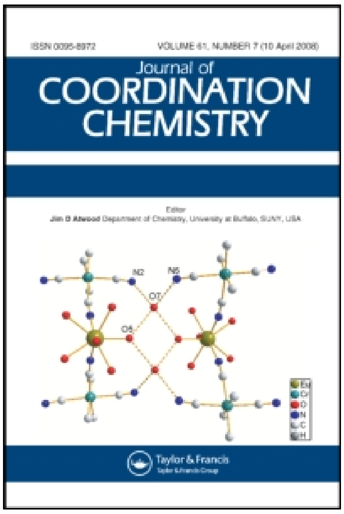

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Anion channel structure through packing of cucurbit[5]uril-Pb^{2+} or cucurbit[5]uril-Hg^{2+} complexes

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Anion channel structure through packing of cucurbit[5]uril-Pb^{2+} or cucurbit[5]uril-Hg^{2+} complexes

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In this study, complexes $\{[Pb_4(C_{30}H_{30}N_{20}O_{10})_2Cl_2]Cl_2(H_2O)_2\}PbCl_6 \cdot 12H_2O$ (**1**) and $[Hg(C_{30}H_{30}N_{20}O_{10})Cl_2]HgCl_4^{2-}(H_3O)_2^{2+} \cdot 6H_2O$ (**2**) have been synthesized and structurally characterized. Single-crystal X-ray diffraction analyses reveal that water-soluble toxic metal ions, Pb^{2+} and Hg^{2+}, can be chelated by cucurbit[5]uril to form molecular capsule and molecular bowl. Moreover, solid-state packing of these molecular capsule or molecular bowl shows the formation of a channel, in which octahedral $[PbCl_6]^{4-}$ or tetrahedral $[HgCl_4]^{2-}$ anions were encapsulated.

Keywords: Anion channel; Cucurbit[5]uril; Crystal structure

1. Introduction

Design and synthesis of anion receptors is of great interest in supramolecular chemistry. The fundamental and practical reasons for this interest have been discussed thoroughly and many host molecules that include anions have been studied [1–16]. Cucurbit[$n = 5$–$8, 10$]uril (figure 1), which has a hollow core and identical carbonyl-fringed portals on each side, having a barrel shape, is one kind of fascinating organic macrocyclic cavitand [17–19]. Obviously, the large inner void of the unique macrocyclic host is ideal for the encapsulation of various anions. In fact, the anion inclusion of the cucurbit[*n*]uril family has been demonstrated in many studies [20–28]. Although the intramolecular cavity of cucurbit[*n*]uril has been extensively investigated for anion inclusion, little attention has been paid to intermolecular void space formed by the solid-state packing of cucurbit[*n*]uril molecules or cucurbit[*n*]uril complexes [29, 30].

A number of cucurbit[5]uril complexes with encapsulated chloride or nitrate were reported [26–28]. The attribute that cucurbit[5]uril can coordinate to many kinds of metal ions of dissimilar ionic radii attracted our interest. Complexation of cucurbit[5]uril by adjusting the portal semidiameter and putting metal ions at different

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out-of-plane sites was concluded in [28], prompting us to investigate whether toxic heavy metal ions, such as Pb^{2+} and Hg^{2+}, can be chelated by cucurbit[5]uril too, because they are especially dangerous to health [31, 32]. Herein, we present the synthesis and crystal structure of cucurbit[5]uril coordinated to Pb^{2+} and Hg^{2+} ions. Moreover, this study shows octahedral $[PbCl_6]^{4-}$ or tetrahedral $[HgCl_4]^{2-}$ anions encapsulated inside the channel formed by the solid-state aggregation of cucurbit[5]uril–Pb^{2+} or cucurbit[5]uril–Hg^{2+}(scheme 1).

2. Experimental

2.1. *Materials and methods*

All reagents and solvents were commercially available and used as received. Cucurbit[5]uril was synthesized by published procedures [18, 19]. The C, H, and N microanalyses were carried out with a CE instruments' EA 1110 elemental analyzer.

