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Silver Ion Inclusion by Calix[4]arene Ethers

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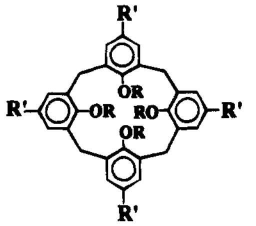
Tetra-*O*-alkylcalix[4]arenes are shown to act as hosts for the Ag^+ ion primarily through π-arene–silver(I) complexation. The structure of one silver(I) complex has been determined by an X-ray structure analysis. The silver ion is held in the cavity of the calixarene and is weakly coordinated to two arene groups and one methoxy group. The calixarene is in the partial cone conformation. This conformation also predominates in solution. Variable-temperature NMR studies show that the silver ion can influence both the distribution and the rate of interconversion of the calixarene conformers compared to the free ligands, by locking the calixarene in the partial cone conformation. The interaction between the included silver ion and tetra-*O*-alkylcalix[4]arene is weak, and the silver ion can be displaced easily by other ligands, such as MeCN, alkenes, and alkynes.

Introduction

Calix[4]arenes are cyclic molecules which contain four phenyl rings linked by methylene bridges. There has been much recent interest in their ability to act as hosts for cations since they display high affinity and high selectivity for cation inclusion.[1,2] Calix[4]arenes are useful building blocks for more complex molecules with unusual properties, but their ability to act as hosts is strongly influenced by their conformations. Four different orientations of the phenyl rings of the cyclic tetramer are possible.[2,3] These conformational isomers of the cyclic tetramers are named the "cone", "partial cone", "1,2-alternate", and "1,3-alternate" conformations, as shown in Figure 1. Most calix[4]arenes with OH groups, such as compounds **1** and **2**, exist preferentially in the cone conformation because of hydrogen-bonding effects. However, *O*-methylcalix[4]arenes, such as the methyl ethers shown in Figure 1, are often conformationally flexible at room temperature. Dynamic ^1H NMR measurements of several *O*-alkylcalix[4]arenes have shown that the conformational isomers can interconvert by rotation of the aryl groups at room temperature with a rate of ca. 100 s^{-1}.[3] Control of the conformation of O-alkylated calix[4]arenes is highly desirable.



1. R = H, R' = H; **2**. R = H, R' = Bu^t
3. R = Me, R' = H; **4**. R=Me, R' = Bu^t

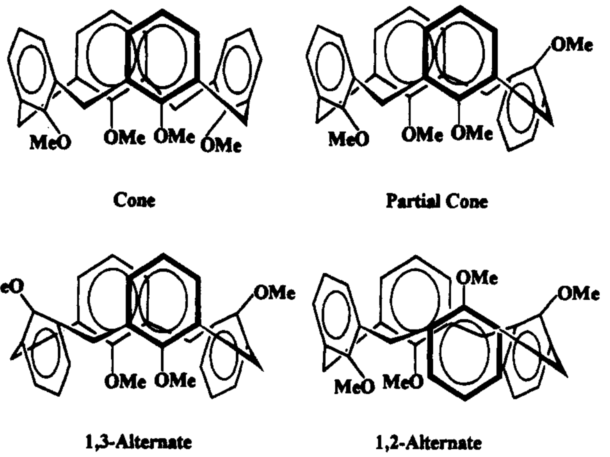


Figure 1. Conformations of calix[4]arene ethers.

Calix[4]arenes are already known to form complexes with some transition metals. For example, several complexes with oxophilic transition metals coordinated to the oxygen atoms at the bottom rim of calix[4]arenes have been reported.[4-6] Some functionalized calix[4]arenes (such as these functionalized with >PPh, $-PPh_2$, or $-NH_2$ groups) also show a strong affinity for transition metal cations.[7-10] In most of these cases, the

