Novel Cadmium(II) Adipate Coordination Polymers with Structural Transformation via Oxalate Ligand: Syntheses, Structures and Fluorescence Properties

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Two novel cadmium adipate coordination polymers $[Cd\{O_2C(CH_2)_4CO_2\}\{1,10\text{-phen}\}]_n$ (**1**) and $[Cd_2(C_2O_4)\{O_2C(CH_2)_4CO_2(OH_2)_2\}\{2,2'\text{-bipy}\}]\cdot H_2O$ (**2**) [adipic acid = $HO_2C(CH_2)_4CO_2H$] have been hydrothermally synthesized and characterized by elemental analyses, IR spectroscopy, thermogravimetric analysis and single-crystal X-ray diffraction. Crystallographic data for **1**: monoclinic, $C2/c$, a = 16.186(3) Å, b = 15.487(3) Å, c = 14.052(3) Å, β = 112.73(3)°, Z = 8. Crystal data for **2**: monoclinic, Cc, a = 23.448(5) Å, b = 11.826(2) Å, c = 8.3163(17) Å, β = 99.08(3)°, Z = 4. The structural analysis reveals that **1** forms a novel one-dimensional chain in which the binuclear Cd centers are linked by adipate anions. Compound **2** is the first example in which both a 2,2′-bipy ligand and an oxalate group are found in the {M/adipate} system. Compound **2** possesses one-dimensional sine- or cosine-type chains, which are alternately connected together by the oxalate group to form a three-dimensional framework. The structural determination reveals that the introduction of the oxalate ligand causes the dimensional transformation of the compounds. Compounds **1** and **2** show strong fluorescent properties at room temperature.

Introduction

Research on metal-templated coordination polymers with different dimensions is of current interest in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also because of their potential applications due to their unique electro-conductive, nonlinear optical and magnetic properties.[1−6] In this respect, the selection of inorganic and organic building blocks possessing specific features to fulfil special needs of transition metals, such as versatile binding modes and coordination abilities to form hydrogen bonding, is the key to the construction of a desired framework.[7,8] It is noteworthy that dicarboxylates such as malonate, fumarate and 1,4-benzenedicarboxylate have been widely used in constructing novel different dimensional metal-organic hybrid compounds.[9] In contrast, the dicarboxylate ligand adipate has rarely been used. There are at least three intriguing structural features of the adipate ligand. In the first place, it contains two bridging moieties, which leads to a variety of connection modes with transitional metal centers and provides abundant structural motifs. In the second place, it can act both as a hydrogen-bond donor and acceptor. And finally, it contains six carbon atoms that may construct high dimensional and pore structures. Although several interesting compounds containing adipate have been reported by Jung, Ribas, Bakalbassis and their co-workers,[10] the introduction of chelating ligands containing N- or O-donors, such as 2,2′-bipy, 1,10-phen and oxalate anion ($C_2O_4^{2-}$), to the {M/adipate} system has not been explored hitherto. A chelating N-containing ligand usually inhibits the expansion of polymeric frameworks due to the "passivation" of the metal sites by the N donors of the organic groups, which may decrease the dimensionality of these metal-organic hybrid compounds.[11,12] However, the O-containing ligand $C_2O_4^{2-}$ has more geometrical coordination modes to provide both rigidity and preferred coordination specificity for metal centers,[7] thus making it easier to form 1-D chains and thereby allow the formation of higher-dimensional frameworks. Taking into account these factors, we became motivated to design and synthesize novel metal-organic coordination polymers containing adipate and one or more kind of organic ligands containing N- or O-donors under hydrothermal conditions.

In this paper, we report two novel cadmium-containing coordination polymers $[Cd\{O_2C(CH_2)_4CO_2\}\{1,10\text{-phen}\}]_n$ (**1**) and $[Cd_2(C_2O_4)\{O_2C(CH_2)_4CO_2(OH_2)_2\}\{2,2'\text{-bipy}\}]\cdot H_2O$ (**2**). Compounds **1** and **2** possess different dimensionality due to the introduction of the oxalate ligand. Compound **1**

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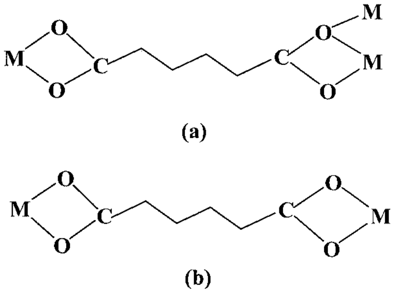
exhibits an interesting 1-D chain in which the binuclear Cd centers are linked by adipate anions. Compound **2** not only has 1-D sine- or cosine-type chains, but also exhibits a novel three-dimensional framework in which the sine- and cosine-type curves are connected alternately by oxalate anions along the *c* axis. Furthermore, both compounds show intense fluorescence at room temperature.

