Hydrothermal Synthesis, Crystal Structure and Properties of a Novel 3D Metal-Organic Cd(II) Coordination Polymer Based on Helical Units

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A metal-organic framework based on 4-methylphthalic acid (H_2L) and 4,4′-bipyridine (bpy), namely $\{[Cd(L)(bpy)_{1.5}]\cdot 2(H_2O)\}_n$ (**1**), has been synthesized hydrothermally and characterized by IR spectroscopy, elemental analysis, thermogravimetry, and single-crystal X-ray crystallography. Complex **1** exhibits a 3D coordination network based on layers. Each layer consists of left- or right-handed $\{Cd\text{-}L\text{-}Cd\text{-}bpy\text{-}Cd\text{-}L\text{-}Cd\text{-}bpy\}_n$ double helices. Water molecules are also incorporated in the network. Compound **1** shows fluorescence at *ca.* 360 nm upon excitation at 304 nm.

Key words: 4-Methylphthalic Acid, Cd(II) Coordination Polymer, Double-helical Chain, Fluorescence

Introduction

The investigation of coordination polymers has achieved remarkable progress in the last decade, not only for intriguing structural and topological diversities, but also for their diverse applications in gas storage, molecular separations, ion exchange, luminescence, and catalysis [1 – 13]. Helical assemblies such as protein bundles and DNA are prevalent in biological systems and play key roles in molecular recognition, replication, and catalysis [14]. This has prompted the synthesis of artificial helical structures [15 – 17]. Generally, there are two methods to build a helical structure: one is the possibility of introducing chiral centers in ligands, and the other is the use of achiral ligands for spontaneous resolution without any chiral auxiliaries. The latter one has been proved to be much more difficult to achieve helical structures [18].

Many coordination polymers have been constructed from aromatic di- and tri-carboxylate ligands such as isophthalate [19], 1,2,3-benzenetricarboxylate [20 – 23], or 1,3,5-benzenetricarboxylate [24 – 29]. Compared with these multicarboxylic acids, 4-methylphthalic acid (H_2L) has remained largely unexplored in the construction of metal-organic frameworks [30, 31]. Many coordination polymers based on helical units using analogous benzene- and naphthalene-based dicarboxylic acids and neutral dipyridyl-type coligands have been reported [32 – 35], while helical architectures based on 4-methylphthalic acid are very rare. The use of auxiliary nitrogen containing ligands is also an effective method for framework formation of coordination polymers. Neutral dipyridyl-type coligands, such as 4,4′-bipyridine (bpy), can pillar dicarboxylate coordination polymer motifs into higher dimensions, and the structural diversity and utility of these phases can then be enhanced [36 – 40].

With the aim of constructing unusual coordination architectures, we began to study the reactions of versatile H_2L and 4,4′-bipyridine mixed ligands with cadmium salts. In this paper, we report the synthesis, structure, thermogravimetric analysis (TGA), and photoluminescence properties of $\{[Cd(L)(bpy)_{1.5}]\cdot 2(H_2O)\}_n$ (**1**), which exhibits a new 3D coordination network built up from layers constructed from alternating double-helical chains and linked by the bpy ligands.

Experimental Section

Materials and measurements

Reagents purchased commercially were used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range

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

Empirical formula	$C_{24}H_{22}CdN_3O_6$
Formula weight	560.85
Crystal color and habit	colorless block
Crystal size, mm^3	$0.20 \times 0.18 \times 0.18$
Temperature, K	293(2)
Crystal system	monoclinic
Space group	$C2/c$
a, Å	20.6101(6)
b, Å	11.7137(3)
c, Å	20.2991(7)
β, deg	107.481(3)
V, Å^3	4674.3(2)
Z	8
D_{calcd}, g cm^{-3}	1.60
μ(MoK_α), mm^{-1}	1.0
F(000), e	2264
θ range data collection, deg	3.14 – 25.00
Reflns. collected / independent / R_{int}	9600 / 4099 / 0.0294
Index ranges *hkl*	$-22 \le h \le 24$, $-13 \le k \le 13$, $-24 \le l \le 22$
Param. refined	316
$R1$[a] /$wR2$[b] [$I > 2\,\sigma(I)$]	0.0385 / 0.1085
$R1$[a] /$wR2$[b] (all data)	0.0477 / 0.1143
GoF[c] (F^2)	1.06
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.95 / −0.95