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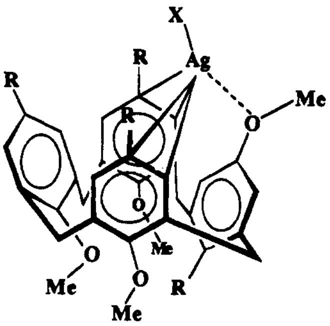
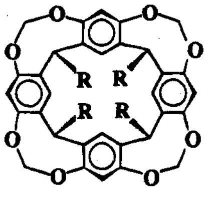
transition metals have been firmly bound and the coordination is irreversible. This paper reports the reversible inclusion of transition metal cations and the effects of their complexation on the conformations and fluxionality of the calix[4]arene host. The π-electron-rich calix[4]arene ethers, which possess two sets of face-to-face benzene rings, offer an interesting site for complexation. It will be shown that the reciprocal recognition between the calix[4]arene hosts and silver ion guest involves coordination of the silver cation to the electron-rich aryl groups of the calix[4]arene ethers and so gives unusual organometallic derivatives.

Experimental Section

The calix[4]arenes (**1**),[3] 5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**),[11] 25,26,27,28-tetramethoxycalix[4]arene (**3**),[3] 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene (**4**),[3] 1,21,23,25-tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin (**7**)[12] were prepared by literature methods. Melting points of all compounds were taken in unsealed capillary tubes using an electrothermal melting point apparatus. NMR spectra were collected by using a Varian XL300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. Since the abundances of the cone, 1,3-alternate, and 1,2-alternate conformers were low, only the spectral data of the dominant partial cone conformer are listed. IR spectra were recorded by using a Bruker IFS32 FTIR spectrometer with KBr mulls. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Mass spectra were recorded by using a Finnegan MAT 8230 spectrometer.



5a: R=H, X=AgNO$_3$; 5b: R=H, X=AgO$_2$CCF$_3$; 5c: R=H, X=AgPF$_6$;
6a R=Bu^t, X=AgNO$_3$; 6b: R=Bu^t, X=AgO$_2$CCF$_3$; 6c: R=Bu^t, X=AgPF$_6$



7. R = CH$_2$CH$_2$Ph

Table 1. Crystallographic Data for (Tetra-*O*-methylcalix[4]arene)silver Nitrate (5a)

empirical formula	(C$_{32}$H$_{32}$O$_4$)AgNO$_3$
fw	650.48
space group	$P2_1/c$
cell dimens	a = 10.0693(7) Å b = 24.6923(10) Å c = 11.4950(4) Å β = 92.609(4)° V = 2855.1(3) Å^3
molecules in unit cell	4
D_{calc}, g cm^{-3}	1.513
crystal dimensions	0.53 × 0.45 × 0.45 mm^3
temp, °C	27.5
radiation	Mo Kα
wavelength, Å	0.710 73
μ(Mo Kα), cm^{-1}	7.45
data collection range, θ	0–30.5
absorption factors (on F)	0.78–1.44
no. of unique reflns with $I > 3\sigma(I)$	4563
no. of params refined	370
discrepancy factor, R	0.052
R_w	0.064
largest shift/esd	0.08
range of values in final diff synthesis, e Å^{-3}	1.1–1.0

(25,26,27,28-Tetramethoxycalix[4]arene)AgNO$_3$ (5a). A suspension of AgNO$_3$ (0.17 g, 1 mmol) in a solution of compound **3** (0.48 g, 1 mmol) in THF (30 mL) was stirred for 12 h at room temperature. A clear colorless solution was obtained. The volume of solvent was reduced, and the remaining solution was then allowed to evaporate slowly over a period of 1 week. Colorless crystals of **5a** (0.5 g, yield 77%) was obtained. Anal. Calc for C$_{32}$H$_{32}$AgNO$_7$: C, 59.09; H, 4.96. Found: C, 58.79; H, 4.75. NMR in CDCl$_3$: $\delta(^1\text{H})$ = 2.86 [s, 3H, OC*H*$_3$], 3.75 [s, 6H, OC*H*$_3$], 3.92 [s, 3H, OC*H*$_3$], 3.18 [d, $^1J_{\text{H-H}}$ = 13.5 Hz, 2H, C*H*$_2$], 4.07 [d, $^1J_{\text{H-H}}$ = 13.5 Hz, 2H, C*H*$_2$], 3.66 [dd, AB system, 4H, $^1J_{\text{H-H}}$ = 14.2 Hz, C*H*$_2$], 6.62–7.36 [m, 12H, *Ar*]; $\delta(^{13}\text{C})$ = 30.30 [s, 2C, *C*H$_2$], 35.47 [s, 2C, *C*H$_2$], 59.85 [s, 1C, *C*H$_3$], 61.02 [s, 1C, *C*H$_3$], 61.27 [s, 2C, *C*H$_3$], 113.1–160.8 [m, 24C, *Ar*]. IR: $\nu_{\text{N-O}}$ = 1290, 1208, 1173 cm^{-1}. FAB-MS: *m*/*e* 587, *m*/*e* calc for C$_{32}$H$_{32}$AgO$_4$$^+$ 587.

