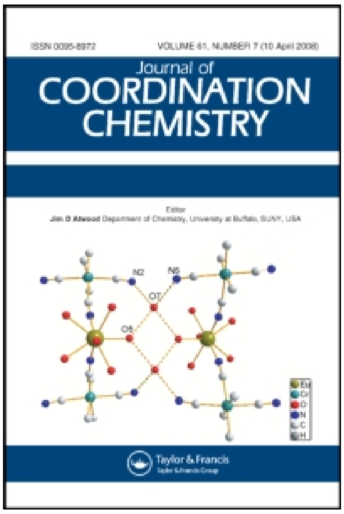

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and structures of copper benzene-1,4-dioxydiacetate complexes with 4,4'-bipyridine and 1,10-phenanthroline

Yun-Nan Gong[a]; Chong-Bo Liu[a]; Yuan Ding[a]; Zhi-Qiang Xiong[b]; Lian-Ming Xiong[a]
[a] School of Environment and Chemical Engineering, Nanchang Hangkong University, Nanchang 330063, P.R. China [b] Center for Analysis and Testing, Nanchang Hangkong University, Nanchang 330063, P.R. China

First published on: 25 June 2010

To cite this Article Gong, Yun-Nan , Liu, Chong-Bo , Ding, Yuan , Xiong, Zhi-Qiang and Xiong, Lian-Ming(2010) 'Syntheses and structures of copper benzene-1,4-dioxydiacetate complexes with 4,4'-bipyridine and 1,10-phenanthroline', Journal of Coordination Chemistry, 63: 11, 1865 — 1872, First published on: 25 June 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.495776

URL: http://dx.doi.org/10.1080/00958972.2010.495776

Journal of Coordination Chemistry
Vol. 63, No. 11, 10 June 2010, 1865–1872

Taylor & Francis
Taylor & Francis Group

Syntheses and structures of copper benzene-1,4-dioxydiacetate complexes with 4,4′-bipyridine and 1,10-phenanthroline

YUN-NAN GONG†, CHONG-BO LIU*†, YUAN DING†,
ZHI-QIANG XIONG‡ and LIAN-MING XIONG†

†School of Environment and Chemical Engineering, Nanchang Hangkong University,
Nanchang 330063, P.R. China
‡Center for Analysis and Testing, Nanchang Hangkong University,
Nanchang 330063, P.R. China

(*Received 6 February 2010; in final form 16 March 2010*)

Two new copper complexes, $[Cu_2(BDOA)(4,4'\text{-bpy})_2]\cdot 2H_2O$ (**1**) and [Cu(BDOA)(phen)] (**2**) (H_2BDOA = benzene-1,4-dioxydiacetic acid; 4,4′-bpy = 4,4′-bipyridine; phen = 1,10-phenanthroline), were synthesized and characterized by IR, elemental analysis, and single-crystal X-ray diffraction. Complex **1** exhibits a 2-D three-connected network structure with 6^3 topology. Complex **2** displays a 1-D chain structure. Furthermore, the 3-D supramolecular networks of **1** and **2** are constructed *via* rich hydrogen bonds. Thermal stability of **1** is discussed in this article.

Keywords: Benzene-1,4-dioxydiacetic acid; Copper complexes; Hydrogen bonds; Topology

1. Introduction

Supramolecular coordination polymers are of interest for their intriguing architectures and potential applications in magnetism, absorption, luminescence, catalysis, and optical properties [1–6]. In particular, much attention has been focused on designing and synthesizing supramolecular coordination polymers based on polycarboxylate ligands [7–10]. As a polycarboxylate ligand, benzene-1,4-dioxydiacetic acid (H_2BDOA) exhibits several interesting features: (1) It combines the characteristics of both flexibility and rigidity, important to construct metal-organic frameworks (MOFs) [11, 12]. The $–OCH_2–$ group makes it more flexible than benzenedicarboxylate [13–15], while the existence of the benzene ring provides a rigid element. (2) Two $–OCH_2COOH$ groups at opposite positions on the benzene ring make H_2BDOA a long spacer, which assists in the generation of porous MOFs [16]. (3) It represents an excellent candidate for the assembly of high-dimensional supramolecular polymers because the coordination sites of H_2BDOA can be used as hydrogen-bond donors as well as acceptors [17].

