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Tube-Type Coordination Polymers: Two- and Four-Silver(I)-Mediated Linear Networking of Calix[4]arene Tetracarboxylates

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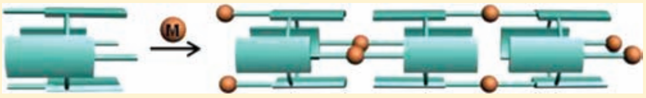
Supporting Information



ABSTRACT: Two calix[4]arene tetracarboxylates, [calix[4]arene tetraacetate (K_4CTA) and calix[4]arene tetrabenzoate (K_4CTB)] as their potassium salts, have been prepared. Employing these as precursors, two Ag(I) coordination polymers incorporating calix[4]arene units have been successfully prepared and their X-ray crystal structures have been determined. In these, the CTA and CTB derivatives are linearly bound to two and four silver atoms, respectively, to generate unusual tubular nanostructures. A comparative NMR study was undertaken to investigate the nature of the metal ion blocking of the tube as observed in the CTA-derived structure. The thermal properties for both coordination polymers were also examined.

INTRODUCTION

Tubular nanostructures have attracted considerable attention due to their ability to transport ions or molecules as well as their potential biomedical utility.[1−5] Various types of molecular or supramolecular tubes have been reported. These include tubes that are assembled via H-bonds from cyclic peptides,[1] lipid tubes,[2] dendrimer-based tubes,[3] and calixarene-based tubes,[4,5] as well as tubes involving metal coordination bonds.[6] Calixarenes are one of the most popular macrocyclic host molecules for constructing supramolecular assemblies;[7] however, to the best of our knowledge, examples of molecular tubes based on the self-assembly of calixarene derivatives with metal ions are still rare.[5a−c] In a related study of this type, Hosseini et al.[5a] constructed an infinite tubular coordination network based on tetracyanocyclophane which shows a 1,3-alternate conformation similar to the typical calix[4]arene derivatives. Atwood[5d] and Dalgarno[5c−e] also reported *p*-carboxylatocalix[4]arene-based nanotubes with large core diameters assembled by noncovalent bonds.

We have been interested in the assembly of supramolecular networks based on the exocoordination of macrocyclic ligand systems, including thiacrowns and calix[4]thiacrowns because the sulfur donors are expected to favor the binding of soft metal ions in an exocyclic mode.[8] In extending this work, we have also been interested in a ligand-directed approach for the construction of a new family of tubelike networks involving the modification of calix[4]arene. Sometimes simple calix[4]arene derivatives show a 1,3-alternate conformation in both solution and the solid state.[6,8] Owing to its internal cavity and the pairs of phenol groups directed from each end, the calix[4]arene framework is clearly a promising building block for further structural elaboration at each end. In particular, this approach appears quite feasible when Ag^+, with its tendency for linear coordination, is used as a linking metal ion. The modification of the four phenol groups by appending carboxylate groups tends to be more advantageous than the appending of a neutral functional group, since in the former case this may avoid the need for a separate counterion, which if it bound to the metal might act to block the assembly process.[9] We have employed calix[4]arene tetraacetate (K_4CTA) and calix[4]arene tetrabenzeoate (K_4CTB) as their potassium salts as the modified carboxylates in the present study (Scheme 1). Employing the tetra-potassium form improved both the reactivity and solubility of this precursor and led to the formation of a tubelike product.

Herein, we report the synthesis and characterization of the new tubular networks **1** and **2** incorporating different linking modes obtained by one-pot reaction of Ag(I) with the corresponding calix[4]arene tetracarboxylates. The thermal properties of the complexes are also described. In addition to solid state X-ray studies, the result of a comparative NMR study of the complexation of **1** in CD_3OD/D_2O (1:1) solution is reported.

RESULTS AND DISCUSSION

K_4CTA and K_4CTB were prepared by hydrolysis of the corresponding calix[4]arene tetraester[10,11] by KOH in a EtOH/THF mixture. Hosseini et al.[11] reported the synthesis and crystal structure of thiacalix[4]arene tetraester and the corresponding tetraacid and confirmed their 1,3-alternate arrangement.

The reaction of silver perchlorate in methanol layered onto an aqueous solution of K_4CTA yielded the colorless crystalline product **1**. X-ray analysis revealed that **1** is a tubular Ag^+ coordination network of formula $\{[Ag_2(Ag_2@CTA)]\cdot 4H_2O\}_n$, with no potassium(I) binding present (Figure 1).

