

Syntheses and Crystal Structures of Five Cadmium(II) Complexes Derived from 4-Aminobenzoic Acid

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Five cadmium(II) complexes, $[\text{CdClL}\cdot\text{H}_2\text{O}]_n$ (**1**), $[\text{CdBrL}\cdot\text{H}_2\text{O}]_n$ (**2**), $\text{CdI}_2(\text{HL})_2$ (**3**), $\{[\text{Cd}(\text{dca})_2(\text{HL})_2]\cdot 2\text{H}_2\text{O}\}_n$ ($\text{dca}^- = \text{dicyanamide}$) (**4**), and $(\text{H}_2\text{L})_2[\text{CdCl}_4(\text{H}_2\text{O})_2]$ (**5**), have been synthesized by the reaction between 4-aminobenzoic acid (HL) and Cd^{2+} . In **1** and **2**, L^- serves as a tridentate ligand and bridges six-coordinate Cd^{II} centers to form $[\text{Cd}^{\text{II}}\text{-L}]_n$ chains; halide anions link adjacent chains into two-dimensional layers. Complex **3** is a typical metallic carboxylic acid synthon. In **3**, HL acts as a monodentate ligand coordinating to Cd^{II} through the nitrogen atom, and the head-to-tail hydrogen bonds of carboxylic groups result in a zigzag chain. The weak $\text{Cd}\cdots\text{I}$ interactions between adjacent chains extend

the zigzag chain-like structure into a two-dimensional structure. Complex **4** consists of $[\text{Cd}(\text{dca})_2(\text{HL})_2]_n$ chains and free water molecules. The twelve-membered rings formed by water molecules and carboxylic groups through hydrogen bonds link the adjacent chains to yield a two-dimensional layer. Complex **5** consists of discrete $[\text{CdCl}_4(\text{H}_2\text{O})_2]^{2-}$ anions and H_2L^+ organic cations, which are linked by intermolecular hydrogen-bonding interactions to form a three-dimensional structure.

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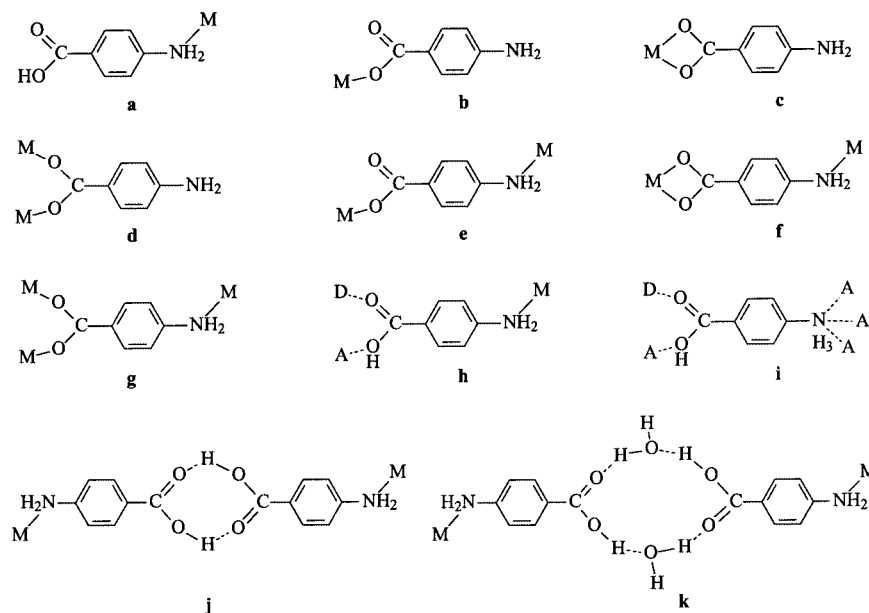
Introduction

The design and synthesis of novel complexes with unusual and tailorable structures are fundamental steps for the discovery and fabrication of various functional supramolecular devices or technologically useful materials.^[1] Recently, a great deal of attention has been paid to the design and construction of organic-inorganic hybrid frameworks from synthons or building blocks, owing to their fascinating structural diversity and promising potential application in chemistry, biology, and material science.^[2,3] Coordination covalent bonds, hydrogen bonds, and combinations of the two have been powerful tools for linking synthons or building blocks into extended structural topologies;^[2–5] likewise, organic counterions are frequently used as templating agents – based on their shape and hydrogen-bonding capability – to form frameworks such as perovskites.^[6] Through careful selection of organic ligands with hydrogen-bonding functionalities, structural frameworks can be confidently established and predicted, and their physical properties, such as magnetic, optical, and electronic properties, can be controlled and tailored.^[2,4–6] By the aforementioned synthetic methods, it is possible to prepare and modify complexes with different structural frameworks through

control of synthetic conditions such as counterions, pH value, reaction temperature, solvent, template, and the ratio of metal/ligand.

In previous studies, we have synthesized a series of novel organic-inorganic hybrid complexes based on covalent bonds through the use of simple organic ligands such as pyridine-2-thiol and pyrimidine-2-thiol.^[7] Recently, we have extended our work by the selection of multifunctional organic ligands that may form both coordination covalent bonds and hydrogen bonds as synthons or building blocks. 4-Aminobenzoic acid (HL) has been extensively studied in coordination chemistry, thanks to the richness of its coordination modes (Scheme 1, **a–i**): 1) HL can act as a carboxylic acid synthon and also as a good monodentate ligand through the amine group.^[8] 2) deprotonated 4-aminobenzoic acid (L^-) can act as a monodentate ligand through a carboxylate oxygen atom,^[9] chelating and/or bridging ligands through its amide and/or carboxylate groups,^[10,11] and 3) HL may be protonated to form organic cation templating agents. Previous reports showed that the association of d^{10} -configured cadmium(II) with HL resulted in two kinds of complexes, in which HL acts as a carboxylic acid synthon^[8] and as a bridging ligand.^[11] Our aim is to study self-assembly processes of $\text{Cd}^{\text{II}}\text{-HL}$ complexes, especially the influence of co-ligand and reaction medium on the coordination behaviour of HL and thereby the structural topology of the complexes obtained. Here we report the syntheses and crystal structures of five cadmium complexes: $[\text{CdClL}\cdot\text{H}_2\text{O}]_n$ (**1**), $[\text{CdBrL}\cdot\text{H}_2\text{O}]_n$ (**2**), $\text{CdI}_2(\text{HL})_2$ (**3**),

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Scheme 1. Possible coordination modes of HL, L⁻ and H₂L⁺; M = metal ion, A = hydrogen bond acceptor, D = hydrogen bond donor

{[Cd(dca)₂(HL)₂·2H₂O]_n} (4), and (H₂L)₂[CdCl₄(H₂O)₂] (5).