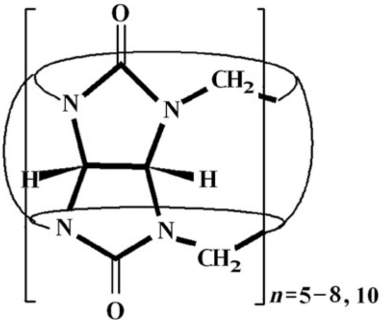
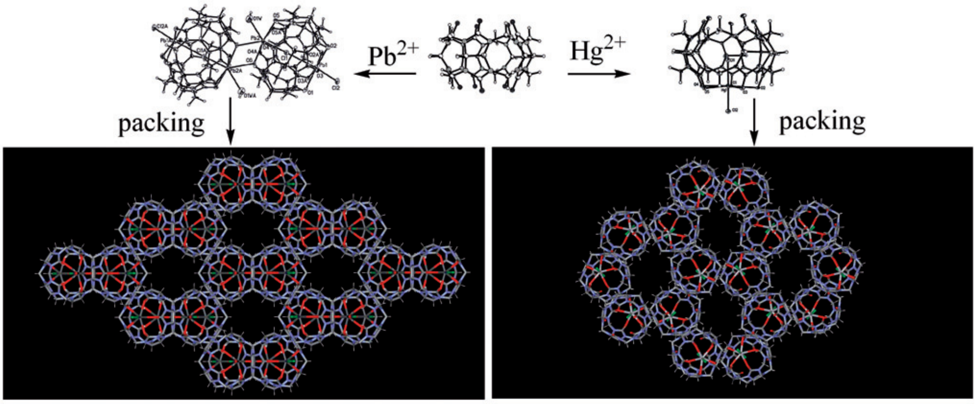


Figure 1. Molecular structure of cucurbit[$n = 5$–8, 10]uril.



Scheme 1. Two anion channel structures generated by packing of cucurbit[5]uril–Pb^{2+} or cucurbit[5]uril–Hg^{2+} complexes were synthesized and structurally characterized.

2.2. *Syntheses*

2.2.1. $\{[Pb_4(C_{30}H_{30}N_{20}O_{10})_2Cl_2]Cl_2(H_2O)_2\}PbCl_6 \cdot 12H_2O$ (1). Cucurbit[5]uril (0.083 g, 0.10 mmol) and $Pb(NO_3)_2$ (0.033 g, 0.10 mmol) were dissolved in 5.0 mL of 3.0 mol HCl solution with stirring at room temperature. Then the mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150°C, held at that temperature for 50 h, cooled to 100°C at a rate of $3^\circ C\,h^{-1}$ and held for 16 h, followed by further cooling to 30°C at a rate of $5^\circ C\,h^{-1}$. Purple crystals of **1** were collected in 65% yield. Anal. Calcd (found) for $\{[Pb_4(C_{30}H_{30}N_{20}O_{10})_2Cl_2]Cl_2(H_2O)_2\}PbCl_6 \cdot 12H_2O$ **1**: C, 21.69 (21.81), N, 16.81 (16.96), and H, 2.61 (2.68).

2.2.2. $[Hg(C_{30}H_{30}N_{20}O_{10})Cl_2]HgCl_4^{2-}(H_3O)_2^{2+} \cdot 6H_2O$ (2). $HgCl_2$ (0.5 mL, 0.1 mol L^{-1}) was added to a solution of cucurbit[5]uril (5 mL, 0.02 mol L^{-1}) in HCl (3 mol L^{-1}) and kept at room temperature in an open beaker. X-ray quality colorless crystals of **2** were separated after 2 weeks and were collected in 76% yield. Anal. Calcd (found) for $[Hg(C_{30}H_{30}N_{20}O_{10})Cl_2]\ HgCl_4^{2-}(H_3O)_2^{2+} \cdot 6H_2O$ **2**: C, 22.65 (22.49), N, 17.61 (17.55), and H, 3.04 (3.13).

2.3. *X-ray crystallography*

Single-crystal X-ray data were collected on a Bruker Apex-2000 diffractometer at 123 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with $\omega/2\theta$ scan mode. Lorentz-polarization and absorption corrections were applied. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package [33, 34], respectively. All non-hydrogen atoms were refined anisotropically. Idealized positions of the hydrogens were located by using a "riding" model with $U_{iso} = 1.2U_{eq}$ of the carrier atom. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. A summary of crystallographic data, data collection, and refinement parameters for **1** and **2** is given in table 1.

