

Difference of Coordination between Alkali- and Alkaline-Earth-Metal Ions to a Symmetrical $\alpha,\alpha',\delta,\delta'$ -Tetramethylcucurbit[6]uril

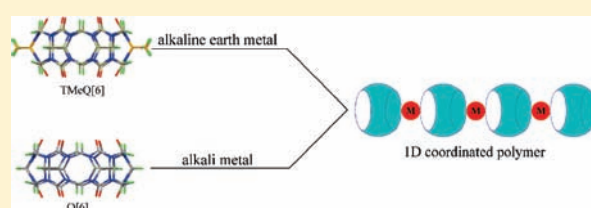
Wen-Jian Chen,[†] Da-Hai Yu,[†] Xin Xiao,[†] Yun-Qian Zhang,[†] Qian-Jiang Zhu,^{*,†} Sai-Feng Xue,[†] Zhu Tao,[†] and Gang Wei^{*,†}

[†]Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, People's Republic of China

[‡]CSIRO Materials Science and Engineering, P.O. Box 218, Lindfield, New South Wales 2070, Australia

S Supporting Information

ABSTRACT: To explore differences in coordination between alkali- and alkaline-earth-metal ions and cucurbit[*n*]urils, a water-soluble $\alpha,\alpha',\delta,\delta'$ -tetramethylcucurbit[6]uril (TMeQ[6]) was used to synthesize a series of complexes and their supramolecular assemblies, based on the coordination of TMeQ[6] with alkali- and alkaline-earth-metal ions. The complexes and corresponding supramolecular assemblies were structurally characterized by single-crystal X-ray diffraction. Unlike cucurbituril (Q[6]), which formed the metal–Q[6] polymers based on the direct coordination of carbonyl oxygen atoms to the alkali-metal ions, TMeQ[6] formed metal–TMeQ[6] polymers based on the direct coordination of carbonyl oxygen atoms with the alkaline-earth-metal ions rather than the alkali-metal ions.



INTRODUCTION

Cucurbit[*n*]urils (Q[*n*]s)¹ and their alkyl-substituted derivatives² are a relatively new family of macrocycles that have proven to be a promising class of ligands and organic building blocks because these macrocycles have two open portals with a unique cavity rimmed with carbonyl groups and they readily coordinate with metal ions such as alkali- and alkaline-earth-metal ions,^{1a,c,3} transition-metal ions,^{3a,4} lanthanide metal ions, uranyl metal ions and their complexes^{3a,5} or clusters^{3a,6} to form various supramolecular entities and frameworks, which are aesthetics as well as the potential for nanoscale applications toward molecular devices and new materials.⁷ Among these metal–Q[*n*] complexes are a few Q[*n*]-based polymers or metal–Q[*n*] frameworks based on the direct coordination of the Q[*n*]s to metal ions. The first example of such polymers was reported by Kim and co-workers, and the crystal structure showed that rubidium and cucurbit[6]uril (Q[6]) formed a one-dimensional polymer by direct coordination through alternate rubidium ions and the portal carbonyl oxygen atoms of Q[6]s. In addition, the coordinating polymer chains were arranged to form a honeycomb structure with large linear hexagonal channels parallel to the polymer chains.⁸ Later, Kim and co-workers also reported similar coordinated polymer chains based on direct coordination through alternative potassium ions and portal carbonyl oxygen atoms of Q[6]s.⁹ Fedin and co-workers first demonstrated the crystal structure of the Q[6] complex with an 4f element of composition $\{[\text{Sm}(\text{H}_2\text{O})_4]_2\text{Q}[6]\}_3^{6+}$ in which triple-decker sandwiches $\{\text{Q}[6][\text{Sm}(\text{H}_2\text{O})_4]\text{Q}[6][\text{Sm}(\text{H}_2\text{O})_4]\text{Q}[6]\}_3^{6+}$ were built from the direct coordination of cucurbituril molecules and Sm^{3+} cations.¹⁰ They also found a new polymer $[\{\text{Nd}(\text{NO}_3)(\text{H}_2\text{O})_4\}_2(\text{NO}_3@Q[6])][\text{Nd}(\text{NO}_3)_6]$ by directly

coordinating alternate Q[6] and neodymium(III) cations.^{5b} Chen and her co-workers demonstrated one-dimensional supramolecular chains constructed from the direct coordination of Q[6] with sodium ions in the presence or absence of organic species.¹¹ Liu and co-workers have reported that the unsubstituted cucurbit[5]uril (Q[5]) can form a one-dimensional supramolecular chain.^{3c} More recently, Thuery has reported a series of lanthanide complexes with cucurbit[*n*]urils ($n = 5-7$) and perchlorate ligands. Among these complexes were some samples of polymers constructed by the direct coordination of Q[6] with lanthanide ions.^{5e}

Alkyl-substituted cucurbit[*n*]urils (SQ[*n*]s) as Q[*n*] derivatives are generally more soluble than the unsubstituted Q[*n*]s in water. In particular, cyclohexanocucurbit[*n*]urils ($n = 5, 6$) are soluble not only in water but also in some organic solvents.^{2b} Our group has reported a series of supramolecular structures with alkyl-substituted cucurbit[5]urils (SQ[5]s) as “beads” arranged in rings in which the “beads” were also directly interconnected by the metal ions, in particular, by the potassium ions.¹² To date, there have not been many investigations of the SQ[*n*]-based polymers based on the direct coordination of SQ[*n*]s and metal ions. We need to consider the following: What kind of metal ion can lead to the metal–SQ[*n*] frameworks? What kind of SQ[*n*] is ready to form the metal–SQ[*n*] frameworks? What factors are responsible for the formation of the metal–SQ[*n*] frameworks? Consequently, the chemical and physical behaviors of the

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metal–SQ[*n*] frameworks remain unknown and need to be explored.

We previously reported the controlled synthesis of $\alpha,\alpha',\delta,\delta'$ -tetramethylcucurbit[6]uril (TMeQ[6]), which was ellipsoidal and water-soluble (Figure 1).^{2e} In the present study, we demonstrate a series of crystal structures of complexes constructed of TMeQ[6] with alkali- and alkaline-earth-metal ions. Unlike the unsubstituted cucurbituril (Q[6]), which coordinates directly with the alkali-metal ion that leads to the formation of a columnar one-dimensional coordinated polymer, the partial methyl-substituted cucurbituril, TMeQ[6], coordinates directly with alkaline-earth-metal ions, instead of alkali-metal ions, and forms a columnar one-dimensional coordinated polymer (Scheme 1).