Choice of suitable auxiliary ligands, such as 4,4′-bipyridine and 1,10-phenanthroline, often have a significant effect on the formation and structure of polycarboxylate

---

*Corresponding author. Email: cbliu2007@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.495776

coordination polymers [18–21]. Herein, we report the syntheses and crystal structures of two new copper coordination polymers $[Cu_2(BDOA)(4,4'\text{-bpy})_2] \cdot 2H_2O$ (**1**) and [Cu(BDOA)(phen)] (**2**).

2. Experimental

2.1. *Materials and physical measurements*

All materials and reagents were obtained commercially and used without purification. The elemental analysis of C, H, and N were carried out with an Elementar Vario EL analyzer. IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets. Thermal stability studies were carried out on a ZRY-2P thermal analyzer.

2.2. *Synthesis of $[Cu_2(BDOA)(4,4'\text{-bpy})_2] \cdot 2H_2O$ (1)*

A mixture of $CuSO \cdot 5H_2O$ (0.025 g, 0.1 mmol), H_2BDOA (0.023 g, 0.1 mmol), 4,4′-bipyridine (0.016 g, 0.1 mmol), NaOH (0.3 mL, 0.65 mol L^{-1}), and distilled water (10 mL) was sealed in a teflon-lined stainless reactor (23 mL) and heated at 150°C for 72 h under autogenous pressure. Red block crystals were obtained. Yield: 42.5%. Anal. Calcd for $C_{30}H_{28}Cu_2N_4O_8$ (%): C, 51.50; H, 4.03; and N, 8.01. Found (%): C, 51.25; H, 4.21; and N, 8.37. IR data (KBr pellet, ν cm^{-1}): 3419m, 1603s, 1510m, 1483m, 1401s, 1345w, 1227m, 1049m, 823w, 799m, 726w, and 675w.

2.3. *Synthesis of [Cu(BDOA) (1,10-phen)] (2)*

A mixture of $CuSO_4 \cdot 5H_2O$ (0.025 g, 0.1 mmol), H_2BDOA (0.023 g, 0.1 mmol), 1,10-phenanthroline (0.020 g, 0.1 mmol), NaOH (0.3 mL, 0.65 mol L^{-1}), and distilled water (10 mL) was sealed in a teflon-lined stainless reactor (23 mL) and heated at 120°C for 72 h under autogenous pressure. Blue block crystals were obtained. Yield: 30.5%. Anal. Calcd for $C_{22}H_{16}CuN_2O_6$ (%): C, 56.52; H, 3.45; and N, 5.99. Found (%): C, 56.71; H, 3.65; and N, 5.73. IR data (KBr pellet, ν cm^{-1}): 1606s, 1510m, 1424m, 1400s, 1344m, 1227m, 1147 m, 1050s, 853m, 804w, 720m, and 682w.

2.4. *X-ray crystallographic study*

X-ray single-crystal data of **1** and **2** were recorded on a Bruker APEX II area detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied using SADABS [22]. The structures were solved by direct methods [23] and refined by full-matrix least-squares on F^2 using SHELXL-97 [24]. All nonhydrogen atoms were refined anisotropically. Hydrogens were placed in geometrically calculated positions. Experimental details for X-ray data collection of **1** and **2** are presented in table 1, selected bond lengths and angles are presented in table 2, and the types of hydrogen bonds are presented in table 3.

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

Complex	**1**	**2**
Empirical formula	$C_{30}H_{28}Cu_2N_4O_8$	$C_{22}H_{16}CuN_2O_6$
Formula weight	699.64	467.91
Temperature (K)	296(2)	296(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions (Å, °)		
a	9.5054(6)	13.1377(11)
b	9.9757(6)	9.9365(8)
c	16.4659(10)	15.2527(13)
α	105.825(10)	90
β	101.614(10)	105.8250(10)
γ	99.638(10)	90
Volume (Å^3), Z	1429.88(15), 2	1915.7(3), 4
Absorption coefficient μ (mm^{-1})	1.547	1.185
F(000)	716	956
θ range for data collection (°)	2.17–25.50	2.61–25.50
Calculated density (mg m^{-3})	1.625	1.622
Independent reflection	$[R(\text{int}) = 0.0481]$	$[R(\text{int}) = 0.0216]$
Goodness-of-fit on F^2	1.004	1.018
Number of data collected	11,150	7244
Number of unique data	5266	1774
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0369$, $wR_2 = 0.1018$	$R_1 = 0.0277$, $wR_2 = 0.0732$
R indices (all data)	$R_1 = 0.0462$, $wR_2 = 0.1055$	$R_1 = 0.0323$, $wR_2 = 0.0761$
Largest difference peak and hole (e Å^{-3})	0.571, −0.330	0.240, −0.178

$R_1 = \sum\|F_o|-|F_c\|/\sum|F_o|$, $wR_2 = [\sum(w(F_o^{2-} - F_c^2)^2)/\sum wF_o^2)^2]^{1/2}$.