Results and Discussion

The hydrothermal reaction of a solution of $Cd(NO_3)_2{\cdot}4H_2O$, adipic acid, 1,10-phenanthroline (1,10-phen), NaOH and H_2O gives rise to **1** as colorless crystals. Single crystal X-ray diffraction analysis reveals that **1** is a 1-D chain-like polymer with one crystallographically unique Cd center in the asymmetric unit (see Figure S1 in the Supporting Information). The Cd(1) site coordinates to two nitrogen atoms of one 1,10-phen group and five carboxyl oxygen atoms of different adipate ligands. The average Cd−N bond length is 2.346 Å and the $Cd-O_{(carboxyl)}$ bond lengths are in the range 2.289(2)−2.587(3) Å. The N(O)−Cd−O(N) bond angles range from 80.65(9)° to 153.85(10)° (see Table S2 in the Supporting Information). Thus, the Cd center displays a distorted pentagonal bipyramidal geometry to form one $[CdO_5N_2]$ unit. Two such $[CdO_5N_2]$ units are connected together by μ_3-O atoms in an edge-sharing mode to form dinuclear Cd centers. In addition, two carboxylate groups of the adipate ligand exhibit two kinds of coordination modes with Cd centers (see a in Scheme 1) — one carboxylate group acts as a bis-chelating ligand to bridge one Cd center, while the other exhibits an unusual bidentate bridging mode to link two Cd centers. Thus, one adipate ligand is connected to three different Cd centers, which has not been observed previously. To the best of our knowledge, this is the first example for adipate anions in which the carboxylates exhibit a bis-chelating and bidentate bridging mode toward metal centers. On the basis of this connection mode, all dinuclear Cd centers are linked by four bridging adipate ligands to form a 1-D chain along the *a* axis (see Figure 1). In contrast to the reported compounds in the {M/adipate} (M = transition metal ions) system, compound **1** is the first dinuclear compound connected by mixed adipate and 1,10-phen ligands. In the packing arrangement of **1**, the adjacent 1-D chains are parallel to each other and construct a 2-D framework through π-π interactions between the aromatic groups of the 1,10-phen ligands.[13a] The narrowest interplanar distance of the aromatic units is about 3.41 Å. Adjacent 2-D frameworks are further connected together to form a 3-D network by hydrogen-bonding interactions. The π-π interactions and the hydrogen bonds enhance the stability of the compound.

Valence-sum calculations give a value of 1.92 for the Cd atom, indicating that the Cd center is in the +2 oxidation state. Atoms O(1)−O(4) have bond-valence sums of 1.66,



Scheme 1. Coordination modes of the adipate ligand in compounds **1** (a) and **2** (b)