EXPERIMENTAL SECTION

Synthesis. Chemicals such as lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, sodium bromide, potassium bromide, potassium sulfate, potassium iodide, potassium nitrate, potassium fluoride, calcium chloride, cadmium chloride, strontium nitrate, and barium chloride were of reagent grade and were used without further purification. TMeQ[6] was prepared by procedures reported elsewhere.^{2e} Elemental analysis was carried out on a EURO EA-3000 elemental analyzer. A series of crystal structures of TMeQ[6] with alkali-metal ions (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺) and alkaline-earth-metal ions (Ca²⁺, Sr²⁺, and Ba²⁺) were obtained. Generally, a similar process is used in the preparation of related crystals of TMeQ[6] with alkali- or alkaline-earth-metal ions. A solution of TMeQ[6] (0.50 g, 0.48 mmol) and the corresponding salt (2.01 mmol) in water (20 mL) was filtered to remove insoluble impurities. The filtrate was filled in a small beaker (50 mL) and was allowed to stand at room temperature by slow evaporation until X-ray-quality crystals were obtained. In some cases, the aqueous solution is acidic. For {[Li₂(H₂O)₆(TMeQ[6])]₂·4Cl·2H₃O·10H₂O} (1), the salt is LiCl (0.09 g); for {[Na₂(H₂O)₈(TMeQ[6])₂·2Cl·24H₂O} (2), the salt is NaCl (0.12 g); for {[Na₂(H₂O)₈(TMeQ[6])₂·4Br·2H₃O·17H₂O} (3), the salt is NaBr (0.21 g, 0.1 M HCl); for {[K₄(H₂O)₇Cl₂(TMeQ[6])₂·4Cl·2H₃O·8H₂O} (4), the salt is KBr (0.15 g, 0.1 M HCl); for {[K₂(H₂O)₅Cl(H₂O@TMeQ[6])₂·2Br·H₃O·H₂O} (5), the salt is KBr (0.24 g, 0.1 M HCl); for {[K₂(H₂O)₆(H₂O@TMeQ[6])₂·2I·12H₂O} (6), the salt is KI (0.335 g); for {2[K(H₂O)₃(NO₃@TMeQ[6])₂·(TMeQ[6])·Cl·H₃O·77H₂O} (7), the salt is KNO₃ (0.206 g); for {[Rb₂(H₂O)₃Cl·K(H₂O@TMeQ[6])₂·3Cl·H₃O·2H₂O} (8), the salts are RbCl (0.21 g) and KCl (0.15 g); for {[Cs(H₂O)₂(TMeQ[6])₂·Cl·9H₂O} (9), the salt is CsCl (0.34 g); for the compounds 10–12 with formulas {[Ca₂(H₂O)₁₀(TMeQ[6])₂·5Cl·H₃O·H₂O·10H₂O}, {[Sr₂(H₂O)₁₀(TMeQ[6])₂·2(NO₃)₂·4Br·2Cl·16H₂O}, and {[Ba₂(H₂O)₆(TMeQ[6])₂·2Cl·8H₂O}, respectively, the alkaline-earth-metal salts are CaCl₂ (0.23 g, 0.1 M HCl), Sr(NO₃)₂ (0.48 g, 0.1 M HCl/HBr), and BaCl₂ (0.42 g), respectively. Elemental analysis results for all compounds 1–12 are given in Table 1.

X-ray Crystallography. A suitable corresponding single crystal (~0.2 × 0.2 × 0.1 mm³) was picked up with paratone oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$, $\mu = 0.828 \text{ mm}^{-1}$) radiation source in the ω -scan mode and a nitrogen cold stream (–50 °C). The data were corrected for Lorentz and polarization effects (SAINT),^{13a} and semiempirical absorption corrections based on equivalent reflections were applied (SADABS).^{13a} The structure was elucidated by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 and SHELXL-97 program packages, respectively.^{13b,c} All of the non-hydrogen atoms were refined anisotropically, and the carbon-bound hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Because we focus on the coordination of metal ions to the portal carbonyl oxygen atoms, most water molecules in the unit cell have been taken into account by the SQUEEZE option of the PLATON program (referring to Table 1), except the coordinated water molecules. Details of the crystal parameters, data collection conditions, and refinement parameters for compounds 1–12 are summarized in Table 2. In addition, the crystallographic data for the reported structures were recorded in the Cambridge Crystallographic Data Centre as supplementary publications CCDC 807587 (1), 807590 (2), 807591 (3), 807592 (4), 807593 (5), 807594 (6), 807595 (7), 807596 (8), 807597 (9), 653912 (10), 807588 (11), and 807589 (12). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44 1223 336033).

RESULTS AND DISCUSSION

Complexes of Alkali-Metal Ions with TMeQ[6]. Previous work has revealed that coordination of the alkali-metal ions, such as sodium,¹¹ potassium,⁹ and rubidium,⁸ with the unsubstituted cucurbituril (Q[6]) led to the formation of the one-dimensional polymer in which the metal ions coordinated directly to the carbonyl oxygen atoms of Q[6]s. In particular, the honeycomblike

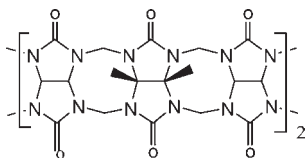


Figure 1. Structure of the TMeQ[6] ligand.

Scheme 1

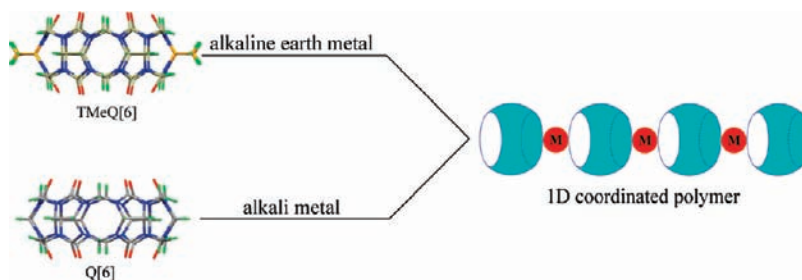


Table 1. Elemental Analysis Results (%)

results	1	2	3	4	5	6	7	8	9	10	11	12
squeezed water molecules in the cell	10	24	13	8		12	78		9	10	15	8
C calcd	31.30	34.33	32.46	34.52	32.65	27.81	29.34	31.36	33.84	28.13	26.55	27.91
C found	31.85	34.88	32.63	33.38	32.45	28.03	29.95	31.55	34.18	28.35	26.83	27.35
H calcd	5.38	5.47	4.90	4.49	4.18	4.79	6.18	3.88	4.69	5.25	4.46	4.22
H found	5.16	5.34	4.71	4.24	4.36	4.65	5.93	4.08	4.44	5.06	4.25	4.07
N calcd	21.90	24.02	22.71	24.16	22.84	19.46	21.11	21.94	23.68	19.68	19.35	19.53
N found	22.48	24.58	22.13	24.76	22.42	20.03	21.43	22.45	24.16	20.02	19.53	20.40

supramolecular assembly was observed in coordination of the rubidium ions and Q[6], and the hexagonal channels were filled with water molecules.⁸ However, most of the compounds contained TMeQ[6], and the alkali-metal ions used in this study did not show the expected assemblies in which the one-dimensional polymer would be formed by the direct coordination of the cucurbituril “beads” with the alkali-metal ions, and only a partial direct coordination of TMeQ[6] to the potassium ion in the acidic solution was observed in the present research. The compounds comprising TMeQ[6], the alkali-metal ions, such as Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ ions, with different anions, such as Cl⁻, Br⁻, I⁻, and NO₃⁻, were synthesized, and the crystal structures of these compounds were unambiguously determined.

