Hydrothermal Synthesis, Crystal Structure and Properties of a 2D Network of Cd(II) Coordination Polymers with Helical Chains

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Z. Naturforsch. **2010**, *65b,* 1169 – 1172;
received March 8, 2010

Hydrothermal reaction of Cd(II) acetate with the bridging ligand m-H_4bptc (m-H_4bptc = biphenyl-2,3′,3,4′-tetracarboxylic acid) yielded a new 2D metal-organic coordination polymer with helical chains in the solid state namely $\{[Cd_2(\text{m-bptc})(H_2O)_6]\cdot(H_2O)_5\}_n$ (**1**). The helices are further connected through hydrogen bonds to give a three-dimensional supramolecular network. The thermal stability of complex **1** was studied by thermogravimetric (TG) and differential thermal analysis (DTA). Compound **1** exhibits photoluminescence with an emission maximum at *ca.* 399 nm upon excitation at 360 nm.

Key words: Cadmium(II), Biphenyl-2,3′,3,4′-tetracarboxylic Acid, Helical Chain, Coordination Polymer, Crystal Structure

Introduction

Metalorganic framework (MOF) coordination polymers are of growing interest not only because of their fascinating and complex structural topologies, but also for their potential applications as functional materials including porosity, magnetism, nonlinear optical activity, catalysis, *etc.* [1 – 3]. Helical coordination polymers are receiving much attention owing to their many novel structures analogous to the helical arrays in biological DNA chains [4]. The self-assembly of multidentate organic ligands and metal ions is currently the most efficient approach towards the design of one-, two-, and three-dimensional coordination polymeric frameworks, the structures of which are influenced by the subtle interplay of many factors such as geometric preference of metal ions, sizes and shapes of organic building blocks, templates, and solvent systems. The selection or design of suitable ligands containing certain features like flexibility or versatile binding modes is crucial to the construction of metal-organic coordination polymers. Multicarboxylate ligands exhibit many coordination modes due to multicarboxylate groups separated by various rigid or flexible spacers. Multidimensional metal-organic coordination polymers with interesting structures including helices and interpenetrating networks have been constructed [5 – 9].

Up to now, to the best of our knowledge, only one metal-organic compound has been obtained from biphenyl-2,3′,3,4′-tetracarboxyl acid (m-H_4bptc) [9]. However, with the aim of further understanding the coordination chemistry of the m-H_4bptc ligand and preparing new materials with interesting structural topologies and physical properties, we have recently become engaged in the research of coordination polymers based on m-H_4bptc. In this paper, we report a synthetic and structural study on the a new compound $\{[Cd_2(\text{m-bptc})(H_2O)_6]\cdot(H_2O)_5\}_n$ (**1**).

Experimental Section

Materials and physical measurements

All starting materials were of analytical grade and were obtained from commercial sources without further purification. Elemental analyses were carried out on an Elementar Vario EL III analyzer. The infrared spectra were recorded from KBr pellets in the range 4000 ∼ 400 cm^{-1} on a Bruker model Vector22 FT-IR spectrometer. Thermogravimetric measurements were carried out from r. t. to 700 ℃ on crystalline samples in a nitrogen stream using a TA Instruments SBT Q600 apparatus at a heating rate of 10 ℃ min^{-1}.

Synthesis of $\{[Cd_2(\text{m-bptc})(H_2O)_6]\cdot(H_2O)_5\}_n$ (1)

A mixture of m-H_4bptc (0.1 mmol, 33.0 mg) and $Cd(OAc)_2\cdot 4H_2O$ (0.2 mmol, 52.0 mg) in distilled water (8 mL) was placed in a Teflon-lined stainless-steel vessel, heated to 120 ℃ for 3 d, and then cooled to r. t. over 24 h. Colorless crystals of complex **1** were obtained. Yield: 70 %. – $C_{16}H_{22}Cd_2O_{16}$: calcd. C 27.62, H 3.16; found C 27.55, H 3.09. – IR (KBr, cm^{-1}): ν = 3420 (w), 1563 (w), 1449 (w), 1390 (w), 1289 (s), 909 (w), 885 (w), 796 (s), 740 (s), 640 (s).

Crystallography data collection and structure determination

Single-crystal X-ray diffraction analysis of complex **1** was carried out at r. t. on a Bruker SMART APEX II CCD

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Table 1. Crystallographic data for complex **1**.