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

1			
Cu(1) –O(1)	2.193(2)	Cu(2)–O(6)$^{\#2}$	2.344(2)
Cu(1)–N(1)	1.930(2)	Cu(2)–N(2)	1.926(2)
Cu(1)–N(3)	1.924(2)	Cu(2)–N(4)$^{\#1}$	1.923(2)
O(1)–Cu(1)–N(1)	101.14(9)	O(6)$^{\#2}$–Cu(2)–N(2)	101.26(9)
O(1)–Cu(1)–N(3)	104.65(9)	O(6)$^{\#2}$–Cu(2)–N(4)$^{\#1}$	98.77(9)
N(1)–Cu(1)–N(3)	154.19(10)	N(2)–Cu(2)–N(4)$^{\#1}$	158.13(10)
2			
Cu(1)–O(3)	1.969(14)	Cu(1)–O(3)$^{\#1}$	1.969(14)
Cu(1)–N(1)	1.999(17)	Cu(1)–N(1)$^{\#1}$	1.999(17)
O(3)–Cu(1)–O(3)$^{\#1}$	93.03(9)	O(3)–Cu(1)–N(1)	166.36(7)
O(3)–Cu(1)–N(1)$^{\#1}$	93.68(7)	O(3)$^{\#1}$–Cu(1)–N(1)	93.68(7)
O(3)$^{\#1}$–Cu(1)–N(1)$^{\#1}$	166.36(7)	N(1)–Cu(1)–N(1)$^{\#1}$	82.34(10)

Symmetry codes: **1**: $^{\#1}x+1$, y − 1, $z-1$; $^{\#2}x$, $y-1$, z, **2**: $^{\#1}-x+1$, y, $-z+3/2$.

3. Results and discussion

3.1. *Description of the crystal structures*

Single-crystal structural analysis reveals that the asymmetric unit of **1** contains two Cu(I) ions, one BDOA^{2-} ligand, two 4,4′-bpy molecules, and two lattice waters (figure 1). Each Cu(I) is coordinated to one carboxylate oxygen from one BDOA^{2-} ligand and two

Table 3. Hydrogen bonding geometry (Å and °) for **1** and **2**.

D–H	*d*(D–H)	*d*(H···A)	∠DHA	*d*(D···A)	A	Symmetry codes
1						
O(7)–H(1W)	0.83	2.60	124.9	3.146(4)	O(5)	
O(7)–H(2W)	0.83	2.09	173.8	2.912(4)	O(2)	$x+1$, y, z
2						
C(5)–H(5)	0.93	2.49	145.0	3.290	O(5)	$1/2+x$, $-1/2+y$, z
C(9)–H(9)	0.93	2.57	138.0	3.320	O(5)	$1/2-x$, $1/2+y$, $1/2-z$

