Synthesis, Crystal Structure and Fluorescence of Two Novel Mixed-Ligand Cadmium Coordination Polymers with Different Structural Motifs

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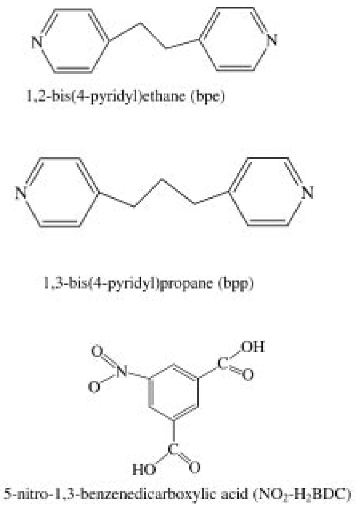
Two novel cadmium(II) coordination compounds, [Cd(bpe)$_{1.5}$(NO$_2$-BDC)]·0.25H$_2$O (**1**) and [Cd(bpp)(NO$_2$-BDC)(H$_2$O)]·0.25H$_2$O (**2**) [NO$_2$-BDCH$_2$ = 5-nitro-1,3-benzenedicarboxylic acid, bpe = 1,2-bis(4-pyridyl)ethane, bpp = 1,3-bis(4-pyridyl)propane] have been hydrothermally synthesized by reaction of cadmium chloride and NO$_2$-BDC with the homologous ligands bpe and bpp, respectively. The former compound displays a remarkable three-dimensional architecture sustained by the catenation of 2D bilayers, while the latter exhibits a unique twofold interpenetrating three-dimensional architecture. The thermal and fluorescence properties associated with their crystal structures have been measured.

Introduction

Polymeric coordination compounds have recently received much attention due to their interesting potential applications and various coordination architectures,[1,2] in which supramolecular polymeric architectures containing topological bonds, such as polycatenanes and polyrotaxanes, are of special interest for chemists.[3,4] The structural topology of coordination polymers can be specially designed by the careful selection of the coordination geometry of the metals, the structure of the spacer ligands, the counteranions, and the reaction conditions.[5−7] To date, of diverse elegant efforts to find key factors in the development of the polymers, the main rational synthetic strategy has been the use of unique spacer ligands where the network topology can be controlled and modified by changing the chemical structure of the organic ligand.[8,9] *N*,*N*′-bipyridine-type ligands are convenient linkers for constructing metal-organic frameworks, and a wide range of one-, two-, and three-dimensional coordination polymers has been generated with them.[10−12] At the same time, phenyldicarboxylates, which can serve as bifunctional ligands, have been effectively utilized to build coordination networks.[13,14] We anticipated using the mixed phenyldicarboxylate/*N*,*N*′-bipyridine-type ligand system [(NO$_2$-BDC)/(bpe or bpp); Scheme 1] to generate some coordination polymers with interesting topologies. Here, we report the crystal structure and fluorescence properties of two novel mixed organic ligand coordination polymers [Cd(bpe)$_{1.5}$(NO$_2$-BDC)]·0.25H$_2$O (**1**) and [Cd(bpp)(NO$_2$-BDC)(H$_2$O)]·0.25H$_2$O (**2**).


1,2-bis(4-pyridyl)ethane (bpe)

1,3-bis(4-pyridyl)propane (bpp)

5-nitro-1,3-benzenedicarboxylic acid (NO$_2$-H$_2$BDC)

Scheme 1.

Results and Discussion

1,2-Bis(4-pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (bpp) were selected as starting materials as they have different linkers between the two pyridine rings and show different structures. The two *N*,*N*′-bipyridine-type ligands react with NO$_2$-BDC (NO$_2$-BDCH$_2$ = 5-nitro-1,3-benzene-

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dicarboxylic acid) and a cadmium salt under the same reaction conditions. The two *N*,*N*′-bipyridine-type ligands have different structures, which finally results in different coordination frameworks as in **1** and **2**.