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; [c] $\mathrm{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

from 4000 to 400 cm^{-1} on a Nicolet NEXUS 470-FTIR spectrometer. Thermal analysis was performed on a SDT 2960 thermal analyzer from room temperature to 800 °C with a heating rate of 20 °C min^{-1} under nitrogen flow. Luminescence spectra of solid samples were recorded on a FluoroMax-4 spectrofluorometer.

*Preparation of {[Cd(L)(bpy)$_{1.5}$]·2(H$_2$O)}$_n$ (**1**)*

A mixture of 4-methylphthalic acid (H_2L) (0.009 g, 0.05 mmol), 4,4′-bipyridine (0.012 g, 0.075 mmol), $Cd(NO_3)_2{\cdot}4H_2O$ (0.012 g, 0.05 mmol), and NaOH (0.004 g, 0.1 mmol) in distilled water (7 mL) was placed in a Teflon-lined stainless-steel container, heated to 120 °C for 3 d, and then cooled to room temperature. Colorless block-like single crystals of **1** were obtained in 65 % yield based on Cd. Anal. for $C_{24}H_{22}CdN_3O_6$ (560.85): calcd. C 51.40, H 3.95, N 7.49; found C 51.46, H 4.14, N 7.42. – IR (KBr, cm^{-1}): ν = 3372 (m), 1605 (w), 1532 (s), 1414 (s), 1219 (m), 1068 (w), 1042 (w), 1004 (w), 849 (w), 808 (m), 624 (w), 501 (w).

Crystallographic studies

Single-crystal X-ray diffraction data of complex **1** was collected on a Bruker Smart Apex CCD diffractometer [40] with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. An empirical absorption correction was applied to the intensities using the program SADABS [41]. The structure was solved using the program SHELXS-97 [42, 43] and refined with SHELXL-97 [44, 45]. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms of the organic ligands were included in the structure factor calculation in idealized positions using a riding model and refined isotropically. The hydrogen atoms of the coordinated and solvate water molecules were located from difference Fourier maps, and then restrained at fixed positions and refined isotropically. Space group, lattice parameters and other relevant information are listed in Table 1. The relevant bond lengths and bond angles are listed in Table 2.

CCDC 888389 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

Spectroscopic studies

In the IR spectrum of complex **1**, the observed strong and broad peak at 3372 cm^{-1} is attributed to

Cd(1)–N(1)	2.456(3)	Cd(1)–N(2)$^{\#1}$	2.437(3)
Cd(1)–N(3)	2.334(3)	Cd(1)–O(1)$^{\#2}$	2.351(3)
Cd(1)–O(2)$^{\#2}$	2.431(2)	Cd(1)–O(3)	2.262(1)
Cd(1)–O(4)	2.578(1)		
O(3)–Cd(1)–N(3)	122.9(2)	O(3)–Cd(1)–O(1)$^{\#2}$	135.82(14)
N(3)–Cd(1)–O(1)$^{\#2}$	94.43(11)	O(3)–Cd(1)–O(2)$^{\#2}$	87.8(2)
N(3)–Cd(1)–O(2)$^{\#2}$	148.59(11)	O(1B)–Cd(1)–O(2)$^{\#2}$	54.88(10)
O(3)–Cd(1)–N(2)$^{\#1}$	81.8(3)	N(3)–Cd(1)–N(2)$^{\#1}$	78.50(12)
O(1)$^{\#2}$–Cd(1)–N(2)$^{\#1}$	83.89(11)	O(2)$^{\#2}$–Cd(1)–N(2)$^{\#1}$	101.97(11)
O(3)–Cd(1)–N(1)	119.3(3)	N(3)–Cd(1)–N(1)	83.96(12)
O(1)$^{\#2}$–Cd(1)–N(1)	84.24(11)	O(2)$^{\#2}$–Cd(1)–N(1)	86.15(11)
N(2)$^{\#1}$–Cd(1)–N(1)	157.94(12)	O(3)–Cd(1)–O(4)	55.7(3)
N(3)–Cd(1)–O(4)	84.1(2)	O(1)$^{\#2}$–Cd(1)–O(4)	162.88(19)
O(2)$^{\#2}$–Cd(1)–O(4)	123.0(2)	N(2)$^{\#1}$–Cd(1)–O(4)	112.35(17)
N(1)–Cd(1)–O(4)	78.64(19)		

