Syntheses, Crystal Structures and Characterization of Two New Pb(II) and Cu(II) Coordination Polymers Based on 2-(4-Fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline and Benzenedicarboxylate Ligands

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Two new coordination polymers, [Pb(L)(1,3-bdc)] ·2.5H_2O (**1**) and [Cu(L)(1,4-bdc)] (**2**) (L = 2-(4-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline; 1,3-bdc, 1,4-bdc = 1,3- and 1,4-benzenedicarboxylate), have been hydrothermally synthesized and characterized by elemental analysis, IR spectra and single-crystal X-ray diffraction. Crystal data for **1**: $C_{54}H_{40}F_2N_8O_{13}Pb_2$, triclinic, space group $P\bar{1}$, a = 9.3468(19), b = 9.4607(14), c = 15.581(3) Å, α = 90.44(4), β = 101.13(3), γ = 113.97(3)°, V = 1229.6(4) Å^3, Z = 1. Crystal data for **2**: $C_{27}H_{15}CuFN_4O_4$, triclinic, space group $P\bar{1}$, a = 9.640(6), b = 10.941(8), c = 11.865(5) Å, α = 62.694(4), β = 69.776(3), γ = 79.915(5)°, V = 1043.2(11) Å^3, Z = 2. In **1**, the Pb(II) atoms are bridged by the 1,3-bdc ligands to yield a chain structure. The ligands L are only located on one side of the chain, where $\pi\cdots\pi$ interactions among neighboring chains result in a supramolecular ladder, and the O–H···O hydrogen bonding interactions further stabilize this structure. Compound **2** shows a layer structure, with stacking by π-π interactions to give a three-dimensional (3D) supramolecular architecture. N–H···O hydrogen bonding further stabilizes the structure of **2**.

Key words: Coordination Polymer, Crystal Structure, 1,3-Benzenedicarboxylate, 2-(4-Fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline

Introduction

Coordination polymers are of current interest not only for their potential applications in microelectronics, nonlinear optics, zeolite-like materials for molecular selection, ion exchange, and catalysis but also for their intriguing variety of architectures and topologies [1, 2]. So far, large numbers of coordination polymers with one- (1D), two- (2D), and three- (3D) dimensional structures have been synthesized by hydrothermal methods. It is well known that the construction of the coordination polymers can be influenced by several factors, such as pH value of solution, temperature, geometric requirements of metal atoms, and the organic ligands [3]. In particular, the choice of the organic ligand is a key factor that may be utilized in determining the framework topology. Organic ligands with aromatic polycarboxylate groups are especially attractive because carboxylate groups can bridge two or more metal centers to produce polymers with versatile structural motifs [4]. Benzenedicarboxylates, such as 1,4- (1,4-bdc) and 1,3-benzenedicarboxylate (1,3-bdc), have been well investigated by Yaghi *et al.* [5]. However, coordination polymers constructed by both benzenedicarboxylate and 1,10-phenanthroline-like (phen-like) ligands have not been well investigated [6 – 8]. Among the phen-like ligands, 2-(4-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L) is a good candidate for *N*-donor ligands, which has excellent coordinating ability and a large conjugated system that can easily form π-π interactions [9 – 13]. In this work, we report two new coordination polymers, [Pb(L)(1,3-bdc)] ·2.5H_2O (**1**) and [Cu(L)(1,4-bdc)] (**2**).

Results and Discussion

*Structure description of **1***

Selected bond lengths and angles for [Pb(L)-(1,3-bdc)] ·2.5H_2O (**1**) and [Cu(L)(1,4-bdc)] (**2**) are listed in Table 1. As shown in Fig. 1, there are one Pb(II) atom, one 1,3-bdc anion, and two and a half water molecules in the asymmetric unit of **1**. The Pb(II) atom is coordinated by two nitrogen atoms from one