Crystal Structures

Single-crystal X-ray diffraction revealed a unique 2D bilayer structure of **1** with molecular formula $[Cd(bpe)_{1.5}(NO_2\text{-}BDC)_2]\cdot 0.25H_2O$. Each Cd^{II} center is heptacoordinated with a distorted $\{CdN_3O_4\}$ pentagonal bipyramidal coordination sphere, as shown in Figure 1. Four oxygen atoms belonging to two chelating didentate carboxylate groups from two NO_2-BDC moieties and one nitrogen atom from a bpe molecule coordinate to the cadmium center in the equatorial plane, with two nitrogen atoms from another two bpe ligands located at the axial positions of the coordination sphere. The Cd−O distances range from 2.322(10) to 2.599(9) Å, and the Cd−N distances are 2.328(13) and 2.345(12) Å. All the bpe ligands adopt an *anti* conformation and link the cadmium(II) ions into a $[Cd(bpe)_{1.5}]_n$ ladder as shown in Figure 2. The bpe ligands adopt two ligand conformations (A and B) in the ladder: the sides of the ladder adopt conformation A (bpe^A), with a dihedral angle of the two pyridyl rings of 44.1°; the rungs of the ladder adopt conformation B (bpe^B), where the two pyridyl rings are coplanar. The NO_2-BDC ligand acts as a μ_2-bridge through two chelating didentate carboxylate groups to link the ladders into a 2D bilayer (Figure 3). As seen in Figure 3b, the bpe^A and NO_2-BDC moieties in the also the link the cadmium ions into a (4,4) net sheet where the bpe^B ligands act as pillars forming bilayer galleries in which the planar sheets separated by them define 1D channels with dimensions of 13.848×14.054 Å^2. In the 2D bilayer structure of **1**, a cuboidal box containing eight cadmium(II) ions at the corners, connected by four short NO_2-BDC and eight long bpe linkers, making up the 12 edges, forms the fundamental building unit of **1** (Figure 4). This cuboidal structural motif is clearly different from the tetrahedral building blocks used to form other bilayer structures.[15,16] Interpenetration occurs in **1**, and each bilayer is interlocked by two adjacent identical frameworks (the upper and the lower identical motifs) as seen in Figure 5. This threefold interpenetration means that the void volume in **1** is very small; it is filled by the free water molecules. The resulting 3D array is, therefore, an infinite catenane of decked layers of an unprecedented interwoven type.

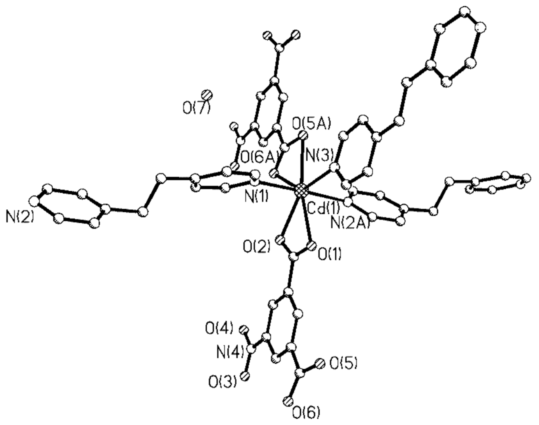
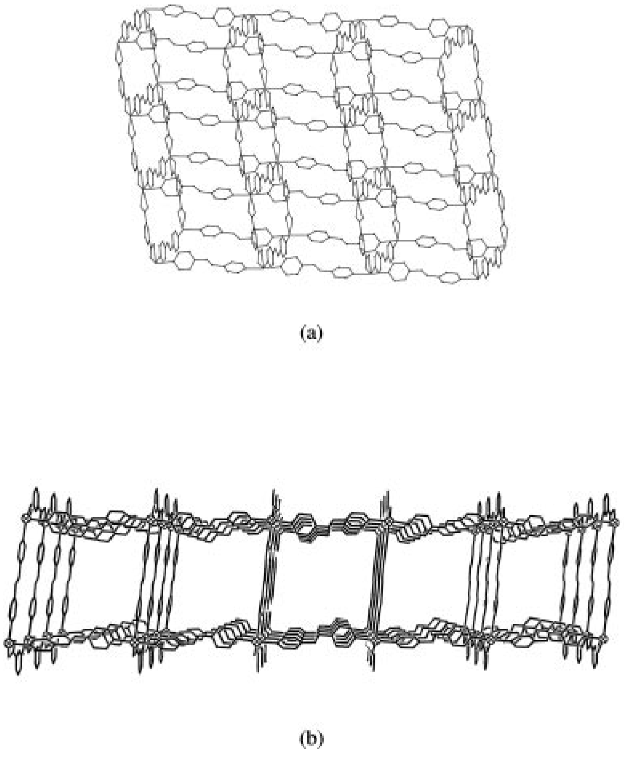