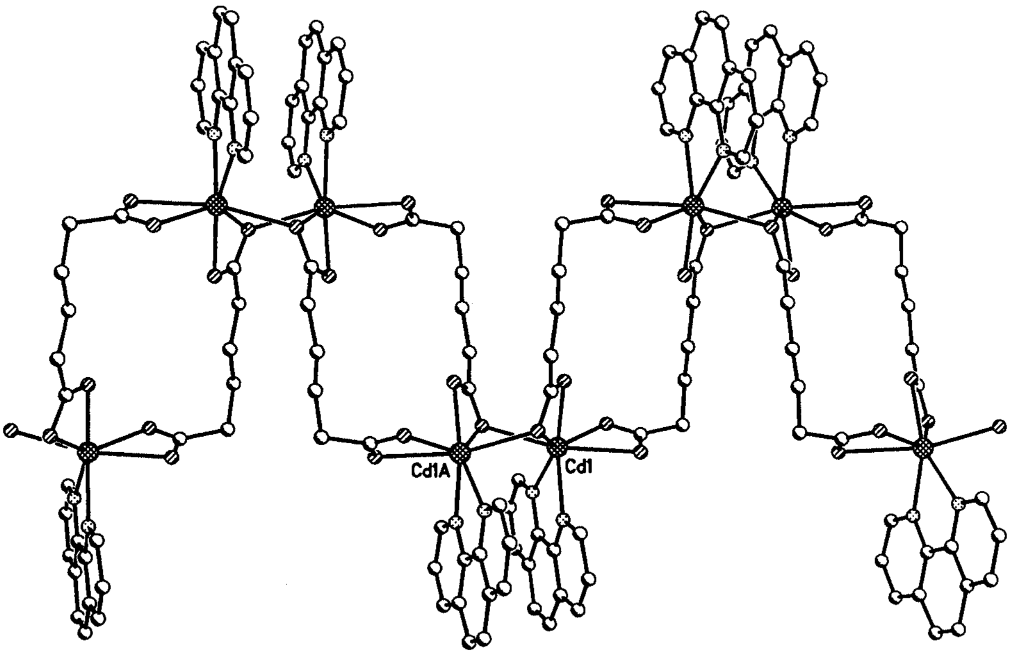
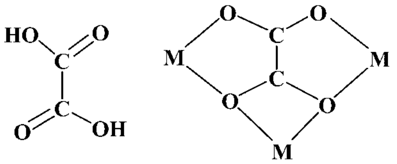


Figure 1. The 1-D chain of compound **1** viewed along the *b* axis

1.79, 1.85, and 1.62, respectively, suggesting that all carboxyl groups are deprotonated.[13b] These results are consistent with the charge-balance considerations and alkaline synthetic conditions of compound **1**.

The hydrothermal reaction of a solution of $Cd(NO_3)_2 \cdot 4H_2O$, adipic acid, 2,2′-bipy, $H_2C_2O_4$, NaOH and H_2O gives rise to **2** as colorless crystals. X-ray crystallographic analysis reveals that compound **2** forms an interesting 3-D network. There are two crystallographically unique Cd centers in the asymmetric unit (see Figure S2). The Cd(1) center is coordinated by two oxygen atoms [Cd(1)−O(3) 2.438(6) Å, Cd(1)−O(4) 2.302(6) Å] of one carboxylate group, four oxygen atoms of two different oxalate anions, including one μ_3-oxygen atom [Cd(1)−O(6) 2.630(6) Å], and one oxygen atom of a water molecule [$Cd(1)-O_{(water)}$ 2.267(6) Å]. The O−Cd(1)−O bond angles range from 52.66(17)° to 166.6(2)°. The Cd(2) center is bonded to two nitrogen atoms of one 2,2′-bipy ring with an average Cd(2)−N bond length of 2.347(6) Å, two oxygen atoms [Cd(2)−O(1) 2.467(6) Å, Cd(2)−O(2) 2.320(6) Å] of one carboxylate group, and two oxygen atoms of one oxalate anion [Cd(2)−O(5) 2.406(5) Å, Cd(2)−O(6) 2.353(5) Å]. The O−Cd(2)−O bond angles range from 54.1(2)° to 156.29(19)°, and the O(N)−Cd(2)−N(O) bond angles range from 81.1(2)° to 166.9(2)° (shown in Table S3). Therefore, both Cd centers display a distorted pentagonal bipyramidal geometry. The $[CdO_7]$ unit and $[CdO_5N_2]$ unit are linked by $C_2O_4^{2-}$ anions to form a pseudo-binuclear Cd center through the μ_3-O(6) atom. The Cd(1)···Cd(2) distance bridged by one μ_3-O(6) atom is 4.881 Å. As opposed to compound **1**, the two carboxyl groups of the adipate ligand in compound **2** exhibit another kind of coordination mode with the Cd atoms, as shown in Scheme 1b — all the carboxyl groups adopt a bis-chelating mode to connect the two Cd atoms. These pseudo-binuclear Cd centers are connected to each other by adipate anions to form a 1-D wave-like chain along the *c* axis, just like a sine- or cosine-type curve (see Figure 2). Furthermore, the $C_2O_4^{2-}$ anions also display two interesting kinds of connection mode with the Cd centers, as shown in Scheme 2. One carboxylate group binds in a bis-chelating mode to bridge one Cd center, while the two oxygen atoms from two different carboxyl groups exhibit an unusual bidentate bridging mode to link with another Cd center. Thus, one $C_2O_4^{2-}$ anion is connected with three Cd centers, as shown in Figure 3. To the best of our knowledge, this is the first example containing $C_2O_4^{2-}$ anions in which the oxalate group binds in both a bis-chelating and a bridging mode toward the metal centers. Based on the connection mode of $C_2O_4^{2-}$ anions, the sine-type and cosine-type chains are connected alternately by $C_2O_4^{2-}$ anions, forming a novel 3-D framework (see Figure 4). It is noteworthy that this 3-D network contains approximately square channels constructed by the adipate and oxalate ligands and the Cd centers, where the 2,2′-bipy ligands reside.



