cu(1)–N(3)	91.65(7)	O(1)–Cu(1)–N(3)	100.94(7)
O(3)–Cu(1)–N(3)	96.93(7)	O(2)–Cu(1)–N(3)	95.75(6)
2			
Zn(1)–O(1)	2.0337(18)	Zn(1)–O(4)	2.0338(18)
Zn(1)–O(2)	2.0412(17)	Zn(1)–O(3)	2.0527(17)
Zn(1)–N(5)	2.0594(17)	Zn(1)–Zn(1)#1	2.9939(5)
O(1)–Zn(1)–O(4)	157.73(7)	O(1)–Zn(1)–O(2)	89.05(9)
O(4)–Zn(1)–O(2)	86.76(9)	O(1)–Zn(1)–O(3)	87.42(8)
O(4)–Zn(1)–O(3)	88.25(9)	O(2)–Zn(1)–O(3)	157.79(7)
O(1)–Zn(1)–N(5)	101.97(7)	O(4)–Zn(1)–N(5)	100.30(7)
O(2)–Zn(1)–N(5)	102.03(7)	O(3)–Zn(1)–N(5)	100.14(7)

Symmetry transformation used to generate equivalent atoms: 1: #1 $-x$, $-y$, $-z$; 2: #1 $-x$, $-y+1$, $-z+1$.

From figure 2, the 2-D networks are constructed by hydrogen-bonding interactions, including intramolecular hydrogen bonds between –NH$_2$ and COO$^-$ groups (N4$\cdots$O2 2.902(3) Å, N5$\cdots$O1 3.280(3) Å, table 3), and intermolecular hydrogen bonds between –NH$_2$ groups and uncoordinated triazine–N (N4$\cdots$N2#1 3.072(3) Å, N5$\cdots$N1#2 3.140(3) Å, table 3). The π–π stacking interaction is observed between two phenyl rings from two ba ligands, in which the vertical plane–plane distances and the centroid–centroid distances between two rings are about 3.51 Å and 3.99 Å, respectively,

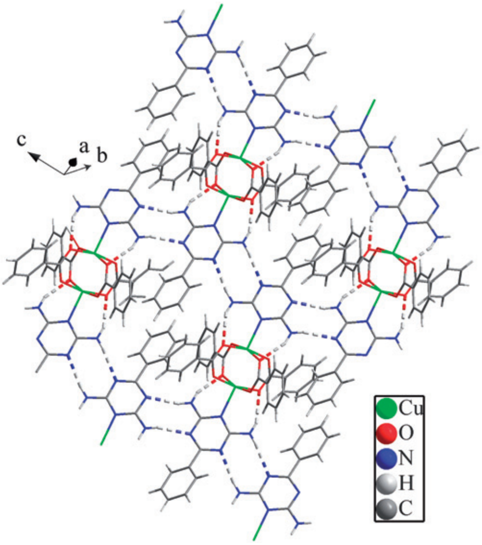

Figure 2. The hydrogen bond motif in **1**; N4–H4B···N2#1, N4–H4C···O2, N5–H5B···O1, N5–H5C···N1#2 are indicated as dashed. Symmetry codes: #1, $-x-1$, $-y-1$, $-z$; #2, $-x-1$, $-y-1$, $-z-1$.

Table 3. Important hydrogen-bonding interactions present in **1** and **2**.

D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
1			
N4–H4B···N2#1	2.27	3.072(3)	154.3
N4–H4C···O2[a]	2.09	2.902(3)	156.1
N5–H5B···O1[a]	2.51	3.280(3)	150.0
N5–H5C···N1#2	2.34	3.140(3)	154.4
2			
N1–H1A···N3#1	2.44	3.276(3)	165.9
N1–H1B···O4[a]	2.33	3.051(3)	141.6
N2–H2A···N4#2	2.15	3.008(3)	178.1
N2–H2B···O3[a]	2.21	2.946(3)	143.2

Symmetry transformations used to generate equivalent atoms: **1**: #1, $-x-1$, $-y-1$, $-z$; #2, $-x-1$, $-y-1$, $-z-1$; **2**: #1, x, $-y+1/2$, $z-1/2$; #2, x, $-y+1/2$, $z+1/2$.

[a] Intramolecular hydrogen bonds.

compared with other reports [12]. The 3-D networks are built up by weak interactions (figure 3).