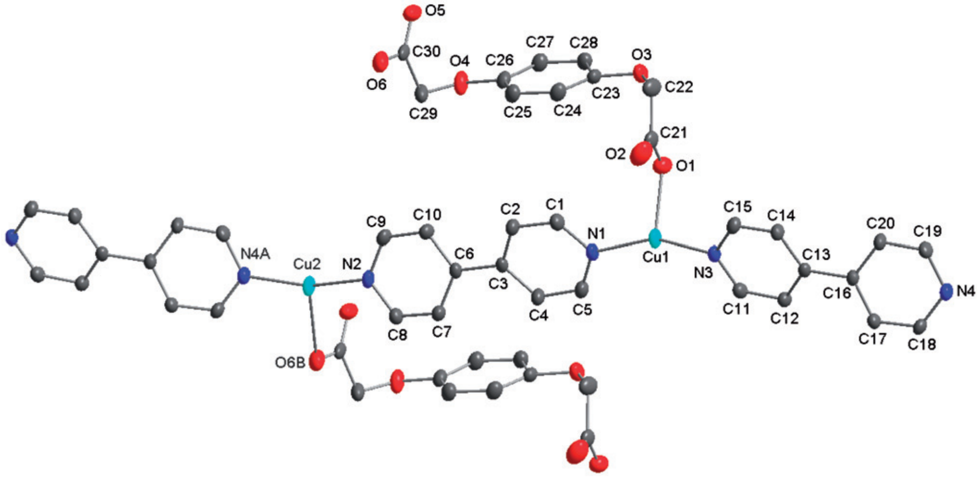

Figure 1. The coordination environment of Cu(I) in **1** with 30% thermal ellipsoids; hydrogens are omitted for clarity.

nitrogens from two 4,4′-bpy. The coordination environments of the two Cu(I) ions are similar, but the bond lengths of Cu1–N and Cu2–N, Cu1–O, and Cu2–O are slightly different. The Cu1–N1 [1.930(2) Å] and Cu1–N3 [1.924(2) Å] distances are close to the Cu2–N2 [1.926(2) Å] and Cu2–N4 [1.923(2) Å], while the Cu1–O1 [2.193(2) Å] distance is shorter than the Cu2–O6B [2.344(2) Å]. Two Cu(I) ions of the asymmetric unit are linked by 4,4′-bpy molecules with Cu1···Cu2 distance of 10.93(8) Å. The BDOA^{2-} are bis-monodentate bridging ligands, linking $[\mathrm{Cu_2(4,4'\text{-}bpy)_2}]^{2+}$ to form a 2-D grid-like layer with dimensions of *ca* 10.82 × 21.59 $Å^2$ (based on the distances between metal ions) along the *a*-axis, and the lattice waters are enclathrated in the cavities *via* O–H ··· O hydrogen bonds (figure 2a). In the 2-D net, the copper center is a three-connected node, and the BDOA^{2-} ligand and 4,4′-bpy molecule are two kinds of linkers, the 2-D layer can be further simplified as a three-connected 6^3 topology. As shown in figure 2(b), the 2-D metal-organic layers are further extended into 3-D supramolecular network *via* O–H···O hydrogen-bond interactions [O(7)···O(5) = 2.911 Å, O(7)···O(2) = 3.146 Å, and <O(7)–H(1W)···O(5) = 124.9°, <O(7)–H(2W)···O(2) = 173.8°] between the carboxylate oxygens and the lattice waters along the *b*-axis.

The X-ray crystal structure of **2** is shown in figure 3, Cu(II) is four-coordinate by two carboxylate oxygens from two BDOA^{2-} ligands and two nitrogens from one phen.