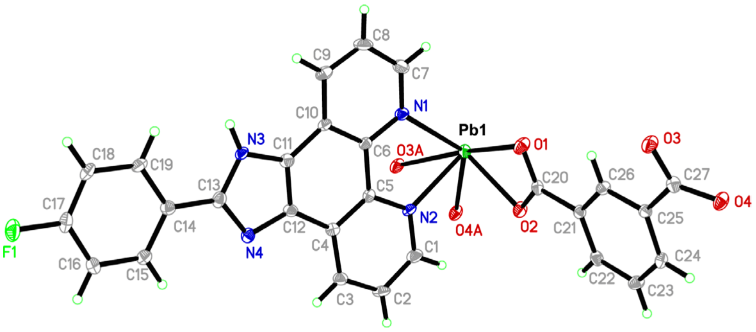

Fig. 1 (color online). The coordination environment of the Pb(II) center in **1**.

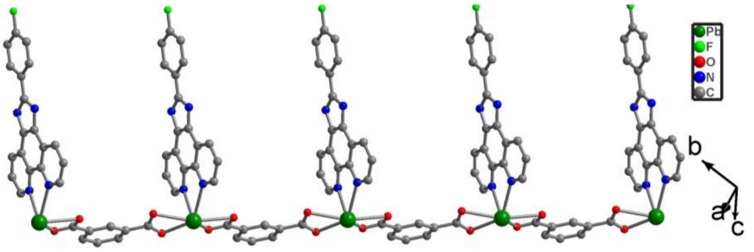

Fig. 2 (color online). View of the chain structure of **1**.

Table 1. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses[a].

Compound **1**			
Pb1–O2	2.398(4)	Pb1–O4$^{\mathrm{i}}$	2.475(4)
Pb1–N2	2.507(4)	Pb1–N1	2.629(4)
Pb1–O3$^{\mathrm{i}}$	2.646(4)	Pb1–O1	2.669(4)
O2–Pb1–O4$^{\mathrm{i}}$	79.30(12)	O2–Pb1–N2	78.16(14)
O4$^{\mathrm{i}}$–Pb1–N2	77.23(14)	O2–Pb1–N1	117.14(14)
O4$^{\mathrm{i}}$–Pb1–N1	131.05(13)	N2–Pb1–N1	63.60(14)
O2–Pb1–O3$^{\mathrm{i}}$	127.35(12)	O4$^{\mathrm{i}}$–Pb1–O3$^{\mathrm{i}}$	51.28(12)
N2–Pb1–O3$^{\mathrm{i}}$	74.63(14)	N1–Pb1–O3$^{\mathrm{i}}$	89.18(14)
O2–Pb1–O1	51.40(12)	O4$^{\mathrm{i}}$–Pb1–O1	130.69(12)
N2–Pb1–O1	90.71(14)	N1–Pb1–O1	79.99(14)
O3$^{\mathrm{i}}$–Pb1–O1	164.63(13)		
Compound **2**			
Cu1–O2	1.979(2)	Cu1–O3	1.953(2)
Cu1–O3$^{\mathrm{i}}$	2.450(2)	Cu1–N1	2.014(3)
Cu1–N2	2.029(3)		
O3–Cu1–O2	89.93(10)	O3–Cu1–O3$^{\mathrm{i}}$	80.87(9)
O2–Cu1–O3$^{\mathrm{i}}$	95.54(10)	O3–Cu1–N1	169.25(10)
O2–Cu1–N1	90.91(10)	O3–Cu1–N2	100.70(10)
O2–Cu1–N2	162.14(10)	N1–Cu1–N2	81.33(10)
N1–Cu1–O3$^{\mathrm{i}}$	88.39(9)	N2–Cu1–O3$^{\mathrm{i}}$	100.27(10)

[a] Symmetry transformations used to generate equivalent atoms for **1**: (i) $x-1$, $y-1$, z; for **2**: (i) $-x+1$, $-y$, $-z+2$.