Results and Discussion

Syntheses and IR Spectra

Treatment of L⁻ with CdCl₂·2.5H₂O and CdBr₂·4H₂O in MeOH/H₂O (2:1) resulted in the formation of the corresponding mixed-anion cadmium(II) complexes **1** and **2**, respectively. However, treatment of L⁻ with CdI₂ under the same conditions failed to produce the expected complex containing mixed-anion ligands. Instead, a straightforward reaction between HL and CdI₂ in MeOH/H₂O (2:1) yielded a two-dimensional complex **3**, formed by head-to-head carboxylic acid hydrogen bonding (Scheme 1, j) and weak Cd···I interactions. The successful isolation of **3** prompted us to replace I⁻ with bridging ligands, such as SCN⁻, dca⁻, and N₃⁻, in order to obtain layer complexes containing head-to-head carboxylic acid hydrogen bonds. Use of Cd(NO₃)₂·6H₂O, NH₄SCN, and HL in MeOH/H₂O (2:1) generated the expected complex [Cd(SCN)₂(HL)₂]_n,^[8b] but employment of Cd(NO₃)₂·6H₂O, Na(dca), and HL in MeOH/H₂O (2:1) produced complex **4**, comprising twelve-membered rings made up of water molecules and carboxylic groups through hydrogen bonds (Scheme 1, k). Isolation of [Cd(N₃)₂(HL)₂]_n from the reaction between Cd(NO₃)₂·6H₂O, NaN₃, and HL in EtOH/H₂O (2:1) was not successful; instead, HL was deprotonated by NaN₃ and a known compound [(CdL₂·H₂O)·2H₂O]_n^[11] was obtained. As mentioned above, HL may be protonated to form an organic ammonium ion H₂L⁺, which can act as an organic cation templating agent for perovskite complexes. When the reaction between CdCl₂·2.5H₂O and HL was carried out in aqueous HCl solution, HL did accept a proton to form H₂L⁺ and produced a perovskite-type complex **5**.

The IR spectra of complexes **1** and **2** confirm the presence of the carboxylate group, by the strong peaks at 1608 and 1398 cm⁻¹ for **1** and at 1610, 1597, 1414 and 1402 cm⁻¹ for **2**. The separations (Δ) between the antisymmetric stretching ν_{asym}(COO) and the symmetric stretching ν_{sym}(COO) are 210 cm⁻¹ for **1**, and 197 and 195 cm⁻¹ for **2**. The characteristic carboxylic acid group bands are observed at 1684, 1441, and 1423 cm⁻¹ for **3** and at 1678, 1626, 1443 (m), and 1423 (m) cm⁻¹ for **4**. Moreover, the IR spectrum in complex **4** displays a very strong absorption band at 2175 cm⁻¹, indicating the presence of C≡N in dca⁻. The carboxylic group in complex **5** is characterized by the presence of strong peaks at 1701 and 1678 cm⁻¹ for antisymmetric stretching and at 1487 and 1433 cm⁻¹ for symmetric stretching. Several strong bands in the 3550 to 2750 cm⁻¹ range may be assigned to N–H and O–H stretching frequency in H₂L⁺.

Structures

[CdCIL·H₂O]_n (1)

Complex **1** consists of two-dimensional layers formed by interconnection of neighboring [Cd^{II}–L]_n chains through bridging Cl⁻ in a *trans* mode. As shown in Figure 1 (a), each Cd^{II} is coordinated by two chelating carboxylate oxygen atoms from one L⁻ ligand, a nitrogen atom from the other L⁻ ligand, two bridging Cl⁻ ions, and one coordinated water molecule in a distorted octahedral geometry. The two bridging Cl⁻ ions stand at the apical positions [Cd–Cl = 2.580(1) and 2.646(1) Å, Cl–Cd–Cl(A) = 171.13(2)°], while the two carboxylate oxygen atoms [O(1) and O(2)], the nitrogen atom [N(0B)], and the water oxygen atom (O_w) form the equatorial plane. Cd^{II} is approximately coplanar with the mean plane of O1, O2, O_w, and N(0B), with a deviation of 0.0625 Å. L⁻ adopts a chelating/

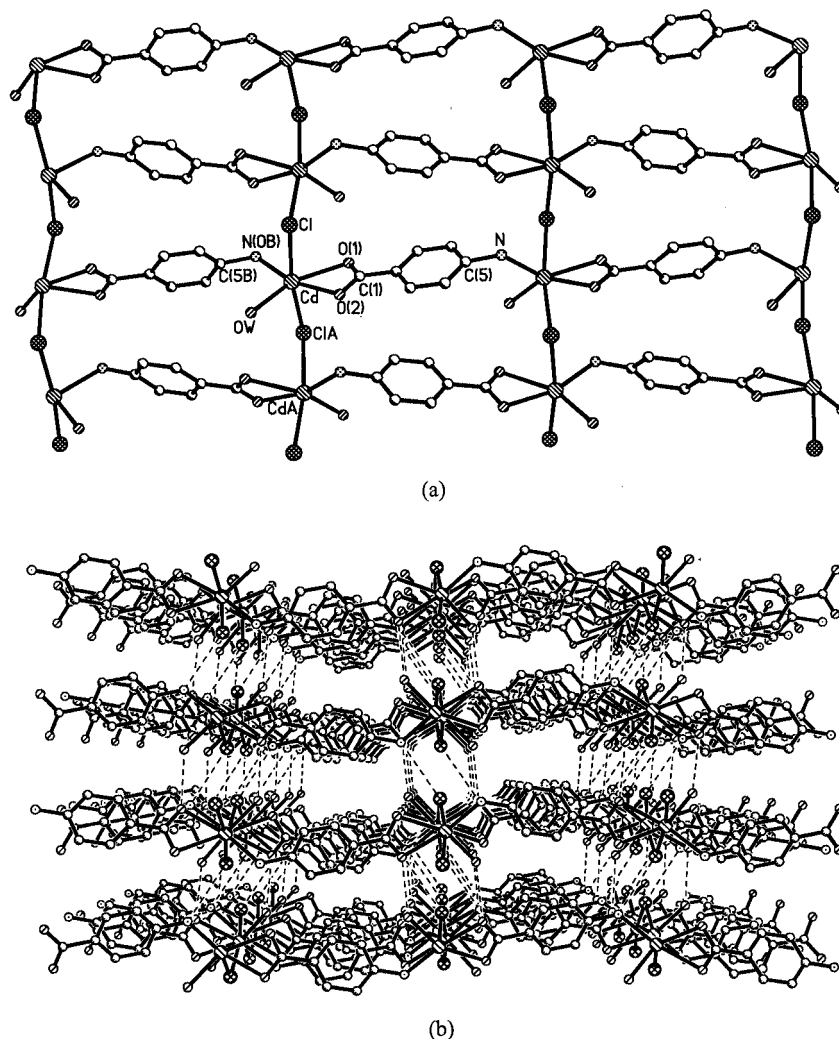


Figure 1. (a) View of the two-dimensional layer in **1** along the *b* axis with atomic numbering; (b) view of a packing diagram showing the three-dimensional structure of **1** along the *a* axis