Figure 1. Perspective view of the coordination environment of the cadmium atom in **1**


(a)

(b)

Figure 3. View of the 2D bilayer of **1**: a) along the *b* axis to show the rectangular channels; b) along the *a* axis

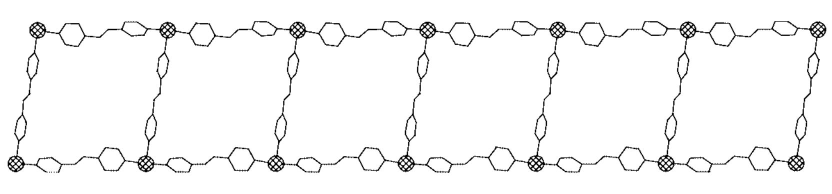


Figure 2. View of the $[Cd(bpe)_{1.5}]_n$ ladder in **1**

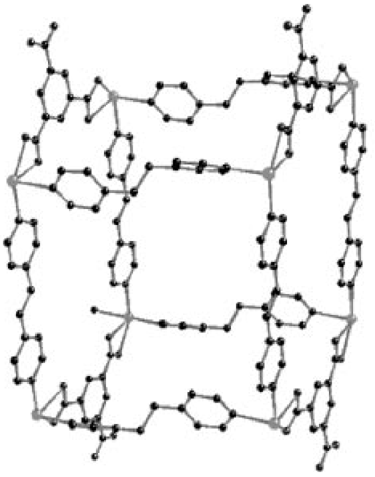


Figure 4. View of the cuboidal structural motif in **1**

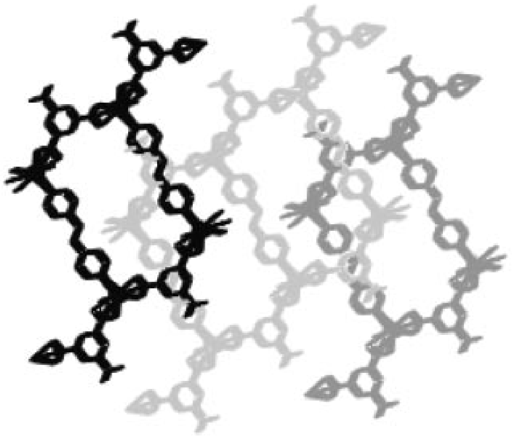


Figure 5. View of the interpenetration in **1**

The structure of **2** is a remarkable extended three-dimensional framework with molecular formula [Cd(bpp)(NO_2-BDC)(H_2O)]·0.25H_2O, in which the cadmium(II) atoms are bridged by mixed NO_2-BDC and bpe ligands. The asymmetric unit contains one cadmium(II) atom, one coordinated NO_2-BDC molecule, one coordinated bpp molecule, one coordinated water molecule and 0.25 free water molecules. All the Cd atoms are equivalent and each cadmium center is six-coordinate in a distorted octahedral geometry. Three carboxylate oxygens (O1, O2 and O3a) belonging to one chelating didentate carboxylate group, a monodentate carboxylate group from two NO_2-BDC molecules and one pyridyl N atom from a bpe ligand coordinate to the Cd center in the equatorial plane with *cis*-bond angles around the Cd center ranging from 54.2(2) to 128.9(2)°; the water molecule (O7) and another pyridyl N atom (N2b) from one bpe ligand are located at the axial positions of the distorted octahedral coordination sphere of Cd, with an O7−Cd−N2b bond angle of 167.7(2)° as shown in Figure 6. The Cd−$O_{carboxylate}$ distances range from 2.204(5) to 2.450(6) Å, and the Cd−N distances are 2.284(6) and 2.330(7) Å. Two NO_2-BDC and four bpp ligands link six Cd atoms to form a Cd_6 ring, which may be taken as the basic building block for the whole 3D framework of **2** (Figure 7). In the Cd_6 ring, the bpp ligands separate the Cd atoms at a distance of 11.598 Å; the two pyridine rings in dpp are almost perpendicular (dihedral angle of 97.2°), which is very different from the values found in **1** (44.1° or 0°). At the same time, the two pyridine rings coordinated to the same Cd atom are also almost perpendicular (dihedral angle of 79.4°). The Cd_6 rings are fused to form the ultimate unique 3D framework of **2**, which contains large channels with dimensions of 17.814 × 6.596 Å^2 (Figure 8). The 3D networks interlock with each other displaying a twofold-interpenetrating mode, which means that the void volume in **2** is very small; it is filled by the free water molecules (Figure 9).