L ligand (Pb(1)–N(1) = 2.629(4) and Pb(1)–N(2) = 2.507(4) Å) and four carboxylate oxygen atoms from two different 1,3-bdc anions (Pb(1)–O(1) = 2.669(4), Pb(1)–O(2) = 2.398(4), Pb(1)–O(4)$^{\mathrm{i}}$ = 2.475 (4) and Pb(1)–O(3)$^{\mathrm{ii}}$ = 2.646(4) Å; symmetry operations of equivalent atoms: (i) $x-1$, $y-1$, z; (ii) $-x+1$, $-y$, $-z+2$). The two carboxylate groups are in a bidentate chelating coordination mode and bridge two neighboring Pb(II) atoms to yield a chain structure (Fig. 2). In the chain, the Pb···Pb distance bridged by the 1,3-bdc anion is about 10.248 Å. The ligands L play an important role in the formation of the chain structure. They only decorate one side of the chain and the L ligands from adjacent chains furnish strong π-*pi* interactions (centroid-to-centroid distance 3.47 Å and face-to-face distance 3.30 Å), which extend the chains into supramolecular ladders (Fig. 3). Moreover, O–H···O hydrogen bonding interactions further stabilize the structure of **1**.

It is well known that the geometries of Pb(II) complexes can be classified as holo- and hemidirected [14]. Holodirected refers to Pb(II) complexes in which the bonds to the ligand atoms are located throughout the surface of an encompassing sphere, whereas hemidirected refers to those cases in which the bonds to the ligand atoms are directed through only part of an encompassing sphere [13]. In compound **1**, the arrangement of O and N atoms for Pb(II) suggests a gap or hole in the coordination geometry around this atom, and its coordination sphere is, thus, hemi-directed.

Structure description of **2**

As shown in Fig. 4, the asymmetric unit of **2** contains one Cu(II) cation, one L molecule, and two half 1,4-bdc anions. The 1,4-bdc ligand resides around a crystallographic center of inversion. Each Cu(II)

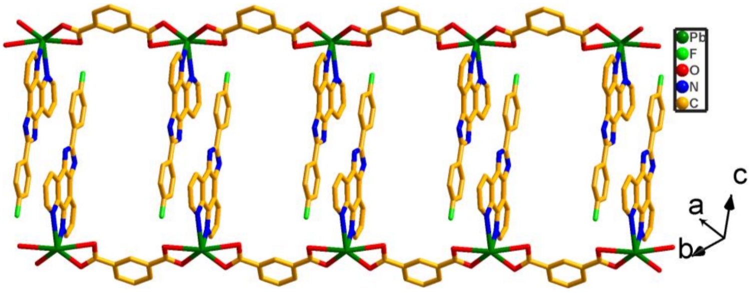

Fig. 3 (color online). View of the supramolecular ladder constructed by π-π interactions in **1**.

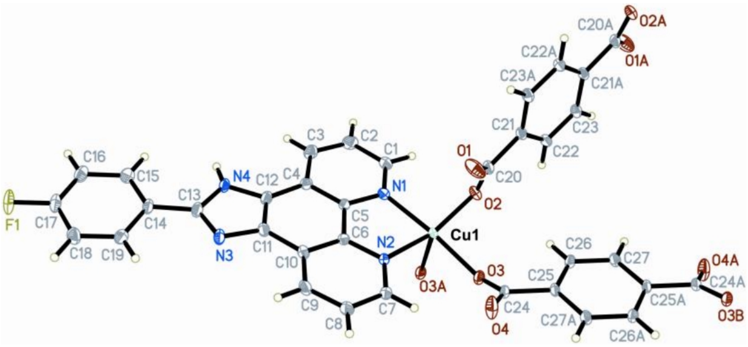

Fig. 4 (color online). The coordination environment of the Cu(II) center in **2**.

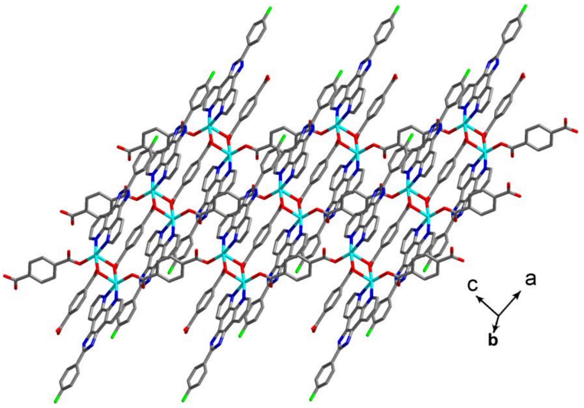

Fig. 5 (color online). A view of the layer structure of complex **2**.

