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Open dimeric and capped polymeric container molecules: calixarene and resorcinarene complexes of Ag^{I} co-ordinated by participation of the upper-rim carbon atoms

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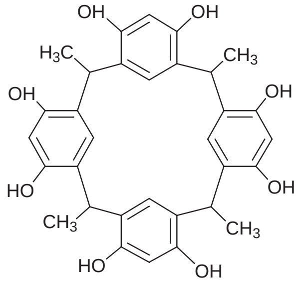
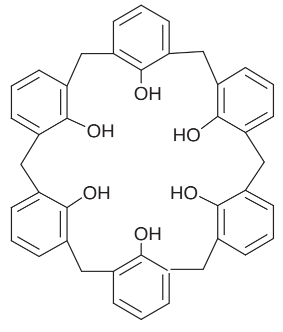
The reactions of *C*-methylcalix[4]resorcinarene (L^1), calix[6]arene (L^2) and calix[4]arene (L^3) with silver(I) salts have resulted in the isolation and structural characterization of three dimeric and one polymeric silver derivatives of calixarene based on cation π interactions. The dinuclear cation in $[Ag_2(L^1)(C_6H_6)_2][ClO_4]_2\cdot 5C_4H_8O$ **1** contains two symmetry-related metal centers, each involving a rather distorted tetrahedral co-ordination with, in addition to one benzene molecule, both the aryl OH groups and the aromatic rings of resorcinarene. The two dimeric calix[6]arene structures, $\{[Ag(L^2)X]\cdot 2C_6H_6\}_2$, where X = ClO_4^- **2** or $CF_3SO_3^-$ **3**, display similar characteristics with two ligand groups inversely linked by the co-ordination of the silver ion to the phenyl carbons. The solvent molecules or the counter anions are not included in the cavity generated by the dimeric unit, but intercalated into calixarene or resorcinarene bilayers. In the calix[4]arene complex $[Ag_2(L^3)(ClO_4)_2]$ **4** each of the four phenyl rings is bound to one metal atom which in turn bridges between the two calixarenes leading to an infinite two-dimensional arrangement. The polyoxo anion bridging between silver ions partially caps the container cavity of the calixarene. The factors controlling the selectivity of complexation and inclusion properties of calixarenes are discussed.

Calixarenes are a family of macrocycles possessing soft π-donor cavities composed of benzene rings and hard oxygen cavities constructed on the hydroxyl lower rim. Among the various properties of calixarenes their unique chemical architecture plays a prominent role and opens the way to practical designing of complexants for metal ions.[1,2] The two most frequently used types of calixarenes are the cyclic tetramers and hexamers, both of which can undergo co-ordination at the phenolic oxygen centers or engage in cation π interactions. To date, calixarenes chemically modified at the phenolic lower rim by the attachment of functional groups with donor atoms appropriate for the co-ordination of metal ions predominate and have produced numerous σ-bonded metallocalixarenes.[3–6] By contrast, there is a paucity of structural data for the metallocalixarenes involving π-donor participation in complexation of cations. These limited examples include alkali-metal and silver(I) derivatives of calix[4]arene with inclusion of metal cations in the π-base cavity,[7,8] and the recently reported bi- and tetra-metalated calixarene complexes involving *exo* binding of Rh, Ru and Ir.[9]

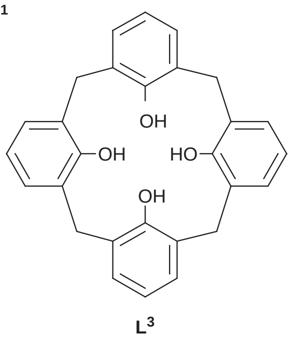
As part of a research program aimed at designing new types of copper(I) and silver(I) complexes with macrocyclic polyhapto organic ligands,[10,11] we have chosen the readily available *C*-methylcalix[4]resorcinarene (L^1), calix[6]arene (L^2) and calix[4]arene (L^3) as subunits further to investigate the unique metal-binding properties of the calixarenes. We report herein the syntheses and structures of three unprecedented open dimeric and one capped polymeric container molecules of calixarene built up by the co-ordination of silver(I) to the phenyl carbons outside the calixarene cavity.