Crystal Structure of 1. In the crystal structure of compound 1, one can see a one-dimensional chain comprising TMeQ[6] molecules and [Li₂(OH₂)₃]⁺ complex cations with a 1:2 ratio of TMeQ[6] to Li⁺ ion. Each TMeQ[6] molecule coordinates with two Li⁺ aqua complex cations, and a coordinated water molecule (O2W) in the [Li₂(OH₂)₃]⁺ cation interacts with a portal carbonyl oxygen (O6) of the neighboring TMeQ[6] through hydrogen bonding; this interaction leads to the formation of the TMeQ[6]–[Li₂(OH₂)₃]⁺ supramolecular chain (Figure 2). Interaction of the coordinated water molecule (O3W) with a portal carbonyl oxygen (O2) of TMeQ[6] further strengthens the supramolecular chain. The bond lengths of Li–O (water molecules) are in the range of 2.826–2.940 Å, and the hydrogen-bonding lengths of O(water molecules) with O(carbonyl oxygen atom) are in the range of 1.897–1.946 Å.

Crystal Structure of 2. A TMeQ[6] pair linked by two sodium pairs can be observed in the crystal structure of compound 2 (Figure 3). Each sodium cation Na1 (with 50% occupancy) in the sodium pair has an octahedral structure with six oxygen atoms, four water molecules (2O1W, O2W, and O3W), and two of the portal carbonyl oxygen atoms of TMeQ[6] (O2 and O3). The Na–O bond lengths are in the range of 2.192–2.439 Å. In addition, the coordinated water molecule O2W plays the role of a bridge to link the two TMeQ[6] molecules in the TMeQ[6] pair, and the water molecule O1W interacts with a portal carbonyl oxygen atom of TMeQ[6] (O1) through hydrogen bonding. It should be noted that there are no metal ions at the other portal of each TMeQ[6] in the TMeQ[6] pair. Thus, one can see that the interaction of TMeQ[6]s with sodium cations does not form the expected 1D supramolecular chain through the direct coordination of Na⁺ cations to TMeQ[6] molecules.

Compound 3 of TMeQ[6] with NaBr was also obtained in this study. The crystal structure of this compound reveals that compounds 3 and 2 are isomorphous. A similar TMeQ[6] pair linked by the sodium pairs to that in compound 2 can also be observed in compound 3. The experimental results suggest that the presence of the counterion Cl⁻ or Br⁻ would not influence

coordination of Na⁺ to TMeQ[6] and the arrangement of their assemblies.

Complexes of TMeQ[6] with Potassium Salts. In this study, we have tried to synthesize the complexes of TMeQ[6]–K⁺ with different counterions, such as Cl⁻, Br⁻, I⁻, and NO₃⁻, or mixtures of them, in order to understand the influence of the anions on the coordination of K⁺ to TMeQ[6].

Crystal Structure of 4. We start by introducing the system of TMeQ[6] with KCl. The crystal structure of compound 4 obtained in a HCl solution containing TMeQ[6] and KCl shows a one-dimensional supramolecular chain comprising TMeQ[6] “beads” and K⁺ linkages with a 1:2 ratio of TMeQ[6] to K⁺ ions (Figure 4). A close inspection reveals that there are two different K⁺-coordination manners in the chain: potassium cations K1 are directly coordinated to the carbonyl oxygen atoms of a portal from two neighboring TMeQ[6]s, while potassium cations K2, which coordinate to carbonyl oxygen atoms of another portal from two neighboring TMeQ[6]s, connect by sharing water molecules O4W. The K1 cation (with 50% occupancy) is directly coordinated with four carbonyl oxygen atoms of a portal from two neighboring TMeQ[6] molecules (2O2 and 2O3), three water molecules (2O3W and O7W disordered over four positions with 25% occupancy), and a chloride anion (Cl2). The K1–O (carbonyl oxygen) bonds are 2.780 (K1–O2) and 2.803 (K1–O3) Å in length, respectively, the K1–O (water molecules) bond lengths are in the range of 2.590–3.955 Å, and the K1–Cl2 bond is 2.980 Å in length. The K2 cation (disordered over two positions with 50% occupancy) is coordinated with six oxygen atoms, three portal carbonyl oxygen atoms (O4, O5, and O6) of a TMeQ[6] molecule, and three water molecules (2O4W and O5W). The bond lengths of K2–O (carbonyl oxygen atom) are in the range of 2.776–2.980 Å, and the bond lengths of K2–O (water molecule) are in the range of 2.801–2.888 Å.

The crystal structure of compound 5 obtained in a HCl solution containing TMeQ[6] and KBr shows structural features similar to those of compound 4. The crystallographic data suggest that compounds 5 and 4 are isomorphous. Solid structural characteristics similar to those of compound 4 can be observed in compound 5, and one-dimensional supramolecular chains of TMeQ[6] and the K⁺ aqua complex with a 1:2 ratio of TMeQ[6] to K⁺ ions are formed.