bridging coordination mode to link two Cd^{II} centers (Scheme 1, f), similar to those in reported Cd^{II} complexes.^[11] Cl⁻ acts as a μ_2 -bridge and lies at the apical site occasionally reported in Cd^{II} complexes with mixed carboxylate and Cl⁻ ligands.^[12] The Cd^{II} components can thus be viewed as linkers connecting L⁻ and Cl⁻ to form a two-dimensional layer consisting of rectangular grids with dimensions of 4.397×9.881 Å based on Cd^{II}–Cd^{II} distances. It should be noted that the water ligand forms hydrogen bonds with carboxylate oxygen atoms of L⁻ [O_w–H⁺⋯O(1)ⁱ 2.776(4) Å and O_w–H⁺⋯O(2)ⁱⁱ 2.773(5) Å; symmetry modes: i: $x + 1/2, -y + 1/2, -z + 1$; ii: $-x + 1, -y + 1, -z + 1$], and the amide of L⁻ also forms a hydrogen bond with Cl⁻ [N–H⁺⋯Clⁱⁱⁱ 3.186(4) Å; symmetry mode: iii: $-x + 1/2, -y + 1, z - 1/2$]. Such hydrogen bonding interactions consolidate the structural architecture and further extend the two-dimensional layers into a three-dimensional structure (Figure 1, b).

[CdBrL·H₂O]_n (**2**)

Complex **2** consists of two-dimensional layers formed by the interconnection of neighboring [Cd^{II}–L]_n chains through bridging Br⁻ in a *cis* mode. As shown in Figure 2 (a), each Cd^{II} is coordinated by two chelating carboxylate oxygen atoms of one L⁻, a nitrogen atom of the other L⁻, two bridging Br⁻ moieties, and one coordinated water molecule in a highly distorted octahedral geometry; the equatorial plane is formed by the two carboxylate oxygen atoms [O(1) and O(2)], a nitrogen atom [N(0A)], and one bromide ion (Br) [with the shorter Cd–Br distance of 2.787(1) Å], while the water oxygen atom (O_w) and the other bromide ion [with the longer Cd–Br(B) distance of 2.829(1) Å] occupy the axial positions. The deviation of Cd^{II} from the equatorial plane defined by O(1), O(2), N(0A), and Br is 0.197 Å. Two adjacent Cd^{II} atoms are bridged by two Br⁻ moieties to form a Cd₂Br₂ four-membered ring^[13] with a Cd^{II}–Cd^{II} separation of 3.795 Å. Such four-membered rings

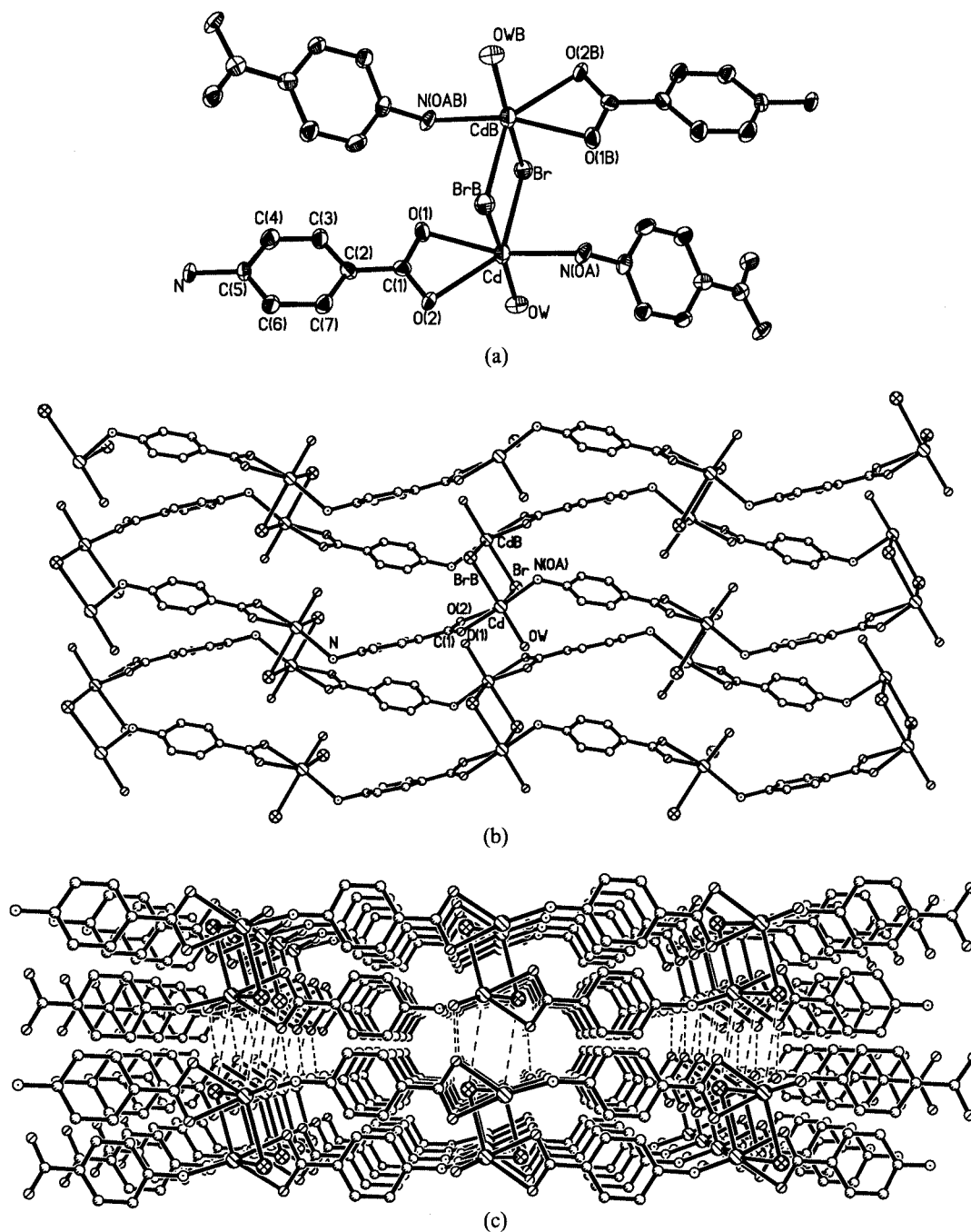


Figure 2. (a) The coordination geometry of Cd^{II} in **2**, thermal ellipsoids are shown with 50% probability; (b) view of the two-dimensional layer in **2** along the a axis; (c) view of the stacking layers in **2** along the b axis

act as nodes, and L^- links the nodes to yield a two-dimensional layer. The coordination mode of L^- is the same as in **1** (Scheme 1, f), but the layer is very different from that of **1** owing to the *cis* orientations of Br^- in **2**. The $\text{Cd}\cdots\text{Cd}$ distance separated by L^- (9.907 Å) is close to that in **1** (9.881 Å). It is noteworthy that the weak inter-layer $\text{Br}\cdots\text{Cd}$ interaction (3.798 Å) and hydrogen bonding interactions may play important roles in consolidating the crystal architecture. As shown in Figure 2 (c), hydrogen bonds of the water ligand and two oxygen atoms of different L^- ligands [$\text{O}_w\text{-H}\cdots\text{O}^{\text{I}}$ 2.716(7) and $\text{O}_w\text{-H}\cdots\text{O}^{\text{II}}$ 2.818(7) Å; sym-

metry modes: i: $1-x, 1-y, -z$; ii: $-x, 1-y, -z$], and of Br^- and amide [$\text{Br}\cdots\text{H}-\text{N}^{\text{III}}$ 3.376(6) Å; symmetry mode: iii: $-x, y-0.5, -0.5-z$] along with the weak $\text{Br}\cdots\text{Cd}$ interaction extend the two-dimensional layers into a three-dimensional structure.