Scheme 4. Coordination modes of the oxalate ligand in compound **2**

Compound **2** is the first example in which both 2,2′-bipy and oxalate ligands are introduced into the {M/adipate} system. Furthermore, the introduction of the oxalate ligand leads to the dimensional transformation of the metal adipate coordination polymers.

Valence-sum calculations give values of 2.17 and 1.98 for the Cd(1) and Cd(2) atoms, respectively, indicating that each Cd center is in the +2 oxidation state. The coordinated oxygen atoms Ow(1) and Ow(2) have bond-valence sums of 0.27 and 0.37, respectively, suggesting that Ow is a coordinated water molecule. Atoms O(1)−O(8) have bond valence sums of 1.69, 1.77, 1.78, 1.83, 1.73, 1.71, 1.76 and 1.76, respectively, showing that all the carboxyl groups have been deprotonated.[13b] These results are consistent with charge-balance considerations and the alkaline synthetic conditions of compound **2**.

The IR spectrum of compound **1** shows characteristic bands of carboxyl groups at 1560 cm^{-1} for the antisymmetric stretching and at 1447 and 1409 cm^{-1} for symmetric

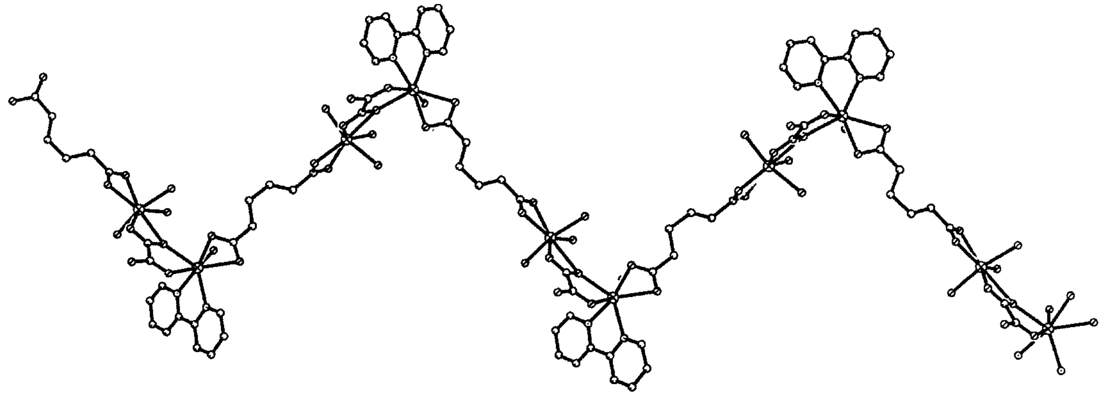


Figure 2. The 1-D chain of compound **2** viewed along the *c* axis

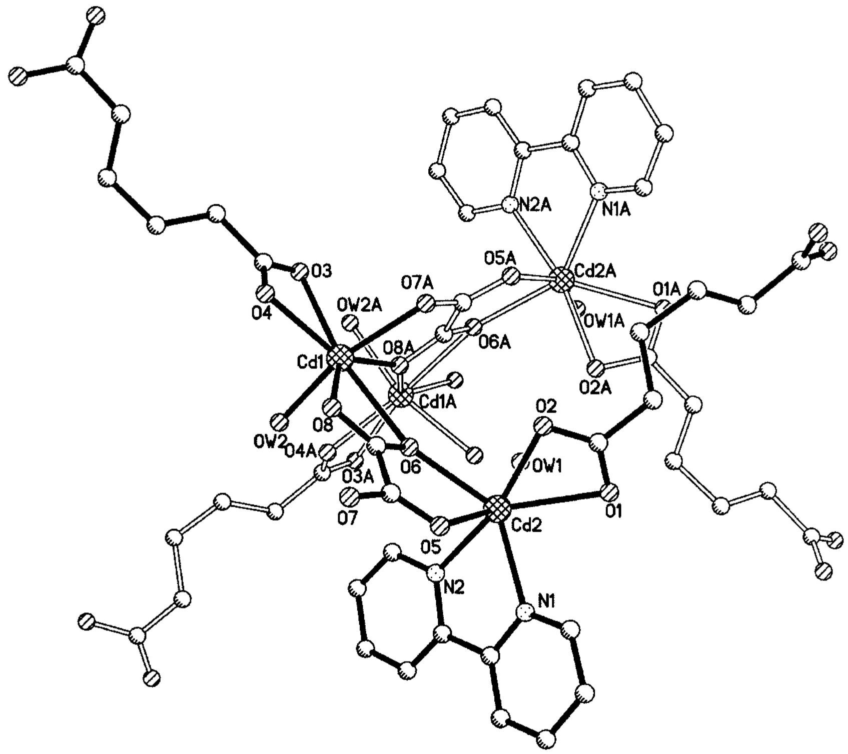


Figure 3. Perspective view of the connection mode of sine- and cosine-type chains connected to each other by oxalate in compound **2**

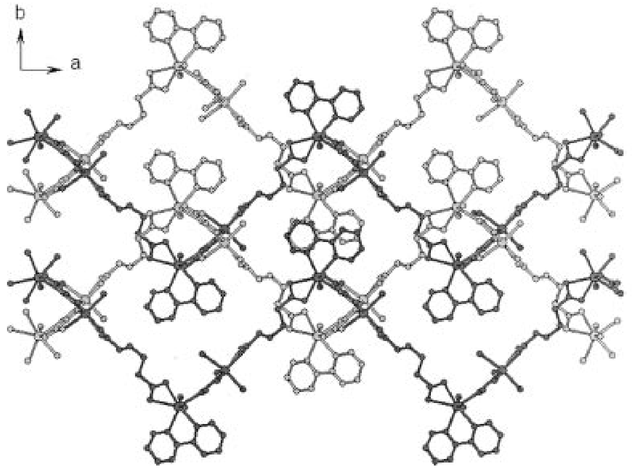


Figure 4. The 3-D framework of compound **2** along the *c* axis