Crystal Structure of 6. In the crystal structure of compound 6 obtained in a solution containing TMeQ[6] and KI, each TMeQ[6] coordinates with two potassium cations K1 and forms a so-called molecular capsule including a water molecule (Figure 5). Each K1⁺ ion is coordinated with seven oxygen atoms, three carbonyl oxygen atoms (O1, O2, and O3) of a TMeQ[6] portal, four water molecules [O1W with 70% occupancy and O1W' with 30% occupancy (omitted for clarity), O2W, O3W, and O4W (captured in the cavity of the TMeQ[6]

Table 2. Crystal Data and Structure Refinement Details for Compounds 1–12

	1	2	3	4	5	6	7	8	9	10	11	12
empirical formula	C ₄₀ H ₈₂ O ₃₀ N ₂₄ ⁺ Li ₂ Cl ₄	C ₈₀ H ₁₅₂ O ₅₆ N ₄₈ ⁻ Na ₂ Cl ₂	C ₈₀ H ₁₄₄ O ₅₁ N ₄₈ ⁻ Na ₂ Br ₄	C ₈₀ H ₁₂₄ O ₄₁ ⁻ N ₄₈ K ₄ C ₁₆	C ₄₀ H ₆₁ O ₂₀ N ₂₄ ⁺ K ₂ Br ₂ Cl	C ₄₀ H ₈₂ O ₃₁ ⁻ N ₂₄ K ₂ I ₂	C ₁₂₀ H ₃₀₁ O ₁₂₆ ⁻ N ₇₄ K ₂ Cl	C ₄₀ H ₅₉ O ₁₉ ⁻ N ₂₄ Rb ₂ KCl ₄	C ₄₀ H ₆₆ O ₂₃ ⁻ N ₂₄ CsCl	C ₄₀ H ₈₉ O ₃₄ ⁻ N ₂₄ Ca ₂ Cl ₅	C ₈₀ H ₁₆₀ O ₆₆ ⁻ N ₅₀ Sr ₄ Cl ₂ Br ₄	C ₄₀ H ₇₂ O ₂₆ ⁻ N ₂₄ Ba ₂ Cl ₄
fw	1534.98	2799.38	2960.05	2783.37	1471.60	1727.30	4911.00	1531.94	1419.53	1707.76	3619.60	1721.70
cryst syst	triclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	triclinic	triclinic	orthorhombic	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>Fddd</i>	<i>Fddd</i>	<i>Fddd</i>	<i>Fddd</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Fddd</i>	<i>P21</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C2/m</i>
<i>a</i> , Å	11.085(2)	22.947(5)	23.0629(16)	22.0717(17)	22.0414(17)	11.8214(14)	14.3377(17)	22.291(6)	13.0365(18)	10.4540(17)	10.6622(6)	23.055(6)
<i>b</i> , Å	12.567(3)	31.395(6)	31.7424(16)	31.444(3)	31.670(3)	12.9387(8)	14.3877(18)	31.654(9)	16.629(2)	12.914(2)	13.1800(8)	10.464(2)
<i>c</i> , Å	13.011(3)	32.718(7)	32.528(3)	32.9292(17)	32.9490(17)	13.0732(8)	27.836(4)	32.854(9)	13.4697(18)	15.172(2)	26.7320(16)	16.667(4)
α , deg	70.445(7)	90	90	90	90	117.784(2)	81.131(4)	90	90	65.459(2)	87.093(2)	90
β , deg	69.832(7)	90	90	90	90	94.009(3)	89.708(4)	90	100.572(2)	73.521(2)	80.497(2)	117.976(2)
γ , deg	80.217(7)	90	90	90	90	104.474(3)	65.254(4)	90	90	73.497(2)	73.618(2)	90
<i>V</i> , Å ³	1600.3(6)	23571(8)	23813(3)	22854(3)	23000(3)	1671.9(2)	5141.3(11)	23182(11)	2870.5(7)	1754.1(5)	3554.6(4)	3551.1(14)
<i>Z</i>	1	8	8	8	16	1	1	16	2	1	1	2
<i>D</i> _{calc} , g cm ⁻³	1.593	1.578	1.651	1.618	1.700	1.716	1.586	1.755	1.642	1.617	1.691	1.627
<i>T</i> , K	223(2)	223	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
μ , mm ⁻¹	0.292	0.182	1.473	0.404	1.697	1.169	0.192	2.039	0.793	0.460	2.765	1.344
unique reffns	5495	5578	5861	5573	5636	6349	19 584	5520	9233	5980	12 316	3335
obsd reffns	5129	3736	3514	4654	4453	5218	8101	2711	8364	5845	8675	3032
no. of param	407	382	426	437	435	416	1105	426	731	430	907	239
<i>R</i> _{int}	0.0689	0.0449	0.0774	0.0374	0.0552	0.0389	0.1088	0.1381	0.0223	0.0219	0.0494	0.0306
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.1174	0.0787	0.0861	0.0781	0.0849	0.0429	0.0641	0.0960	0.0402	0.0444	0.0620	0.0333
wR [<i>I</i> > 2 σ (<i>I</i>)] ^b	0.3089	0.2197	0.2670	0.2455	0.2652	0.1141	0.1445	0.2788	0.1019	0.1172	0.1763	0.0927
<i>R</i> (all data)	0.1367	0.1081	0.1243	0.0874	0.1027	0.0532	0.1376	0.1896	0.0445	0.0536	0.0879	0.0364
wR (all data)	0.3187	0.2350	0.2914	0.2555	0.2774	0.1198	0.1662	0.3195	0.1044	0.1228	0.1905	0.0944
GOF on <i>F</i> ²	1.057	1.045	1.047	1.074	1.081	1.069	0.803	1.021	1.052	1.099	1.110	1.118

^a Conventional *R* on $F_{hk\ell}$: $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b Weighted *R* on $|F_{hk\ell}|^2$: $\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]^{1/2}$.

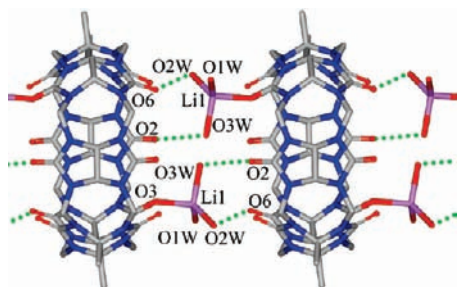


Figure 2. View of the partial atom-numbering scheme in the supramolecular chain in **1**. Carbon-bound hydrogen atoms are omitted for clarity. Dashed lines indicate hydrogen-bonding interactions.

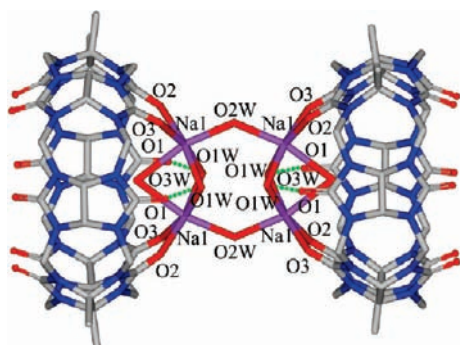


Figure 3. View of the TMeQ[6] pair linked by the Na⁺ metal ion pairs with a partial atom-numbering scheme in **2**. Carbon-bound hydrogen atoms are omitted for clarity. Dashed lines indicate hydrogen-bonding interactions.

molecule with 50% occupancy)]. Moreover, the coordinated water molecule O1W also interacts with three portal carbonyl oxygens (O4, O5, and O6) through hydrogen bonding and aids the coordinated K1 cations to form the molecular capsule. The bond lengths of K1–O are in the range of 2.542–3.120 Å, and the bond lengths of O1W–O (carbonyl oxygen atoms) are in the range of 2.896–2.951 Å.