The asymmetric unit of **1** in its coordination sphere contains one CTA^{4-} and four silver(I) ions. In the unit cell, two crystallographically nonequivalent Ag atoms (Ag1 and Ag2) are present. Notably, the tubular network is formed by the bridging of consecutive dinuclear $(Ag1)_2@CTA^{2-}$ complex units by two bridging Ag2 atoms. Each Ag2 atom is two-coordinated, being bound by two monodentate carboxylate oxygen atoms from different ligands via

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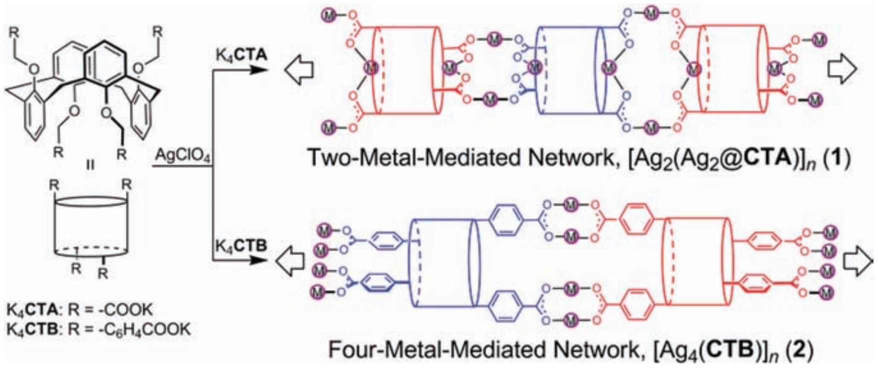
Scheme 1. Linear Networking Modes of Calix[4]arene Units in This Work



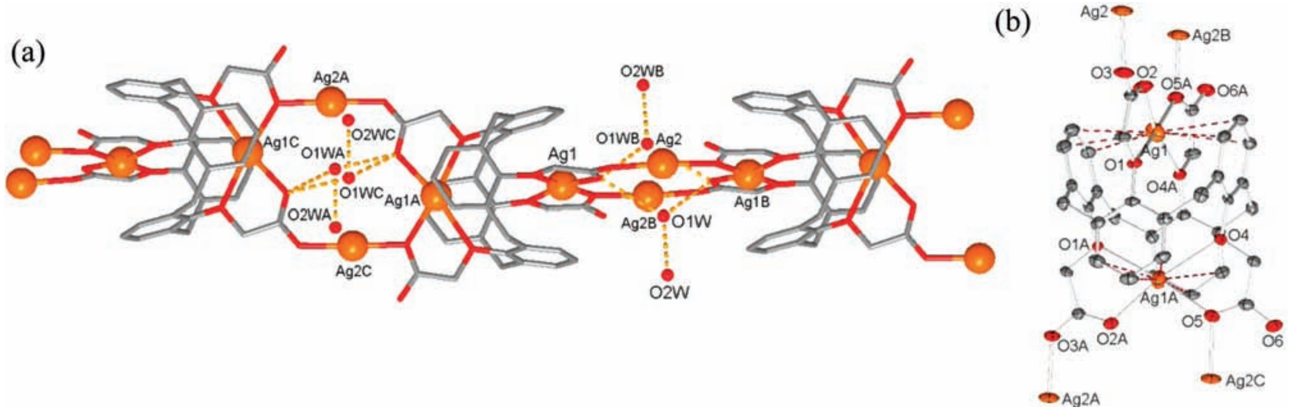


Figure 1. (a) Two-silver(I)-mediated tubular network **1**, $\{[Ag_2(Ag_2@CTA)]\cdot 4H_2O\}_n$ and (b) another view of the Ag^+ coordination environments. The displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. [Symmetry codes: (A) $1 - x, y, 0.5 - z$; (B) $0.5 - x, 1.5 - y, 1 - z$; (C) $0.5 + x, 1.5 - y, -0.5 + z$.].