L^1



L^2



L^3

Results

The reactions of resorcinarene and calixarene with an appropriate silver(I) salt under mild conditions readily afforded the complexes **1**–**4**. In order to obtain single crystals for each compound a number of experiments have been conducted by varying the solvent, temperature and diffusion solvent. Similar reactions to that described in the Experimental section but performed in other solvents led to a mixture of precipitate and tiny single crystals unsuitable for X-ray analysis. The infrared spectra were recorded in the region 4000–400 cm^{-1} on KBr disks. Complexes **2**–**4** exhibit strong absorptions due to ν(OH) at 3130–3170 cm^{-1} and ν(C=C) at 1450–1466 cm^{-1}, as expected for the presence of calixarenes. The corresponding absorption of ν(OH) for complex **1** moved to 3400 cm^{-1} due to co-ordination

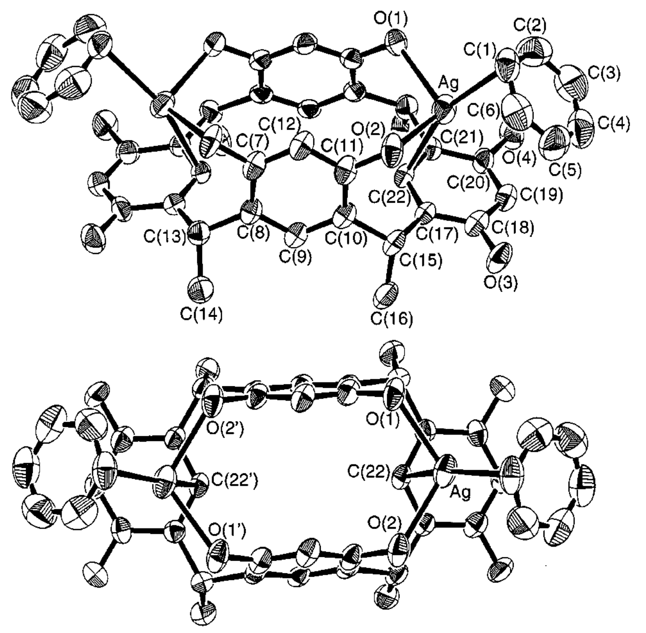


Fig. 1 An ORTEP[12] drawing of the cation $[Ag_2(L^1)(C_6H_6)_2]^{2+}$ in complex **1**, with labeling scheme (top) and the cavity size in the dimeric unit (bottom), C(22)···C(22′) 5.35, O(1)···O(2) 4.09 Å. Thermal ellipsoids are at the 30% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

1			
Ag–O(1)	2.442(6)	Ag–O(2)	2.458(7)
Ag–C(1)	2.45(1)	Ag–C(22)	2.528(8)
O(1)–Ag–C(1)	106.5(5)	O(1)–Ag–C(22)	89.1(2)
O(2)–Ag–C(1)	100.1(6)	O(2)–Ag–C(22)	84.6(3)
C(1)–Ag–C(22)	160.3(4)	O(1)–Ag–O(2)	111.9(2)
2			
Ag–O(7)	2.399(3)	Ag–O(7′)	2.469(4)
Ag–C(29)	2.427(4)	Ag–C(35)	2.399(4)
O(7)–Ag–O(7′)	80.7(1)	O(7)–Ag–C(29)	122.7(1)
O(7)–Ag–C(35)	110.5(1)	O(7′)–Ag–C(29)	117.8(1)
O(7′)–Ag–C(35)	104.2(1)	C(29)–Ag–C(35)	115.1(1)
3			
Ag–O(7)	2.449(7)	Ag–O(7′)	2.483(7)
Ag–C(29)	2.434(10)	Ag–C(35)	2.44(1)
O(7)–Ag–O(7′)	87.8(2)	O(7)–Ag–C(29)	116.9(3)
O(7)–Ag–C(35)	115.6(3)	O(7′)–Ag–C(29)	113.7(3)
O(7′)–Ag–C(35)	108.2(3)	C(29)–Ag–C(35)	112.1(4)
4			
Ag–O(3)	2.460(9)	Ag–O(6)	2.383(6)
Ag–C(1)	2.457(9)	Ag–C(13)	2.542(8)
O(3)–Ag–O(6)	91.7(4)	O(3)–Ag–C(1)	115.1(3)
O(6)–Ag–C(1)	104.6(5)	O(3)–Ag–C(13)	121.5(3)
O(6)–Ag–C(13)	112.4(4)	C(5)–Ag–C(13)	110.1(3)