3. Results and discussion

3.1. *Description of the crystal structures*

Conventional solution synthesis, the method we previously used, is not suitable to prepare single crystals of cucurbit[5]uril with Pb^{2+}, because precipitate is formed at once when adding the cucurbit[5]uril solution to the Pb^{2+} solution. Solvothermal reaction of cucurbit[5]uril and Pb^{2+} at 150°C for 50 h leads to single crystals of **1**. Crystal structure analysis reveals 5 Pb^{2+} cations, 10 chlorides, 2 cucurbit[5]uril, and 12 water molecules (figure 2). Four lead ions are coordinated to each portal of the two cucurbit[5]uril molecules. Pb1 is coordinated by five carbonyl oxygens (O1, O2, O3, O2A, and O3A) and a chloride (Cl2) with a distance of 2.583(2) Å. Pb2 is coordinated by six carbonyl oxygens from two different cucurbit[5]uril molecules and one water

(O1W) molecule with a distance of 2.830 Å. In this way, one cucurbit[5]uril and two Pb^{2+} cations form one closed molecular capsule. In the closed molecular capsule, the other chloride (Cl1) is encapsulated and coordinated to Pb2 from inside. Coordinated by six chlorides, Pb3 formed $[PbCl_6]^{4-}$. Selected bond lengths (Å) and angles (°) for **1** are shown in table 2.

The remarkable feature in **1** is that two cucurbit[5]urils and two encapsulated chlorides, four Pb^{2+}, two coordinated chlorides, and two coordinated water molecules lie on special positions of site symmetry *m*. So, Pb2 and Pb2A, as well as O6 and O6A are within a plane and form a parallelogram in which the distance between the two leads (Pb2 and Pb2A) is 4.728 Å. Obviously, the Pb_2O_2 plane is vertical to each plane formed by five oxygens of cucurbit[5]uril. The most interesting feature of the crystal structure of **1** is that two cucurbit[5]uril-based molecular capsules formed a supramolecule in which cucurbit[5]uril molecules link through the coordination of their carbonyl groups to lead.

Table 1. Summary of crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{60}H_{88}N_{40}O_{34}Pb_5Cl_{10}$	$C_{30}H_{48}N_{20}O_{18}Hg_2Cl_6$
Formula weight	3304.20	1590.76
Temperature (K)	123(2)	123(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnnm*	*P2(1)2(1)2(1)*
Unit cell dimensions (Å)		
a	13.643	13.188(3)
b	24.601(4)	14.567(3)
c	13.643(3)	24.366(5)
Volume (Å^3), *Z*	4578.9(13), 2	4680.8(18), 4
Calculated density (g cm^{-3})	2.397	2.257
Crystal size (mm^3)	0.23 × 0.15 × 0.11	0.40 × 0.35 × 0.23
Reflections collected	33681	27543
Independent reflections	4604 [*R*(int) = 0.0419]	8940 [*R*(int) = 0.0801]
Goodness-of-fit on F^2	1.068	1.030
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0467$, $wR_2 = 0.1302$	$R_1 = 0.0682$, $wR_2 = 0.1728$
R indices (all data)	$R_1 = 0.0499$, $wR_2 = 0.1331$	$R_1 = 0.0707$, $wR_2 = 0.1745$

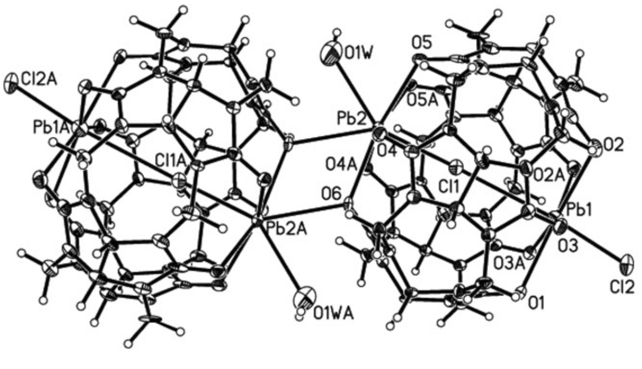


Figure 2. ORTEP diagram of **1**; displacement ellipsoids are drawn at the 50% probability level. Solvate water and $[PbCl_6]^{4-}$ are omitted for clarity.