stretching (see Figure S3a). The separations ($\Delta\nu$) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ indicate the presence of both chelating (113 cm^{-1}) and monodentate (151 cm^{-1}) coordination modes in compound **1**. The IR spectrum of compound **2** exhibits characteristic bands of carboxyl groups at 1630 cm^{-1} and 1603 cm^{-1} for the antisymmetric stretching and at 1437 cm^{-1} for symmetric stretching (see Figure S3b). The separations ($\Delta\nu$) between the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands show that the carboxylate groups bind in a bis-chelating fashion to the metal centers.[14]

In the TGA curve of compound **1** (see Figure S4a), there is only one weight loss of 70.50% in the range 320−540 °C, corresponding to the release of 1,10-phen and adipate ligands (calcd. 70.60%). The remaining weight of 29.50% corresponds to the percentage (29.40%) of Cd and O components, indicating that the final product is CdO. The TGA curve of compound **2** exhibits three weight-loss stages. The first weight loss is 3.09% (calcd. 2.70%) in the range of 133−185 °C, corresponding to the release of water molecules of crystallization. The second weight loss is 18.27% (calcd. 18.59%) in the range 265−360 °C, corresponding to the release of coordinated water and oxalate ligand. The last weight loss is 40.48% (calcd. 40.22%) in the temperature range 375−565 °C, corresponding to the release of 2,2′-bipy and adipate ligands. The residue is CdO. The whole weight loss (61.84%) is in good agreement with the calculated value (61.51%; see Figure S4b).