of the aryl OH group to the metal. Both calix[6]arene and calix[4]arene complexes of **2** and **4** gave an uninformative isotropic ESR signal at room temperature which could be due to a paramagnetic impurity.

Dinuclear complex $[Ag_2(L^1)(C_6H_6)_2][ClO_4]_2\cdot 5C_4H_8O$ 1

Complex **1** crystallizes in the monoclinic system *C*2/*c* with four dinuclear molecules in the unit cell. The structure consists of a dinuclear cation $[Ag_2(L^1)(C_6H_6)_2]$ and two non-interacting perchlorate anions. As shown in Fig. 1, the cation contains two symmetry-related metal centers 7.41 Å apart, each involving co-ordination with two aryl OH groups and one η^1-aromatic ring of resorcinarene and the fourth interaction with one benzene molecule in a rather distorted tetrahedral geometry. The observed Ag–C bond distances are 2.45(1) and 2.528(8) Å for Ag–C(1) and Ag–C(22), respectively, Table 1. The conformation of the resorcin[4]arene is symmetric with two opposite benzene rings facing each other and the other two flattened rings lying between, just like two handles on sides of a saucepan. The co-ordination of the macrocyclic resorcinol tetramer to the silver ions is notable, which is accomplished by both cation π interactions and direct binding through four of the eight aryl OH groups. The dinuclear unit generates a molecular cavity with a cross section of about 5.35 × 4.09 Å, which is not occupied by either the THF solvent molecule or the perchlorate anion. Instead, the THF molecules are situated in a column along with ClO_4^- ions in a region of void space in the lattice. This contrasts to the recently reported crystal structure of the neurotransmitter acetylcholine complex of resorcinarene in which the acetylcholine trimethylammonium moiety is included in the four π rings of the cavitand by multiple cation π interactions.[13] Surprisingly, such an inclusion phenomenon was not observed in complex **1**.

Dinuclear complexes $\{[Ag(L^2)X]\cdot 2C_6H_6\}_2$ ($X = ClO_4^-$ 2 or $CF_3SO_3^-$ 3)

X-Ray single-crystal structure determinations of the perchlorate salt **2** and triflate salt **3** of calix[6]arene revealed that they are isostructural with similar conformations of the molecules. Since the structure data of the perchlorate are somewhat more precise than those of the triflate, all figures concerned are based on the results for **2**. Both structures in the solid state consist of a centrosymmetric dinuclear unit $[Ag(L^2)X]_2$ as illustrated in Fig. 2, in which the two calixarenes are inversely linked by the co-ordination of the silver ions to the phenyl carbons with Ag–C distances of 2.427(4) and 2.399(4) Å for **2** and 2.434(10) and 2.44(1) Å for **3**. In addition, the two silver atoms are symmetrically bridged by two perchlorate anions with Ag–O distances of 2.399(3) and 2.469(4) Å for **2** and 2.449(7) and 2.483(7) Å for **3**. The AgC_2O_2 core has a distinct distorted tetrahedral geometry, evident from the average bond angle C–Ag–O of 113.8 and 113.6° for **2** and **3**, respectively.