Empirical formula	$C_{16}H_{22}Cd_2O_{16}$
Formula weight	695.14
Color, habit	colorless, block
Crystal size, mm^3	0.18 × 0.16 × 0.15
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	10.8870(5)
b, Å	6.3402(3)
c, Å	36.5153(18)
β, deg	91.2850(10)
Volume, Å^3	2519.9(2)
Z	4
Density (calcd.), g cm^{-3}	1.83
Absorption coeff., mm^{-1}	1.8
$F(000)$, e	1368
Temperature, K	293(2)
Index range h, k, l	−13/12, −7/7, −44/42
Refl. collected / independent / R_{int}	13102 / 4927 / 0.0418
Refl. with $[I \geq 2\,\sigma(I)]$	3437
Parameters refined	334
$R1$ / $wR2$ $[I \geq 2\sigma\,(I)]$	0.0547 / 0.1048
$R1$ / $wR2$ (all data)	0.0854 / 0.1106
Goodness of fit (GoF)	1.025
Final diff. peaks (max / min), e Å^{-3}	+0.72 / −1.49

diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) using ω-scans. Lorentz, polarization and absorption corrections were applied. The structure was solved by Direct Methods and refined with the full-matrix least-squares technique using the programs SHELXS-97 and SHELXL-97, respectively [10]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The hydrogen atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restrains. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

CCDC 745108 contains 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.

Results and Discussion

Crystal structure

The metal-ligand connectivity pattern of complex **1** is depicted in Fig. 1a. Selected bond lengths and angles of complex **1** are listed in Table 2. In each unit, there are two crystallographically non-equivalent Cd(II) center ions, one m-bptc^{4-} ligand, six coordinated water molecules, and five solvate water molecules. Cd1 adopts a distorted octahedral coordination environment with the Cd1–O bond lengths in the range 2.215(5) – 2.332(4) Å, including three carboxylic oxygen atoms of monodentate 3′-COO$^-$ and 4′-COO$^-$ groups from three different m-bptc^{4-} ligands and three oxygen atoms from coordinated water

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1**[a].

Cd(1)–O(8)	2.215(5)	Cd(1)–O(9)	2.313(5)
Cd(1)–O(10)	2.315(5)	Cd(1)–O(11)	2.314(5)
Cd(1)–O(5)$^{\#1}$	2.332(4)	Cd(1)–O(5)$^{\#2}$	2.332(4)
Cd(2)–O(1)	2.455(4)	Cd(2)–O(2)	2.311(4)
Cd(2) –O(12)	2.409(4)	Cd(2)–O(13)	2.317(5)
Cd(2)–O(14)	2.301(4)	Cd(2)–O(3)$^{\#3}$	2.469(4)
Cd(2)–O(4)$^{\#3}$	2.315(4)		
O(11)–Cd(1)–O(5)$^{\#1}$	165.93(16)	O(10)–Cd(1)–O(5)$^{\#1}$	88.52(15)
O(9)–Cd(1)–O(5)$^{\#1}$	88.90(14)	O(8)–Cd(1)–O(5)$^{\#1}$	110.35(15)
O(9)–Cd(1)–O(5)$^{\#2}$	82.89(14)	O(5A)–Cd(1)–O(5)$^{\#2}$	74.60(16)
O(8)–Cd(1)–O(5)$^{\#2}$	102.59(16)	O(11)–Cd(1)–O(5)$^{\#2}$	111.88(15)
O(10)–Cd(1)–O(5)$^{\#2}$	161.90(15)	O(11)–Cd(1)–O(10)	83.23(15)
O(8)–Cd(1)–O(9)	160.73(15)	O(8)–Cd(1)–O(11)	81.01(17)
O(9)–Cd(1)–O(11)	79.82(16)	O(8)–Cd(1)–O(10)	89.23(16)
O(9)–Cd(1)–O(10)	90.43(14)	O(14)–Cd(2)–O(12)	174.71(14)
O(12)–Cd(2)–O(4)$^{\#3}$	88.58(15)	O(1)–Cd(2)– O(4)$^{\#3}$	168.29(14)
O(13)–Cd(2)– O(4)$^{\#3}$	85.14(16)	O(14)–Cd(2)–O(4)$^{\#3}$	90.31(15)
O(12)–Cd(2)–O(3)$^{\#3}$	106.43(14)	O(13)–Cd(2)–O(3)$^{\#3}$	136.25(15)
O(1)–Cd(2)–O(3)$^{\#3}$	137.23(14)	O(2)–Cd(2)–O(4)$^{\#3}$	135.26(15)
O(2)–Cd(2)–O(3)$^{\#3}$	87.76(13)	O(14)–Cd(2)–O(3)$^{\#3}$	77.03(14)
O(4C)–Cd(2)–O(3)$^{\#3}$	54.46(15)	O(2)–Cd(2)–O(12)	79.50(14)
O(14)–Cd(2)–O(2)	104.84(15)	O(14)–Cd(2) –O(1)	92.34(15)
O(2)–Cd(2)–O(13)	135.99(16)	O(2)–Cd(2)–O(1)	54.68(14)
O(13)–Cd(2)–O(1)	83.54(15)	O(12)–Cd(2)–O(1)	87.73(14)
O(14)–Cd(2)–O(13)	88.40(16)	O(13)–Cd(2)–O(12)	86.35(16)