When the metal salt and aromatic acid of **1** are replaced by $ZnCl_2$ and naa, complex **2** is obtained. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with binuclear units linked by hydrogen-bonding and $\pi\cdots\pi$ packing interactions. From figure 4, each Zn(II) is coordinated by four oxygen atoms and one nitrogen atom, forming a distorted square pyramidal geometry, of which oxygen atoms are from carboxylate groups and nitrogen atom from the monodentate Phdat ligand. The Zn–O lengths are 2.0337(18)–2.0527(17) Å and the Zn–N distance is 2.0594(17) Å. Zn(1) and Zn(1 A) (A = $-x$, $1-y$, $1-z$) are centrosymmetrical and bridged by four *syn*,*syn*-μ_2:η^1:η^1carboxylate groups

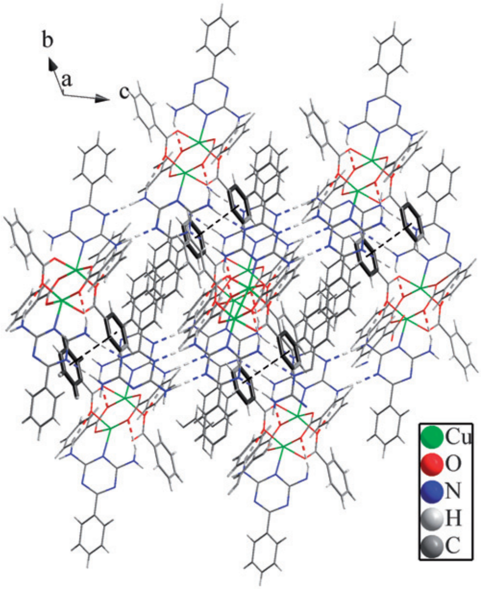

Figure 3. The packing diagram in **1**; $\pi\cdots\pi$ stacking interactions are indicated as dark dashed lines; the hydrogen bonds are indicated as dashed lines (N4–H4B···N2#1, N4–H4C···O2, N5–H5B···O1, N5–H5C···N1#2). Symmetry codes: #1, $-x-1$, $-y-1$, $-z$; #2, $-x-1$, $-y-1$, $-z-1$.

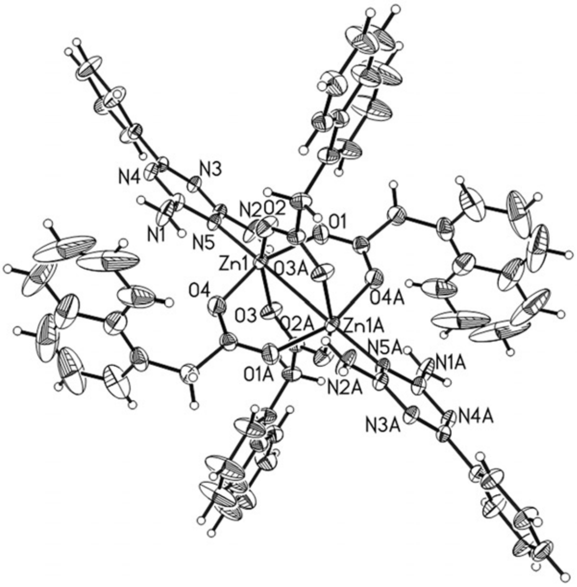

Figure 4. The coordination diagram of **2**. For clarity, all carbon and hydrogen atoms are not labeled. Symmetry code: A: $-x$, $1-y$, $1-z$.

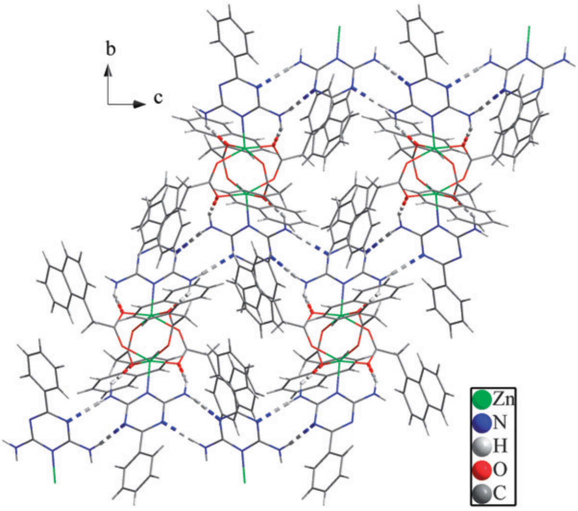

Figure 5. The hydrogen bond motif in **2**; N1–H1A···N3#1, N1–H1B···O4, N2–H2B···O3, N2–H2A···N4#2 are indicated as dashed lines. Symmetry codes: #1: x, $-y+1/2$, $z-1/2$; #2: x, $-y+1/2$, $z+1/2$.

from the naa ligand. Thus a paddle-wheel-shaped binuclear $Zn_2(CO_2)_4$ unit is formed with a Zn···Zn separation of 2.9939(5) Å, longer than that of a similar paddle-wheel-shaped compound $[Zn_2(\mu\text{-4-OBz})_4(py)_2]\cdot 0.5CH_3OH$ [13]. In Phdat, the interplanar angles of two rings are 28.7°, smaller than that (34.5°) of **1**.