Polynuclear complex $[Ag_2(L^3)(ClO_4)_2]$ 4

In complex **4** each calix[4]arene is symmetrically bound to four silver atoms with each of the four carbon atoms in the distal phenyl units of the upper rim co-ordinated to one silver(I) ion, which in turn bridges two calix[4]arenes at Ag–C(1) and Ag–C(13) bond distances of 2.457(9) and 2.542(8) Å, Fig. 3. The next shortest contacts between Ag and C are 2.741(8) Å for Ag···C(14) and 2.950(9) Å for Ag···C(12). These distances are too long to be considered as effective cation π interactions.[8] The two-dimensional polymeric framework of calix[4]arene thus resulting from this arrangement is further stabilized by the ClO_4^- anion bridging between two Ag atoms, which partially caps the cavity at the upper rim of the calixarene giving rise to a capped supramolecular container. Therefore, the silver ion in **4**, as in **2** and **3**, also involves an essentially tetrahedral AgC_2O_2 core, through the two bridging ClO_4^- ligands and two calixarenes with C–Ag–O angles ranging from 104.6(5) to 121.5(3)° and Ag–O bond distances of 2.383(6) and 2.460(9) Å.

Discussion

The four calixarene structures of complexes **1**–**4** are noteworthy in several respects. First, as mentioned in the Introduction, calixarenes possess soft π-donor cavities composed of benzene rings and hard oxygen cavities constructed on the hydroxyl lower rim. The structures of calix[4]arene derivatives of transi-

