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Journal of Molecular Structure 796 (2006) 119–122
Journal of MOLECULAR STRUCTURE
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Self-assembly of alternating left- and right-handed infinite Cd(II) helicates into a 2D open framework structure

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Received 19 January 2006; received in revised form 31 January 2006; accepted 2 February 2006
Available online 27 March 2006

Abstract

Pyrazine-2,3,5,6-tetracarboxylic acid ($ptcH_4$) reacts with $Cd(NO_3)_2 \cdot 6H_2O$ at room temperature in the presence of pyridine to form a 2D open framework built from alternating left- and right-handed helicates with the empirical formula, $\{[Cd_2(ptc)\cdot(py)_5\cdot H_2O]\cdot 5H_2O\cdot py\}_n$, **1**. Lattice water and pyridine molecules form an intricate array of H-bonding with the 2D sheets leading to a 3D structure. This compound crystallizes in the monoclinic space group $C2/c$ with the following lattice parameters—$a=24.103(2)$, $b=13.480(5)$, $c=29.176(4)$ Å, $\beta=109.427(3)°$, $V=8940(4)$ Å^3, $Z=8$, $R1=0.0513$, $wR2=0.1552$, $S=1.085$.

Keywords: X-ray crystallography; Supramolecular chemistry; Self-assembly; Metal-organic framework; Helical structure

1. Introduction

Self-assembled helical structures are essence of life and are of interest in supramolecular chemistry because helical structures are reminiscent of DNA structures. Due to the important roles of helicity in biology as well as in advanced materials, helical organic, inorganic and metal-organic hybrid compounds continue to attract a lot of attention [1–3]. In the field of coordination chemistry, multidentate chelate ligands have been used with great success for this purpose [4]. The propensity for forming coordination polymers in the form of helicates depends on the stereoelectronic molecular information encoded in the ligand and reading of this information by metal ions under suitable experimental conditions. While coordination polymers are of great current interest in the field of catalysis and biology as well as in the development and understanding of self-assembly processes [5–10]. Helical coordination networks in particular, are of great interest owing to their potential utility in chiral separation, asymmetric catalysis and non-linear optical applications [11–13]. We present here, a 2D coordination polymer containing alternate left-handed and right-handed infinite helical structures.

2. Experimental

2.1. General

The metal salts and phenazine were acquired from Aldrich and used as received. Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320; X-ray powder pattern (Cu Kα radiation at a scan rate of 3°/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator; thermogravimetric analysis (heating rate of 5 °C/min) Perkin-Elmer Pyris 6. Microanalyses for the compounds were obtained from the Central Drug Research Institute, Lucknow, India.

2.1.1. Synthesis of pyrazine-2,3,5,6-tetracarboxylic acid ($ptcH_4$)

This compound was synthesized in 55% yield by oxidation of phenazine with aqueous $KMnO_4$.

2.1.2. Synthesis of $\{[Cd_2(ptc)\cdot(py)_5\cdot H_2O]\cdot 5H_2O\cdot py\}_n$, **1**

Reaction of $Cd(NO_3)_2\cdot 4H_2O$ (0.62 g; 2 mmol) and pyrazine-2,3,5,6-tetracarboxylic acid ($ptcH_4$) (0.26 g; 1 mmol) dissolved in 25 mL aqueous pyridine (1:1 v/v) to obtain a colorless solution. After filtering the solution, the filtrate is allowed to evaporate at room temperature whereupon colorless crystals of **1** appeared after 10 days in the form of rectangular parallelopiped in 65% yield. Anal. Calcd for $C_{38}H_{37}N_8O_{14}Cd_2$ (1054.56): C, 43.27; H, 3.53; N, 10.62%. Found: C, 43.32; H, 3.55; N, 10.68%.

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doi:10.1016/j.molstruc.2006.02.008

2.2. X-ray crystallography

Single crystal X-ray data on **1** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT [14] software. An empirical absorption correction was applied to the collected reflections with SADABS [15] using XPREP [16]. The structure was solved by the direct method using SHELXTL [17] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97 [18] program package. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The crystal and refinement data are collected in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, 293349 for **1**. Copies of this information may be obtained free of charge at 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 336066; e-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

Compound $\{[Cd_2(ptc)\cdot(py)_5\cdot H_2O]\cdot 5H_2O\cdot py\}_n$, (**1**) is readily formed by reacting a Cd(II) salt with pyrazine-2,3,5,6-tetracarboxylic acid (ptcH$_4$) at room temperature in presence of pyridine in 65% yield. Once formed, it is stable in air and insoluble in water as well as common organic solvents. High yield of the product indicates that it is thermodynamically stable under the prevailing reaction condition.