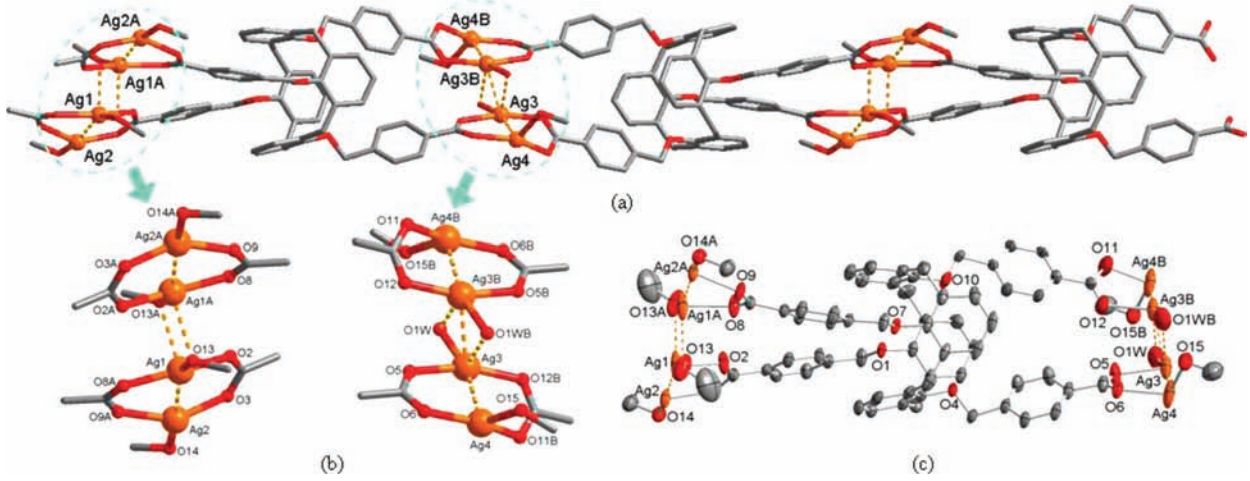


Figure 2. (a) Four-silver(I)-mediated network **2**, $\{[Ag_4(CTB)(H_2O)(CH_3OH)_3]\cdot 2H_2O\}_n$, (b) two views of the Ag^+ coordination geometries, and (c) the basic unit with a thermal ellipsoid plot. The displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. [Symmetry codes: (A) $-x + 2, -y, -z + 1$; (B) $-x - 1, -y + 2, -z$.]

linear C(O)O−(Ag2)−O(O)C linkages [O−Ag2−O 175.5(2)°]. Accordingly, complex **1** adopts a two-silver(I)-mediated tubular structure. The distance between bridging Ag2 atoms is 6.020(1) Å, and the repeating unit of the tubular network has a length of 25.3 Å.

Each Ag1 atom occupies the inside of a calix unit in a distorted square planar array of two monodentate carboxylate oxygens and two phenolic oxygens from different pendants in a *cis* arrangement [∠O−Ag1−O 64.86(10)−118.38(12)°]. The Ag1 atom also interacts with the aromatic rings via η^3-type cation···π interactions (dashed lines in Figure 1b, 3.07−3.30 Å). The Ag1 atoms inside the calix unit are separated by 5.106(1) Å. Water molecules in the lattice form H-bonds with carboxylate oxygen atoms, resulting in each 1D tubular network being weakly linked to form a pseudo-3D framework (Figure 1a and Figure S3 and Table S1 of the Supporting Information).

An unexpected feature of **1** that reflects the need for charge compensation is that two additional Ag atoms are located in the tube, blocking the inside of the tubular structure. We reasoned that this problem might be ameliorated by insertion of an aromatic group between the respective calix phenolic oxygens and the pendent carboxylic oxygens. Accordingly, the potassium salt of calix[4]arene tetrabenzoate (K_4CTB) was proposed as an alternate precursor and the initial reaction was repeated employing K_4CTB and $AgClO_4$ in methanol/water to give crystalline **2**. As illustrated in Figure 2, X-ray analysis revealed that **2** also adopts an infinite tubular structure, with the formula $\{[Ag_4(CTB)(H_2O)(CH_3OH)_3]\cdot 2H_2O\}_n$ (again without potassium(I) binding). The asymmetric unit of **2** in its coordination sphere consists of four silver atoms, one CTB^{4-}, one water molecule, and three methanol molecules.

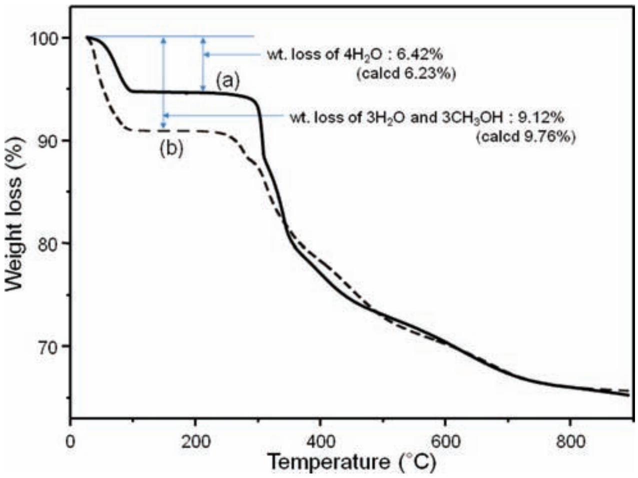


Figure 3. TGA curves for (a) **1** and (b) **2**.

In this case, notably, the consecutive CTB^{4-} tubular units are linked by four bridging Ag atoms. This result illustrates that the tuning of the distance between two binding sites by insertion of the aromatic group was successful in inducing the formation of a perforated tubular structure. This is a consequence of the absence of a carboxyl oxygen near each phenolic oxygen in CTB^{4-} so that chelation of Ag^+ no longer occurs.