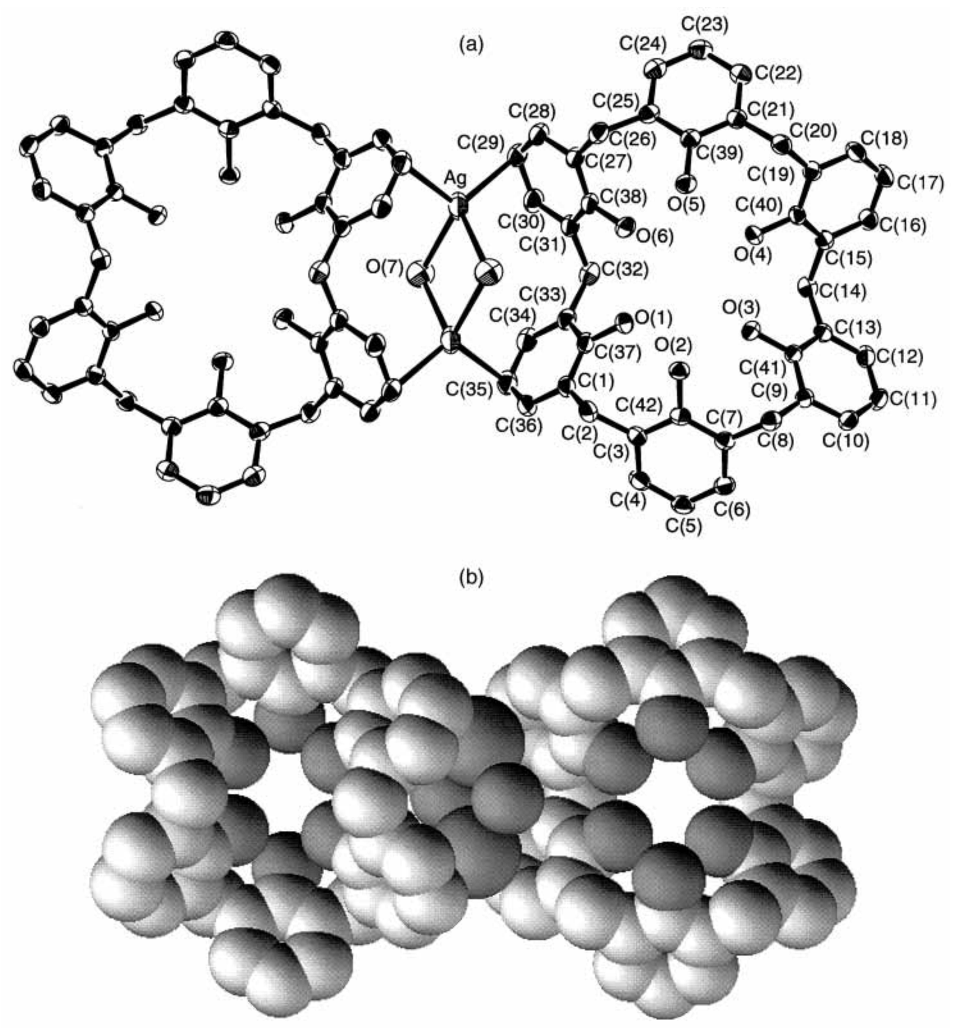


Fig. 2 An ORTEP plot (a) and space-filling model (b) for the dimeric structure of complex **2**. The non-interacting oxygen atoms of the ClO_4^- ions are not shown for clarity. Thermal ellipsoids for the ORTEP drawing are at the 30% probability level.

tion metal ions and trivalent lanthanide cations display similar characteristics with the cation being encapsulated in an oxygen environment of the lower rim.[3–6,14,15] Cation π interaction does occur in the monomeric silver(I) complex of tetra-*O*-propylcalix[4]arene[8b] and bi- and tetra-metalated calixarene complexes of rhodium, ruthenium and iridium.[9] This may be ascribable to the preference of soft metal ions such as Ag^I for a soft donor center. The crystallographic results of the present three silver complexes **2**–**4** lent further support to such an argument as in each case the metal ion is co-ordinated to the carbon atoms of the upper rim rather than to the hydroxyl lower rim of the calixarene. In this respect, the most striking feature of complex **1** is that it is the first example of a system in which the metal ions interact with the calixarene at both the soft donor phenyl carbon atoms and the hard donor aryl OH oxygen atoms. The average Ag–C distances of 2.489 and 2.500 Å observed in **1** and **4**, respectively, are slightly longer than those of 2.413 Å for **2** and 2.437 Å for **3**. Nevertheless, all these values are normal and comparable to those observed in silver(I) complexes of aromatics (average 2.56 Å)[10] and both cone and partial-cone calix[4]arene derivatives (2.395 and 2.405 Å, respectively),[8] confirming unambiguously the co-ordination of Ag to the phenyl carbons in the system.

Secondly, in contrast to their inherent conformational mobility and to the previous report that calix[4]arene can have a partial-cone conformation in the presence of silver(I) ion,[8] the calix[4]arenes and calix[6]arene in the present work are found in the solid state to exhibit the usual cone and a slightly flattened cone conformation, respectively. However, the calix[6]arene molecules in **2** and **3** have two distinct orientations in the unit cell, whereas all calix[4]arenes in **4** are oriented in an identical direction, Fig. 4. Furthermore, in contrast to most calixarene complexes containing solvent in the cavity as the result of host–guest interaction,[3,4,14] the two benzene solvate molecules found in an asymmetric unit $[Ag(L^2)X]$ of both **2** and **3** are not located inside the open container molecular basket but intercalated between the two dimeric units. The reason for this difference in behavior is not immediately clear, since the cone opening in **2** and **3** is expected to be both flexible and wide. This observation implies that the two parallel assemblies of dimers of alternately oriented calix[6]arenes are somewhat associated with each other in an upper rim-to-lower rim fashion which gives rise to a large intermolecular cavity to include two benzene molecules. A similar situation is observed in the supramolecular complex of calixarene with fullerenes in which C_{60} is also intercalated into calixarene bilayers.[16] The mean Ag–O distances of 2.434, 2.466 and 2.422 Å for **2**–**4**, respectively, are significantly shorter than the sum of the ionic radii of Ag^I and O (2.78 Å), suggesting that both dimeric and polymeric frameworks are supported by the effective bridging of ClO_4^- or $CF_3SO_3^-$ between the two Ag atoms. While previous reports suggest that metallocalixarenes can be expected to have various conformations by conventionally controlling the metal ions and the attachment of the functional groups to the macrocycle,[3–9,13,15] this work raises the intriguing point as to the functions of the counter anion and ligand in the versatile co-ordination modes of calixarenes. For example, similar calixarene complexes of silver salts with non-co-ordinating anions such as $AgBF_4$ and $AgPF_6$ might give completely different structures and frameworks.