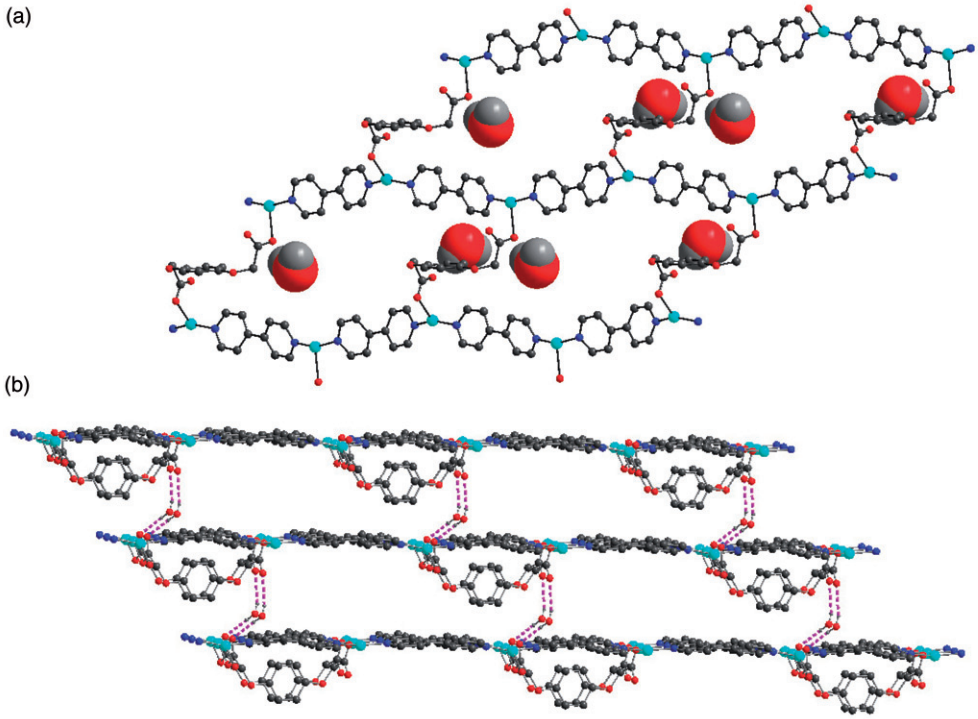

Figure 2. (a) View of the 2-D grid-like layer framework along the *a*-axis; lattice water molecules are shown by space-filling model. (b) The 3-D supramolecular structure of **1** along the *b*-axis; the hydrogen bonding interactions between the layers are indicated as dotted lines (pink in color).

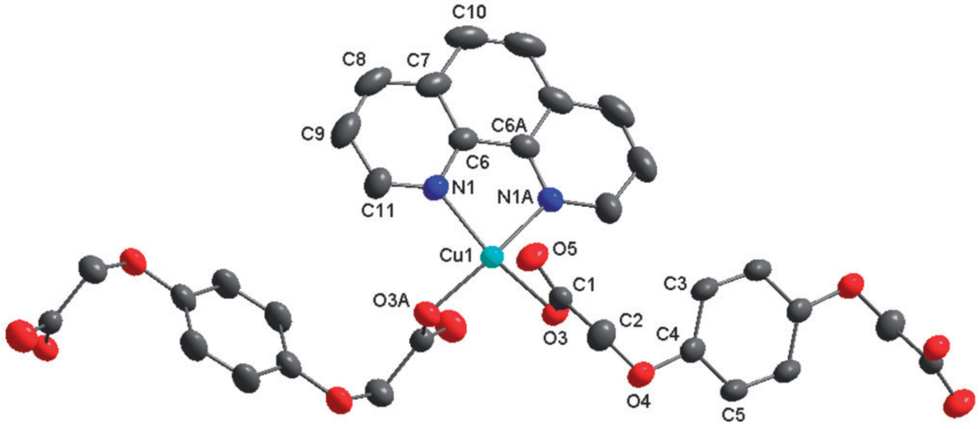

Figure 3. The coordination environment of Cu(II) in **2** with 30% thermal ellipsoids; all hydrogen atoms are omitted for clarity.