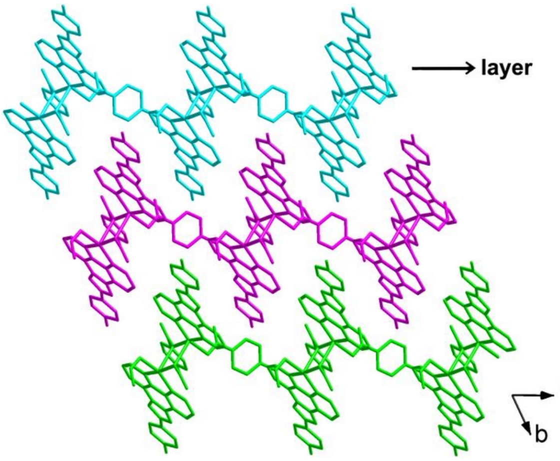

Fig. 6 (color online). A view of the 3D architecture of **2** constructed by π-π interactions.

atom is five-coordinated by two N atoms from one L, and three O atoms from three different 1,4-bdc ligands in a distorted square pyramidal environment. It is interesting to note that the two 1,4-bdc ligands show different coordination modes (Fig. 4). For convenience, the 1,4-bdc anions containing the oxygen atoms labeled O1 and O3 are designated 1,4-bdc1 and 1,4-bdc2, respectively. Each 1,4-bdc1 coordinates to two Cu(II) centers in a bis-monodentate mode. Each carboxylate group of the 1,4-bdc2 anion connects two Cu(II) centers in a bis-bridging mode to form a dimer. The distance between the Cu(II) centers in the dimer is 3.367(4) Å. The dinuclear units are bridged by the backbones of the 1,4-bdc2 ligands to form a chain structure (Fig. 5). The chains are further linked by the 1,4-bdc1 ligands in bis-modentate modes to generate a layer (Fig. 5). The ligands L are attached to both sides of the layers, allowing the formation of π-π stacking interactions (centroid-to-centroid distance of 3.57 Å and face-to-face distance of 3.35 Å), and connect the adjacent layers to a 3D supramolecular architecture (Fig. 6). Obviously, the strong π-π stacking interactions play an important role in stabilizing the supramolecular architecture of **2**. Moreover, the N–H···O hydrogen bonding further support the structure of **2**.

It is noteworthy that the skilful combination of bridging carboxylate anions, phen-like chelating ligands and metal cations has generated a number of interesting coordination compounds so far. Unfortunately, owing to the termination effect of chelating phen-like ligands, such coordination polymers are usually only one- or two-dimensional [6 – 9]. As far as we know, high-dimensional complexes based on dicarboxylate and phen-like ligands have rarely been reported [10 – 13]. Therefore, the structure **2** is a rare example for layers based on dicarboxylate and aromatic *N*-chelating ligands.

IR spectra

The broad band at 3431 cm^{-1} is attributed to the O–H stretching frequency of the free water molecules of compound **1**. In the IR spectra of compounds **1** and **2**, the special peaks at about 1659 and 1658 cm^{-1} are attributed to the protonated carboxylate groups of 1,3-bdc and 1,4-bdc ligands. Peaks at about 1456 and 1450 cm^{-1} could be assigned to ν(C=N) stretching vibration of the ligand L.

Thermogravimetric analyses (TGA)

To characterize the compounds **1** and **2** more fully in terms of thermal stability, their thermal behavior was examined by TGA (Fig. 7). The experiments were performed on samples consisting of numerous single crystals under N_2 atmosphere with a heating rate of 10 °C/min. For **1**, the weight loss corresponding to the release of water molecules is observed from 70 to 140 °C (obsd. 6.9 %, calcd. 6.2 %). The decomposition of the remainder occurred from 250 to 530 °C, leading to the formation of PbO as the residue (obsd. 29.7 %, calcd. 30.6 %). From the TGA curve of **2**, no weight loss was observed below 235 °C, indicating that there are no small molecules of solvent. The host framework starts to decompose in the range from 235 to 575 °C. The remaining weight corresponds to the formation of CuO (obsd. 14.2 %, calcd. 14.7 %).