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

Table 3. Hydrogen bond lengths (Å) and angles (deg) for complex **1**[a,b].

D–H$\cdots$A	d(H$\cdots$A)	d(D$\cdots$A)	∠(DHA)
O(9)–H(9B)$\cdots$O(15) $^{\#2}$	2.58	3.288(10)	141.4
O(10)–H(10C)$\cdots$O(17) $^{\#2}$	2.27	2.933(11)	134.4
O(11)–H(11A)$\cdots$O(1) $^{\#2}$	2.17	2.781(7)	128.7
O(11)–H(11B)$\cdots$O(15) $^{\#2}$	2.10	2.794(13)	138.0
O(12)–H(12C)$\cdots$O(3) $^{\#2}$	1.95	2.791(6)	170.1
O(17)–H(17A)$\cdots$O(6) $^{\#4}$	2.09	2.888(11)	157.1
O(10)–H(10B)$\cdots$O(6) $^{\#1}$	1.96	2.678(6)	141.0
O(13)–H(13B)$\cdots$O(16) $^{\#5}$	2.02	2.773(12)	148.0
O(13)–H(13C)$\cdots$O(11) $^{\#5}$	2.44	3.018(6)	125.4
O(14)–H(14C)$\cdots$O(12) $^{\#5}$	2.11	2.774(6)	134.6
O(14)–H(14B)$\cdots$O(2) $^{\#6}$	2.06	2.847(6)	154.1
O(19)–H(19A)$\cdots$O(6) $^{\#7}$	2.48	3.258(13)	153.0
O(12)–H(12B)$\cdots$O(15)	2.10	2.779(11)	137.0
O(15)–H(15A)$\cdots$O(8)	2.29	2.838(12)	122.2
O(15)–H(15B)$\cdots$O(16)	2.16	2.782(15)	129.4
O(16)–H(16A)$\cdots$O(19)	1.91	2.725(13)	160.3
O(16)–H(16B)$\cdots$O(18)	2.03	2.777(14)	146.1

[a] Symmetry codes: $^{\#1}$ $-x+2$, $-y+1$, $-z$; $^{\#2}$ x, $y-1$, z; $^{\#4}$ $x-1$, y, z; $^{\#5}$ x, $y+1$, z; $^{\#6}$ $-x+3/2$, $y+1/2$, $-z+1/2$; $^{\#7}$ $x-1$, $y-1$, z;
[b] d(D–H) fixed at 0.85 Å.