Table 1
Crystal and structure refinement data for **1**

Empirical formula	$C_{38}H_{37}Cd_2N_8O_{14}$
Formula weight	1054.56
Temperature	100 K
Radiation, wavelength	Mo Kα, 0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	24.103(2)
b (Å)	13.480(5)
c (Å)	29.176(4)
β (°)	109.427(5)
U (Å^3)	8940(4)
Z	8
ρ_{calc} (Mg/m^3)	1.567
μ (mm^{-1})	1.023
F(000)	4232
Refl. collected	29,394
Independent refl.	9314
Refinement method	Full-matrix least-squares on F^2
GOOF	1.085
Final *R* indices	$R1 = 0.0513$
$[I > 2\sigma(I)]$	$wR2 = 0.1552$
R indices	$R1 = 0.0606$
(All data)	$wR2 = 0.1619$

Table 2
Selected bond distances (Å) and bond angles (°) in **1**

Cd1 OW6 2.304(3)	Cd1 N4 2.306(4)
Cd1 N3 2.334(4)	Cd1 N1 2.369(3)
Cd1 O1 2.438(3)	Cd1 O3 2.492(3)
Cd1 O1 2.493(3)	Cd2 N7 2.328(4)
Cd2 N6 2.338(4)	Cd2 N5 2.346(4)
Cd2 O6 2.427(3)	Cd2 O7 2.446(3)
Cd2 O8 2.505(4)	Cd2 O5 2.515(3)
OW6 Cd1 N4 92.04(14)	OW6 Cd1 N3 87.25(14)
N4 Cd1 N3 174.23(13)	OW6 Cd1 N1 142.24(13)
N4 Cd1 N1 92.93(13)	N3 Cd1 N1 91.13(13)
OW6 Cd1 O1 81.59(12)	N4 Cd1 O1 85.75(12)
N3 Cd1 O1 88.49(12)	N1 Cd1 O1 136.11(11)
OW6 Cd1 O3 75.63(11)	N4 Cd1 O3 90.94(13)
N3 Cd1 O3 94.42(13)	N1 Cd1 O3 66.89(11)
O1 Cd1 O3 156.85(10)	OW6 Cd1 O1 150.24(11)
N4 Cd1 O1 85.48(12)	N3 Cd1 O1 92.29(12)
N1 Cd1 O1 67.51(11)	O1 Cd1 O1 68.66(11)
O3 Cd1 O1 133.98(10)	N7 Cd2 N6 90.80(14)
N7 Cd2 N5 177.72(14)	N6 Cd2 N5 91.40(14)
N7 Cd2 O6 90.88(12)	N6 Cd2 O6 91.80(13)
N5 Cd2 O6 89.63(12)	N7 Cd2 O7 89.19(12)
N6 Cd2 O7 82.32(13)	N5 Cd2 O7 90.54(12)
O6 Cd2 O7 174.11(12)	N7 Cd2 O8 91.70(12)
N6 Cd2 O8 135.57(13)	N5 Cd2 O8 86.32(12)
O6 Cd2 O8 132.49(11)	O7 Cd2 O8 53.39(12)
N7 Cd2 O5 83.56(12)	N6 Cd2 O5 144.37(12)
N5 Cd2 O5 94.96(12)	O6 Cd2 O5 53.32(11)
O7 Cd2 O5 132.50(11)	O8 Cd2 O5 79.90(11)

The asymmetric unit of **1** consists of two Cd(II), one *ptc*$^{4-}$, six pyridine and six water molecules. Its structure can be described as a 2D coordination polymer consisting of two different types of hepta-coordinated Cd(II) centers with pentagonal bipyramidal geometry (Fig. 1). The equatorial coordination to Cd(1) ion is provided by two carboxylate O and ring N on one side of the ligand, a bridging carboxylate O from the neighboring ligand and a water molecule.