Photoluminescence Properties

The emission spectra of compounds **1** and **2** in the solid state at room temperature are depicted in Figure 5, with intense emissions at 443 nm (see a in Figure 5, λ_{ex} = 383 nm) for **1** and 422 nm (see b in Figure 5, λ_{ex} = 346 nm) for **2**. The difference between the two emission bands may be due to the different coordination environments of the Cd atom in these compounds. According to the literature,[15] the emissions at 443 nm and 422 nm can be assigned to ligand-to-metal charge-transfer (LMCT) bands. These observations indicate that compounds **1** and **2** may be excellent candidates for photoluminescent materials.

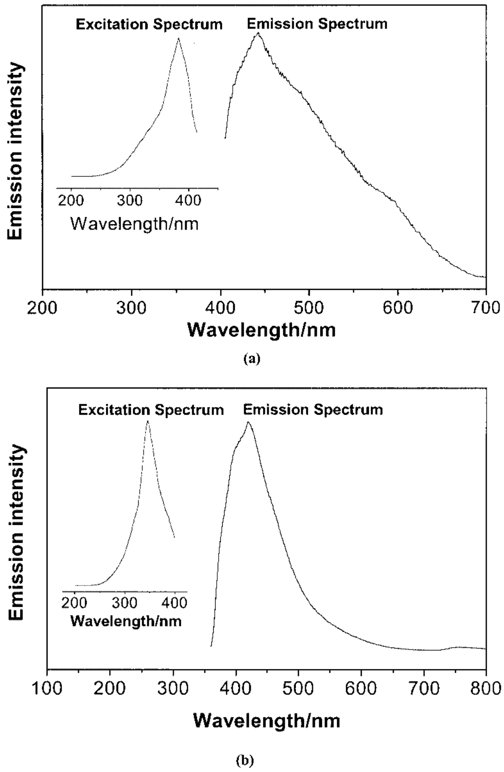


Figure 5. Solid-state emission spectra of the complexes at room temperature: (a) **1**, (b) **2**

Conclusion

We have successfully combined the merits of Cd metal and adipate with other organic ligands and synthesized two novel coordination polymers — $[Cd\{O_2C(CH_2)_4CO_2\}\{1,10\text{-phen}\}]_n$ (**1**) and $[Cd_2(C_2O_4)\{O_2C(CH_2)_4CO_2(OH_2)_2\}\{2,2'\text{-bipy}\}]\cdot H_2O$ (**2**) — with different dimensionalities and different coordination architectures. Comparing the structures of **1** and **2**, it has been found that the different coordination modes of the ligand may have a significant effect on the formation and dimension of the resulting structures. The successful preparation of compounds **1** and **2** provides a valuable approach for the construction of many other coordination polymers with different dimensional structures by the introduction of another kind of organic ligand. Furthermore, the strong fluorescent properties of compounds **1** and **2** make them excellent candidates for potential photoactive materials.

Experimental Section

General Methods: All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed with a Perkin-Elmer 2400 CHN Elemental Analyzer; Cd was determined with a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} with an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. TG analyses were performed with a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C·min^{-1}. Excitation and emission spectra were obtained with a Spex FL-2T2 spectrofluorometer equipped with a 450-W-xenon lamp as the excitation source.

Synthesis of 1: Compound **1** was synthesized from a reaction mixture containing $Cd(NO_3)_2\cdot 4H_2O$ (0.15 g, 0.5 mmol), adipic acid (0.073 g, 0.5 mmol), 1,10-phen (0.018 g, 0.1 mmol), NaOH (0.04 g, 1.0 mmol) and H_2O (6 mL, 333 mmol) in an 18-mL Teflon-lined autoclave under autogenous pressure at 160 °C for four days, followed by slow cooling (10 °C/h) to room temperature. The product was washed with distilled water and air-dried. The product was of high quality in the form of colorless crystals. Yield: 0.112 g (75% based on Cd). Elemental analyses. $C_{18}H_{16}CdN_2O_4$: calcd. C 49.5, H 3.7, N 6.4, Cd 25.7; found C 49.6, H 3.5, N 6.5, Cd 25.9. Selected FT-IR data (KBr pellet): $\tilde{\nu}$ = 3427 (s), 3053 (w), 2991 (m), 1560 (s), 1516 (w), 1418 (s), 1409 (s), 1355 (w), 1316 (m), 1103 (s), 1053 (s), 858 (s), 787 (m), 753 (m), 730 (s), 638 (m), 601 (w), 470 (s), 420 (w) cm^{-1}.