This work provides the first example of polymeric metallo-

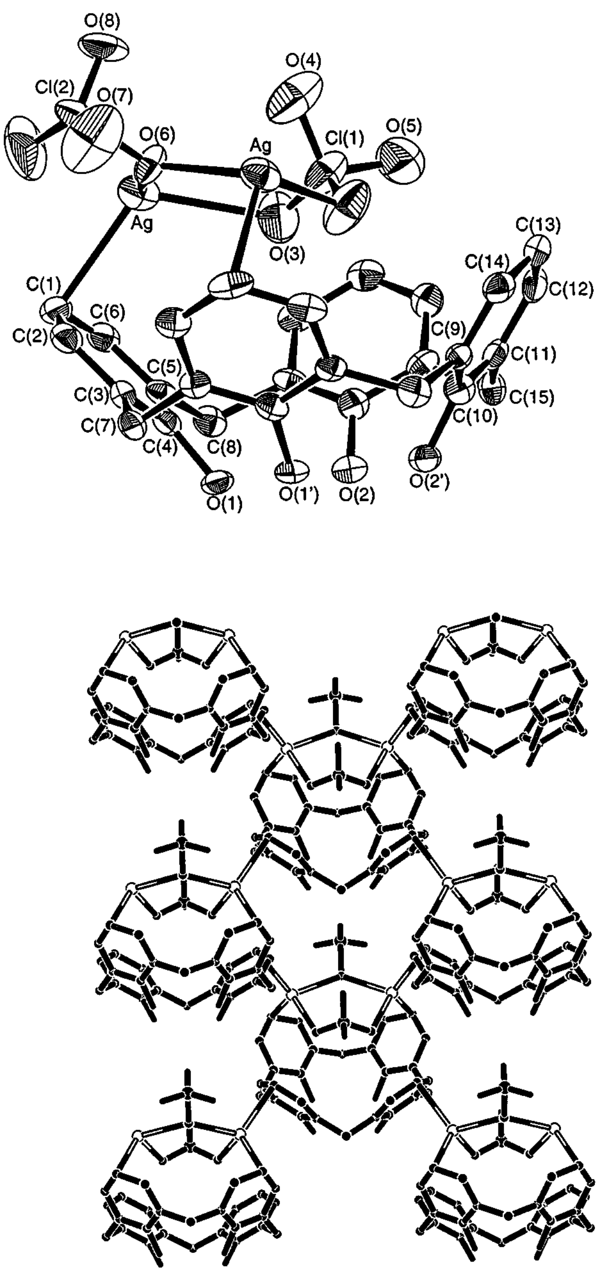


Fig. 3 An ORTEP drawing (top) and perspective plot (bottom) of the crystal structure of complex **4** down the *a* axis. Thermal ellipsoids for the ORTEP drawing are at the 30% probability level.

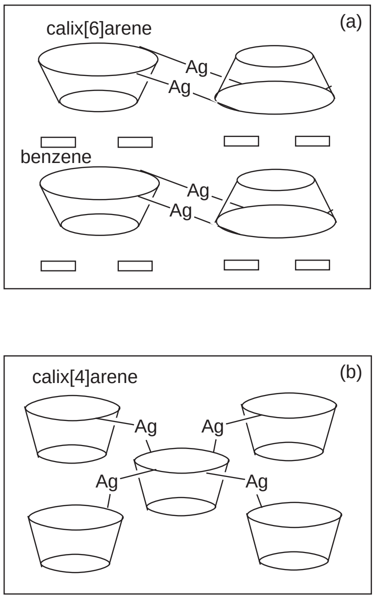


Fig. 4 Schematic representation showing different orientations of the calix[6]arene (a) and calix[4]arene (b) moieties in complexation with silver(I) ions.