$\text{CdI}_2(\text{HL})_2$ (**3**)

The structure of complex **3** is made up of $\text{HL}-\text{CdI}_2-\text{HL}$ metallic synthons. As shown in Figure 3 (a), each Cd^{II} is coordinated by two I^- and two nitrogen atoms of HL in a distorted tetrahedral geometry [$\text{Cd}-\text{N} = 2.347(5)$ Å,

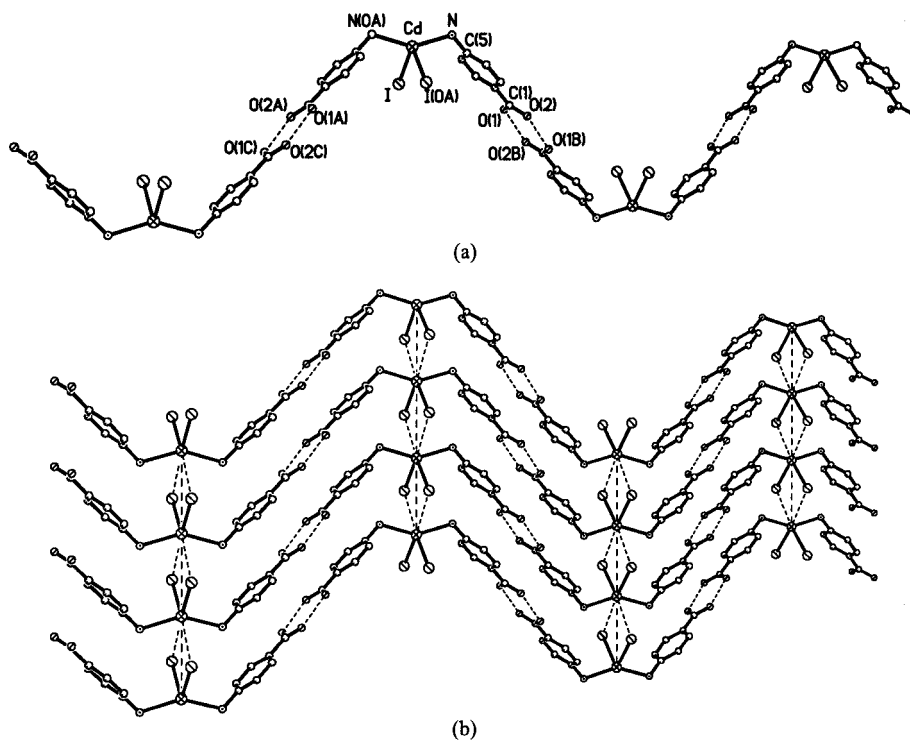


Figure 3. (a) One-dimensional hydrogen bonding zigzag chain in **3**; (b) two-dimensional layer is formed through weak Cd–I and hydrogen bonding interactions in **3**

Cd–I = 2.8276(8) Å, N–Cd–N(0A) = 148.8(3)°. Each HL acts as a monodentate ligand, coordinating to Cd^{II} through its amine nitrogen atom, and forms hydrogen bonds through the carboxylic group (Scheme 1, h). The two HL components coordinated to the same Cd^{II} atom are approximately perpendicular, with a dihedral angle of 83.8°, similar to those in synthons of four-coordinate metal centers and pyridine derivatives.^[5] In **3**, HL–CdI₂–HL units propagate by head-to-head hydrogen bonds between the carboxylic acid groups of HL (Scheme 1, j) into a zigzag chain [O(1)ⁱ⋯H–O(2)^j 2.631(7) Å; symmetry code: i: $-x + 1/2, -y + 5/2, -z + 1$]. Such zigzag chains are further extended into a two-dimensional network through weak inter-chain Cd⋯I interactions [I⋯Cd^{II} 3.3365(9) Å, Cd–I⋯Cd^{II} 93.727(13)°; symmetry code: ii: $x, y + 1, z$] (Figure 3, b). The inter-chain adjacent Cd⋯Cd separation is 4.511 Å.

$\{[\text{Cd}(\text{dca})_2(\text{HL})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**4**)

The crystal structure of complex **4** consists of one-dimensional cadmium chains and free water molecules (Figure 4, a). Each Cd^{II} is coordinated by six nitrogen atoms in a distorted octahedral geometry, in which four nitrogen atoms of different dca[−] moieties form the equatorial plane [average Cd–N_{dca} = 2.326(3) Å] and the nitrogen atoms of two HL units [Cd–N_{HL} = 2.377(3) Å] occupy the apical positions. Each adjacent Cd^{II} pair is bridged by two inversely related dca[−] units to form a neutral one-dimensional cadmium–dca chain consisting of twelve-membered (N–C–N–C–N–Cd)₂ rings with a Cd⋯Cd separation of 7.737 Å, which is slightly larger than those in the complexes

comprising this type of bridge.^[14] The HL ligands are situated at the two sides of the chain to saturate the six-coordinate Cd^{II} centers, adopting a monodentate coordination mode through the nitrogen atoms and forming hydrogen bonds through the carboxylic groups (Scheme 1, h). Unlike in **3**, adjacent one-dimensional chains in **4** are interconnected by hydrogen bonds between free water molecules and carboxylic groups to produce a two-dimensional structure [O_w⋯O(2) 2.608(3), O_w–H⋯O(1)ⁱ 2.783(4) Å; symmetry code: i: $-x + 1, -y + 2, -z + 1$] (Figure 4, b). The O(2)–C(11) bond of 1.327(4) Å in HL is longer than those in **3**, [Cd(SCN)₂(HL)₂]_n^[8b] and the free HL ligand.^[15] Formula **k** in Scheme 1 shows the twelve-membered ring formed by hydrogen bonds of water molecules and carboxylic acid groups. To the best of our knowledge, this is a unique structural motif in supramolecular chemistry. As shown in Figure 4 (c), the two-dimensional layers are further extended into a three-dimensional framework through weak inter-layer hydrogen bonds between free water molecules and oxygen atoms from HL [O_w⋯O(2)ⁱⁱ 2.924(4) Å; symmetry code: ii: $-x + 1, y + 1/2, -z + 1/2$].