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

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

the O–H stretching vibration of the water molecules. The absence of strong bands ranging from 1690 to 1710 cm^{-1} indicates the complete deprotonation of the substituted phthalate dicarboxylic acid moieties. The IR spectrum of the title compound also shows characteristic asymmetric (1605 and 1532 cm^{-1}) and symmetric stretching band (1414 cm^{-1}) of the carboxylate groups. All these agree well with the result of the crystal structure analysis.

Description of the crystal and molecular structure of $\{[Cd(L)(bpy)_{1.5}]\cdot 2(H_2O)\}_n$ ***(1)***

The asymmetric unit of **1** contains one crystallographically unique Cd(II) cation, one dianion L^{2-}, one and a half bpy ligands, and two solvent water molecules (Fig. 1). The Cd1 ion is in a distorted pentagonal-bipyramidal coordination environment, with O1#2, O2#2, O3, O4, and N3 in an equatorial plane, while N1 and N2#1 occupy the axial positions with an N1–Cd1–N2#1 angle of 157.9°. The Cd–O and Cd–N distances are in the range of 2.262 – 2.578 and 2.334 – 2.456 Å, respectively. All bond lengths compare well with CSD averages of similar structures. Selected bond lengths and angles of complex **1** are listed in Table 2. The L^{2-} ligand adopts the bis-bidentate bis-chelating mode linking adjacent Cd atoms to produce an infinite zig-zag chain along the *b* axis. Such chains are cross-linked by bpy ligands (N1–N2) to give rise to a two-dimensional bilayer motif, as shown in Fig. 2. The L^{2-} and bpy ligands link the Cd atoms to form a right-handed double helical chain extending along the *b* axis with the pitch length at 23.4 Å based on the repeating unit containing

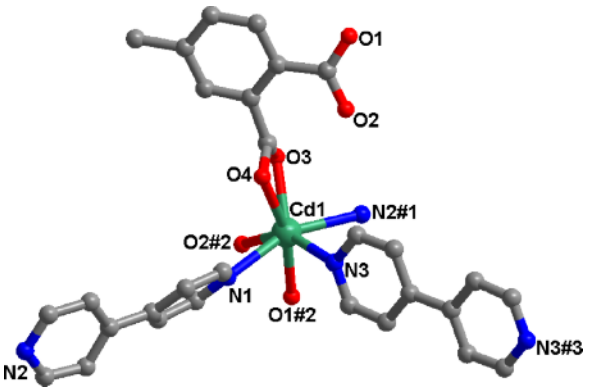

Fig. 1 (color online). Metal coordination and atom labeling in complex **1**. All hydrogen atoms and water molecules are omitted for clarity. Symmetry codes: $^{\#1}$ $x-1/2, y+1/2, z$; $^{\#2}$ $-x+1/2, y-1/2, -z+1/2$; $^{\#3}$ $-x+1/2, -y+5/2, -z$.

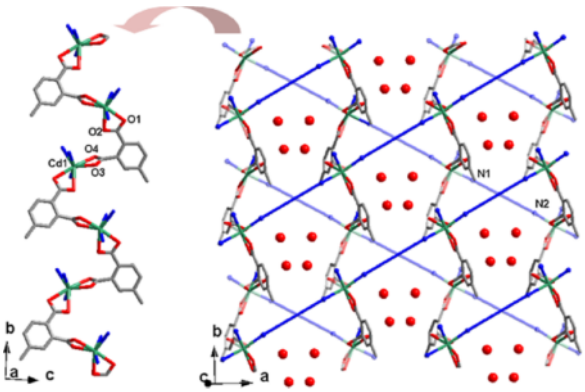

Fig. 2 (color online). Left: view of a zig-zag chain along the *b* axis of **1**; right: view of a bilayer connected by bpy (N1–N2) ligands in the crystal structure of **1**. All irrelevant atoms are omitted for clarity.