Since the two macrocycle molecules linked together resemble a siamese, we suggest the name siamese molecule.

Although the closed molecular capsule in **1** is very similar to its counterparts in $\{[Ba_2(C_{30}H_{30}N_{20}O_{10})Cl](NO_3)(H_2O)_5\}Cl_2 \cdot 2H_2O$ [26], which we previously reported, there are many significant differences between the two closed molecular capsules. First, in **1** the bond length of Pb2−Cl1 (2.709 Å) is much shorter than that of Pb1−Cl1 (3.470 Å), which means the encapsulated chloride is not in the center of the closed molecular capsule. The main reason is that Pb1 and Pb2 possess different coordination geometries and different electrostatic interactions with the encapsulated chloride. Second, each lead cation is almost at the same plane with the five carbonyl oxygen atoms of cucurbit[5]uril in **1**. In the barium compound, each barium ion is out-of-plane. Ba1 is 0.767 Å (Ba2 is 0.722 Å) above the mean plane of the five carbonyl oxygen atoms of the cucurbit[5]uril portal. Third, the portal semidiameter of cucurbit[5]uril in the barium compound (mean value = 2.638 Å) is slightly bigger than that in **1** (mean value = 2.607 Å). This structural behavior can be illustrated by the fact that the ionic radius of barium ion is larger than that of lead ion.

Slow evaporation of hydrochloric acid aqueous solution containing $HgCl_2$ and cucurbit[5]uril, in mole ratio 1:2, results in the formation of crystals of **2**. In the crystal structure (figure 3), one mercury is located at the center of one portal of cucurbit[5]uril, coordinated by five carbonyl oxygens (O1, O2, O3, O4, and O5) and a chloride (Cl2) with a distance of 2.305(3) Å; the cucurbit[5]uril and one mercury cation form a molecular bowl (or opened molecular capsule). In the molecular bowl, the other chloride (Cl1) is encapsulated. The encapsulated chloride is coordinated to mercury from inside. In table 3, relevant bond lengths (Å) and angles (°) for **2** are shown.

Comparison of **2** and $[Cd(C_{30}H_{30}N_{20}O_{10})Cl_2]\ CdCl_4^{2-}(H_3O)_2^{2+} \cdot 2CH_3OH \cdot 4H_2O$ [26] reveals that these two compounds are isomorphous. However, the portal semidiameter of cucurbit[5]uril in **2** (mean value = 2.707 Å) is much bigger than that in the latter (mean value = 2.551 Å), undoubtedly due to the ionic radius of mercury ion (1.16 Å) being larger than that of cadmium ion (1.09 Å) [35].

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

Pb(1)–Cl(2)	2.583(2)	Pb(2)–O(6)	2.577(5)
Pb(1)–O(1)	2.589(5)	Pb(2)–O(4)#1	2.578(3)
Pb(1)–O(3)#1	2.605(4)	Pb(2)–O(4)	2.578(3)
Pb(1)–O(3)	2.605(4)	Pb(2)–O(5)#1	2.638(3)
Pb(1)–O(2)#1	2.639(4)	Pb(2)–O(5)	2.638(3)
Pb(1)–O(2)	2.639(4)	Pb(2)–Cl(1)	2.7086(17)
Cl(2)–Pb(1)–O(1)	83.90(12)	O(5)–Pb(2)–Cl(1)	84.80(8)
Cl(2)–Pb(1)–O(3)#1	89.09(8)	O(6)–Pb(2)–O(1W)	127.4(2)
Cl(2)–Pb(1)–O(3)	89.09(8)	O(4)#1–Pb(2)–O(1W)	102.62(9)
Cl(2)–Pb(1)–O(2)#1	95.42(9)	O(4)–Pb(2)–O(1W)	102.62(9)
Cl(2)–Pb(1)–O(2)	95.42(9)	O(5)#1–Pb(2)–O(1W)	69.24(19)
O(6)–Pb(2)–Cl(1)	84.60(11)	O(5)–Pb(2)–O(1W)	69.24(19)
O(4)#1–Pb(2)–Cl(1)	85.63(7)	Cl(1)–Pb(2)–O(1W)	148.0(2)
O(4)–Pb(2)–Cl(1)	85.63(7)	Cl(1)–Pb(2)–O(6)#2	142.80(11)
O(5)#1–Pb(2)–Cl(1)	84.80(8)	O(1W)–Pb(2)–O(6)#2	69.2(2)

Symmetry transformations used to generate equivalent atoms: #1: x, y, $-z+1$; #2: $-x$, $-y+1$, $-z+1$.