Two Ag atoms (Ag1 and Ag2, or Ag3 and Ag4) which link a pair of bis(carboxylate-O,O′) units form an 8-membered metallacycle. The Ag···Ag distances [2.709(2) and 2.770(1) Å] in the metallacycle are shorter than the sum of the van der Waals radii (3.44 Å) for silver, suggesting the presence of an argentophilic interaction.[12] Solvent molecules are also bound in the coordination sphere of each silver, which adopts a T-shaped coordination geometry (Figure 2a,b). In the packing of **2**, there is an Ag···π interaction [2.628(6) Å] between neighboring

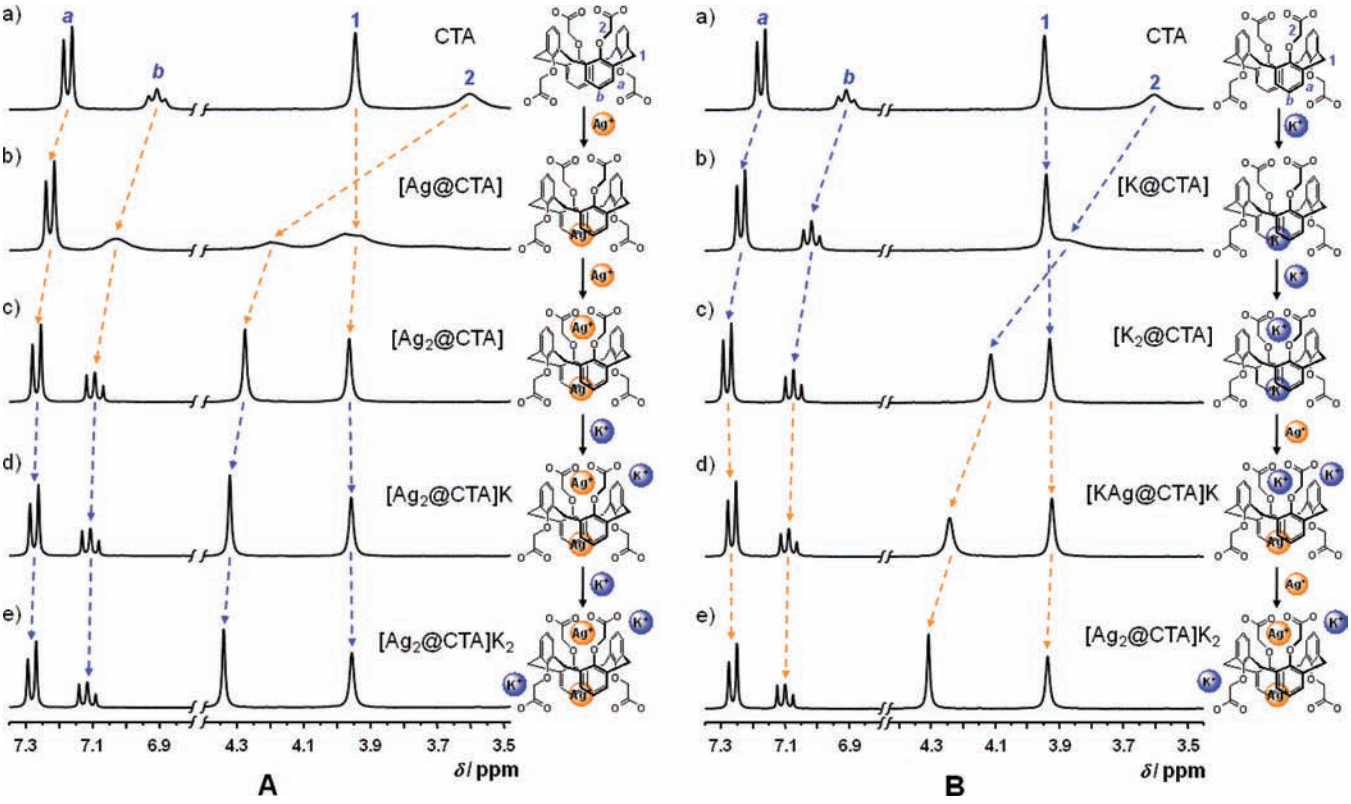


Figure 4. Cation-induced ^1H NMR spectra of CTA^{4+}. (A): stepwise addition of silver(I) and potassium(I); (a) CTA, (b) CTA + 1 equiv $AgClO_4$, (c) CTA + 2 equiv $AgClO_4$, (d) CTA + 2 equiv $AgClO_4$ + 1 equiv $KClO_4$, and (e) CTA + 2 equiv $AgClO_4$ + 2 equiv $KClO_4$. (B): stepwise addition of potassium(I) and silver(I); (a) CTA, (b) CTA + 1 equiv $KClO_4$, (c) CTA + 2 equiv $KClO_4$, (d) CTA + 2 equiv $KClO_4$ + 1 equiv $AgClO_4$, and (e) CTA + 2 equiv $KClO_4$ + 2 equiv $AgClO_4$.

tubular networks leading to the formation of a pseudo-2D framework (Figure S5 of the Supporting Information).

Thermogravimetric analysis performed on **1** and **2** shows respective weight losses of 6.42 and 9.12% until 98 °C, corresponding to the loss of coordinated solvent molecules (expected values: 6.23 and 9.76%) (Figure 3). After the release of all solvent molecules, both compounds are stable up to 280 °C (for **1**) and 260 °C (for **2**), after which a significant weight loss was observed, due to the release of the ligand.