Figure 5 also shows the connection of the neighboring TMeQ[6] molecular capsules, a pair of interactions between the coordinated water molecule O3W and the carbonyl oxygen atom O4 of the two neighboring TMeQ[6] molecules through hydrogen bonding; the bond length of O3W–O4 is 2.967 Å. Thus, a one-dimensional supramolecular chain can be constructed of TMeQ[6]-based molecular capsules.

Crystal Structure of 7. Compound **7** was obtained from an aqueous solution containing TMeQ[6] and KNO₃. The crystal structure of **7** presents two different TMeQ[6] molecules: an uncoordinated TMeQ[6] and a TMeQ[6] coordinated with only one potassium cation K1. The cation (K1) is coordinated to seven oxygen atoms, three portal carbonyl oxygen atoms (O1, O2, and O6) of the TMeQ[6] molecule, three water molecules (O1W, O2W, and O3W), and an oxygen atom (O21) of an included nitrate anion (Figure 6). The coordinated water molecule O2W interacts with three portal carbonyl oxygen atoms (O3, O4, and O5) of the TMeQ[6] molecule. The bond lengths of K1–O (carbonyl oxygen atoms) are in the range of 2.359–2.458 Å, the bond lengths of K1–O (water molecules) are in the range of 2.364–2.384 Å, and the bond lengths of O2W–O (carbonyl oxygen atoms) are in the range of 2.839–3.036 Å.

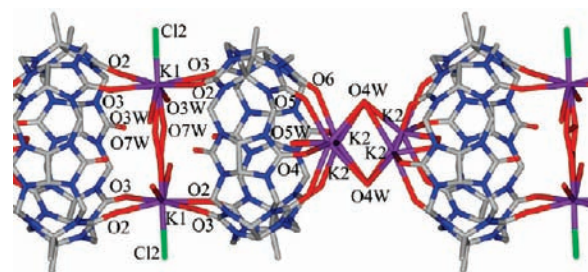


Figure 4. View of a partial atom-numbering scheme in the supramolecular chain in **4**. Carbon-bound hydrogen atoms are omitted for clarity.

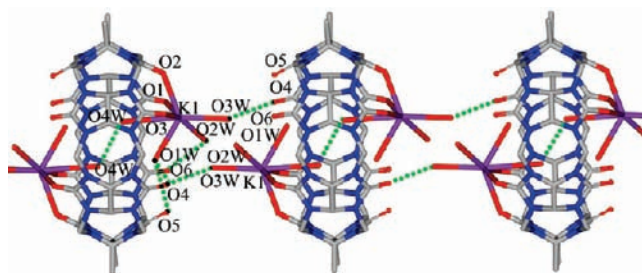


Figure 5. View of a partial atom-numbering scheme in the supramolecular chain constructed of TMeQ[6]–K⁺ capsules through hydrogen bonding in **6**. Carbon-bound hydrogen atoms are omitted for clarity.

On the basis of the above experimental results, one can see that the counteranions and acidic solution could influence the coordination of TMeQ[6] with the potassium cation and the solid structural features. It should be noted that no supramolecular polymers are formed through direct coordination of TMeQ[6] with a potassium cation.

Crystal Structure of 8. Compound **8** was obtained in an aqueous solution containing TMeQ[6], KCl, and RbCl. A comparison of the crystallographic data of compound **8** with those of compounds **4** and **5** reveals that these three compounds are isomorphous. Solid structural characteristics similar to those of compound **4** or **5** can be observed in compound **8**. For example, a one-dimensional supramolecular chain is comprised of TMeQ[6], K⁺, and Rb⁺ aqua complexes with a 1:1:2 ratio of TMeQ[6]–K⁺–Rb⁺, and two rubidium cations Rb1 are directly coordinated to portal carbonyl oxygen atoms (O2 and O3) from two neighboring TMeQ[6] molecules; moreover, a potassium cation K2 coordinates to the portal carbonyl oxygen atoms O1. While two rubidium cations Rb2 from two neighboring TMeQ[6] molecules connect by sharing water molecules O1W, each Rb2 is disordered over two positions with a 50% occupancy and coordinates to portal carbonyl oxygen atoms O4, O5, and O6 (Figure 7).

Crystal Structure of 9. The crystal structure of the complex of TMeQ[6] with the Cs cation in compound **9** shows that each Cs1 cation is coordinated with seven oxygen atoms, two water molecules (O1W and O2W, which are included in the cavity of the TMeQ[6] molecule), and, in particular, five carbonyl oxygen atoms of the portal of a TMeQ[6] molecule due to the larger ionic radius. The bond lengths of Cs1–O (carbonyl oxygen atoms) are in the range of 3.194–3.621 Å; the bond lengths of Cs1–O (water molecules) are in the range of 3.129–3.556 Å (Figure 8). However, no important assembly,

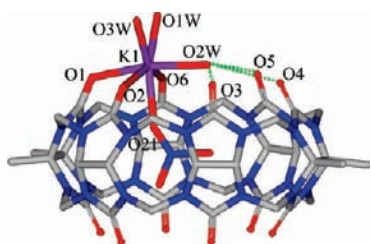


Figure 6. View of the complex of TMeQ[6]–K1. Carbon-bound hydrogen atoms are omitted for clarity. Dashed lines indicate hydrogen-bonding interactions.

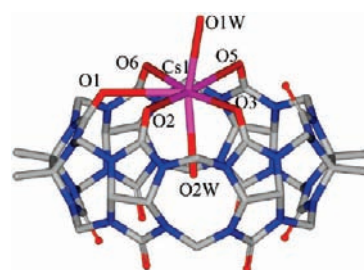


Figure 8. View of the complex of TMeQ[6]–Cs in 9. The carbon-bound hydrogen atoms are omitted for clarity.

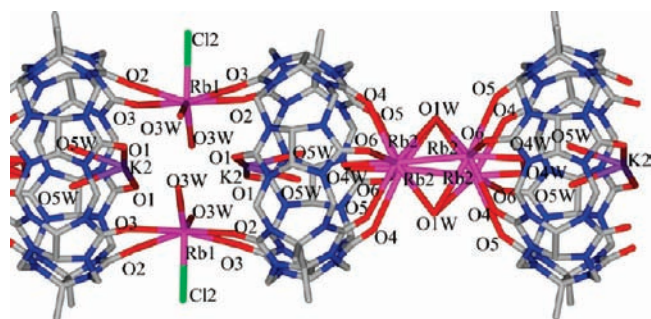


Figure 7. View of a partial atom-numbering scheme in the supramolecular chain in 8. Carbon-bound hydrogen atoms are omitted for clarity.