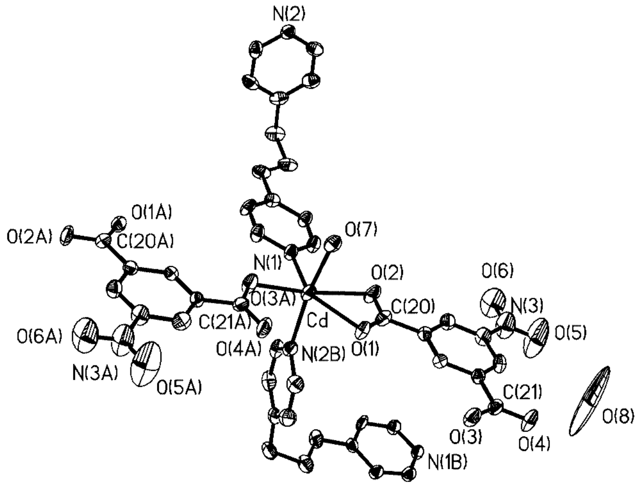


Figure 6. Perspective view of the coordination environment of the cadmium atom in **2**

IR Spectroscopy

The IR spectra of the two compounds show the characteristic bands of the dicarboxylate groups of NO_2-BDC at 1150−1620 cm^{-1} for the asymmetric vibration and at 1390−1420 cm^{-1} for the symmetric vibration. The absence of the expected absorption at 1690−1730 cm^{-1} for the protonated carboxylate groups illustrates the complete deprotonation of NO_2-BDC in the reaction with cadmium.[17]

Thermal and Fluorescent Properties

To study the thermal stability of the two compounds, thermogravimetric analysis (TGA) was performed on them. The TGA results of the two compounds are similar and show a very slow and gradual release of 0.25 water molecules in the 40−135 °C temperature range for **1** and 0.25 water molecules over the temperature range 35−120 °C for **2**. No obvious decomposition was observed until about 410 °C. Compounds **1** and **2** begin to decompose at 418 °C and 426 °C, respectively.

Metal-organic polymer compounds with a d^{10} configuration (such as Zn^{2+} and Cd^{2+}) have been found to exhibit photoluminescent properties,[18,19] and Zaworotko and co-