$(\text{H}_2\text{L})_2[\text{CdCl}_4(\text{H}_2\text{O})_2]$ (**5**)

Complex **5** consists of discrete octahedral [CdCl₄(H₂O)₂]^{2−} anions linked by H₂L⁺ organic cations through extensive intermolecular hydrogen bonding interactions. As shown in Figure 5 (a), cadmium(II) is coordinated by four Cl[−] ions [Cd–Cl = 2.5687(7) or 2.5699(7) Å] and two water oxygen atoms [Cd–O_w = 2.364(2) Å] in a compressed octahedral geometry, in which the Cl[−] units lie in the equatorial plane and the oxygen atoms are situated at

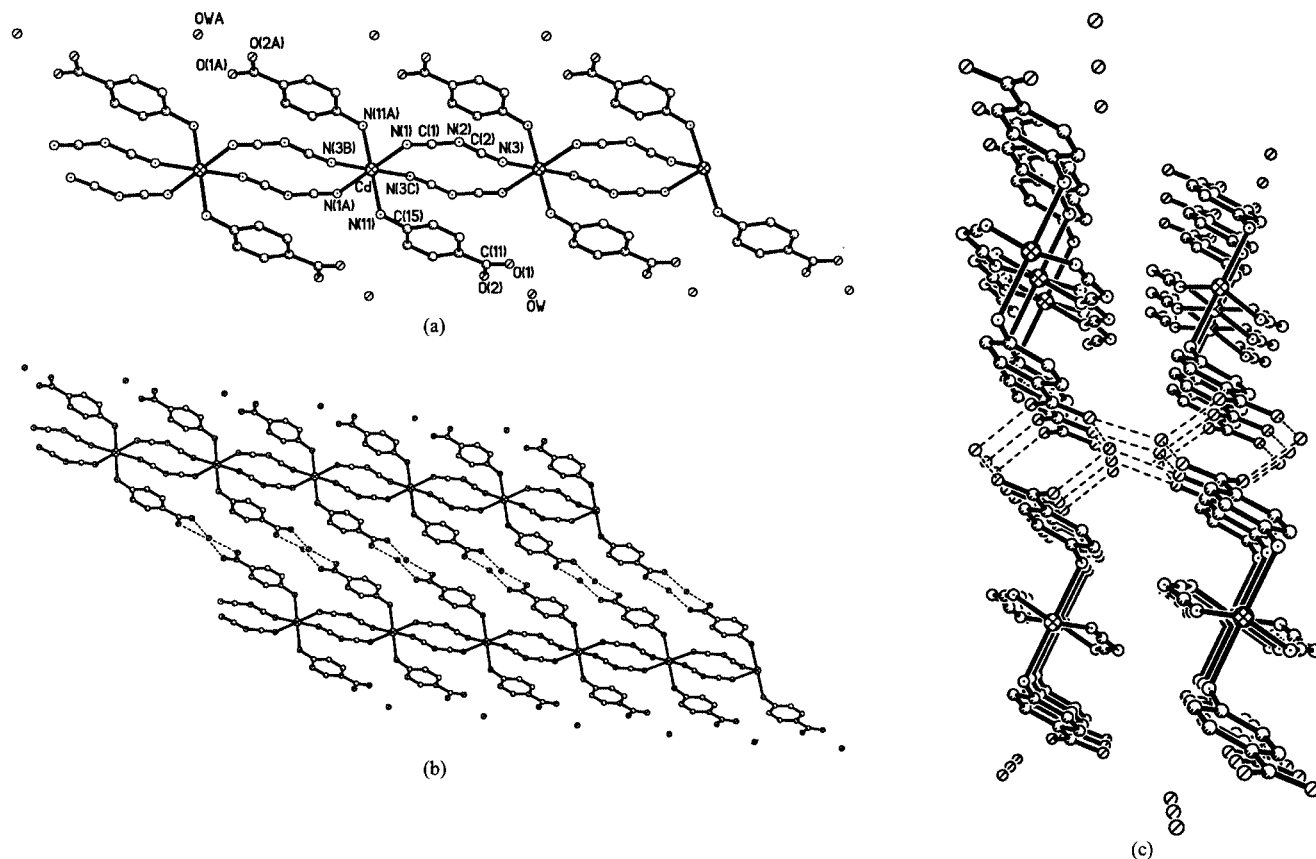


Figure 4. (a) View of one-dimensional chain and lattice water molecules in **5** with atomic numbering; (b) view of the hydrogen bonding between adjacent chains to form a two-dimensional layer along the *c* axis; (c) view of three-dimensional structure in **4** along the *a* axis

the axial positions. The coordination environment around Cd^{II} is similar to that in [CdCl₂(H₂O)₂·2Cyt]_{*n*} (Cyt = cytosine).^[16] Cd^{II} is coplanar with the four Cl⁻ units and lies in the center of the equatorial plane. The bond lengths and angles are very similar to those in [CdCl₂(H₂O)₂·2Cyt]_{*n*}.^[16] As shown in Figure 5 (b), H₂L⁺ cations act as linkers to link discrete [CdCl₄(H₂O)]²⁻ units into a three-dimensional supramolecular structure through hydrogen bonding. There is no interaction between adjacent [CdCl₄(H₂O)]²⁻ units, and the shortest Cd–Cd separation is 5.833 Å. Formula **i** in Scheme 1 shows the hydrogen bonds formed by H₂L⁺: –NH₃⁺ is surrounded by three Cl⁻ units [N–H⋯Cl(2) 3.228(3), N–H⋯Cl(2)ⁱ 3.193(3), N–H⋯Cl(2)ⁱⁱ 3.233(3) Å; symmetry codes: i: *x*, *y* + 1, *z*; ii: –*x* + 1, *y* + 1/2, –*z* + 1/2], –OH forms a hydrogen bond with a Cl⁻ ion [O(1)–H⋯Clⁱⁱⁱ 3.031(3) Å; symmetry code: iii: –*x* + 2, *y* + 1/2, –*z* + 1/2], and –C=O forms a hydrogen bond with a coordinated water molecule (O_w) [O_w–H⋯O(2)^{iv} 2.753(4) Å; symmetry code: iv: *x* – 1, –*y* + 3/2, *z* – 1/2]. To the best of our knowledge, this is the first complex comprising discrete [CdCl₄(H₂O)]²⁻ anions and the first complex to use protonated 4-aminobenzoic acid (H₂L⁺) as an organic cation templating agent.