Similar to **1**, hydrogen-bonding interactions connect the binuclear units into 2-D networks; intramolecular hydrogen bonds exist between $-NH_2$ and COO^- ((N1···O2 3.051(3) Å, N2···O3 2.946(3) Å, table 3) and intermolecular hydrogen bonds between $-NH_2$ groups and the uncoordinated triazine–N atom (N1···N3#1 3.276(3) Å, N2···N4#2 3.008(3) Å, table 3, figure 5). The 2-D networks are further connected into 3-D networks by naphthyl–naphthyl $\pi\cdots\pi$ packing interactions (figure 6). The vertical plane–plane and centroid–centroid distances between the naphthyl rings are 3.56 Å and 3.92 Å, respectively [12].

3.2. *IR spectra*

IR spectra results of **1** and **2** are similar (Supplementary material). The stretching vibrations of N–H and C–H range from 3500 to 3190 cm^{-1}. Because two CO bonds of $-COO^-$ are in resonance, typical C=O stretching vibrations disappear [14]. For example, in **1**, two spectral bands at 1628 and 1407 cm^{-1} are, respectively, from asymmetrical and symmetrical vibrations of COO^-. Peaks at 1550–1000 cm^{-1} are attributed to aromatic ring stretching, 660–850 cm^{-1} for the aromatic ring C–H in-plane vibration and out-of-plane vibration.

3.3. *Luminescence spectra*

The luminescent property of **2** has been studied in the solid state at room temperature (Supplementary material). An emission occurs at 404 nm upon excitation at 304 nm.

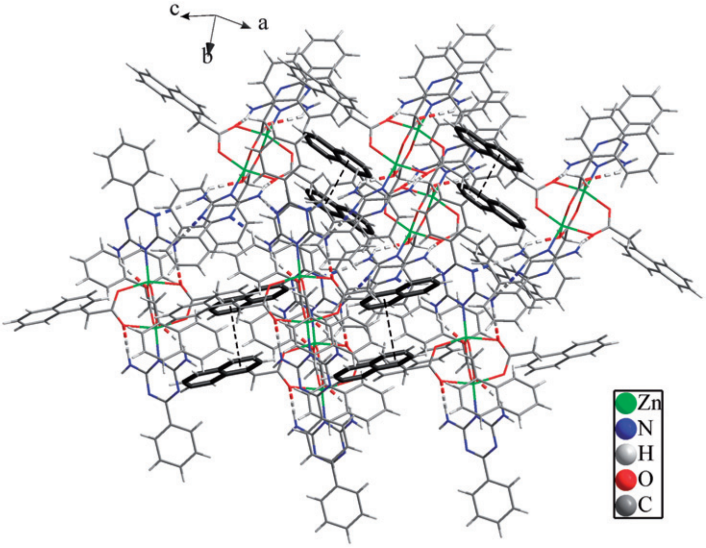

Figure 6. The packing diagram in **2**; $\pi\cdots\pi$ stacking interactions are indicated as dark dashed lines; the hydrogen bonds are indicated as dashed lines (N1–H1A···N3#1, N1–H1B···O4, N2–H2B···O3, N2–H2A···N4#2). Symmetry codes: #1, x, $-y+1/2$, $z-1/2$; #2, x, $-y+1/2$, $z+1/2$.

However, according to the literature [15], ba is non-fluorescent and phdat does not show fluorescence property to a measurable degree. Thus, the emission of **2** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), which should originate from the intraligand π–π^* transition [13].