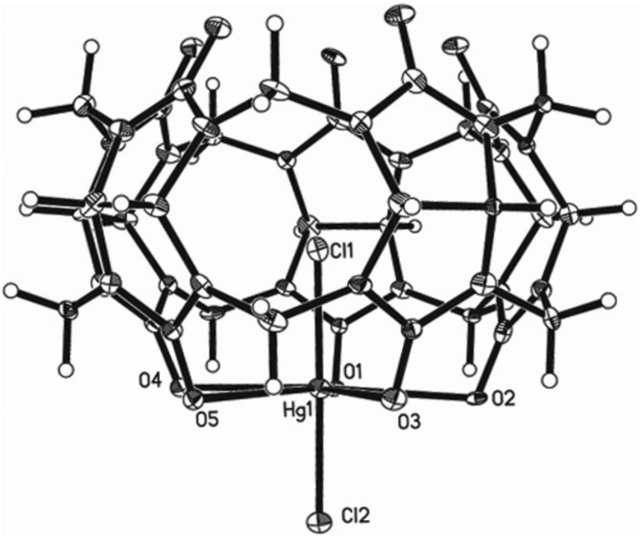


Figure 3. ORTEP diagram of **2**; displacement ellipsoids are drawn at the 50% probability level; and solvate water and $[HgCl_4]^{2-}$ are omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Hg(1)–Cl(1)	2.346(3)	Hg(1)–O(3)	2.604(2)
Hg(1)–Cl(2)	2.305(3)	Hg(1)–O(4)	2.744(15)
Hg(1)–O(1)	2.706(2)	Hg(1)–O(5)	2.756(3)
Hg(1)–O(2)	2.725(3)		
Cl(2)–Hg(1)–Cl(1)	174.86(10)	Cl(1)–Hg(1)–O(4)	90.1(6)
Cl(2)–Hg(1)–O(3)	93.5(2)	Cl(2)–Hg(1)–O(5)	91.64(2)
Cl(1)–Hg(1)–O(3)	91.5(2)	Cl(1)–Hg(1)–O(5)	91.04(1)
Cl(2)–Hg(1)–O(1)	81.98(2)	O(2)–Hg(1)–O(3)	72.38(2)
Cl(1)–Hg(1)–O(1)	93.1(2)	O(1)–Hg(1)–O(2)	74.84(1)
Cl(2)–Hg(1)–O(2)	85.35(2)	O(3)–Hg(1)–O(5)	73.51(15)
Cl(1)–Hg(1)–O(2)	94.91(2)	O(4)–Hg(1)–O(5)	69.73(2)
Cl(2)–Hg(1)–O(4)	86.66(2)	O(1)–Hg(1)–O(4)	69.28(2)

3.2. *Formation of the anion channel*

Analysis of **1** reveals that each siamese molecule is a hydrogen-bond donor to four neighbors through CH or CH_2 groups, and, at the same time, behaves as a hydrogen-bond acceptor to four remaining neighbors through the carbonyl-fringed portals. As a result, each siamese molecule strongly interacts with the eight nearest neighbors. In such a way, the siamese molecules extend in three dimensions to form a stable supramolecular framework. The packing diagram of the siamese molecules is depicted in figure 4. A honeycomb-like structure with 1-D channels along the *a*-axis is generated, in which the octahedral $[PbCl_6]^{4-}$ and water molecules were entrapped. Clearly, extensive hydrogen bonding exist between $[PbCl_6]^{4-}$ and water. Hydrogen bonds for **1** are given in table 4.