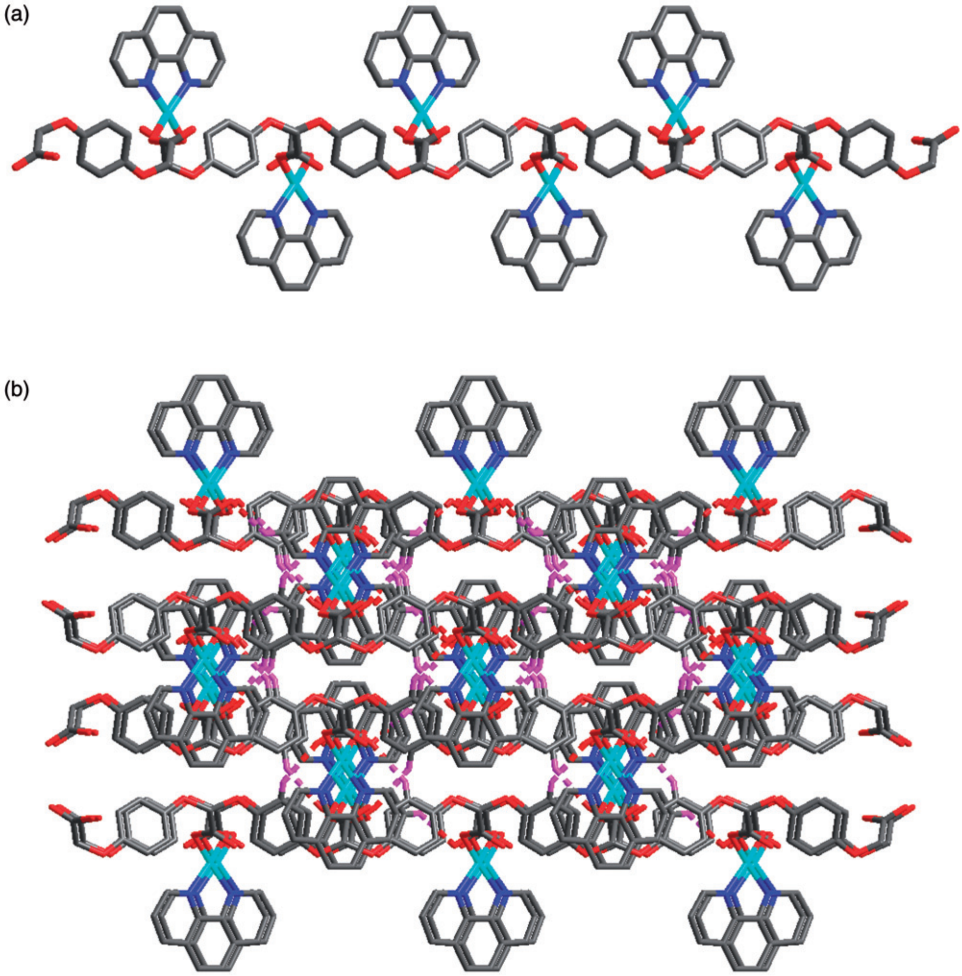

Figure 4. (a) The 1-D chain structure along the *c*-axis. (b) View of the 3-D supramolecular structure of **2** along the *c*-axis; hydrogen bonding interactions between the chains are indicated as dotted lines (pink in color).

The Cu–O and Cu–N distances are 1.969(14) and 1.999(17) Å, respectively. In **2**, H_2BDOA adopts bis-monodentate coordination linking Cu(II) ions to a 1-D chain structure with Cu $\cdots$ Cu distance of 11.88(7) Å along the *c*-axis (figure 4a). The phen molecules cling to both sides of the chain with dihedral angle between the plane of Cu(II) ions and phen of 18.17(2)°. As illustrated in figure 4(b), the 3-D supramolecular network of **2** is constructed *via* C–H $\cdots$ O hydrogen-bond interactions [C(5) $\cdots$ O(5) = 3.29 Å, C(9) $\cdots$ O(5) = 3.32 Å, and $<$C(5)–H(5) $\cdots$ O(5) = 138°, $<$C(9)–H(9) $\cdots$ O(5) = 145°] between carbons on the phenyl/pyridyl rings and carboxylate oxygen atoms along the *c*-axis.

In **1** and **2**, different auxiliary ligands (4,4′-bpy and phen) result in the different structures. In **1**, 4,4′-bpy is a bridging ligand, joining the [Cu_2(BDOA)] building blocks to a 2-D layer structure, while in **2** phen is bidentate chelating to Cu(II), preventing the 1-D chain from extending into higher dimensions. H_2BDOA are bis-monodentate, and carboxylate oxygens coordinate to copper and are hydrogen-bond acceptors to build up rich hydrogen bonds, constructing the 3-D supramolecular structure.

3.2. *Thermogravimetric analysis of 1*

The thermogravimetric (TG) curve of **1** exhibits two steps of weight loss from 50°C to 850°C. The first weight loss of 4.92% from 50°C to 150°C corresponds to a loss of two lattice waters per asymmetric unit (Calcd: 5.15%). The compound is stable at 280°C, and the second weight loss of 74.23% (Calcd: 74.40%) from 280°C to 850°C corresponds to a loss of organic groups; the final residuals are Cu_2O.

3.3. *IR spectra*

IR spectras of **1** and **2** show characteristic bands of carboxylates at 1603 and 1606 cm^{-1} for asymmetric stretches and at 1401 and 1400 cm^{-1} for the symmetric stretches. The separation between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ of 202 cm^{-1} for **1** and 206 cm^{-1} for **2** indicates bis-monodentate mode. The band at 3419 cm^{-1} can be attributed to O–H stretching of lattice water in **1**.

4. Conclusion

Two new copper benzene-1,4-dioxydiacetate complexes with 4,4′-bipyridine and 1,10-phenanthroline have been synthesized and characterized. In **1**, 4,4′-bpy is a bridging ligand joining the [Cu_2(BDOA)] building blocks to form a 2-D layer structure with 6^3 topology; in **2**, phen is a terminal ligand, preventing the 1-D chain structure from extending to higher dimensions. Hydrogen-bond interactions play an important role in the construction of the 3-D supramolecular networks.

Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center with deposition nos CCDC 764222 and 7764223, respectively.

Acknowledgments

This study was supported by the Natural Science Foundation of China (grant no. 20961007) and the Natural Science Foundation of Jiangxi province (grant no. 2008GZH0009).

References

[1] W.J. Zhuang, X.J. Zheng, L.C. Li, D.Z. Liao, H. Ma, L.P. Jin. *CrystEngComm.*, **9**, 653 (2007).

[2] J. Wang, Z.J. Lin, Y.C. Ou, N.L. Yang, Y.H. Zhang, M.L. Tong. *Inorg. Chem.*, **47**, 190 (2008).

[3] P.P. Liu, Y.Q. Wang, C.Y. Tian, H.Q. Peng, E.Q. Gao. *J. Mol. Struct.*, **920**, 459 (2009).

[4] A. Majumder, S. Shit, C.R. Choudhury, S.R. Batten, G. Pilet, D. Luneau, N. Daro, J.P. Sutter, N. Chattopadhyay, S. Mitra. *Inorg. Chim. Acta*, **358**, 3855 (2005).

[5] D.H. Choi, J.H. Yoon, J.H. Lim, H.C. Kim, C.S. Hong. *Inorg. Chem.*, **45**, 5947 (2006).

[6] Y.Q. Wei, Y.F. Yu, K.C. Wu. *Cryst. Growth Des.*, **8**, 2087 (2008).

[7] X. Li, Y.Q. Li, Y.B. Zhang. *J. Coord. Chem.*, **61**, 1720 (2008).

[8] C.B. Liu, M.X. Yu, X.J. Zheng, L.P. Jin, S. Gao, S.Z. Lu. *Inorg. Chim. Acta*, **358**, 2687 (2005).

[9] X.G. Wang, J. Li, B. Ding, E.C. Yang, X.J. Zhao. *J. Mol. Struct.*, **876**, 268 (2008).

[10] Q.R. Wu, X.L. Chen, H.M. Hu, T. Qin, F. Fu, B. Zhang, X.L. Wu, M.L. Yang, G.L. Xue, L.F. Xu. *Inorg. Chem. Commun.*, **11**, 28 (2008).

[11] X.L. Hong, Y.Z. Li, H.M. Hu, Y. Pan, J.F. Bai, X.Z. You. *Cryst. Growth Des.*, **6**, 1221 (2006).

[12] X.F. Li, Z.B. Han, X.N. Cheng, X.M. Chen. *Inorg. Chem. Commun.*, **9**, 1091 (2006).

[13] C.B. Liu, C.Y. Sun, L.P. Jin, S.Z. Lu. *New J. Chem.*, **28**, 1019 (2004).

[14] Y.H. Wan, L.P. Zhang, L.P. Jin, S. Gao, S.Z. Lu. *Inorg. Chem.*, **42**, 4985 (2003).

[15] D.F. Sun, R. Cao, W.H. Bi, J.B. Weng, M.C. Hong, Y.C. Liang. *Inorg. Chim. Acta*, **357**, 991 (2004).

[16] Y.C. Qiu, C. Daiguebonne, J.Q. Liu, R.H. Zeng, N. Kerbellec, H. Deng, O. Guillou. *Inorg. Chim. Acta*, **360**, 3265 (2007).

[17] Y.M. Dai, E. Tang, Z.J. Li, Y.G. Yao. *Acta Crystallogr.*, **C61**, m61 (2007).

[18] C.Y. Gao, S.X. Liu, L.H. Xie, C.Y. Sun, J.F. Cao, Y.H. Ren, D. Feng, Z.M. Su. *CrystEngComm.*, **11**, 177 (2009).

[19] X.L. Hong, J.F. Bai, Y. Song, Y.Z. Li, Y. Pan. *Eur. J. Inorg. Chem.*, 3659 (2006).

[20] X.M. Zhang, M.L. Tong, X.M. Chen. *Angew. Chem. Int. Ed.*, **41**, 1029 (2002).

[21] X. Li, Y.Q. Li, X.J. Zheng, H.L. Sun. *Inorg. Chem. Commun.*, **11**, 779 (2008).

[22] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of the Area Detector Data*, University of Göttingen, Göttingen, Germany (1997).

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

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