Single-Crystal X-ray Analysis of 5a. Single crystals of complex **5a** were obtained as described above. All X-ray measurements were made with graphite-monochromated Mo radiation on an Enraf-Nonius CAD4 diffractometer using a transparent block-shaped crystal which slowly darkened during the course of the experiment. Experimental details are summarized in Table 1.

The unit cell constants were determined by the least-squares treatment of 25 reflections with Bragg angles in the range 20.8 < θ < 23.2°. Intensities for 9092 reflections with h = 0 to 14, k = −35 to 0, and l = −16 to 16 were measured from continuous $\omega/2\theta$ scans. The scan speeds were adjusted to give $\sigma(I)/I$ < 0.03 subject to a time limit of 30 s. Three reflections were used to monitor the stability of the crystal and diffractometer: their mean intensity showed only random fluctuations of 1.5% during data collection. Empirical absorption corrections were made by the method of Stuart and Walker[13] at the end of the isotropic refinement. The internal agreement factor, R_{int}, for merging 435 duplicate intensities was 0.027. Of 8657 unique reflections measured, 4563 for which $I > 3\sigma(I)$ were used in the subsequent analysis.

The positions of the non-hydrogen atoms were obtained using Patterson and difference Fourier methods. Hydrogen atoms were included in calculated positions with C–H = 0.96 Å and were constrained to ride on their parent carbon atoms with their U(isotropic) parameters set at ca. 1.2U_{eq} of the parent carbon atom. mhe structure was refined by full-matrix least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ where $w = \sigma(|F_o|)^{-2}$. Anisotropic displacement parameters were refined for all non-hydrogen atoms. These parameters

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Table 2. Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for 5a

	x	*y*	*z*	U^a
Ag	0.12277(4)	0.19027(2)	0.23204(3)	0.054
O(1)	−0.1482(6)	0.3199(3)	0.2376(4)	0.128
O(2)	0.0007(7)	0.2688(3)	0.1691(6)	0.176
O(3)	−0.0718(7)	0.2521(3)	0.3177(7)	0.193
O(11)	0.4303(3)	0.0901(1)	0.2029(2)	0.045
O(21)	0.5290(3)	0.1284(1)	0.4781(3)	0.048
O(31)	0.0617(3)	0.1317(1)	0.4006(3)	0.043
O(41)	0.2184(3)	−0.0008(1)	0.1505(3)	0.050
N	−0.0731(5)	0.2835(2)	0.2429(4)	0.065
C(11)	0.4915(4)	0.1161(2)	0.1120(4)	0.047
C(12)	0.5862(4)	0.1557(2)	0.1387(4)	0.051
C(13)	0.6447(5)	0.1810(2)	0.0451(6)	0.070
C(14)	0.6087(7)	0.1668(3)	−0.0679(6)	0.080
C(15)	0.5124(6)	0.1296(3)	−0.0903(4)	0.072
C(16)	0.4505(5)	0.1026(2)	−0.0019(4)	0.055
C(17)	0.4969(5)	0.0432(2)	0.2464(4)	0.063
C(18)	0.6171(4)	0.1728(2)	0.2622(5)	0.056
C(21)	0.4525(4)	0.1686(2)	0.4242(4)	0.039
C(22)	0.3311(4)	0.1814(2)	0.4714(3)	0.040
C(23)	0.2585(5)	0.2238(2)	0.4206(4)	0.048
C(24)	0.3008(5)	0.2498(2)	0.3216(5)	0.054
C(25)	0.4160(5)	0.2316(2)	0.2688(4)	0.056
C(26)	0.4933(4)	0.1914(2)	0.3220(4)	0.046
C(27)	0.6179(5)	0.1500(2)	0.5681(4)	0.065
C(28)	0.2744(5)	0.1475(2)	0.5656(3)	0.048
C(31)	0.1332(4)	0.0855(2)	0.4345(3)	0.038
C(32)	0.1054(4)	0.0370(2)	0.3805(4)	0.043
C(33)	0.1776(5)	−0.0078(2)	0.4168(4)	0.052
C(34)	0.2783(6)	−0.0039(2)	0.5031(5)	0.059
C(35)	0.3076(5)	0.0457(2)	0.5533(4)	0.051
C(36)	0.2361(4)	0.0918(2)	0.5207(3)	0.041
C(37)	−0.0572(5)	0.1401(2)	0.4650(5)	0.063
C(38)	0.0038(5)	0.0336(2)	0.2778(4)	0.050
C(41)	0.1589(4)	0.0474(2)	0.1155(3)	0.040
C(42)	0.2124(5)	0.0781(2)	0.0281(4)	0.045
C(43)	0.1505(5)	0.1256(2)	−0.0040(4)	0.052
C(44)	0.0369(5)	0.1434(2)	0.0482(4)	0.050
C(45)	−0.0128(4)	0.1134(2)	0.1380(4)	0.045
C(46)	0.0500(4)	0.0651(2)	0.1743(3)	0.040
C(47)	0.1693(6)	−0.0471(2)	0.0874(6)	0.079
(C48)	0.3412(6)	0.0615(2)	−0.0257(4)	0.063