^{1}H NMR study of the competitive complexation behavior of CTA^{4-} toward K^+ and Ag^+ in CD_3OD-D_2O confirmed the preference for Ag^+ complexation (Figure 4). In this study, the tetra(triethylammonium) salt of CTA^{4-}, $[(Et_3NH)_4CTA]$, was employed in examining the respective metal ion affinities toward the anionic tetracarboxylate, CTA^{4-}.

Addition of 1 or 2 equiv of Ag^+ to this species induced larger downfield shifts for H_2 and H_b than occur for H_1 and H_a (Figure 4A-b,c). This behavior is in accord with the larger coordination affinity of phenolic oxygen and p-carbon atoms toward Ag^+, suggesting that the metal ions are located in the calix unit. The consecutive addition of 1 or 2 equiv of K^+, however, caused no further induced shifts (Figure 4A-d,e). The observed result confirms that since two binding sites in CTA^{4-} are already saturated by two Ag^+ ions to form $[Ag_2@CTA]$, no further interaction with K^+ occurs. For comparison, the NMR spectra of CTA^{4-} were also obtained under conditions in which the reverse order of salt addition was carried out (Figure 4B). Similar to the spectra shown in Figure 4A, addition of 1 or 2 equiv of K^+ causes larger downfield shifts for H_2 and H_b than those for H_1 and H_a (Figure 4A-b,c). In this case, however, the K^+-induced chemical shift changes for each peak were smaller than those for Ag^+, in keeping with K^+ occupying the binding sites, to form $[K_2@CTA]$ but with the binding affinity being weaker than occurs for Ag^+.

The evidence for the proposed 2:1 (K^+/CTA) complexation was also confirmed by ESI-mass spectrometry and additional ^{1}H NMR titration experiments. First, the mass peaks of $[K_2CTA]^{2-}$ and $[HK_2CTA]^-$ suggesting the 2:1 complexation appeared at m/z 365.2 (calcd 365.1) and 731.2 (calcd 731.1), respectively (Experimental Section and Figure S6 of the Supporting Information). Second, the ^{1}H NMR titration of CTA with $KClO_4$ (0−2.4 equiv) and the titration curves in Figure S8 of the Supporting Information exhibit the inflection point around 2 equiv, suggesting the formation of the 2:1 complexation.

Unlike Figure 4A, the consecutive addition of Ag^+ results in further downfield shifts, in keeping with the bound K^+ being replaced by Ag^+, to form $[KAg@CTA]K$ and $[Ag_2@CTA]K_2$ in a stepwise manner. Thus, the NMR peaks in Figure 4B-e exhibit a similar pattern to those shown in Figure 4A-c, once again suggesting that Ag^+ binds more strongly than K^+. This result is also in keeping with the observation mentioned previously that there was no uptake of K^+ during the synthesis of the Ag^+ complex of **1** even though K^+ was present in the reaction solution.

CONCLUSION

Assembly of 1,3-alternate calix[4]arene tetraacetate with $AgClO_4$ afforded a two-metal-mediated tube-type coordination polymer, but the interior of the tube is blocked by Ag^+ ions. By replacing this ligand with the calix[4]arene tetrabenzoate analogue in a parallel reaction, a four-metal-mediated coordination polymer with a perforated tubular structure was isolated. The present results illustrate how the appropriate tuning of the 1,3-alternate calix[4]arene derivative works as a rational approach in preparing desired metallosupramolecular networks. Further exploration of the synthesis and physical properties of novel metallosupramolecular network species based on the modification of the calix[4]arene derivatives is underway in our laboratory.

Table 1. X-ray Crystallographic Data for 1 and 2

	1	2
chemical formula	$C_{36}H_{36}Ag_4O_{16}$	$C_{63}H_{62}Ag_4O_{18}$
formula weight	1156.13	1538.61
crystal system	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a/Å	10.2637(9)	11.7322(5)
b/Å	17.0722(15)	14.9622(6)
c/Å	20.9381(18)	18.2293(7)
a/deg	90	70.221(2)
β/deg	103.271(4)	89.107(2)
γ/deg	90	79.170(2)
V/Å^3	3570.9(5)	2953.6(2)
Z	4	2
D_{calc}/(g/cm^3)	2.151	1.730
μ/mm^{-1}	2.240	1.381
$2\theta_{max}$/deg	52.00	52.00
reflections collected	13640	47067
independent reflections	3466 [R_{int} = 0.0402]	12597 [R_{int} = 0.0353]
absorption correction	semiempirical from equivalents	
max. and min transmission	0.8070 and 0.4322	0.8976 and 0.7892
goodness-of-fit on F^2	1.076	1.052
R_1, wR_2 [$I > 2\sigma(I)$]	0.0577, 0.1438	0.0620, 0.1536
R_1, wR_2 [all data]	0.0596, 0.1449	0.0850, 0.1743

EXPERIMENTAL SECTION

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The ^{1}H NMR spectra were recorded on a Bruker Advance-300 (300 MHz) NMR spectrometer. FT-IR spectra were measured with a ThermoFisher Scientific Nicolet *i*S 10 FT-IR spectrometer. The elemental analyses of K_4CTA, K_4CTB, and **2** were carried out after they were dried in vacuo. TGA was performed under nitrogen on a SDT Q600 thermogravimetric analyzer.