UV/Vis absorption spectra

The UV/Vis absorption spectrum of compound **2** was registered from the crystalline state at r. t. (Fig. 8). The weak band from 550 to 670 nm can be assigned as

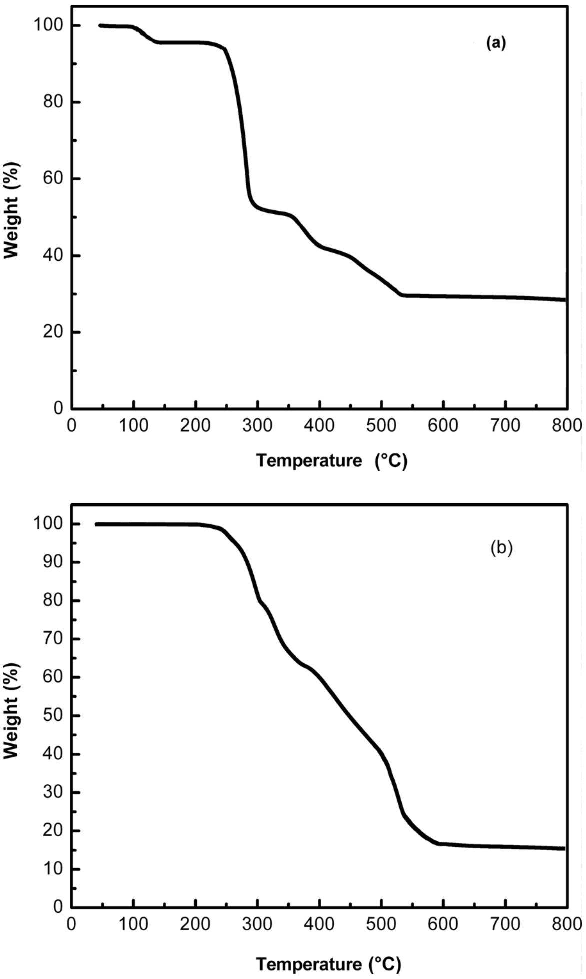

Fig. 7. TG curves of compounds **1** (a) and **2** (b).

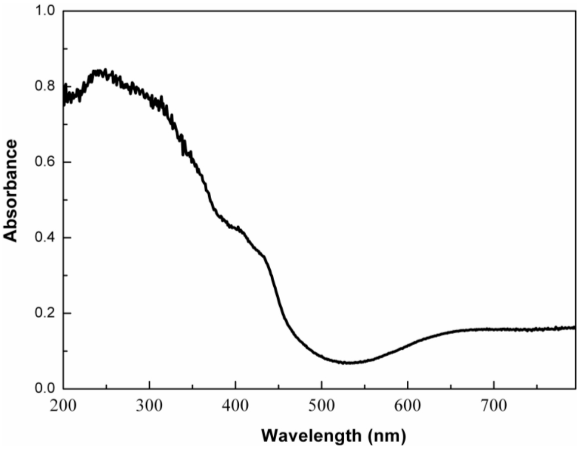

Fig. 8. UV/Vis absorption spectrum of compound **2**.

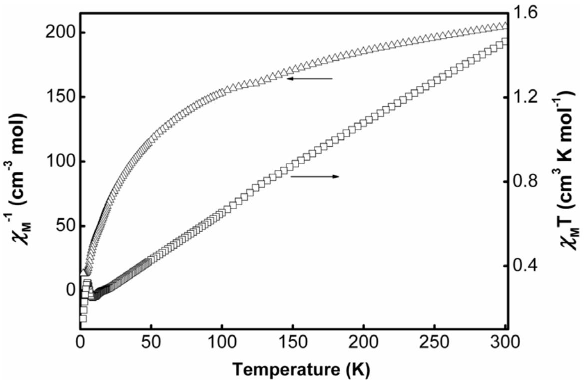

Fig. 9. Plots of the temperature dependence of $\chi_m T$ (squares) and $\chi_m{}^{-1}$ (triangles) for compound **2.**

d-d transitions, while the band from 200 to 400 nm is considered to be due to intraligand transitions [14].