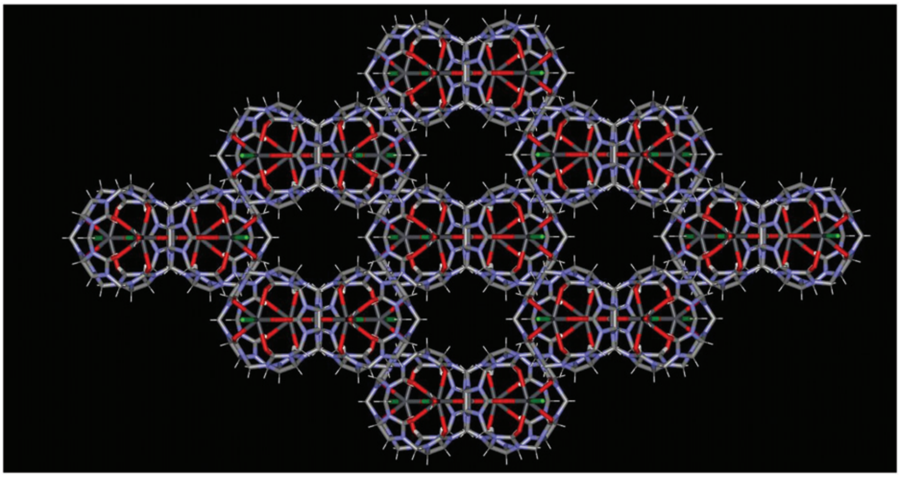


Figure 4. Packing diagram of **1** viewed down the *a*-axis showing the packing of the siamese molecule creating a through channel down the *a*-axis encapsulating the octahedral $[PbCl_6]^{4-}$ inside the cavity. Water and $[PbCl_6]^{4-}$ are omitted for clarity.

Table 4. Hydrogen bonds for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(2W)–H(2)···O(3W)	0.85	2.02	2.78(2)	148.3
O(2W)–H(3)···O(4W)#6	0.85	1.58	2.34(2)	147.3
O(3W)–H(4)···O(2)#7	0.85	2.42	3.159(12)	146.5
O(4W)–H(5)···Cl(3)#8	0.85	2.49	3.298(11)	160.0
O(5W)–H(6)··· Cl(3)#8	0.85	2.67	3.436(13)	150.5
O(5W)–H(7)···O(4W)	0.85	1.97	2.735(15)	149.1
O(6W)–H(8)···O(5)#9	0.85	2.17	3.012(17)	170.7
O(6W)–H(9)···O(5W)#9	0.85	2.10	2.94(2)	167.0

Symmetry transformations used to generate equivalent atoms: #6: $-x$, $-y+1$, $-z$; #7: $-x-1/2$, $y+1/2$, $-z+1/2$; #8: x, $y+1$, z; #9: $-x-1/2$, $y-1/2$, $-z+1/2$.

In the crystal structure of **2**, each isolated mercury-capped molecular bowl strongly interacts with the six nearest neighbors as in **1** and a hexagonal arrangement of the cucurbit[5]uril molecular bowls forms 1-D channels along the *a*-axis (figure 5). The channels are filled with tetrahedral $[HgCl_4]^{2-}$ anions and water molecules. The molecular bowls, $[HgCl_4]^{2-}$, and water interact to form a 3-D hydrogen-bonded structure. Hydrogen bonds for **2** are listed in table 5. Examples of cucurbit[*n*]uril channels in solid-state structures remain rare. Such channels have many potential applications including catalysis, ion delivery, gas storage, and separation.

4. Conclusion

A number of structures of Pb^{2+} and Hg^{2+} complexes have been published in the past few years [36–44]. For example, Marandi *et al.* [36–38] reported a series of Pb^{2+}