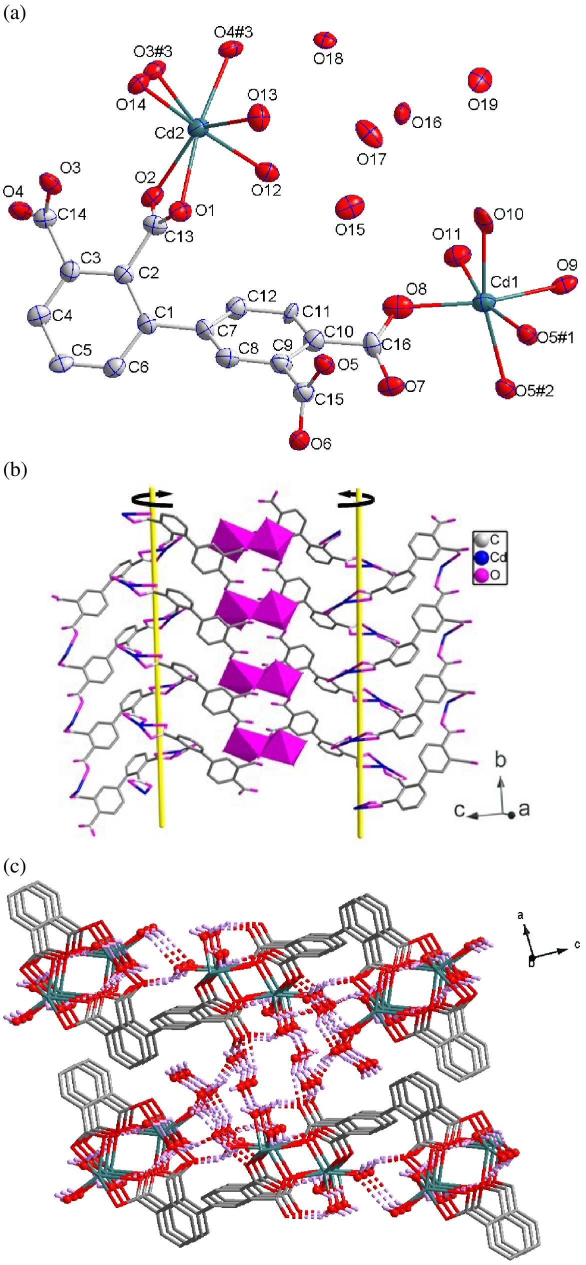
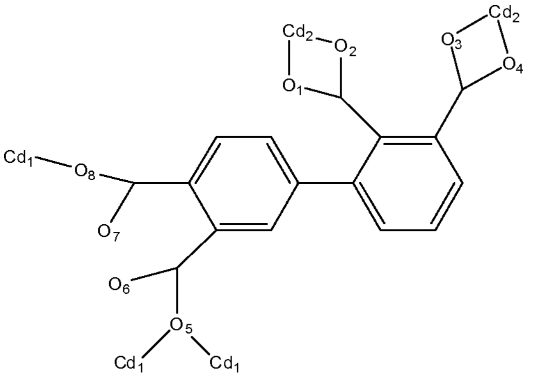


Fig. 1. (a) The connectivity pattern in the asymmetric unit of complex **1** (all hydrogen atoms omitted for clarity); (b) layer structure formed by binuclear Cd clusters and m-bptc^{4-} anions parallel to the *bc* plane; (c) 3D metal-organic framework formed by hydrogen bonding interactions.



Scheme 1. The coordination mode of the m-bptc^{4-} ligand in complex **1**.

molecules. The coordination geometry for the seven-coordinate Cd2 is close to pentagonal bipyramidal with Cd2–O bonds ranging from 2.047 to 2.409 Å, including four oxygen atoms of two chelating carboxylate groups (2-COO$^-$ and 3-COO$^-$) from two neighboring bptc^{4-} ligands and three oxygen atoms from water molecules. The crystal structure of complex **1** exhibits a 2D network composed of binuclear Cd1 cluster nodes as well as left- and right-handed helical chains containing the Cd2 ions (Fig. 1b).

As to the m-bptc^{4-} ligand, the dihedral angle between two phenyl rings is 48.9°, the four carboxylate groups (2-, 3′-, 3-, and 4′-COO$^-$) have dihedral angles of 58.8, 61.8, 74.5, and 34.1° towards the plane of the corresponding phenyl rings. The 3′-COO$^-$ and 4′-COO$^-$ groups in the anion m-bptc^{4-} have a dihedral angle of 65.85°, and a dramatic twisting is observed between 2-COO$^-$ and 3-COO$^-$ groups with the dihedral angle of 44.1°. This twisting leads to chiral helical chains.

The 2- and 3-COO$^-$ bidentate groups of the m-bptc^{4-} ligand chelate two adjacent Cd2 ions (Scheme 1) to form two types of helical chains with opposite chirality (Fig. 1b). The helices occur in equal numbers due to the centrosymmetric space group. The 3′- and 4′-COO$^-$ groups are monocoordinated to three different Cd1 ions, but O5 of the 3′-COO$^-$ group bridges two adjacent Cd1 ions (Scheme 1) to form a ribbon of binuclear Cd1 clusters (Fig. 1b). However, the two types of helical chains containing Cd2 ions are further bridged by the ribbon containing the Cd1 clusters to produce an interesting 2D layer structure. The screw axes of these helices are all parallel to the crystallographic *b*axis, and the opposite chirality helices are arranged in an alternate fashion so that the layer is achiral in general, as shown in Fig. 1b.