Magnetic properties

The temperature-dependent magnetic susceptibility data of compound **2** have been measured from polycrystalline samples at an applied magnetic field of 1000 Oe in the temperature range of 2 – 300 K (Fig. 9). According to the structure, **2** can be approximately regarded as a dicopper(II) complex [15]. Upon cooling, the values of $\chi_m T$ keep smoothly decreasing in the 300 – 8 K range, and then exhibit a maximum value of 0.6406 cm^3 mol^{-1} K at 5 K before going down quickly to a minimum value of 0.3001 cm^3 mol^{-1} K at 2 K. This behavior is indicative of antiferromagnetic coupling [16]. The inflexion at 5 – 8 K may be due to a small canting of the sub-lattice [16].

Experimental Section

General

All materials were of analytical grade and used as received without further purification. The IR spectra were obtained on a Perkin-Elmer 2400LSII spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer in the range from 40 to 800 °C under nitrogen gas. The UV/Vis absorption spectrum of **2** was collected on a finely ground sample with a Cary 500 spectrophotometer equipped with a 110 mm diameter integrating sphere. Temperature-dependent magnetic susceptibility data for polycrystalline compound **2** was obtained on a Quantum Design MPMSXL SQUID magnetometer under an applied field of 1000 Oe over the temperature range of 2 – 300 K.

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

Compound	**1**	**2**
Formula	$C_{54}H_{40}F_2N_8O_{13}Pb_2$	$C_{27}H_{15}CuFN_4O_4$
M_r	1461.02	541.97
Crystal size, mm^3	$0.20 \times 0.17 \times 0.13$	$0.24 \times 0.21 \times 0.18$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.3468(19)	9.640(6)
b, Å	9.4607(14)	10.941(8)
c, Å	15.581(3)	11.865(5)
α, deg	90.44(4)	62.694(4)
β, deg	101.13(3)	69.776(3)
γ, deg	113.97(3)	79.915(5)
V, Å^3	1229.6(4)	1043.2(11)
Z	1	2
D_{calcd}, g cm^{-3}	1.97	1.73
μ(MoK_α), mm^{-1}	6.9	1.1
F(000), e	706	550
hkl range	$-8 \le h \le 11$ $-11 \le k \le 11$ $-16 \le l \le 18$	$-12 \le h \le 12$ $-14 \le k \le 13$ $-15 \le l \le 15$
θ range, deg	2.37 – 25.03	3.05 –27.48
Refl. collect.	6173	10329
unique	3796	3691
R_{int}	0.0192	0.0431
Data / ref. parameters	4239 / 379	4729 / 334
$R1$ / $wR2[I \ge 2\sigma(I)]$	0.0297 / 0.0684	0.0459 / 0.1220
$R1$ / $wR2$ (all data)	0.0356 / 0.0706	0.0639 / 0.1311
GoF (F^2)	1.071	1.120
$\Delta\rho_{max/min}$, e Å^{-3}	1.17 / −0.57	0.55 / −0.67

*Syntheses of compounds **1** and **2***

A mixture of $Pb(NO_3)_2$ (0.5 mmol), 1,3-H_2bdc (0.5 mmol) and L (0.5 mmol) was dissolved in 12 mL distilled water. The pH value of the system was adjusted to between 5 and 6 by using triethylamine. The resulting solution was stirred for about 0.5 h at r. t., sealed in a 23-mL Teflon-lined stainless-steel autoclave and heated at 464 K for 3 d under autogeneous pressure. The reaction system was slowly cooled to r. t. Pale-yellow crystals of **1** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield: 37 % based on Pb(II). – Anal. for $C_{54}H_{40}F_2N_8O_{13}Pb_2$ (1461.02): calcd. C 44.38, H 2.76, N 7.67; found C 44.70, H 2.26, N 7.84. – IR (KBr, cm^{-1}): ν = 3431m, 2169m, 1659s, 1613m, 1456s, 1400w, 1221w, 1161m, 841w, 781w, 591w.