The two axial sites on the metal are occupied by two pyridine molecules. The Cd(2) ion is equatorially coordinated to two

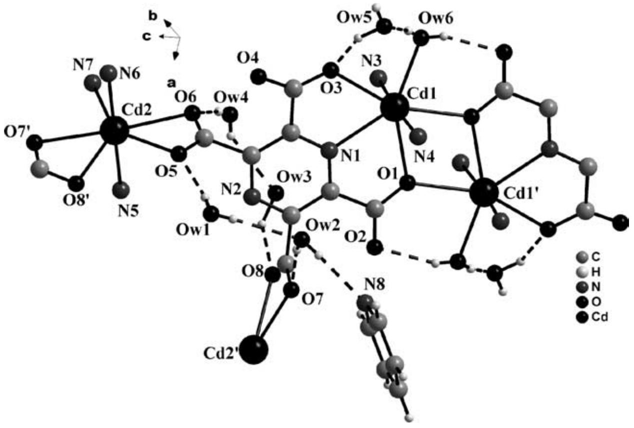

Fig. 1. An illustration showing the binding mode of the ligands with metals and presence of three different type of water dimeric clusters.

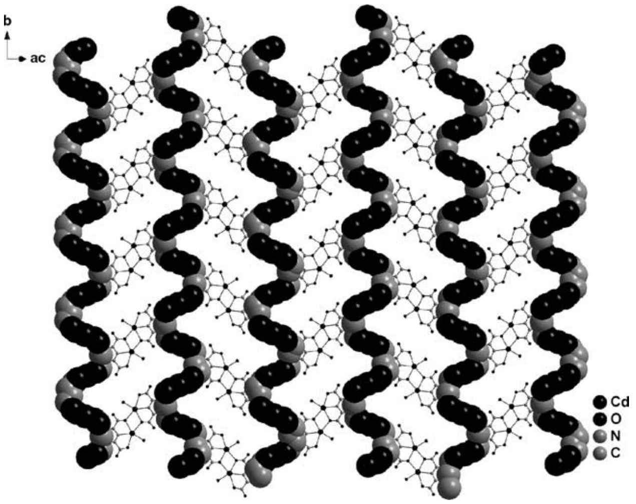

Fig. 2. The 2D structure including two types of helical chains.

Table 3
Geometrical parameters of hydrogen-bonds (Å, °) of the three different dimers in **1**

Ow1···Ow2	2.909(1)	Ow1–H···Ow2	168.02(6)
Ow3···Ow4	2.770(3)	Ow4–H···Ow3	144.37(2)
Ow5···Ow6	2.684(2)	Ow6–H···Ow5	160.77(3)
Ow1···O5	2.905(4)	Ow1–H···O5	168.02(2)
Ow2···O7	2.892(2)	Ow2–H···Ow2	168.02(4)
Ow2···N8	2.864(2)	Ow2–H···N8	175.03(3)
Ow3···O8	2.941(3)	Ow3–H···O8	145.06(2)
Ow4···O8	2.846(3)	Ow4–H···O6	172.43(2)
Ow5···O4	2.754(2)	Ow5–H···O4	159.31(3)
Ow5···O3	2.790(3)	Ow5–H···O3	148.83(4)
Ow6···O2	2.790(3)	Ow6–H···O2	161.25(2)

carboxylate O from two different *ptc*$^{4-}$ ligands in the bi-dentate fashion and one pyridine molecule. The two axial sites are again occupied by two pyridine molecules. Two Cd(1) ions form a carboxylate-bridged dimer. All Cd–O and Cd–N bond distances are within normal ranges as found in other Cd(II) complexes [19]. The same ligand and other similar ligands systems are also used to make many MOF structures [20].