^{a} $U = {}^1/_3\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*(\vec{a}_i\cdot\vec{a}_j)$.

(see Table 2) indicate apparent mean-square displacements, *U*, of up to 0.37 Å^2 for the nitrate oxygen atoms in the direction normal to the NO_3^- plane and suggest slight positional disorder of the nitrate anion. The GX program package[14] was used for all calculations; atomic scattering factors and anomalous dispersion corrections were taken from ref 15.

(25,26,27,28-Tetramethoxycalix[4]arene)AgOCOCF$_3$ (5b). This was prepared similarly from $AgOCOCF_3$ (0.22 g, 1 mmol) and compound **3** (0.48 g, 1 mmol) in THF (30 mL) and was isolated as a colorless crystalline solid **5b** (0.55 g, yield 79%). Anal. Calc for $C_{34}H_{32}AgF_3O_6$: C, 58.22; H, 4.60. Found: C, 57.96; H, 4.41. NMR in CD_2Cl_2: $\delta(^1H)$ = 2.70 [s, 3H, OCH_3], 3.71 [s, 6H, OCH_3], 3.95 [s, 3H, OCH_3], 3.20 [d, $^1J_{H-H}$ = 14.6 Hz, 2H, CH_2], 4.11 [d, $^1J_{H-H}$ = 14.6 Hz, 2H, CH_2], 3.75 [dd, AB system, 4H, $^1J_{H-H}$ = 14.1 Hz, CH_2], 6.57−7.32 [m, 12H, *Ar*]; $\delta(^{13}C)$ = 30.63 [s, 2C, CH_2], 35.81 [s, 2C, CH_2], 60.15 [s, 1C, CH_3], 60.90 [s, 1C, CH_3], 61.44 [s, 2C, CH_3], 113.8−159.42 [m, 24C, *Ar*], 157.70 [q, 1C, CF_3], 159.84 [s, 1C, CF_3CO_2]. IR: ν_{C-O} = 1630 (br), 1290, 1203 cm^{-1}.