Conclusion

Through the use of the multifunctional 4-aminobenzoic acid (HL) ligand and different synthetic strategies, we have

successfully synthesized five Cd^{II} complexes that display hydrogen-bonding interactions. Complexes **1** and **2** may be regarded as extensions of the one-dimensional chain structure of [(CdL₂·H₂O)·2H₂O]_{*n*}^[11] into two-dimensional networks through bridging Cl⁻ or Br⁻ instead of L⁻ and are further extended into three-dimensional structures by inter-layer hydrogen bonding interactions. Moreover, Cl⁻ and Br⁻, occupying different coordination sites around Cd^{II}, result in two completely different structural topologies. Complex **3** is a typical metallic carboxylic acid synthon. The twelve-membered ring formed by H₂O and the carboxylic acid group of HL through hydrogen bonding in **4** is a unique structural motif in supramolecular chemistry. In complex **5**, N–H⋯Cl, O–H⋯Cl, O_w–H⋯Cl, and O_w–H⋯O hydrogen bonds link compressed octahedral [CdCl₄(H₂O)]²⁻ anions and H₂L⁺ cations into a three-dimensional structure. To the best of our knowledge, this is the first complex comprising discrete [CdCl₄(H₂O)]²⁻ anions and the first complex to use protonated 4-aminobenzoic acid (H₂L⁺) as an organic cation templating agent. In summary, this work demonstrates that the combination of coordination covalent bonds and hydrogen bonds is an important tool for the construction of supramolecular architectures, and that the presence of counterions or co-ligands in the synthetic reaction plays an important role in the formation of different structures.

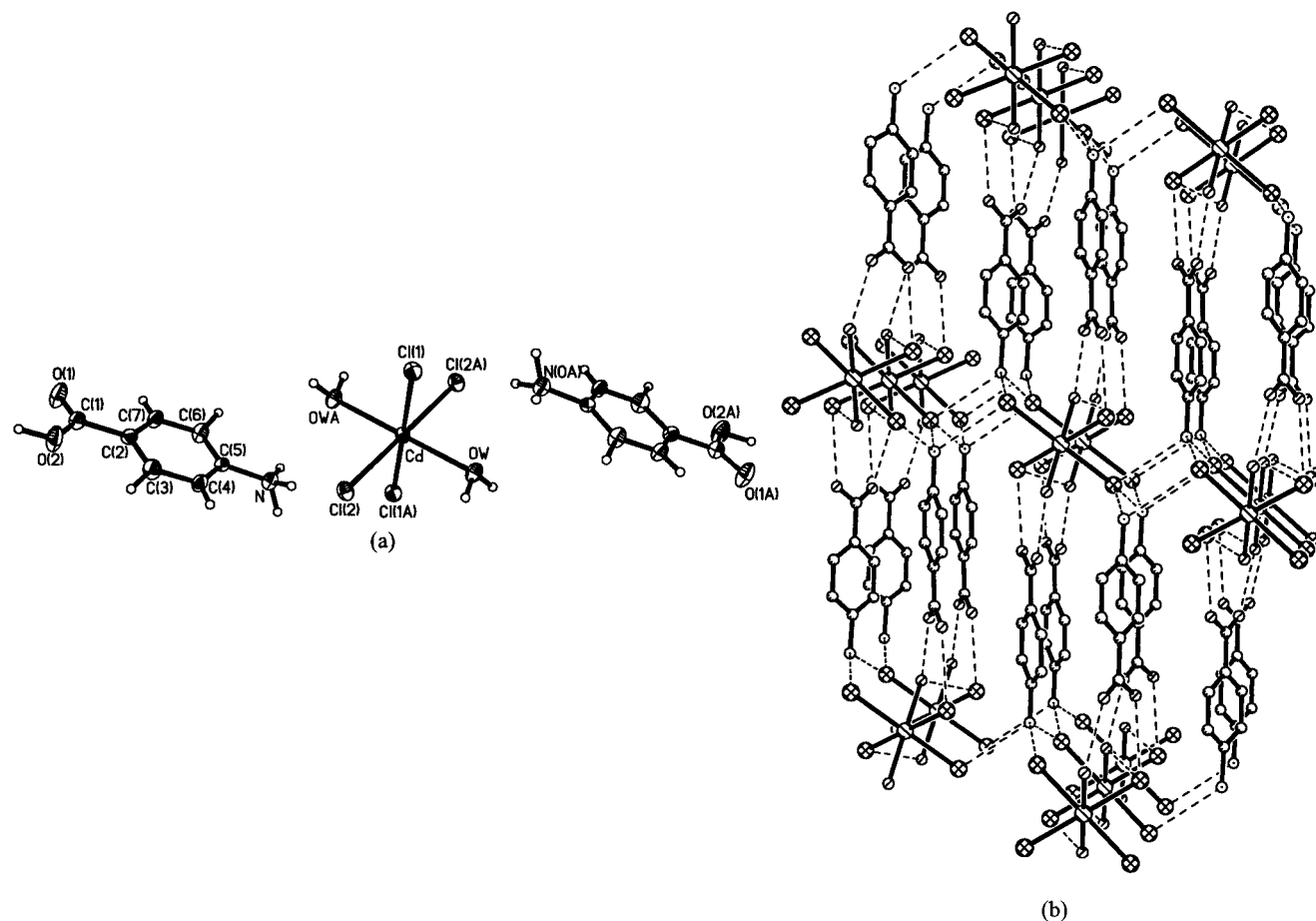


Figure 5. (a) View of discrete $[\text{CdCl}_4(\text{H}_2\text{O})_2]^{2-}$ and H_2L^+ organic cations in **5**; thermal ellipsoids are shown with 30% probability; (b) packing diagram in **5** along the a axis

Table 1. Crystallographic data for the five crystal structures

Compound	1	2	3	4	5
Empirical formula	$\text{C}_7\text{H}_8\text{CdCl}_3\text{NO}_3$	$\text{C}_7\text{H}_8\text{BrCdNO}_3$	$\text{C}_7\text{H}_7\text{Cd}_{0.5}\text{INO}_2$	$\text{C}_9\text{H}_6\text{Cd}_{0.50}\text{N}_4\text{O}_3$	$\text{C}_7\text{H}_{10}\text{Cd}_{0.5}\text{Cl}_2\text{NO}_3$
Formula mass	301.99	346.45	320.24	277.40	283.26
Crystal size [mm]	$0.64 \times 0.50 \times 0.12$	$0.58 \times 0.36 \times 0.09$	$0.62 \times 0.20 \times 0.14$	$0.48 \times 0.35 \times 0.19$	$0.68 \times 0.60 \times 0.44$
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pbca$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a [Å]	8.7606(3)	6.4357(2)	15.8720(2)	11.5381(10)	12.0794(11)
b [Å]	10.6930(3)	7.2533(3)	4.5115(1)	7.7374(6)	5.8333(5)
c [Å]	19.7616(7)	19.7258(6)	25.0187(7)	12.4261(11)	14.8963(13)
β [°]		90.890(2)	97.474(2)	90.979(2)	100.376(1)
V [Å ³]	1851.21(10)	920.69(6)	1776.28(7)	1109.18(16)	1032.47(16)
Z	8	4	8	4	4
D_c [g·cm ⁻³]	2.167	2.499	2.395	1.661	1.822
μ [mm ⁻¹]	2.619	6.683	4.724	1.037	1.608
$F(000)$	1168	656	1192	556	564
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
$\lambda(\text{Mo-}K_\alpha)$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Reflns. collected	5826	2833	2852	3332	2995
Unique reflns.	1646	1596	1555	1918	1825
Obsd. reflns. [$F > 4.0\sigma(F)$]	1418	1333	1259	1591	1744
Parameters	119	119	106	151	165
S on F^2	1.176	1.020	1.024	1.098	1.194
R_1	0.0348	0.0539	0.0453	0.0309	0.0245
wR	0.1056	0.1413	0.1206	0.0914	0.0713
$\Delta\rho_{\text{min. and max.}}$ [e Å ⁻³]	0.863 and -0.639	1.276 and -1.453	1.143 and -1.043	0.565 and -0.629	0.388 and -0.718

Experimental Section

General: All reagents are commercially available and were used as purchased without further purification. The IR spectra were recorded with a Magna 750 FT-IR spectrophotometer from KBr disks. Elemental analyses were recorded with an Elementar Vario ELIII elemental analyzer.