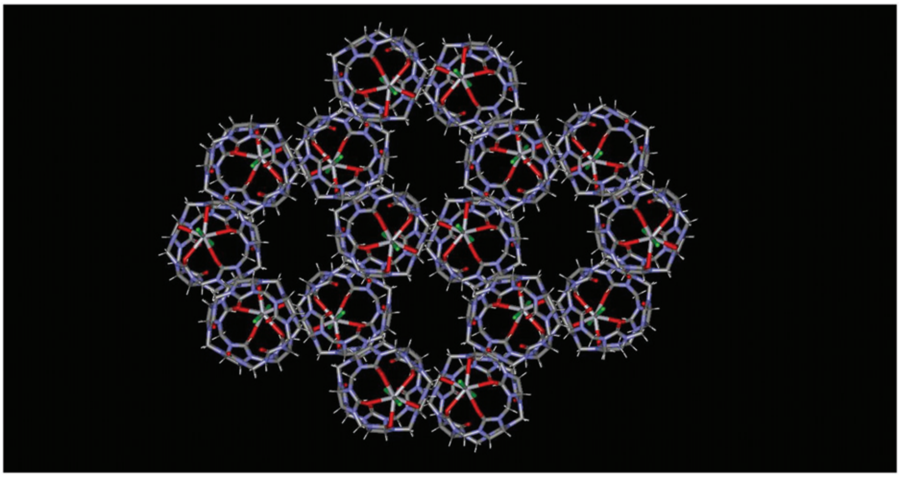


Figure 5. Packing diagram of **2** viewed down the *a*-axis showing the packing of the siamese molecule creating a through channel down the *a*-axis encapsulating the tetrahedral $[HgCl_4]^{2-}$ inside the cavity. Water and $[HgCl_4]^{2-}$ are omitted for clarity.

Table 5. Hydrogen bonds for **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1W)–H(1WA)···O(7)	0.85	2.28	3.044(12)	150.5
O(1W)–H(1WB)··· Cl(2)	0.85	2.60	3.366(10)	151.4
O(2W)–H(2WA)···Cl(4)#1	0.85	2.30	3.136(12)	165.7
O(2W)–H(2WB)···Cl(5)#2	0.85	2.40	3.230(12)	166.3
O(3W)–H(3WA)···O(2W)	0.85	1.83	2.656(16)	164.5
O(3W)–H(3WB)···O(5)	0.85	2.10	2.932(12)	165.5
O(4W)–H(4WA)···Cl(6)	0.85	2.24	3.080(10)	170.7
O(4W)–H(4WB)···O(6W)#3	0.85	1.79	2.632(14)	170.2
O(5W)–H(5WC)···O(7W)	0.85	1.57	2.412(16)	169.5
O(5W)–H(5WA)···O(3W)	0.85	1.63	2.476(14)	174.9
O(5W)–H(5WB)···O(6)#4	0.85	1.79	2.637(13)	174.9
O(6W)–H(6WA)···O(2)	0.85	1.89	2.710(13)	161.4
O(6W)–H(6WB)···Cl(5)#5	0.85	2.41	3.230(11)	162.5
O(7W)–H(7WA)···O(1)	0.85	2.38	2.987(13)	129.4
O(7W)–H(7WA)···Cl(2)	0.85	2.44	3.169(11)	144.0
O(7W)–H(7WB)···O(4W)#3	0.85	1.87	2.592(14)	141.4
O(8W)–H(8WA)···O(2)	0.85	1.95	2.750(12)	156.6
O(8W)–H(8WB)···O(6)	0.85	2.17	2.975(12)	157.3

Symmetry transformations used to generate equivalent atoms: #1: $-x+3/2$, $-y+1$, $z-1/2$; #2: $-x+1$, $y-1/2$, $-z+1/2$; #3: $x-1/2$, $-y+3/2$, $-z+1$; #4: $x-1$, y, z; #5: $x+1/2$, $-y+3/2$, $-z+1$.

complexes with many ligands. Gao *et al.* [39] synthesized Hg^{2+} complexes with substituted 1,10-phenanthroline and studied its luminescent properties. Similar to these ligands, cucurbit[5]uril can coordinate to Pb^{2+} and Hg^{2+}. However, it must be mentioned that cucurbit[5]uril is a macrocyclic cryptand, in which the anion is easily encapsulated.

In summary, we have reported that toxic Pb^{2+} and Hg^{2+} can be chelated by cucurbit[5]uril, further confirming the cucurbit[5]uril complexation mechanism that we had previously proposed [28]. Unambiguously, complexation of cucurbit[5]uril with toxic metal ions has important potential applications to the filtration of drinking water and environmental remediation. More importantly, we have demonstrated octahedral $[PbCl_6]^{4-}$ and tetrahedral $[HgCl_4]^{2-}$ encapsulation inside the channels formed by the solid-state aggregation of cucurbit[5]uril with Pb^{2+} and with Hg^{2+}. The discovery of the anion channel structure in a supramolecular framework sheds light on designing organic molecular porous materials based on non-covalent interactions.

Supplementary material

CCDC Nos 704472 and 704473 contain the supplementary crystallographic data for this article. The datum can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

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