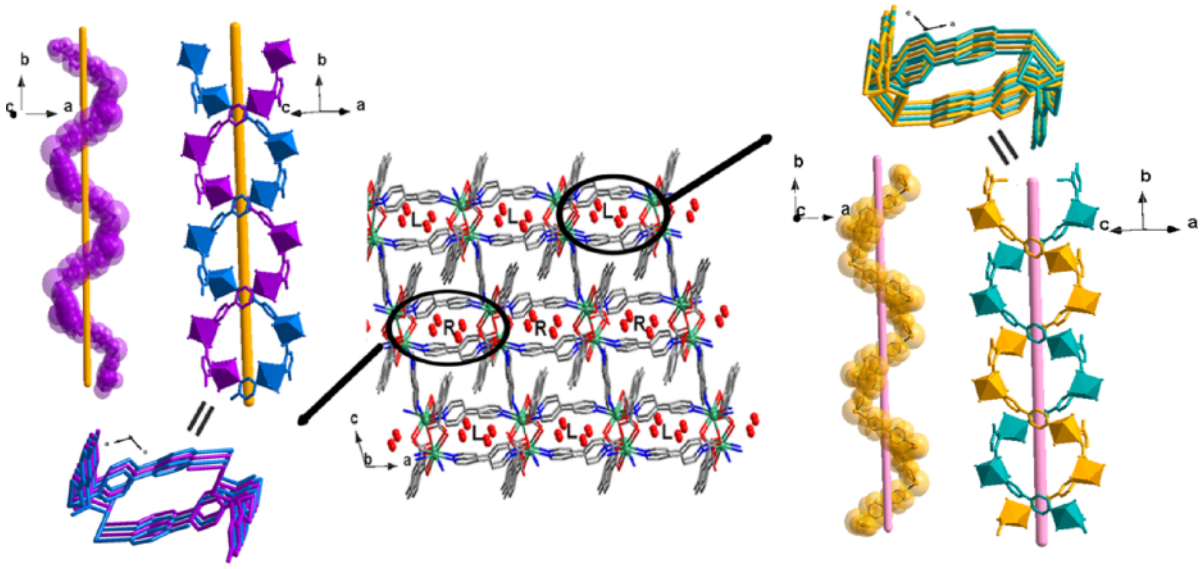

Fig. 3 (color online). 3D Framework of **1** connected by bpy (N3–N3#3) ligands showing its chiral layers and micropores. Schematic representations of right-handed (left) and left-handed (right) double helices.

four metal centers, two L^{2-} and two bpy ligands. Adjacent right-handed double helical chains share zig-zag chains developing homochiral helical two-dimensional sheets. Notably, each double-helix constructs a parallel channel in which the free water molecules are filled, as illustrated in Fig. 3. Contrarily, its adjacent sheets are made up of left-handed double helical chains with the same pitch as the former right-handed double helical chain. Adjacent layers possess opposite chirality. The layers with opposite chirality are cross-linked by the second type of bpy (N3–N3#3) ligands which act as pillars, to give a 3D framework (Fig. 3). In the reported two examples of cadmium polymers, $[Cd(HPT)_2(4,4'\text{-bpy})]_n$ [32] (PTZ = phthalate) and $\{[Cd(ndc)(bpp)_2](H_2O)_3\}$ [33] (ndc = naphthalene-2,3-dicarboxylate, bpp = 1,3-bis(4-pyridyl)propane), the complexes exhibit homochiral three-dimensional coordination architectures constructed by an alternating assembly of vertical chiral layers or chiral chains using achiral bridging ligands. However, in this case, the alternating horizontal layers possess opposite chirality forming an achiral 3D array.