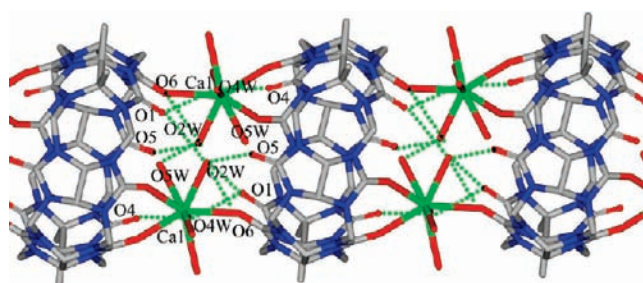


Figure 9. View of a partial atom-numbering scheme in the supramolecular chain in 10. The carbon-bound hydrogen atoms are omitted for clarity, and dashed lines indicate hydrogen-bonding interactions.

such as the one-dimensional chain constructed of TMeQ[6] molecules and Cs^+ complexes through hydrogen bonding or direct coordination, is observed in compound 9.

Complexes of the Alkaline-Earth-Metal Ions with TMeQ[6]. It has been shown that the alkali-metal ions can form a one-dimensional polymer by direct coordination with the unsubstituted Q[6], and to date, no research has shown that the alkaline-earth-metal ions could form a polymer by direct coordination with the unsubstituted Q[6].^{14,15} Unexpectedly, in the present research, we have not found a polymer by the direct coordination of the alkali-metal ions with TMeQ[6]. However, the interaction between TMeQ[6] and the alkaline-earth-metal ions, such as those of calcium, strontium, and barium, has revealed that such a polymer can be formed through direct coordination of these metal ions to the TMeQ[6] ligand.

Crystal Structure of 10. The crystal structure of compound 10 shows a one-dimensional supramolecular chain formed by the direct coordination of TMeQ[6] with the Ca^{2+} ions with a 1:2 ratio of TMeQ[6] to Ca^{2+} ions (Figure 9). A close inspection reveals that each calcium dication (Ca1) in the supramolecular chain is coordinated with eight oxygen atoms, five water molecules (O1W, O2W, O3W, O4W, and O5W), and three carbonyl oxygen atoms from two neighboring TMeQ[6] molecules (O2, O3 belonging to TMeQ[6], and O6 belonging to a neighboring TMeQ[6]). The bond lengths of $\text{Ca}-\text{O}$ (water molecules) are in the range of 2.396–2.715 Å, and the bond lengths of $\text{Ca}-\text{O}$ (carbonyl oxygen atoms) are in the range of 2.382–2.446 Å. Two neighboring TMeQ[6] molecules are bridged by two Ca^{2+} ions (Ca1) through direct coordination; the two Ca^{2+} ions (Ca1) are separated by 5.881 Å. Moreover, the water molecules coordinated with the Ca^{2+} ions form a hydrogen-bonding network among themselves and also with the portal carbonyl oxygen atoms of the TMeQ[6] molecules. The bond lengths are in the

range of 2.681–3.040 Å. Combining the direct coordination of the TMeQ[6] molecules with the Ca^{2+} ions and the hydrogen-bonding network between the two neighboring TMeQ[6] molecules leads to the formation of a one-dimensional coordination polymer, and such a supramolecular chain is different from those constructed from TMeQ[6] and alkali-metal ions.

Crystal Structure of 11. Coordination and assembly similar to those of compound 10 have been observed in the crystal structure of compound 11. A close inspection reveals that two slightly different one-dimensional coordination polymers of alternating TMeQ[6] and the Sr^{2+} aqua complex with a 1:2 ratio of TMeQ[6] to Sr^{2+} ions are formed (Figure 10a,b). Both strontium dications (Sr1 and Sr2) in the two different one-dimensional supramolecular polymers are also coordinated with eight oxygen atoms, five water molecules, and three carbonyl oxygen atoms from two neighboring TMeQ[6] molecules (two belonging to TMeQ[6] and one belonging to the neighboring TMeQ[6]). The bond lengths of $\text{Sr}-\text{O}$ (water molecules) vary within the range of 2.554–2.651 Å, and the bond lengths of $\text{Sr}-\text{O}$ (carbonyl oxygen atoms) vary within the range of 2.526–2.583 Å. Two neighboring TMeQ[6] molecules are bridged by two Sr^{2+} ions through direct coordination; the two Sr^{2+} ions are separated by 6.909 Å (for $\text{Sr1}-\text{Sr1}$) and 6.030 Å (for $\text{Sr2}-\text{Sr2}$). Moreover, the water molecules coordinated with the Sr^{2+} ions form a hydrogen-bonding network among themselves and also with the portal carbonyl oxygen atoms of the TMeQ[6] molecules. These networks could further strengthen the coordination of Sr cations to the TMeQ[6] molecules.

Crystal Structure of 12. The single-crystal structure of compound 12 reveals a one-dimensional supramolecular chain comprised of alternating TMeQ[6] molecules and a $\text{Ba}_2-(\mu\text{-OH}_2)_2(\text{OH}_2)_4\text{Cl}_2$ complex with a 1:2 ratio of TMeQ[6] to Ba^{2+} ions (Figure 11). The two neighboring TMeQ[6]

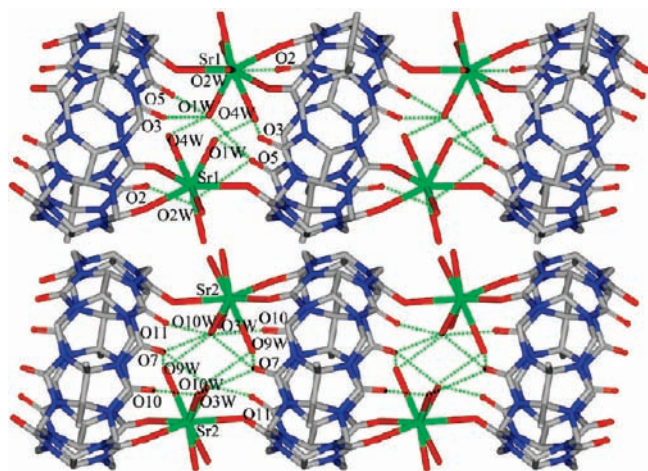


Figure 10. (a and b) Views of two partial atom-numbering schemes in the supramolecular chains in **11**. The carbon-bound hydrogen atoms are omitted for clarity, and dashed lines indicate hydrogen-bonding interactions.