calixarene complexes based on cation π interaction although formation of π complexes with the metal outside the cavity is not novel. Compared with the considerable interest during recent years in the use of calixarene monomers as platforms for the construction of supramolecular receptor assemblies,[17] there are few studies on calixarene-containing polymers, most of which exhibit the macrocycle moiety as an appendage of the polymer chain.[18] The unique two-dimensional framework, which is based on multiple cation π interaction of calixarene and metal ions, observed in the present polymeric calix[4]arene complex allows the possibility of using π-metalated calixarenes as building blocks for synthetic supramolecular receptors. In fact, complex **4** is a rarely observed capped molecular container, where among the four silver atoms attached to the upper rim of a calixarene two are bridged in pairs by two $\mathrm{ClO_4}^-$ ions as shown in Fig. 4. The perchlorate ions partially cap the container cavity and lead to no inclusion of guest molecules in the bowl. The measured cavity size as an interatomic distance is 8.64 Å at the upper rim [C(1) ··· C(13)] and 3.73 Å at the lower rim [O(1) ··· O(2′)]. These four atoms compose a trapezium, from this and the separation of 4.13 Å between C(1) and O(1) a bowl depth of *ca.* 3.32 Å was calculated. Therefore, the calix would have a cavity large enough to encapsulate selectively some small gaseous molecules such as dioxygen and methane. Such applications are the subject of ongoing investigations in our laboratory.[16,19]

In summary, silver(I) ion is shown to form open dimeric and capped polymeric container molecules with calixarenes based on cation π interactions, in particular, the co-ordination of resorcinarene involving both σ bonding at an aryl OH group and π bonding on the phenyl ring is quite unique. Although there still are challenges in understanding why solvent molecules or counter anions are not included in the open cavity of each dimeric structure, it is unambiguously demonstrated that the perchlorate anion can act as a gate blocking the guest molecules entering into the host cavity in the calix[4]arene system. Further studies of metal–calixarene compounds with different metal salts and with inclusion of small gaseous molecules are currently underway.

Experimental

All reactions and manipulations were carried out under an argon atmosphere using the standard Schlenk vacuum line techniques. Solvents were dried using standard procedures and distilled under an argon atmosphere prior to use. Reagent grade *C*-methylcalix[4]resorcinarene, calix[4]arene and calix[6]arene were from Aldrich. All other chemicals were from Wako Pure Chemical, Inc. and used without further purification. Microanalyses were performed by the Department of Chemistry, Tokyo Metropolitan University. The IR spectra were recorded as KBr discs on a JASCO 8000 FT-IR spectrometer, ESR spectra on a JEOL JES-TE200 spectrometer.

CAUTION: although no problems were encountered during the preparation of the perchlorate salt described below, suitable care should be taken when handling such potentially hazardous compounds.

Syntheses

$[\mathrm{Ag_2(L^1)(C_6H_6)_2}][\mathrm{ClO_4}]_2\cdot5\mathrm{C_4H_8O}$ 1. A solution of $\mathrm{AgClO_4}$ (20.7 mg, 0.1 mmol) in 5 cm^3 of benzene was added dropwise to a solution of *C*-methylcalix[4]resorcinarene (27.2 mg, 0.05 mmol) in 5 cm^3 of tetrahydrofuran (THF). After stirring for 10

Table 2 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{64}H_{80}Ag_2Cl_2O_{21}$	$C_{108}H_{96}Ag_2Cl_2O_{20}$	$C_{110}H_{96}Ag_2F_6O_{18}S_2$	$C_{28}H_{24}Ag_2Cl_2O_{12}$
M	1471.96	2000.58	2099.80	839.14
Crystal color, habit	Colorless, brick	Colorless, prisms	Yellow, brick	Colorless, prisms
Crystal size/mm	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.30	0.20 × 0.20 × 0.30	0.25 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhomic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$Pnma$
a/Å	25.049(8)	21.164(2)	21.379(4)	19.488(6)
b/Å	15.247(2)	11.606(2)	11.788(4)	13.359(3)
c/Å	17.934(2)	10.146(1)	10.324(2)	10.547(6)
α/°		71.62(1)	70.91(2)	
β/°	95.40(2)	80.302(10)	80.33(1)	
γ/°		79.11(1)	78.74(2)	
U/Å^3	6818(2)	2306.6(6)	2396(1)	2745(1)
Z	4	1	1	4
D_c/g cm^{-3}	2.868	2.880	2.910	4.060
F(000)	6080	2064	2160	3328
μ(Mo-Kα)/cm^{-1}	14.44	11.10	10.66	33.72
No. data collected	8297	11108	11554	3292
No. data in refinement [$I > 3.00\sigma(I)$]	2803	6731	5120	1636
No. refined parameters	402	595	602	216
Final R (R')	0.059 (0.070)	0.048 (0.075)	0.083 (0.115)	0.063 (0.087)
Goodness of fit	2.20	1.81	2.41	1.95
Maximum, minimum peaks in final difference map/e Å^{-3}	0.57, −0.47	0.57, −0.56	1.54, −1.22	1.46, −0.79