Preparation of K_4CTA. An aqueous solution of KOH (8 equiv) was slowly added to a refluxing solution of calix[4]arene tetraethylacetate (**3**, Supporting Information)[10,11] in EtOH/THF (1:1 v/v, 100 mL), and refluxing was continued for 12 h. The white precipitate formed was further filtered off, washed with EtOH/THF (1:1 v/v) and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{36}H_{28}K_4O_{12}$ (%): C, 53.45; H, 3.49. Found: C, 53.11; H, 3.68. ^{1}H NMR (CD_3OD, 300 MHz, 295 K): δ = 7.36 (d, 8H, Ar), 7.18 (t, 4H, Ar), 4.34 (s, 8H, CH_2OAr), 3.94 (s, 8H, $ArCH_2Ar$). M_p: 308 °C (dec). IR (KBr pellet, cm^{-1}): 3419.4, 2919.9, 1610.4, 1458.1, 1409.8, 1326.9, 1313.4, 1247.8, 1199.6, 1091.6, 1027.9, 933.4, 914.2, 846.6, 773.3, 736.7, 678.8, 595.9, 570.8, 551.5, 516.8. Mass spectrum m/z (ESI): 847.0 for $[K_5CTA]^+$ (Calcd 847.0), 365.2 for $[K_2CTA]^{2-}$ (Calcd 365.1), 731.2 for $[HK_2CTA]^-$ (Calcd 731.1), and 769.2 for $[K_3CTA]^-$ (Calcd 769.1).

Preparation of K_4CTB. The synthetic procedure used for K_4CTB was the same as that for K_4CTA except for the use of calix[4]arene

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**[a]

Ag1−O1	2.569(4)	Ag1−O2	2.379(5)
Ag1−O4^i	3.618(4)	Ag1−O5^i	2.324(4)
Ag2−O3	2.145(4)	Ag2−O5^{ii}	2.172(4)
O1−Ag1−O2	66.25(14)	O1−Ag1−O4^i	121.12(12)
O2−Ag1−O5^i	107.26(15)	O4^i−Ag1−O5^i	65.01(13)
O5^i−Ag1−O1	173.18(14)	O2−Ag1−O4^i	169.50(15)
O3−Ag2−O5^{ii}	175.5(2)		

[a] Symmetry operations: (i) $-x + 1, y, -z + {}^{1}/_{2}$; (ii) $x - {}^{1}/_{2}, -y + {}^{3}/_{2}, z + {}^{1}/_{2}$.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

Ag1−O2	2.214(4)	Ag1−O8^i	2.228(4)
Ag1−O13	2.466(6)	Ag1−O1^i	2.698(7)
Ag2−O3	2.240(4)	Ag2−O9i	2.189(4)
Ag2−O14	2.545(4)	Ag3−O5	2.209(5)
Ag3−O12^{ii}	2.180(8)	Ag3−O1W	2.489(7)
Ag3−O1W^{ii}	2.721(8)	Ag4−O6	2.219(4)
Ag4−O11^{ii}	2.192(13)	Ag4−O15	2.459(5)
Ag1···Ag2	2.7695(8)	Ag3···Ag4	2.7087(19)
Ag3···Ag3^{ii}	2.630(6)		
O2−Ag1−O8^i	158.8(2)	O2−Ag1−O13	106.1(2)
O2−Ag1−O13^i	90.1(2)	O8^i−Ag1−O13	94.92(19)
O8^i−Ag1−O13^i	88.8(2)	O13−Ag1−O1^i	85.9(3)
O3−Ag2−O9^i	148.00(17)	O3−Ag2−O14	88.97(14)
O9^i−Ag2−O14	97.56(15)	O5−Ag3−O1W	87.7(2)
O5−Ag3−O12^{ii}	162.0(3)	O5−Ag3−O1W^{ii}	89.3(2)
O12^{ii}−Ag3−O1W	106.1(3)	O12^{ii}−Ag3−O1W^{ii}	93.8(3)
O1W−Ag3−O1W^{ii}	119.56(19)	O6−Ag4−O11^{ii}	151.5(5)
O6−Ag4−O15	105.47(16)	O11^{ii}−Ag4−O15	102.9(5)

[a] Symmetry operations: (i) $-x + 2, -y, -z+1$; (ii) $-x - 1, -y + 2, -z$.