*Thermal analysis of complex **1***

Thermogravimetric analysis (TGA) was conducted to study the thermal stability of the title complex, which is an important aspect of metal-organic frameworks. TGA was performed on crystalline samples of **1** in the range of 30 – 800 °C, as depicted in Fig. 4. The TGA curve of **1** has two major degradation steps in the range 30 – 800 °C. The first weight loss of 6.6 % occurs between 29 and 157 °C (calcd: 6.4 %), corresponding to the loss of the two water molecules per formula unit. Then, a plateau region is observed from 157 to 264 °C. The host framework starts to decompose above 264 °C.

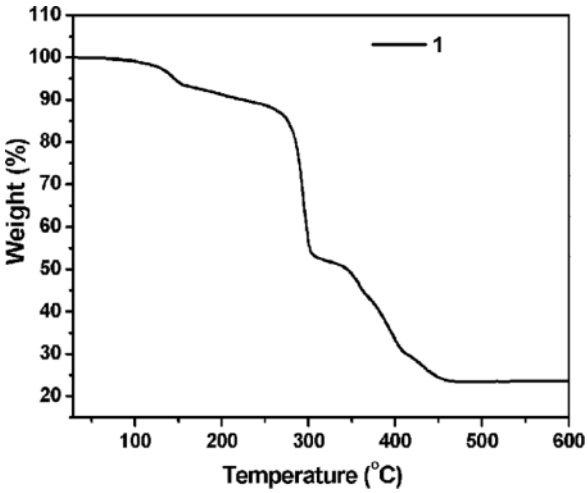

Fig. 4. Thermogravimetric analysis (TGA) curve for **1**.

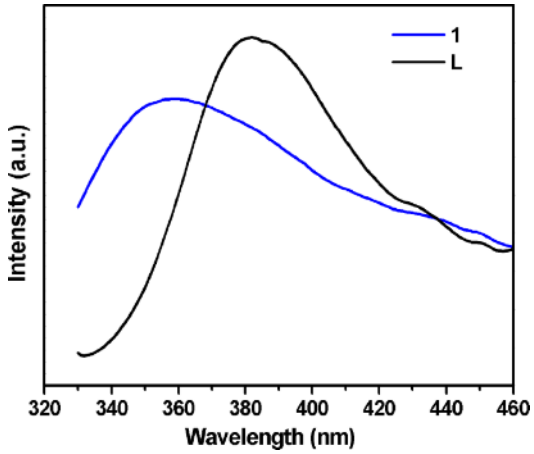

Fig. 5 (color online). The emission spectra of **1** and the free ligand (H_2L) in the solid state at room temperature.

*Luminescence properties of complex **1***

Luminescent compounds composed of d^{10} metal centers and organic ligands are of great interest because of their potential applications in the areas of chemical sensors and photochemistry. These crystalline solids usually display regular photoluminescence properties. Therefore, in the present work, the luminescence properties of compound **1** and the free ligand H_2L were investigated in the solid state at room temperature. As shown in Fig. 5, complex **1** exhibits photoluminescence with an emission maximum at *ca.* 360 nm upon excitation at 304 nm. The emission for complex **1** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Cd^{2+} ions are difficult to oxidize or to reduce due to their d^{10} configuration, and can probably be assigned to the intraligand (π–π^*) fluorescent emission because similar emissions are observed for the free ligand at 382 nm ($\lambda_{ex} = 300$ nm). The blue shift of emission in **1**, compared with the free ligand, is probably due to the complexation together with the fact that complex **1** is more rigid than the free ligand, reducing the loss of energy by radiationless decay.

Conclusions

In summary, a new cadmium coordination network containing left- and right-handed double helices has been synthesized by the self-assembly of 4-methylphthalic acid (H_2L) with 4,4′-bipyridine and cadmium nitrate in aqueous alkaline solution. The double-helical structure builds up chiral channels which are filled by water solvate molecules. Adjacent layers possess opposite chirality so that the compound is overall achiral. Our studies not only further confirm that the 4-methylphthalate ligand is a favorable building block for coordination polymers, but also illustrate the influence of the auxiliary ligands on the structure. Moreover, complex **1** displays an optical emission and may be an candidate for luminescent materials.

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