min the reaction mixture was filtered. The filtrate was introduced into a 6 mm diameter glass tube and layered with 2 cm^3 of *n*-pentane as a diffusion solvent. The glass tube was sealed under Ar and after standing at room temperature for 2 d colorless brick crystals of complex **1** were obtained (41 mg, 55%) (Found: C, 51.26; H, 5.29. $C_{64}H_{80}Ag_2Cl_2O_{21}$ requires C, 52.18; H, 5.43%).

{[Ag(L^2)(ClO$_4$)]·2C$_6$H$_6$}$_2$ 2. A solution of calix[6]arene (50.8 mg, 0.08 mmol) in benzene (10 cm^3) was treated with $AgClO_4$ (16.6 mg, 0.08 mmol). After stirring for 10 min the reaction mixture was filtered. The filtrate was introduced into a 6 mm diameter h-shape glass tube and layered with 2 cm^3 of *n*-pentane as a diffusion solvent. The glass tube was sealed under Ar and after standing at 50 °C for 4 d colorless plate crystals of complex **2** were obtained (52 mg, 65%) (Found: C, 64.64; H, 4.79. $C_{54}H_{48}AgClO_{10}$ requires C, 64.78; H, 4.80%).

{[Ag(L^2)(CF$_3$SO$_3$)]·2C$_6$H$_6$}$_2$ 3. The yellow brick crystals of complex **3** were prepared in the same way as for **2** using Ag-CF_3SO_3 instead of silver(I) perchlorate and *n*-hexane as the diffusion solvent (50 mg, 60%) (Found: C, 62.27; H, 4.48. $C_{55}H_{48}AgF_3O_9S$ requires C, 62.86; H, 4.57%).

[Ag$_2$(L^3)(ClO$_4$)$_2$] 4. To a solution of calix[4]arene (42.5 mg, 0.3 mmol) in benzene (30 cm^3) was added $AgClO_4$ (41.4 mg, 0.2 mmol). The mixed solution was treated in the same way as that for complex **2** and yielded colorless plate crystals of **4** (48 mg, 57%) (Found: C, 38.01; H, 2.83. $C_{14}H_{12}AgClO_6$ requires C, 40.04; H, 2.86%).

Crystallography

All measurements were carried out at room temperature on a Rigaku AFC5R diffractometer for complex **1**, and on an AFC7R diffractometer for **2**–**4**. Crystallographic data are given in Table 2. Periodic remeasurement of three standard reflections revealed no significant crystal decay or electronic instability in each case. Intensities were measured from continuous ω–2θ scans. All intensity data were corrected for Lorentz polarization effects. The structures were solved by a direct method[20] and refined by full-matrix least-squares analysis on F. All the full-occupancy non-hydrogen atoms were refined anistropically except the three F atoms in **3** which were refined isotropically. The counter anions ClO_4^- and $CF_3SO_3^-$ were found to have high thermal motions in each case, and partial occupancy was introduced to account for the very disordered atom O(6) in the refinement of **4**. The highest residual peaks for **3** and **4** resulted from this disorder. Hydrogen atoms of the four structures were introduced in their calculated positions; they were included, but not refined, in the refinement. In **1** and **2** the hydrogen atoms of THF and benzene molecules were excluded. Computations were carried out using TEXSAN.[21]

CCDC reference number 186/1272.

See http://www.rsc.org/suppdata/dt/1999/373/ for crystallographic files in .cif format.

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