tetra(methyl 4-methylbenzoate) (**4**, Supporting Information)[10,11] instead of **3**. Anal. Calcd for $C_{60}H_{44}K_4O_{12}$ (%): C, 64.73; H, 3.98. Found: C, 64.39; H, 4.23. ^{1}H NMR (D_2O, 300 MHz, 295 K): δ = 7.99 (d, 8H, Ar), 7.18 (d, 8H, Ar), 6.72 (d, 8H, Ar), 6.60 (t, 4H, Ar), 4.72 (s, 8H, ArCH_2OAr), 3.41 (s, 8H, ArCH_2Ar). M_p: 301−302 °C (dec). IR (KBr pellet, cm^{-1}): 3396.3, 2918.0, 1593.1, 1548.7, 1452.3, 1388.6, 1249.8, 1191.9, 1093.5, 1031.8, 1016.4, 956.6, 918.0, 840.9, 813.9, 771.5, 715.5, 646.1, 615.2, 569.0, 551.6, 518.8, 451.3. Mass spectrum m/z (ESI): 1151.2 for $[K_5CTB]^+$ (Calcd 1151.1), 517.3 for $[K_2CTB]^{2-}$ (Calcd 517.1), and 498.3 for $[HKCTB]^-$ (Calcd 498.1).

Preparation of 1, $\{[(\mu_2\text{-Ag})_2(Ag_2@CTA)]\cdot 4H_2O\}_n$. $AgClO_4$ (51.3 mg, 0.25 mmol) in methanol (2 mL) was layered onto an aqueous solution (2 mL) of K_4CTA (25.0 mg, 0.031 mmol) at room temperature. X-ray quality single crystals were obtained in 42% yield. IR (KBr pellet, cm^{-1}): 3411.9, 2921.8, 1606.5, 1458.1, 1413.6, 1330.7, 1317.2, 1249.7, 1199.6, 1091.6, 1029.8, 935.3, 916.1, 846.6, 773.3, 738.6, 680.8, 595.9. Anal. Calcd for $\{[Ag_2(Ag_2@C_{36}H_{28}O_{12})]\cdot 4H_2O\}_n$: C, 37.40; H, 3.14. Found: C, 37.63; H, 3.36. M_p: 305 °C (dec).

Preparation of 2, $\{[(\mu_2\text{-Ag})_4(CTB)(H_2O)(CH_3OH)_3]\cdot 2H_2O\}_n$. $AgClO_4$ (36.5 mg, 0.18 mmol) in methanol (2 mL) was layered onto an aqueous solution (2 mL) of K_4CTB (25.0 mg, 0.022 mmol) at room temperature. X-ray quality single crystals were obtained in 24% yield. IR (KBr pellet, cm^{-1}): 3424.9, 1606.4, 1436.7, 1417.4, 1328.7, 1222.6, 1012.5, 937.2, 848.5, 802.2, 761.7, 701.9, 561.18. Anal. Calcd for $[Ag_4(C_{60}H_{44}O_{12})]_n$: C, 51.90; H, 3.19. Found: C, 51.63; H, 3.41. M_p: 292−293 °C (dec).

X-ray Crystallographic Analysis. Crystal data for **1** and **2** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spots (from 36 collected frames). Data collection, data reduction, and semiempirical absorption correction were carried out using the software package of APEX2.[13] All of the calculations for the structure determination were carried out using the SHELXTL package.[14] In all cases, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms, except all water molecules for **1** and **2**, were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. In the case of water molecules, the initial positions of the hydrogen atoms were obtained from difference electron density maps and refined with riding constraints. Relevant crystal collection data, refinement data for the crystal structures, and the selected bond lengths and angles of **1** and **2** are summarized in Tables 1−3. In the refinement procedure for **2**, the Ag3 atom and one methylbenzoate pendant arm are disordered over two sites occupied in a 57:43 ratio (Figure S4 of the Supporting Information).

CCDC 826730 (**1**) and 826731 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic data in CIF format, synthetic procedures and ^{1}H NMR spectra of ligands, the additional crystal structures, ESI mass spectra for K_4CTA and K_4CTB, ^{1}H NMR titration data, and geometric parameters for H-bondings. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 988. (b) Ghadiri, M. R.; Granja, J. R.; Milligan, R. A.; McRee, D. E.; Khazanovich, N. *Nature* **1993**, *366*, 324.

(2) Schnur, J. M. *Science* **1993**, *262*, 1669.

(3) (a) Kim, Y.; Mayer, M. F.; Zimmerman, S. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 1121. (b) Yan, D.; Zhou, Y.; Hou, J. *Science* **2004**, *303*, 65.