[CdCIL·H₂O]_n (1): A solution of CdCl₂·2.5H₂O (0.11 g, 0.5 mmol) in H₂O (5 mL) was added slowly to a solution of HL (0.07 g, 0.5 mmol) in MeOH (10 mL). Aqueous NaOH (1 mol·L⁻¹) was then added dropwise to the reaction mixture until a small amount of precipitate had formed. The precipitate was filtered off and the clear filtrate was allowed to stand at room temperature. After one week, light yellow crystals were obtained. Yield: 68%. C₇H₈CdClNO₃ (302.0): calcd. C 27.84, H 2.65, N 4.64; found C 28.27, H 2.76, N 4.52. IR (KBr): $\tilde{\nu}$ = 3329 (s), 3280 (s), 3217 (s), 3134 (m), 1928 (vw), 1693 (vw), 1637 (vw), 1608 (vs), 1597 (m), 1520 (s), 1518 (s), 1433 (m), 1398 (vs), 1327 (w), 1302 (w), 1240 (w), 1176 (w), 1142 (w), 1076 (s), 1034 (m), 964 (w), 856 (m), 843 (vw), 787 (m), 777 (m), 702 (vw), 636 (m), 617 (vw), 517 (vw), 503 (vw) cm⁻¹.

[CdBrL·H₂O]_n (2): The procedure was similar to the synthesis of complex 1, except that CdBr₂·4H₂O (0.17 g, 0.5 mmol) was used instead of CdCl₂·2.5H₂O. Yield: 53%. C₇H₈BrCdNO₃ (346.5): calcd. C 24.27, H 2.31, N 4.04; found C 24.32, H 2.43, N 4.12. IR (KBr): $\tilde{\nu}$ = 3286 (br, vs), 1923 (vw), 1911 (vw), 1668 (w), 1610 (vs), 1597 (vs), 1502 (vs), 1414 (vs), 1402 (vs), 1302 (m), 1246 (s), 1184 (m), 1146 (w), 1101 (m), 1055 (vs), 951 (w), 868 (s), 852 (s), 785 (s), 702 (m), 636 (s), 596 (m), 530 (m) cm⁻¹.

CdI₂(HL)₂ (3): A solution of CdI₂ (0.09 g, 0.25 mmol) in H₂O (5 mL) was added slowly to a solution of HL (0.07 g, 0.5 mmol) in MeOH (10 mL). The reaction mixture was stirred for 30 min and the resulting colourless solution was filtered. Light yellow crystals of complex 3 were obtained by allowing the filtrate to stand in air for one week. Yield: 56%. C₇H₇Cd_{0.5}INO₂ (320.2): calcd. C 26.25, H 2.19, N 4.37; found C 26.37, H 2.24, N 4.43. IR (KBr): $\tilde{\nu}$ = 3460 (s), 3363 (s), 3329 (s), 3215 (m), 2978 (m), 2669 (m), 2551 (m), 1684 (s), 1605 (s), 1574 (m), 1512 (vw), 1441 (m), 1423 (m), 1387 (w), 1319 (s), 1290 (s), 1261 (m), 1174 (s), 1128 (w), 1097 (vw), 1012 (w), 1018 (w), 964 (w), 899 (vw), 843 (w), 773 (m), 694 (vw), 617 (w), 550 (vw), 499 (vw) cm⁻¹.

{[Cd(dca)₂(HL)₂]·2H₂O}_n (4): A solution of Cd(NO₃)₂·6H₂O (0.15 g, 0.5 mmol) and Na(dca) (0.09 g, 1 mmol) in H₂O (5 mL) was added slowly to a solution of HL (0.07 g, 0.5 mmol) in MeOH (10 mL). The reaction mixture was stirred for 30 min and gave a colourless solution. After filtration, the filtrate was allowed to stand in air for two weeks to give light yellow crystals of complex 4. Yield: 50%. C₉H₉Cd_{0.5}N₄O₃ (277.4): calcd. C 38.97, H 3.24, N 20.19; found C 39.02, H 3.27, N 20.23. IR (KBr): $\tilde{\nu}$ = 3575 (vw), 3460 (m), 3383 (w), 3365 (m), 3307 (w), 3165 (vw), 2663 (vw), 2291 (m), 2268 (m), 2235 (w), 2175 (vw), 1678 (s), 1626 (s), 1605 (s), 1576 (vw), 1518 (vw), 1443 (w), 1423 (w), 1365 (vw), 1327 (s), 1315 (s), 1292 (s), 1263 (w), 1176 (m), 1128 (vw), 1012 (vw), 964 (vw), 943 (vw), 918 (vw), 845 (vw), 771 (vw), 698 (vw), 619 (vw), 553 (vw), 509 (vw) cm⁻¹.

(H₂L)₂[CdCl₄(H₂O)₂] (5): An aqueous solution (10 mL) of CdCl₂·2.5H₂O (0.11 g, 0.5 mmol) was added slowly to a solution of HL (0.07 g, 0.5 mmol) in HCl (6 mol·L⁻¹, 20 mL). After stirring for 30 min, the colourless reaction mixture was filtered. Light yellow crystalline complex 5 was obtained by keeping the filtrate in

Table 2. Selected bond lengths [Å] and angles [°] for the five complexes; symmetry codes: **1** (A): $x + 1/2, -y + 1/2, -z + 1$; (B): $x, -y + 1/2, z + 1/2$; **2** (A): $x, -y + 1/2, z + 1/2$; (B): $-x, -y, -z$; **3** (A): $-x + 1, y, -z + 1/2$; **4** (A): $-x, -y, -z + 1$; (B): $-x, -y + 1, -z + 1$; (C): $x, y - 1, z$; **5** (A): $-x + 1, -y + 1, -z$