(25,26,27,28-Tetramethoxycalix[4]arene)AgPO$_2$F$_2$ (5c). This was prepared similarly from $AgPF_6$ (0.253 g, 1 mmol) and compound **3** (0.48 g, 1 mmol) in THF (30 mL). Yield: 0.6 g, 84%. Anal. Calc for $C_{32}H_{32}AgF_2O_6P$: C, 55.75; H, 4.68. Found: C, 55.83; H, 4.44. NMR in CD_2Cl_2: $\delta(^1H)$ = 2.67 [s, 3H, OCH_3], 3.81 [s, 6H, OCH_3], 4.04 [s, 3H, OCH_3], 3.34 [d, $^1J_{H-H}$ = 14.6 Hz, 2H, CH_2], 4.12 [d, $^1J_{H-H}$ = 14.6 Hz, 2H, CH_2], 3.86 [dd, AB system, 4H, $^1J_{H-H}$ = 13.5 Hz, CH_2], 6.72−7.48 [m, 12H, *Ar*]; $\delta(^{13}C)$ = 30.67 [s, 2C, CH_2], 35.45 [s, 2C, CH_2], 60.47 [s, 1C, CH_3], 60.90 [s, 1C, CH_3], 61.93 [s, 2C, CH_3], 109.31−160.93 [m, 24C, *Ar*]; $\delta(^{31}P)$ = −17.1 [t, $^1J_{P-F}$ = 1047.5 Hz].

The following compounds were similarly prepared.

(5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]AgNO$_3$ (6a). Yield: 74%. Anal. Calc for $C_{48}H_{64}AgNO_7$: C, 65.90; H, 7.37. Found: C, 65.61; H, 7.50. NMR in CD_2Cl_2 at −40 °C: $\delta(^1H)$ = 1.08 [s, 9H, $C(CH_3)_3$], 1.16 [s, 18H, $C(CH_3)_3$], 1.34 [s, 9H, $C(CH_3)_3$], 2.03 [s, 3H, OCH_3], 3.47 [s, 6H, OCH_3], 3.42 [s, 3H, OCH_3], 3.15 [d, $^1J_{H-H}$ = 12.6 Hz, 2H, CH_2], 4.16 [d, $^1J_{H-H}$ = 12.6 Hz, 2H, CH_2], 3.80 [s, br, 4H, CH_2], 6.79−7.25 [m, 12H, *Ar*].

(5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene)AgO$_2$CCF$_3$ (6b). Yield: 76%. Anal. Calc for $C_{50}H_{64}AgF_3O_6$: C, 64.86; H, 6.97. Found: C, 64.96; H, 6.78. NMR in CD_2Cl_2 at −40 °C: $\delta(^1H)$ = 1.12 [s, 9H, $C(CH_3)_3$], 1.20 [s, 18H, $C(CH_3)_3$], 1.35 [s, 9H, $C(CH_3)_3$], 2.19 [s, 3H, OCH_3], 3.81 [s, 6H, OCH_3], 4.11 [s, 3H, OCH_3], 3.44 [d, $^1J_{H-H}$ = 12.7 Hz, 2H, CH_2], 4.15 [d, $^1J_{H-H}$ = 12.7 Hz, 2H, CH_2], 3.86 [s, br, 4H, CH_2], 6.90−7.18 [m, 12H, *Ar*].

(5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene)AgPF$_6$ (6c). Yield: 77%. Anal. Calc for $C_{48}H_{64}AgF_6O_4P$: C, 60.19; H, 6.73. Found: C, 59.93; H, 6.48. NMR in CD_2Cl_2 at room temperature: $\delta(^1H)$ = 1.23 [s, 9H, $C(CH_3)_3$], 1.30 [s, 18H, $C(CH_3)_3$], 1.36 [s, 9H, $C(CH_3)_3$], 2.10 [s, 3H, OCH_3], 3.15 [s, 6H, OCH_3], 3.89 [s, 3H, OCH_3], 3.46 [d, $^1J_{H-H}$ = 12.6 Hz, 2H, CH_2], 4.15 [d, $^1J_{H-H}$ = 12.6 Hz, 2H, CH_2], 3.78 [s, br, 4H, CH_2], 6.92−7.43 [m, 12H, *Ar*].