The preparation of **2** was similar to that of **1** except that 1,4-H_2bdc and $Cu(NO_3)_2 \cdot 2.5H_2O$ were used instead of 1,4-H_2bdc and $Pb(NO_3)_2$, respectively. Yield: 31 % based on Cu(II). – Anal. for $C_{27}H_{15}CuFN_4O_4$ (541.97): calcd. C 59.83, H 2.79, N 10.34; found C 59.41, H 2.50, N 10.71. – IR (KBr, cm^{-1}): ν = 2160m, 1658s, 1612w, 1450m, 1409w, 1221w, 1201w, 1168m, 847w, 784w.

X-Ray structure determination

Single-crystal X-ray diffraction data for complex **1** (Table 2) were recorded at a temperature of 293(2) K on a Bruker Apex CCD diffractometer, using the *omega* scan technique with MoK_α radiation (*lambda* = 0.71073 Å). Single-crystal X-ray diffraction data for **2** (Table 2) were collected on a Rigaku RAXIS-RAPID diffractometer using ω scans with MoK_α radiation. The structures were solved by Direct Methods with SHELXS-97 [17] and refined by full-matrix least-squares techniques using SHELXL-97 [18]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms of the ligands were refined as part of rigid groups. The H atoms of the water molecules in **1** were located from a difference Fourier map.

CCDC 821322 (**1**) and 782105 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176 – 182.

[2] J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117 – 138.

[3] G. Férey, *Chem. Mater.* **2001**, *13*, 3084 – 3098.

[4] S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558 – 1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460 – 1494.

[5] J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213 – 1214.

[6] X. L. Wang, Y. Q. Chen, Q. Gao, H. Y. Lin, G. C. Liu, J. X. Zhang, A. X. Tian, *Cryst. Growth Des.* **2010**, *10*, 2174 – 2184.

[7] J. Yang, G. D. Li, J. J. Cao, Q. Yue, G. H. Li, J. S. Chen, *Chem. Eur. J.* **2007**, *13*, 3248 – 3261.

[8] Z.-G. Kong, X.-Y. Ma, Z.-L. Xu, *Z. Naturforsch.* **2010**, *65b,* 1173 – 1176.

[9] Q. Qiao, G. Q. Wu, T. D. Tang, S. W. Ng, *Acta Crystallogr.* **2009**, *C65*, m146 – m148.

[10] Z.-G. Kong, X.-Y. Wang, L. Carlucci, *Inorg. Chem. Commun.* **2009**, *12*, 691 – 694.

[11] X.-L. Wang, Y.-F. Bi, H.-Y. Lin, G.-C. Liu, *Cryst. Growth Des.* **2007**, *7*, 1086 – 1091.

[12] X.-Y. Wang, M. Wang, X.-Y. Ma, *Acta Crystallogr.* **2009**, *C65*, m459 – m462.

[13] X.-Y. Wang, S. Ma, T. Li, S. W. Ng, *Z. Naturforsch.* **2011**, *66b,* 103 – 106.

[14] H.-Y. Bai, J.-F. Ma, J. Yang, L.-P. Zhang, J.-C. Ma, Y.-Y. Liu, *Cryst. Growth Des.* **2010**, *10*, 995 – 1016.

[15] Z.-G. Gu, X.-H. Zhou, Y.-B. Jin, R.-G. Xiong, J.-L. Zuo, X.-Z. You, *Inorg. Chem.* **2007**, *46*, 5462 – 5464.

[16] M. Biswas, G. M. Rosair, G. Pilet, S. Mitra, *Inorg. Chim. Acta* **2007**, *360* 695 – 699

[17] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

[18] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.