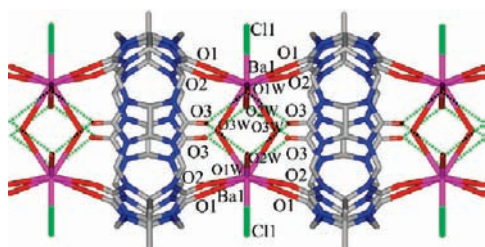


Figure 11. View of a partial atom-numbering scheme in the supramolecular chain in **12**. The carbon-bound hydrogen atoms are omitted for clarity, and dashed lines indicate hydrogen-bonding interactions.

molecules in the supramolecular chain are bridged by a $\text{Ba}_2(\mu\text{-OH}_2)_2(\text{OH}_2)_4\text{Cl}_2$ complex through direct coordination of barium dications (Ba1) to the portal carbonyl oxygen atoms (O1 and O2) of TMeQ[6] s. Each barium cation (Ba1) in the supramolecular chain has a dodecahedral structure with eight oxygen atoms, four water molecules (O1W , O2W , and O3W), four from the dipolar carbonyl of two neighboring TMeQ[6] molecule portals (2O1 and 2O2), and a Cl anion (Cl1). The $\text{Ba}-\text{O}$ bonds were 2.756–2.978 Å in length, and the $\text{Ba}-\text{Cl1}$ bonds were 3.169 Å in length. The two Ba^{2+} in the $\text{Ba}_2(\mu\text{-OH}_2)_2(\text{OH}_2)_4\text{Cl}_2$ complex are separated by 5.049 Å (Figure 11).

Coordination of TMeQ[6] with Alkali- or Alkaline-Earth-Metal Ions. Generally, as a ligand, the unsubstituted cucurbituril (Q[6]) or partially methyl-substituted cucurbituril (TMeQ[6]) can coordinate with either alkali- or alkaline-earth-metal ions and with certain complexes. However, the assembly of the complexes of metal ions with cucurbiturils (Q[n] s) could depend upon the ligands Q[n] s. Previous work^{8,9,11} and the present experimental results reveal that the unsubstituted Q[6] ligand can coordinate with the alkali-metal ions and form a one-dimensional supramolecular assembly alternating between Q[6] molecules and metal ions through direct coordination, while the TMeQ[6] ligand can coordinate with the alkaline-earth-metal ions and form a one-dimensional supramolecular assembly of alternating TMeQ[6] molecules and metal ions through direct coordination.

Our previous work revealed that the alkyl-substituted Q[5] s have a strong tendency to arrange into a ring by direct coordination of the alkyl-substituted Q[5] s to the Sr^{2+} and K^+ metal ions. The observed solid-state affinity of the metal ion in the supramolecular rings for the carbonyl oxygen atom of the substituted glycoluril moiety indicates a likely increased electron density as a consequence of the electron-donating effect of the alkyl substituents.^{12a} Indeed, the calculated results showed that the Mulliken atomic charges of the carbonyl oxygen atoms on the alkyl-substituted Q[5] s are generally more negative than those of the carbonyl oxygen atoms on the unsubstituted Q[5] s.¹⁶ A comparison of the Mulliken atomic charges of the carbonyl oxygen atoms on the cyclohexano-substituted Q[5] s to the unsubstituted Q[5] s in their potassium complexes shows a 5–9% increase; this subtle difference in the atomic charges of the carbonyl oxygen atoms could lead to a change in the affinity of the metal ions in the cases of the alkyl-substituted Q[n] s.¹⁷

Among the TMeQ[6] –metal ion interaction systems in the present study are different architectures, such as the one-dimensional supramolecular chain of alternating TMeQ[6] molecules and metal ions through direct coordination (in compounds **10**–**12**) or hydrogen-bonding networks (in compounds **1**–**3** and **6**) or alternative direct coordination and hydrogen-bonding networks (in compounds **4**, **5**, and **8**). The TMeQ[6] – Cs^+ interaction system even shows no special assembled architecture. Some additional reasons leading to the formation of such different architectures could relate to the impact of the ionic radius, ion electron-shell structure, counteranion, and acidic solution.

On the other hand, as a center metal ion, coordination to the ligands, Q[n] s, or SQ[n] s, could be dependent upon the radius, charge, or electron-shell structure of the metal ion. The ionic radii of the alkali-metal ions are 0.60 Å (Li^+), 0.95 Å (Na^+), 1.33 Å (K^+), 1.49 Å (Rb^+), and 1.69 Å (Cs^+), and the ionic radii of the alkaline-earth-metal ions are 0.18 Å (Be^{2+}), 0.50 Å (Mg^{2+}), 1.01 Å (Ca^{2+}), 1.13 Å (Sr^{2+}), and 1.34 Å (Ba^{2+}). The bond lengths of these metal ions with the carbonyl oxygen atom of TMeQ[6] are in the range of 1.9 ($\text{Li}-\text{O}$)–3.6 ($\text{Ce}-\text{O}$) Å. For metal ions with ionic radii in the range of 0.95–1.49 Å, such as Na^+ , K^+ , Rb^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+} , the bond lengths are generally in the range of 2.3–2.9 Å. So far, no assembled architectures of Q[n] s with beryllium and magnesium metal ions have been reported. Although the complex of TMeQ[6] with lithium was synthesized, a one-dimensional polymer of alternating TMeQ[6] s and Li^+ ions through direct coordination has not been observed in compound **1**. Obviously, the radii of these metal ions are too small to effectively coordinate to two adjacent cucurbituril molecules. Otherwise, strong repulsion would occur between the two portals of the two adjacent cucurbituril molecules bridged by the metal ions with small ionic radii. The cesium metal ion has the largest ionic radius of these metal ions. The crystal structure of compound **9** reveals that a cesium metal ion covers almost a whole portal of TMeQ[6] and coordinates with five carbonyl oxygen atoms of the portal of the TMeQ[6] molecule. The cesium metal ion seems to be a favored coordinate with the TMeQ[6] molecule but bridges two adjacent TMeQ[6] molecules through direct coordination. The experimental results reveal that a metal ion (M^{n+}) has an ionic radius in the range of 0.95–1.49 Å or the $\text{Me}-\text{O}$ (carbonyl oxygen) bond is within the range of 2.3–2.9 Å in a complex of metal ion to cucurbit[n]uril; a one-dimensional polymer could be formed as a consequence of the direct coordination of the metal ions with the TMeQ[6] molecules.