The Cd(2) ions are arranged in infinite helices in spite of the fact that the ligand has no intrinsic tendency to form such structures. The Cd(1) dimers are present in between two helicates to make the 2D sheet structure (Fig. 2). Interestingly, the structure shows alternate right- and left-handed helical chains extending along the crystallographic *b* axis (Fig. 2). The helical structure is a result of metal–ligand interactions coupled with stereoelectronic characteristics of the ligand and the conditions prevailing during the synthesis. The stability of the final helical structure relies on the coordinate bonds that each metal makes with the ligand. An inspection of the structure of **1** leads to the belief that the metal coordinated pyridine molecules play key roles in the formation of the helices by acting as structure-directing agents to induce a helical array. The width of each helix is calculated to be 13.5 Å and the pitch is 10.4 Å with two Cd(2) ions per turn at a distance of 7.87 Å, while the distance between Cd ions in two helices are either 16.477 or 17.426 Å. Both the width and the pitch are large that is a result of the topology of the ligand and the electrostatic repulsive interactions among Cd(III) ions. Similar kind 2D structure with both left- and right-handed helicate are reported [3,4c]. In one report [3], they synthesized a layered coordination polymer of Co(II) containing two helical chains and the resultant crystals were not racemic as evidenced by the observation of strong signals in vibrational circular dichroism (VCD) spectra. In other report [4c], carboxylate-bridged two terpyridine complex are reported. Three different types of water dimers present in the lattice are involved in H-bonding interactions (Table 3) with free

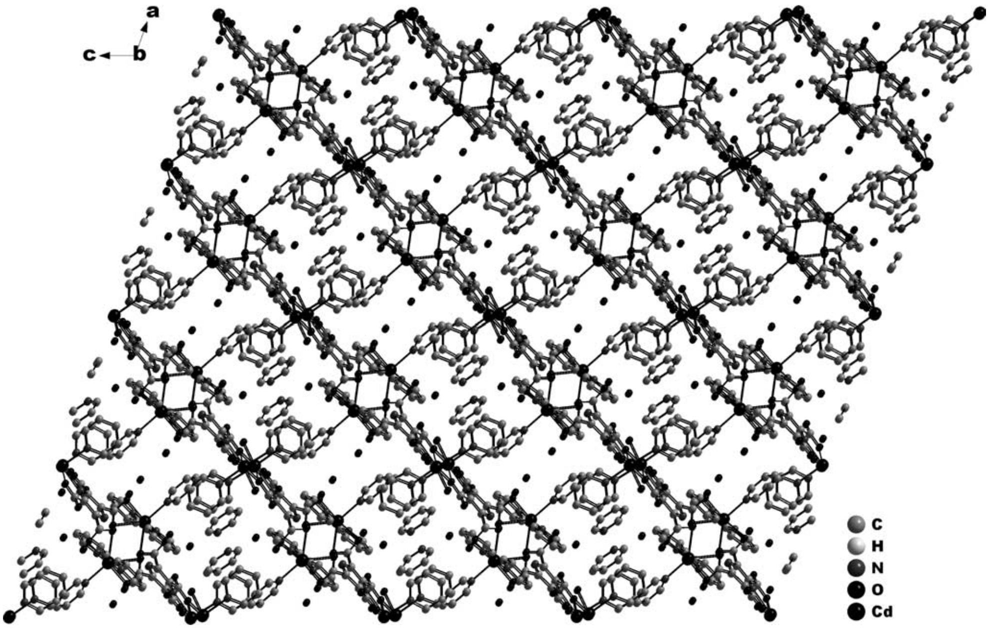

Fig. 3. A view of the overall 3D structure of **1** omitting H atoms for clarity.

carboxylate O of the sheet structures leading to a 3D motif (Fig. 3).

Thermal gravimetric analyses performed under N_2 atmosphere show that the compound **1** lost the encapsulated free water and pyridine molecule within 200 °C. The FTIR spectrum of **1** shows a broad band centered around $3500\ \mathrm{cm}^{-1}$ due to water molecules that vanishes on heating the compound under vacuum (0.1 mm) at 180 °C for 2 h. Powder X-ray diffraction patterns of **1** show changes in peak positions as well as their intensities before and after water expulsion although sharp peaks remain in the diffraction pattern indicating a crystalline solid remains after water and pyridine expulsion.

4. Conclusions

The structure of the compound **1** reported herein not only contains helical chains but also possess left- and right-handed helical chains in one compound. The structures of the compound reported here show that infinite single helical chains can be constructed with simpler ligand.

Acknowledgements

We gratefully acknowledge the financial support received from the Department of Science and Technology, New Delhi, India (to P.K.B.) and Council of Scientific and Industrial Research, New Delhi, India for a SRF to S.G.

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