3.4. *Magnetism of 1*

The temperature dependence of the molar susceptibility of **1** was carried out in an applied field of 1000 G ranging from 300 K to 2 K. As shown in figure 7, $\chi_M T$ is 0.73 cm^3 mol^{-1} K at room temperature, close to the value of non-interacting Cu$_2$ units (0.75 cm^3 mol^{-1} K, $g=2$). Upon cooling, $\chi_M T$ decreases to 0.28 cm^3 mol^{-1} K at 16 K, similar to other compounds containing paddle-wheel copper units [10], typical antiferromagnetic interactions between the magnetic centers. Below 16 K, the $\chi_M T$ value rapidly rises to 0.81 cm^3 mol^{-1} K at 4.4 K, followed by a sharp drop to 0.52 cm^3 mol^{-1} K at 2 K. Within the binuclear unit, there is only one magnetic exchange pathway, four *syn,syn*-μ_2-carboxylate bridges, which provides small metal–metal distances and results in good overlap of the magnetic orbitals, inducing anti-ferromagnetic coupling as observed in other structurally relevant binuclear Cu carboxylato-bridge compounds [16].

3.5. *Thermal analysis*

The thermal behaviors of **1** and **2** have been studied by TGA (Supplementary material). Due to the similarities in **1** and **2**, they show similar decomposition patterns. With no thermal degradation till 208°C, several successive weight losses are observed (for **1**, 208–515°C; for **2**, 208–586°C), which correspond to the loss of phdat and aromatic

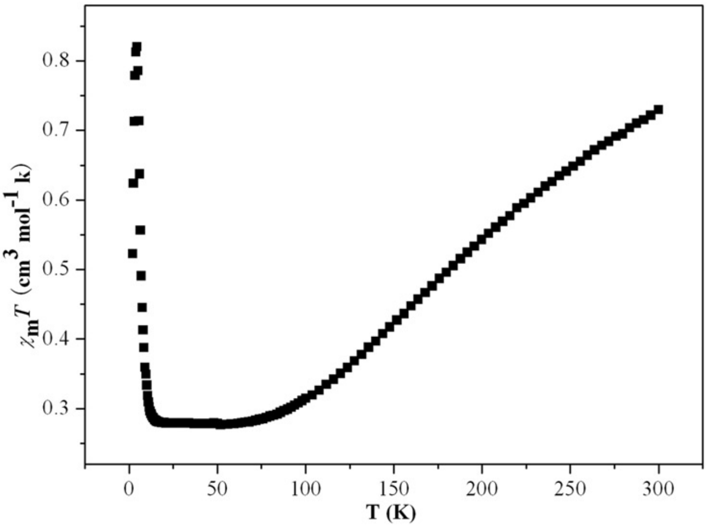

Figure 7. The plot of $\chi_M T$ *vs.* T under an applied magnetic field of 1000 G for **1**.

acids, respectively. The residual weights of 16.3% in **1** and 13.1% in **2** are assumed as CuO (Calcd 16.1%) and ZnO (Calcd 12.6%), respectively.

4. Conclusion

Two binuclear complexes have been prepared with an aromatic acid and phdat as ligands, which contain paddle-wheel-shaped binuclear $[M_2(CO_2)_4]$ units (M=Cu (**1**) and Zn (**2**)), and are further connected into 3-D networks by N–H···N, N–H···O hydrogen-bonding and $\pi\cdots\pi$ stacking interactions. The magnetic measurements of **1** show anti-ferromagnetic interactions between Cu(II). Compound **2** exhibits solid state emission at 404 nm upon excitation at 304 nm.

Supplementary material

CCDC numbers for **1** and **2** are 858033 and 858034, respectively. The crystallographic data for this article can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk).

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References

[1] (a) K.L. Mulfort, J.T. Hupp. *J. Am. Chem. Soc.*, **129**, 9604 (2007); (b) S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O.M. Yaghi, H. Berke. *Chem. Commun.*, **46**, 7981 (2010); (c) S.C. Xiang, W. Zhou, J.M. Gallegos, Y. Liu, B.L. Chen. *J. Am. Chem. Soc.*, **131**, 12415 (2009).

[2] (a) J. Jia, X. Lin, C. Wilson, A.J. Blake, N.R. Champness, P. Hubberstey, G. Walker, E.J. Cussen, M. Schröder. *Chem. Commun.*, 840 (2007); (b) S.C. Xiang, S.M. Hu, T.L. Sheng, R.B. Fu, X.T. Wu, X.D. Zhang. *J. Am. Chem. Soc.*, **129**, 15144 (2007).

[3] D.M. Rudkevich. *Angew. Chem., Int. Ed. Engl.*, **43**, 558 (2004).