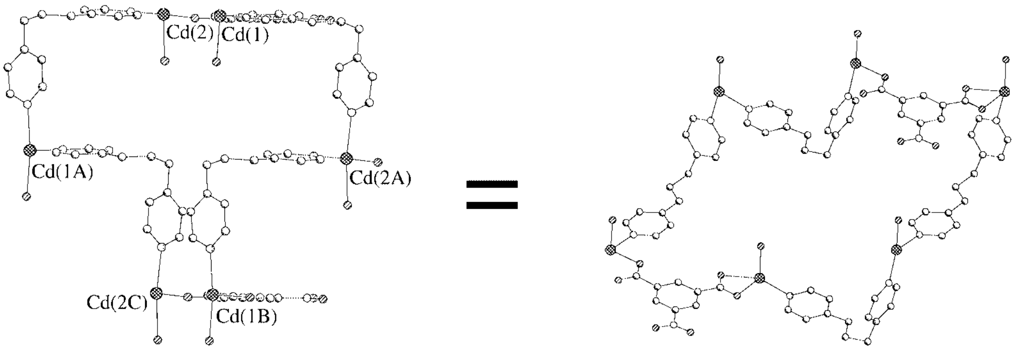


Figure 7. View of the Cd_6 ring in **2**

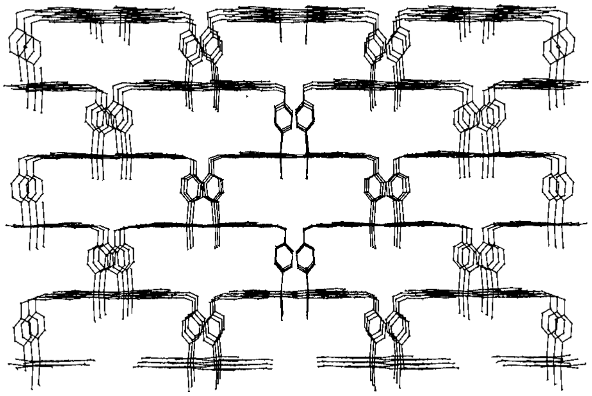


Figure 8. View of the 3D framework in **2** with large channels

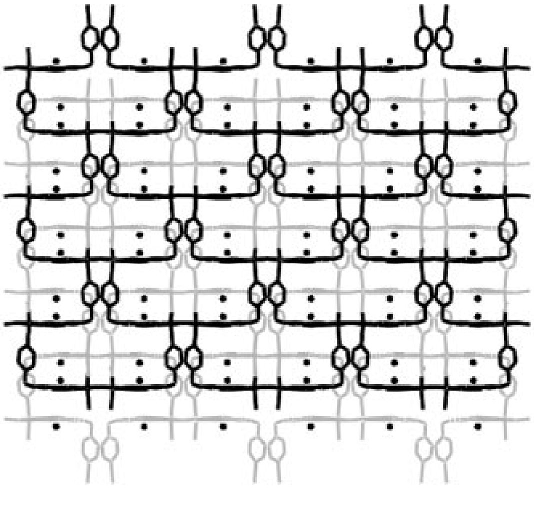
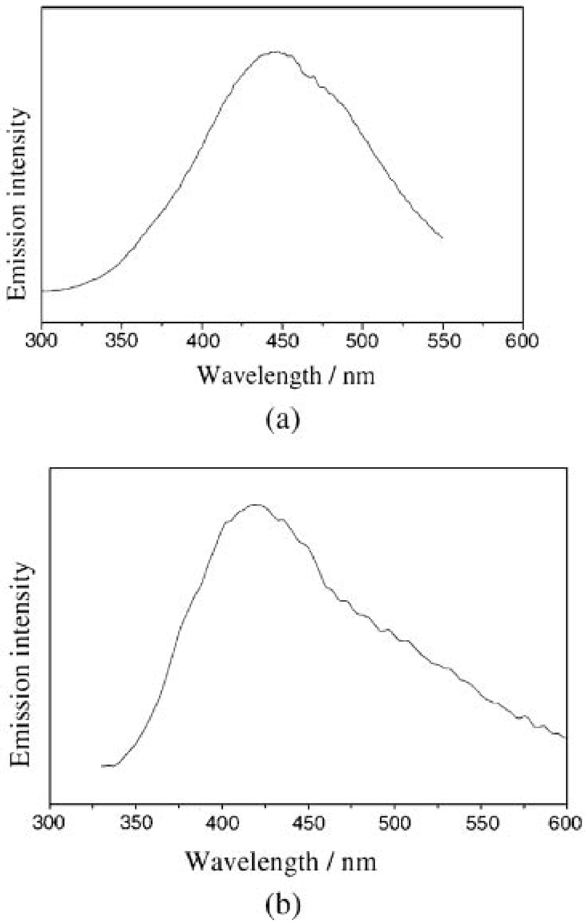


Figure 9. View of the interpenetration in **2** and the free water molecules in the void volumes

workers recently reported the first coordination polymer that traps a fluorescent guest.[20] Here, we want examine the photoluminescence of **1** and **2**. The solid-state emission spectra of complexes **1** and **2** at room temperature are shown in Figure 10. It can be seen that the maximum of the emission bands of **1** is located at 435 nm (λ_{ex} = 280 nm), while **2** also exhibits an intense photoluminescence emission at 439 nm (λ_{ex} = 310 nm). These emissions bands may be due to σ-donation from the cooperation of NO_2-BDC and bpp or bpe to the Cd center,[18a] and may be assigned to the ligand-to-metal charge-transfer (LMCT) band.[18,19] It is noticeable that **1** and **2** exhibit quenching of the fluorescence, with τ = 3.45 ns for **1** and τ = 3.64 ns for **2**.