At the same time, six coordinated water molecules of each asymmetric unit of complex **1** form a rich hydrogen-bonding network including the carboxylate oxygen atoms, the coordinated and the solvate water molecules. The five solvate water molecules form a water cluster $(H_2O)_5$ which fills the space between adjacent layers with inter- and intralayer hydrogen bonds. The hydrogen bonds exist not only among the $(H_2O)_5$ cluster but also between the $(H_2O)_5$ cluster and the coordinated water molecules and the carboxylate oxygen atoms to form a 3D metal-organic framework, as shown in Fig. 1c. The hydrogen bond lengths (Å) and angles (deg) are listed in Table 3.

*Thermogravimetric analysis of complex **1***

The thermogravimetric analysis (TGA) was conducted to determine the thermal stability of this complex, which is an important aspect for metal-organic frameworks. TGA was performed on crystalline samples of **1** in the range of 25 ∼ 700 °C. The results have indicated that a weight loss of 28.0 % below 132 °C corresponds to the loss of solvent and coordinated water molecules per formula unit (calcd. 28.4 %), and that the framework collapsed in the temperature range of 340 – 530 °C.

*Photoluminescence properties of complex **1***

The photoluminescence properties of complex **1** were studied in the solid state at room temperature. The complex shows luminescence with an emission maximum at 399 nm upon excitation at 360 nm. The emission can probably be assigned to the intraligand (π-π^*) fluorescent emission because similar emissions are observed at 392 nm for the free m-H_4bptc ligand and at 406 nm for the reported complex $[Cd_2$(m-bptc)(4,4-bpy)$_{0.5}(H_2O)_4]\cdot H_2O$ [9]. The shift of the emission of complex **1** is probably due to the difference of the coordination environment around the metal ions.

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[1] a) R. J. Hill, D.-L. Long, N. R. Champness, P. Hubberstey, M. Schröder, *Acc. Chem. Res.* **2005**, *38*, 337; b) D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, *36*, 770; c) R. Robson, *Dalton Trans.* **2008**, 5113.

[2] a) B. F. Abrahams, M. Moylan, S. D. Orchard, R. Robson, *Angew. Chem.* **2003**, *115*, 1892; *Angew. Chem. Int. Ed.* **2003**, *42*, 1848; b) Q. Ye, X.-S. Wang, H. Zhao, R.-G. Xiong, *Chem. Soc. Rev.* **2005**, *34*, 208; c) R. A. Fischer, C. Wöll, *Angew. Chem.* **2008**, *120*, 8285; *Angew. Chem. Int. Ed.* **2008**, *47*, 8164.

[3] a) E. K. Brechin, *Chem. Commun.* **2005**, 5141; b) X.-Y. Wang, Z.-M. Wang, S. Gao, *Chem. Commun.* **2008**, 281; c) J.-P. Zhang, X.-M. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 5516.

[4] a) J. D. Watson, F. H. C. Crick, *Nature* **1953**, *171*, 737; b) D. A. Rusling, V. E. C. Powers, R. T. Ranasinghe, Y. Wang, S. D. Osb, T. Brown, K. R. Fox, *Nucleic Acids Res.* **2005**, *33*, 3025; c) K. M. Vasquezez, L. Narayanan, P. M. Glazer, *Science* **2000**, *290*, 530.

[5] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469; b) M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; c) Y. Qi, Y. Wang, C. Hu, M. Cao, L. Mao, E. Wang, *Inorg. Chem.* **2003**, *42*, 8519.

[6] C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466.

[7] a) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su, C.-W. Hu, *Angew. Chem.* **2004**, *116*, 5146; *Angew. Chem. Int. Ed.* **2004**, *43*, 5036; b) X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li, Z.-M. Su, *Chem. Commun.* **2005**, 5450.

[8] a) S.-Q. Zang, Y. Su, Y.-Z. Li, Z.-P. Ni, Q.-J. Meng, *Inorg. Chem.* **2006**, *45*, 174; b) S.-Q. Zang, Y. Su, Y.-Z. Li, Z.-P. Ni, Q.-J. Meng, *Inorg. Chem.* **2006**, *45*, 2972.

[9] S.-Q. Zang, Y. Su, Y.-Z. Li, Z.-P. Ni, H.-Z. Zhu, Q.-J. Meng, *Inorg. Chem.* **2006**, *45*, 3855.

[10] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; *ibid.* **2008**, *A64*, 112.