[4] (a) Z.-R. Pan, J. Xu, X.-Q. Yao, Y.-Z. Li, Z.-J. Guo, H.-G. Zheng. *CrystEngComm*, **13**, 1617 (2011); (b) L. Zhang, Z.-J. Li, Q.-P. Lin, Y.-Y. Qin, J. Zhang, P.-X. Yin, J.-K. Cheng, Y.-G.Yao. *Inorg. Chem.*, **48**, 6517 (2009); (c) Z.-L. Fang, J.-G. He, Q.-S.Zhang, Q.-K. Zhang, X.-Y. Wu, R.-M. Yu, C.-Z. Lu. *Inorg. Chem.*, **50**, 11403 (2011).

[5] (a) W. Zhao, Y. Song, T.-A. Okamura, J. Fan, W.-Y. Sun, N. Ueyama. *Inorg. Chem.*, **44**, 3330 (2005); (b) Y.-Q. Huang, X.-Q. Zhao, W. Shi, W.-Y. Liu, Z.-L.Chen, P. Cheng, D.-Z. Liao, S.-P. Yan. *Cryst. Growth Des.*, **8**, 3652 (2008).

[6] (a) L.-F. Ma, Q.-L. Meng, L.-Y. Wang, B. Liu, F.-P. Liang. *Dalton Trans.*, **39**, 8210 (2010); (b) E.-C. Yang, Y. Feng, Z.-Y. Liu, T.-Y. Liu, X.-J. Zhao. *CrystEngComm*, **13**, 230 (2011).

[7] B.R. Manzano, F.A. Jalón, M.L. Soriano, M.C. Carrión, M.P. Carranza, K. Mereiter, A.M. Rodrguez, A. de la Hoz, A. Sánchez-Migallón. *Inorg. Chem.*, **47**, 8957 (2008).

[8] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany (1997).

[9] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).

[10] (a) M. BarquÍn, M.J.G. Garmendia, L. LarrÍnaga, E. Pinilla, J.M. Seco, M.R. Torres. *J. Coord. Chem.*, **63**, 1652 (2010); (b) M. BarquÍn, N. Cocera, M.J.G. Garmendia, L. LarrÍnaga, E. Pinilla, M.R. Torres. *J. Coord. Chem.*, **63**, 2247 (2010).

[11] P.M. Selvakumar, E. Suresh, S. Waghmode, P.S. Subramanian. *J. Coord. Chem.*, **64**, 3495 (2011).

[12] (a) S. Balboa, J. Borrás, P. Brandi, R. Carballo, A. Castiñeiras, A.B. Lago, J. Niclós-Gutiérrez, J.A. Real. *Cryst. Growth Des.*, **11**, 4344 (2011); (b) Y.M. Li, L.Y. Jin. *Russ. J. Coord. Chem.*, **36**, 765 (2010); (c) Y.-M. Li, J.-J. Zhang, T.-L. Sheng, R.-B. Fu, S.-M. Hu, Z.-Z. Lai, X.-T. Wu. *Chin. J. Struct. Chem.*, **25**, 891 (2005).

[13] (a) D. Dey, S. Roy, R.N.D. Purkayastha, R. Pallepogu, L. Male, V. McKee. *J. Coord. Chem.*, **64**, 1165 (2011); (b) U. Kumar, J. Thomas, R. Nagarajan, N. Thirupathi. *Inorg. Chim. Acta*, **372**, 191 (2011); (c) A.M. Baruah, A. Karmakar, J.B. Baruah. *Inorg. Chim. Acta*, **361**, 2777 (2008).

[14] (a) M. Melnik. *Coord. Chem. Rev.*, **42**, 259 (1982); (b) M. Kato, Y. Muto. *Coord. Chem. Rev.*, **92**, 45 (1988); (c) P.S. Subramanian, D. Srinivas. *Polyhedron*, **15**, 985 (1996); (d) P.S. Subramanian, P.C. Dave, V.P. Boricha, D. Srinivas. *Polyhedron*, **17**, 443 (1998).

[15] (a) H. Baba, M. Kitamura. *J. Mol. Spectrosc.*, **41**, 302 (1972); (b) I.M. Khasawneh, J.D. Winefordner. *Anal. Chim. Acta*, **184**, 307 (1986).

[16] (a) X.Z. Wang, D.R. Zhu, Y. Xu, J. Yang, X. Shen, J. Zhou, N. Fei, X.K. Ke, L.M. Peng. *Cryst. Growth Des.*, **10**, 887 (2010); (b) Y. Pang, D. Tian, X.-F. Zhu, Y.-H. Luo, X. Zheng, H. Zhang. *CrystEngComm*, **13**, 5142 (2011).