Synthesis of 2: Compound **2** was synthesized from a reaction mixture containing $Cd(NO_3)_2\cdot 4H_2O$ (0.15 g, 0.5 mmol), adipic acid (0.073 g, 0.5 mmol), 2,2′-bipy (0.023 g, 0.15 mmol), $H_2C_2O_4$ (0.009 g, 0.1 mmol), NaOH (0.04 g, 1.0 mmol) and H_2O (6 mL, 333 mmol) in na 18-mL Teflon-lined autoclave under autogenous pressure at 160 °C for four days, followed by slow cooling (10 °C/h) to room temperature. The product was washed with distilled water and air-dried. The product was of high quality in the form of colorless crystals. Yield: 0.108 g (72% based on Cd). $C_{18}H_{22}Cd_2N_2O_{11}$: calcd. C 32.4, H 3.3, N 4.2, Cd 33.7; found C 32.5, H 3.2, N 4.4, Cd 33.9. Selected FT-IR data (KBr pellet): $\tilde{\nu}$ = 3382 (s), 3269 (w), 2876 (w), 1639 (m), 1603 (m), 1550 (s), 1460 (w), 1437 (s), 1361 (w), 1309 (s), 1214 (m), 1176 (w), 1155 (m), 1073 (w), 1060 (w), 1018 (s), 971 (w), 910 (w), 804 (s), 765 (s), 737 (m), 651 (m), 627 (w), 583 (w), 493 (m), 449 (w) cm^{-1}.

X-ray Crystallography: Single crystals of compounds **1** and **2** with dimensions 0.532 × 0.485 × 0.396 mm and 0.467 × 0.413 × 0.345 mm, respectively, were glued onto a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) at 293 K in the range $1.89 < \theta < 27.48°$ and $1.76 < \theta < 27.44°$, respectively. An empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXL crystallographic software package.[16] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. The space group of the compound **2** was selected to be *Cc*. Although *Cc* and *C2/c* possess the same extinction rules, it can be presumed that the structure of compound **2** is noncentrosymmetric based on the lower CFOM value and the mean value of $<E^{2-}1>$ 0.651, which is lower than 0.736. Furthermore, as the value of $<E^{2-}1>$ is very low, the structure may be twinned. Thus, during the structural absolute refinement, a twin refinement was used. The final structural Flack parameter (k = 0.00), suggesting the absolute configuration of compound **2**, was confirmed. Selection of the *C2/c* space group to solve the structure did not give the correct structural model.

Crystal Data for 1: $C_{18}H_{16}CdN_2O_4$, M_r = 436.73, monoclinic, *C2/c*, a = 16.186(3) Å, b = 15.487(3) Å, c = 14.052(3) Å, $\alpha = \gamma$ = 90°, β = 112.73(3)°, U = 3248.7(11) Å^3, Z = 8, D_c = 1.786 g·cm^{-3}, μ = 1.371 mm^{-1}, $F(000)$ = 1744, $R1$ = 0.0305, $wR2$ = 0.0685 and

$S = 0.999$ for 3728 reflections with $I > 2\sigma(I)$ and 226 parameters ($R1 = 0.0464$, $wR2 = 0.0864$ for all 7266 data).

Crystal Data for 2: $C_{18}H_{22}Cd_2N_2O_{11}$, $M_r = 667.18$, monoclinic, Cc, $a = 23.448(5)$ Å, $b = 11.826(2)$ Å, $c = 8.3163(17)$ Å, $\beta = 99.08(3)°$, $U = 2277.3(8)$ Å^3, $Z = 4$, $D_c = 1.928$ g·cm^{-3}, $\mu = 1.928$ mm^{-1}, $F(000) = 1312$, $R1 = 0.0323$, $wR2 = 0.0884$ and $S = 0.996$ for 4775 reflection with $I > 2\sigma(I)$ and 293 parameters ($R1 = 0.0384$, $wR2 = 0.0971$ for all 4778 data).

CCDC-220446 (for **1**) and -223954 (for **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: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: Crystal data and structure refinement, bond lengths and angles, the perspective view of the Cd^{II} coordination environments, the IR spectra, the TGA curves for compounds **1** and **2** (Tables S1−3, Figures S1−S4; see also the footnote on the first page of this article).

Acknowledgments

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