(a)

(b)

Figure 10. Solid-state emission spectra of the two compounds at room temperature: a) compound **1**; b) compound **2**

Although **1** and **2** have different structural motifs, it is interesting to note that they exhibit similar thermal behaviors and emission bands. As the thermal behaviors and photoluminescence behaviors are closely associated with the metal ions and ligands coordinated around them, we need to compare the coordination environments of the Cd ions in **1** and **2**. The Cd atom in **1** has two chelating bis-didentate carboxylate groups and three bpp ligands, and in **2** there is one chelating bis-didentate carboylate group, one monodentate carboxylate group, and two bpp ligands. These similar environments may be the reason for the similar thermal and fluorescence behaviors of **1** and **2**.

Conclusion

Two coordination polymers formed by a cadmium salt and NO_2-BDC with the homologous ligands bpe and bpp have been prepared and characterized. Because of the different structures of the selected organic ligands (bpe for **1** and bpp for **2**), complex **1** exhibits a remarkable three-dimensional architecture sustained by the catenation of 2D bilayers, while complex **2** displays a unique twofold interpenetrating three-dimensional structural motif. Because of interpenetration, the two compounds all have small void volumes filled by free water molecules. They have similar thermal behaviors and fluorescence spectra.

Experimental Section

General: $CdCl_2 \cdot 2.5H_2O$ and NO_2-BDC were purchased commercially and used without further purification. The bpe and bpp were purchased from Fluka. C, H and N analyses were determined on a Perkin−Elmer 240C analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer in the range 200−4000 cm^{-1}. Thermogravimetric analyses were performed on a NETSCHZ STA-449C thermoanalyser under N_2 (26−750 °C range) at a heating rate of 10 °C/min. Fluorescent characterization was performed on an Edinburgh F900 analytical instrument at Fuzhou University**.** Fluorescence spectra of the solid samples were obtained by direct front-face emission from the solid powder bonded to a quartz support oriented at 40° to both the excitation and emission light paths, with excitation at 280 nm for **1** and 310 nm for **2**.

$[Cd(bpe)_{1.5}(NO_2\text{-}BDC)] \cdot 0.25H_2O$ (1): The pH value of an aqueous mixture (10 mL) containing NO_2-BDC (0.5 mmol), $CdCl_2 \cdot 2.5H_2O$ (0.5 mmol) and bpe (0.5 mmol) was pre-adjusted to about 6 with a 0.1 M aqueous NaOH solution. The mixture was then transferred into an Teflon-lined, stainless-steel autoclave (18 mL), and the vessel was sealed and heated to 180 °C for 72 h, then cooled to room temperature at a rate of 10 °C/h. Colorless crystals of **1** were obtained (0.165 g, 82%). $C_{26}H_{21.5}CdN_4O_{6.25}$ (602.4): calcd. C 51.80, H 3.57, N 9.30; found C 51.41, H 3.62, N 9.24.

$[Cd(bpp)(NO_2\text{-}BDC)(H_2O)] \cdot 0.25H_2O$ (2): The pH value of an aqueous mixture (10 mL) containing NO_2-BDC (0.5 mmol), $CdCl_2 \cdot 2.5H_2O$ (0.5 mmol) and bpp (0.5 mmol) was pre-adjusted to about 6 with a 0.1 M aqueous NaOH solution. The mixture was then transferred into an Teflon-lined, stainless-steel autoclave (18 mL), and the vessel was sealed and heated to 180 °C for 72 h, then cooled to room temperature at a rate of 10 °C/h. Colorless crystals of **2** were obtained (0.213 g, 78%). $C_{21}H_{19.55}CdN_3O_{7.25}$ (542.3): calcd. C 46.47, H 3.60, N 7.74; found C 45.02, H 3.67, N 7.65.

Table 1. Crystallographic data for the compounds **1** and **2**

	1	**2**
Empirical formula	$C_{26}H_{21.5}CdN_4O_{6.25}$	$C_{21}H_{19.5}CdN_3O_{7.25}$
Molecular weight	602.37	542.3
Space group	$P\bar{1}$	$C2/c$
a (Å)	10.2414(8)	14.4774(1)
b (Å)	10.9924(8)	18.3603(6)
c (Å)	13.8482(9)	17.2732(4)
α (°)	109.940(3)	90
β (°)	99.410(3)	105.561(2)
γ (°)	109.142(3)	90
V (Å^3)	1316.3(2)	4423.1(2)
Z	2	8
d_{calcd}, (Mg·m^{-3})	1.520	1.629
μ(Mo-K_α), (mm^{-1})	0.877	1.036
F(000)	607	2180
Reflections collected	3148	4582
Independent reflections	1672	2072
Parameters	343	298
Goodness-of-fit on F^2	1.120	1.129
R_1 indices [$I > 2\sigma(I)$]	0.0553	0.0425
wR_2 indices (all data)	0.1435	0.1113