(4) (a) Wang, W.; Gong, S.; Chen, Y.; Ma, J. *New J. Chem.* **2005**, *29*, 1390. (b) Organo, V. G.; Leontiev, A. V.; Sgarlata, V.; Dias, H. V. R.; Rudkevich, D. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3043. (c) Kim, S. K.; Vicens, J.; Park, K.-M.; Lee, S. S.; Kim, J. S. *Tetrahedron Lett.* **2003**, *44*, 993. (d) Sidorov, V.; Kotch, G. W.; Abdrakhmanova, G.; Mizani, R.; Fettinger, J. C.; Davis, J. T. *J. Am. Chem. Soc.* **2002**, *124*, 2267. (e) Baldini, L.; Sansone, F.; Casnati, A.; Ungaro, F. *J. Supramol. Chem.* **2002**, 219. (f) Hajek, F.; Graf, E.; Hosseini, M. W.; Delaigue, X.; Cian, A. D.; Fischer, J. *Tetrahedron Lett.* **1996**, 37, 1401. (g) Sidorov, V.; Kotch, F. W.; El-Kouedi, M.; Davis, J. T. *Chem. Commun.* **2000**, 2369.

(5) (a) Kleina, C.; Graf, E.; Hosseini, M. W.; Cian, A. D.; Fischer, J. *Chem. Commun.* **2000**, 239. (b) Budka, J.; Lhoták, P.; Stibor, I.; Sýkora, J.;

Císařová, I. *Supramol. Chem.* **2003**, *15*, 353. (c) Kennedy, S.; Karotsis, G.; Beavers, C. M.; Teat, S. J.; Brechin, E. K.; Dalgarno, S. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4205. (d) Dalgarno, S. J.; Warren, J. E.; Antesberger, J.; Glass, T. E.; Atwood, J. L. *New J. Chem.* **2007**, *31*, 1891. (e) Kennedy, S.; Dalgarno, S. J. *Chem. Commun.* **2009**, 5275.

(6) (a) Yamaguchi, T.; Tashiro, S.; Tominaga, M.; Kawano, M.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 10818. (b) Tashiro, S.; Tominaga, M.; Kusukawa, T.; Kawano, M.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3267. (c) Aoyagi, M.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 7457. (d) Loï, M.; Hosseini, M. W.; Jouaiti, A.; De Cian, A.; Fischer, J. *Eur. J. Inorg. Chem.* **1999**, 1981. (e) Hannon, M. J.; Painting, C. L.; Errington, W. *Chem. Commun.* **1997**, 1805.

(7) (a) Vicens, J.; Harrowfield, J. *Calixarenes in the Nanoworld*; Springer: Dordrecht, 2007. (b) Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. *Calixarenes 2001*; Kluwer Academic Publishers: Dordrecht, 2001. (c) Vicens, J.; Böhmer, V. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer Academic Publishers: Dordrecht, 1991.

(8) (a) Park, I.-H.; Park, K.-M.; Lee, S. S. *Dalton Trans.* **2010**, 9696. (b) Lee, S. Y.; Park, S.; Lee, S. S. *Inorg. Chem.* **2009**, *48*, 11335. (c) Jo, M.; Seo, J.; Lindoy, L. F.; Lee, S. S. *Dalton Trans.* **2009**, 6096. (d) Lee, J. Y.; Lee, S. Y.; Park, S.; Kwon, J.; Sim, W.; Lee, S. S. *Inorg. Chem.* **2009**, *48*, 8934. (e) Lee, J. Y.; Kim, H. J.; Jung, J. H.; Sim, W.; Lee, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 13838. (f) Lee, J. Y.; Lee, S. Y.; Sim, W.; Park, K.-M.; Kim, J.; Lee, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 6902.

(9) Ma, B.-Q.; Mulfort, K. L.; Hupp, J. T. *Inorg. Chem.* **2005**, *44*, 4912.

(10) (a) No, K.; Lee, H. J.; Park, K.-M.; Lee, S. S.; Noh, K. H.; Kim, S. K.; Lee, J. Y.; Kim, J. S. *J. Heterocycl. Chem.* **2004**, *41*, 211. (b) Iwamoto, K.; Shinkai, S. *J. Org. Chem.* **1992**, *57*, 7066.

(11) (a) Akdas, H.; Jaunky, W.; Graf, E.; Hosseini, M. W.; Planeix, J.-M.; Cian, A. D.; Fischer, J. *Tetrahedron Lett.* **2000**, *41*, 3601. (b) Akdas, H.; Graf, E.; Hosseini, M. W.; Cian, A. D.; Harrowfield, J. M. *Chem. Commun.* **2000**, 2219.

(12) (a) Zhu, H.-F.; Fan, J.; Okamura, T.-a.; Zhang, Z.-H.; Liu, G.-X.; Yu, K.-B.; Sun, W.-Y.; Ueyama, N. *Inorg. Chem.* **2006**, *45*, 3941. (b) Fei, B.-L.; Sun, W.-Y.; Okamura, T.-a.; Tang, W.-X.; Ueyama, N. *New J. Chem.* **2001**, *25*, 210. (c) Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2000**, *122*, 7608. (d) Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136.

(13) Bruker. *APEX2 Version 2009.1-0 Data collection and Processing Software*; Bruker AXS Inc.: Madison, WI, U.S.A., 2008.

(14) Bruker. *SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc.: Madison, WI, U.S.A., 2001.