Complex 1			
Cd–O(1)	2.395(3)	Cd–N(0B)	2.304(3)
Cd–O(2)	2.351(3)	O(1)–C(1)	1.257(5)
Cd–O _w	2.266(3)	O(2)–C(1)	1.280(5)
Cd–Cl	2.646(1)	N–C(5)	1.435(5)
Cd–ClA	2.580(1)		
O(2)–Cd–O(1)	55.35(10)	O _w –Cd–N(0B)	98.24(13)
O(1)–Cd–Cl	82.53(8)	N(0B)–Cd–O(2)	163.65(12)
O(2)–Cd–Cl	82.26(8)	N(0B)–Cd–O(1)	109.76(11)
O(1)–Cd–ClA	88.62(8)	N(0B)–Cd–ClA	94.34(10)
O(2)–Cd–ClA	92.11(8)	N(0B)–Cd–Cl	89.38(10)
O _w –Cd–O(1)	151.94(12)	ClA–Cd–Cl	171.13(2)
O _w –Cd–O(2)	96.64(12)	CdA–ClA–Cd	114.60(4)
O _w –Cd–Cl	96.35(9)	C(5B)–N(0B)–Cd	119.8(3)
O _w –Cd–ClA	91.09(9)	O(1)–C(1)–O(2)	120.7(4)
Complex 2			
Cd–O(1)	2.392(6)	Cd–Br(B)	2.830(1)
Cd–O(2)	2.413(5)	N–C(5)	1.430(9)
Cd–O _w	2.236(6)	O(1)–C(1)	1.286(9)
Cd–Br	2.7875(9)	O(2)–C(1)	1.266(10)
Cd–N(0A)	2.353(6)		
O(1)–Cd–O(2)	54.57(17)	O _w –Cd–N(0A)	94.8(2)
O(1)–Cd–Br	82.41(12)	N(0A)–Cd–O(1)	164.1(2)
O(2)–Cd–Br	136.98(12)	N(0A)–Cd–O(2)	133.3(2)
O(1)–Cd–Br(B)	87.15(13)	N(0A)–Cd–Br	88.42(15)
O(2)–Cd–Br(B)	84.24(13)	N(0A)–Cd–Br(B)	80.72(15)
O _w –Cd–O(1)	99.4(2)	Br–Cd–Br(B)	95.01(3)
O _w –Cd–O(2)	89.4(2)	Cd–Br–Cd(B)	84.99(3)
O _w –Cd–Br	98.23(13)	O(2)–C(1)–O(1)	119.3(7)
O _w –Cd–Br(B)	165.90(14)		
Complex 3			
Cd–N	2.347(5)	O(1)–C(1)	1.249(7)
Cd–I	2.8276(8)	O(2)–C(1)	1.289(8)
N–C(5)	1.429(8)		
N–Cd–I	103.35(14)	N–Cd–I(0A)	97.57(15)
N(0A)–Cd–N	148.8(3)	I(0A)–Cd–I	95.12(3)
N(0A)–Cd–I	97.57(15)	C(5)–N–Cd	119.7(4)
N(0A)–Cd–I(0A)	103.35(14)	O(1)–C(1)–O(2)	123.3(6)
Complex 4			
Cd–N(1)	2.338(3)	N(11)–C(15)	1.413(4)
Cd–N(11)	2.377(3)	O(1)–C(11)	1.216(4)
Cd–N(3B)	2.314(3)	O(2)–C(11)	1.327(4)
Cd–N(3C)	2.314(3)		
N(1)–Cd–N(11)	90.43(11)	N(3B)–Cd–N(11A)	87.13(11)
N(1)–Cd–N(1A)	180.0	N(3C)–Cd–N(11A)	92.87(11)
N(1)–Cd–N(11A)	89.57(11)	N(3C)–Cd–N(3B)	180.0
N(1A)–Cd–N(11)	89.57(11)	N(3C)–Cd–N(1)	96.36(11)
N(1A)–Cd–N(11A)	90.43(11)	N(3C)–Cd–N(1A)	83.64(11)
N(11A)–Cd–N(11)	180.0	N(3C)–Cd–N(11)	87.13(11)
N(3B)–Cd–N(1)	83.64(11)	C(15)–N(11)–Cd	115.1(2)
N(3B)–Cd–N(1A)	96.36(11)	O(1)–C(11)–O(2)	121.4(3)
N(3B)–Cd–N(11)	92.87(11)		
Complex 5			
Cd–O _w	2.364(2)	Cd–Cl(2)	2.5687(7)
Cd–Cl(1)	2.5699(7)	N–C(5)	1.464(4)
O(2)–C(1)	1.188(4)	O(1)–C(1)	1.310(4)
O _w –Cd–O _w A	180.00(9)	Cl(2A)–Cd–Cl(1)	86.90(2)
O _w –Cd–Cl(2A)	86.52(7)	Cl(2)–Cd–Cl(1)	93.10(2)
O _w A–Cd–Cl(2A)	93.48(7)	O _w –Cd–Cl(1A)	92.83(6)
O _w –Cd–Cl(2)	93.48(7)	O _w A–Cd–Cl(1A)	87.17(6)
O _w A–Cd–Cl(2)	86.52(7)	Cl(2A)–Cd–Cl(1A)	93.10(2)
Cl(2A)–Cd–Cl(2)	180.00(3)	Cl(2)–Cd–Cl(1A)	86.90(2)
O _w –Cd–Cl(1)	87.17(6)	Cl(1)–Cd–Cl(1A)	180.00(3)
O _w A–Cd–Cl(1)	92.83(6)	O(2)–C(1)–O(1)	124.6(3)

air for one month. Yield: 65% (based on HL). $C_{14}H_{18}CdCl_6N_2O_4$ (603.4): calcd. C 27.87, H 2.98, N 4.64; found C 27.91, H 2.93, N 4.69. IR (KBr): $\tilde{\nu}$ = 3496 (m), 3275 (m), 3066 (br, s), 2920 (br, s), 2677 (m), 2617 (m), 2546 (m), 1950 (vw), 1701 (vs), 1678 (vs), 1612 (vs), 1589 (s), 1558 (m), 1522 (m), 1510 (s), 1487 (m), 1433 (m), 1419 (m), 1387 (w), 1319 (m), 1284 (s), 1211 (m), 1182 (m), 1119 (m), 1107 (m), 1063 (vw), 1020 (w), 957 (vw), 906 (vw), 856 (w), 833 (vw), 762 (s), 739 (w), 692 (w), 638 (w), 596 (w), 542 (w), 525 (w), 480 (m) cm^{-1} .

X-ray Crystallography: Intensity data for the five complexes were measured with a Siemens Smart CCD diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. Empirical absorption corrections were applied by use of the SADABS program. The structures were solved by direct methods and all calculations were performed with the aid of the SHELXL PC program. The positions of H atoms in complexes **1–4** were generated geometrically (C–H bond fixed at 0.96 \AA) and the positions of H atoms in complex **5** were generated from difference Fourier maps, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The structures were refined by full-matrix, least-squares minimization of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except the H atoms. The crystallographic data for complexes **1–5** are listed in Table 1, selected bond lengths and angles in Table 2. CCDC-180374 to -180376 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].

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