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

$[Cd(bpe)_{1.5}(NO_2\text{-}BDC)_2] \cdot 0.25H_2O$ (**1**)[a]			
Cd(1)−N(2b)	2.328(13)	Cd(1)−N(1)	2.361(12)
Cd(1)−N(3)	2.345(12)	Cd(1)−O(2)	2.322(10)
Cd(1)−O(1)	2.599(9)	Cd(1)−O(6a)	2.315(11)
Cd(1)−O(5a)	2.592(10)		
O(6a)−Cd(1)−O(2)	85.0(5)	N(3)−Cd(1)−O(5a)	85.1(5)
O(6a)−Cd(1)−N(2b)	96.6(6)	N(1)−Cd(1)−O(5a)	96.3(4)
O(2)−Cd(1)−N(2b)	92.1(4)	O(6a)−Cd(1)−O(1)	137.8(4)
O(6a)−Cd(1)−N(3)	136.9(5)	O(2)−Cd(1)−O(1)	52.8(4)
O(2)−Cd(1)−N(3)	138.0(5)	N(2b)−Cd(1)−O(1)	85.4(5)
N(2b)−Cd(1)−N(3)	86.6(5)	N(3)−Cd(1)−O(1)	85.3(5)
O(6a)−Cd(1)−N(1)	89.2(5)	N(1)−Cd(1)−O(1)	89.8(4)
O(2)−Cd(1)−N(1)	87.8(4)	O(5a)−Cd(1)−O(1)	168.5(4)
O(6a)−Cd(1)−O(5a)	52.3(4)	N(2b)−Cd(1)−N(1)	174.1(6)
O(2)−Cd(1)−O(5a)	136.9(5)	N(3)−Cd(1)−N(1)	89.5(5)
N(2b)−Cd(1)−O(5a)	87.8(5)		
$[Cd(bpp)(NO_2\text{-}BDC)(H_2O)] \cdot 0.25H_2O$ (**2**)[b]			
Cd−O(3a)	2.204(5)	Cd−N(2b)	2.330(7)
Cd−N(1)	2.284(6)	Cd−O(1)	2.340(5)
Cd−O(7)	2.326(5)	Cd−O(2)	2.450(6)
O(3a)−Cd−N(1)	90.1(2)	N(1)−Cd−O(1)	141.0(2)
O(3a)−Cd−O(7)	86.4(2)	O(7)−Cd−O(1)	84.99(19)
N(1)−Cd−O(7)	96.8(2)	N(2b)−Cd−O(1)	84.7(2)
O(3a)−Cd−N(2b)	94.9(2)	O(3a)−Cd−O(2)	173.1(2)
N(1)−Cd−N(2b)	95.4(2)	N(1)−Cd−O(2)	86.9(2)
O(7)−Cd−N(2b)	167.7(2)	O(7)−Cd−O(2)	87.86(19)
O(3a)−Cd−O(1)	128.9(2)	N(2b)−Cd−O(2)	91.5(2)
O(1)−Cd−O(2)	54.17(19)		

[a] Symmetry codes: (a) $x - 1, y, z$; (b) $x, y, z + 1$. [b] Symmetry codes: (a) $x, -y, z + 1/2$; (b) $x - 1/2, -y + 1/2, z - 1/2$.

X-ray Crystallography: Single crystals of **1** and **2** were selected for an X-ray diffraction study. The unit-cell parameters and intensities were collected at 299 K on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073Å) and a graphite monochromator using the ω-scan mode. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXTL software suite.[21] All non-hydrogen atoms were refined anisotropically. All H-atoms were located theoretically and not refined. A summary of the crystallographic data of **1** and **2** is presented in Table 1, with selected bond lengths and angles in Table 2.

CCDC-203638 (**1**) and -203639 (**2**) contain the supplementary crystallographic data for this paper. These data can 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: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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