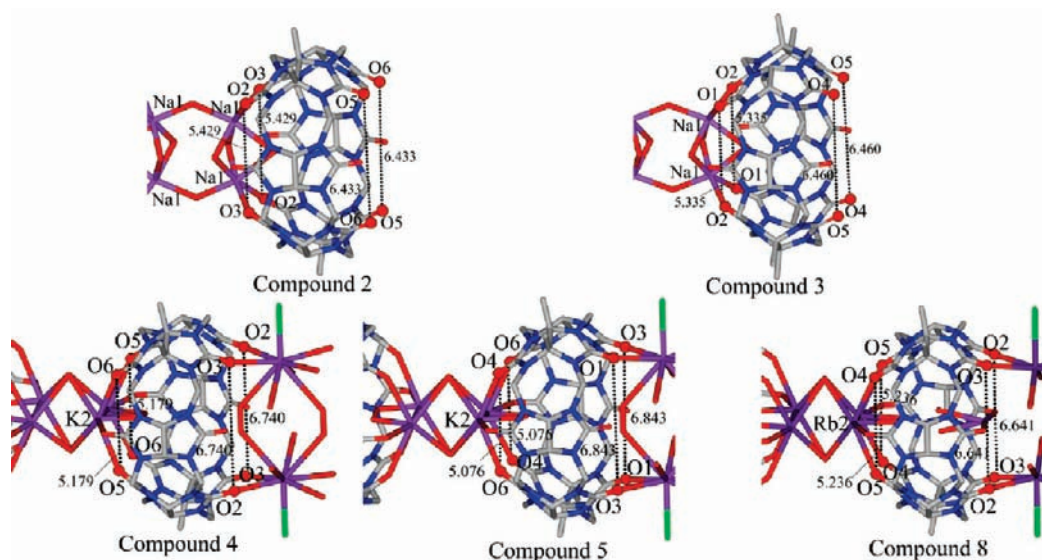


Figure 12. Crystal structures of the TMeQ[6]–metal complexes of five isomorphous compounds (2–5 and 8), in particular, for a comparison of the sizes of two portals.

From the crystallographic data, it appears that five of the compounds are isomorphous (2–5 and 8). The crystal structural demonstration for these five compounds shows a common feature that one portal of TMeQ[6] is fully covered with two metal ions, and such a coordination appears to lead to a size enhancement of the other TMeQ[6] portal. Figure 12 shows that the distances of the selected carbonyl oxygen atoms of the portal covered with the two metal ions are in the range of 5.076–5.429 Å, while the distances of the corresponding carbonyl oxygen atoms of the other portal are in the range of 6.433–6.843 Å; there is about a 1.4 Å difference. However, this difference or the portal enhancement could make (1) it difficult to fully coordinate the rest of the metal ions to the other portal of the TMeQ[6] molecule and results in the formation of the molecular bowl conformation, as shown in compound 2 or 3, and (2) the rest of the metal ions coordinate partially to the other portal of the TMeQ[6] molecule, as shown in compounds 4 or 5 and 8. This suggests that the formation of these isomorphs could be a consequence of the full coverage of the portal of TMeQ[6]. As for the lithium (with the smallest radius) or cesium (with the largest radius), different conformations can be observed in the corresponding compounds.

The ion electron-shell structure of the metal ions could also influence the coordination of the metal ions with the TMeQ[6] molecules. For example, the electronic structure of Li^+ is $1s^2 2s^0 2p^0$; the Li^+ ion has four empty orbitals and coordinates with four oxygen atoms; as shown in Figure 2. Other metal ions have empty d or f orbitals and present a strong capacity for multiple coordination. In the present study, the sodium ion is six-coordinate, the potassium ion can be up to nine-coordinate, the rubidium ion is a seven-coordinate ligand, the cesium ion is eight-coordinate, etc.

Although counteranions such as Cl^- , Br^- , I^- , NO_3^- , etc., are not involved in direct coordination in the formation of a one-dimensional polymer, the size, coordination capacity with the metal ion, and interaction with the latticed water molecules of the counteranions could influence the coordination of Q[n]s with the metal ions, the formation of a supramolecular polymer, and even the assembled architectures of the supramolecular polymer.

For example, the Cl^- anion seems to have a tendency to coordinate with the metal ions. One can see such coordination in compounds 4, 5, 8, and 12, but it does not affect the formation of one-dimensional chains. However, coordination of the NO_3^- anion with the metal ions or inclusion in the cavity of a Q[n] generally could interrupt the formation of a one-dimensional chain. A NO_3^- anion can offer more than one oxygen atom to coordinate with a metal ion that could reduce the capacity of the metal ion to coordinate with other atoms, such as carbonyl oxygen atoms or water molecules. The NO_3^- anion also has a tendency to be included in the cavity of a Q[n]; coordination of the captured NO_3^- anion to the metal ion that coordinates with the portal carbonyl oxygen atoms of Q[n]s could significantly affect this metal ion to further coordinate with other atoms, such as carbonyl oxygen atoms or water molecules.

In addition, the acidic solution could lead to the direct coordination of the metal ions with TMeQ[6] molecules. For example, compound 4 or 5 obtained in the HCl solution shows that the two neighboring TMeQ[6] molecules are bridged by the K^+ cations through direct coordination in the one-dimensional supramolecular chains.

CONCLUSION

In the present study, we have presented 12 complexation systems based on the TMeQ[6] molecules with alkali- and alkaline-earth-metal ions. It is unexpected that the TMeQ[6] molecule coordinates directly with the alkaline-earth-metal ion, which leads to the formation of a one-dimensional coordination polymer in compounds 10–12. Such one-dimensional coordination polymers were only observed in compounds comprising the unsubstituted Q[6] and the alkali-metal ions.^{8,9,11} The coordination polymers comprising Q[n] and the metal ion are formed as a consequence of a combination of a certain cucurbit-[n]uril, a suitable metal ion with suitable counteranion, and a suitable acidic aqueous solution. Generally, cucurbit[n]uril is ready to coordinate with metal ions, but the alkyl-substituted group girding on the surface of cucurbit[n]uril could influence the capacity for coordination of the portal carbonyl oxygen atoms

and lead to the formation of different supramolecular architectures. The metal ion should have a suitable ionic radius and form a bond of sufficient length to keep two neighboring cucurbit[*n*]urils at a suitable distance. The counteranion and acidic condition are also factors to be considered in the synthesis of supramolecular architectures based on the direct coordination of TMeQ[6] and alkali- or alkaline-earth-metal ions. Synthesis in the presence of some other species, such as a transition-metal ion and small organic molecules, and their corresponding properties are being examined further to ascertain the predictability of the formation of such supramolecular architectures relative to the alkyl-substituted cucurbit[*n*]urils.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gzutao@263.net (Z.T.), gang.wei@csiro.au (G.W.).
Tel: +86-851-3623903 (Z.T.), 61294137704 (G.W.). Fax: +86-851-3620906 (Z.T.), +61294137044 (G.W.).

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