Results and Discussion

Preparation of Calix[4]arene−Silver Complexes 5. All previously reported silver complexes of simple arenes, such as the relatively stable complex $[Ag(PhCH_2CH_2Ph)]^+$, decompose rapidly unless they are stored in the presence of excess ligand vapor and protected from moisture.[16,17] The silver complexes of deltaphane, paracyclophane, and stilbene, however, are crystalline solids, which are stabilized by forming two or three coordinate bonds in the complexes **8**−**10**.[18−20] Some of these have been called π-prismands.[21] The present work shows that calix[4]arenes, which have four phenyl rings arranged around a central cavity, can form unusually stable silver(I) complexes which may be considered as π-cryptands.[21] Thus, slow evaporation of a stoichiometric solution of **3** and silver nitrate in dry tetrahydrofuran gave colorless or pale amber crystals of the new complex **5a**. This complex dissolved in CH_2Cl_2 (320 mg mL^{-1}) and $CHCl_3$, in contrast to silver nitrate, which is insoluble. Addition of silver nitrate in excess of the 1:1

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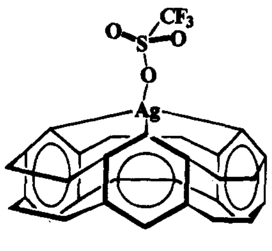
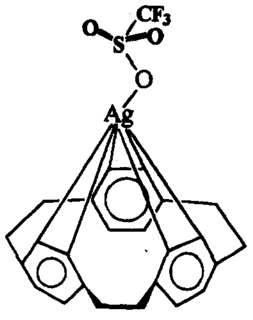
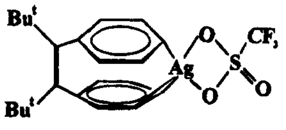
(21) The term π-prismand has been used to describe complexes such as **8** in which a prism-shaped cavity is defined by the planes of π-donor phenyl rings.[19] For species such as **5a** and **10** the shape of the cavity is not obviously prismatic. The terminology π-cryptand seems a more descriptive generic name for such complexes although the term cryptand is already in use for other compounds. An independent report of silver ion complexation by calixarene was recently published, but the nature of the binding was not determined: Bakker, W.; Verboom, W.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1994**, 71.



Deltaphane 8



Paracyclophane 9



Cofacial Stilbene 10

stoichiometry caused no further changes in the ^{1}H NMR spectrum of **5a**. Crystals of the new complex **5a** are stable to moist air. Complex **5a** is photosensitive, since exposure of a solution in THF or CH_2Cl_2 solution over 1 week led to a color change from colorless to amber. The calix[4]arene–silver complexes **5b** and **5c** were prepared in a similar way by reaction of **3a** with silver trifluoroacetate or silver hexafluorophosphate. These calix[4]arene–silver complexes are also stable except that the hexafluorophosphate is rapidly hydrolyzed to give the $PO_2F_2^-$ anion. The sharp ^{1}H NMR signals of **5** at room temperature indicate that the silver–arene bonds are well formed, since the binding between calix[4]arene **3** and silver is strong enough to stop the conformational tumbling of **3** (Figure 2).

Molecular Structure of 5a. X-ray analysis shows that crystals of **5a** obtained from THF/diethyl ether/*n*-hexane solution contain discrete molecules (Figure 3a) in which the silver ion is bound both to the calix[4]arene and to an asymmetrically bidentate nitrate residue. The molecule has an approximate plane of symmetry which contains the $AgNO_3$ unit and bisects phenyl rings 1 and 3 of the calix[4]arene. In addition, the calix[4]arene adopts a partial cone conformation, as shown by the signs of the CH_2–C_{Ar} torsion angle ϕ^1–χ^4 (Table 3). Using the convention proposed by Ugozzoli and Andreetti,[22] its conformation symbol is therefore C_s(+ −, + −, + +, − −). The conformation is such that rings 2 and 4 are nearly cofacial (dihedral angle 12.7(2)°). The silver ion lies in the cleft between these rings: it is bound to them through the edges C(23)–C(24) and C(44)–C(45), and it is also attached to ring 3 through its MeO oxygen atom, O(31). The atoms of the calix[4]arene donor set [C(23), C(24), C(44), C(45), O(31)] are coplanar to within 0.005(5) Å; the silver atom is displaced 0.30 Å from this plane toward O(2), i.e. away from the interior of the calix[4]arene.

The silver ion is thus attached to a rim of the calix[4]arene and does not completely occupy its central cavity as may be seen from Figure 3b. Phenyl ring 1 and its associated methoxy group protect the silver ion from further ligation but do not interact with it covalently: the Ag⋯O(11) contact of 3.989(3) Å roughly *trans* to O(2) is clearly nonbonding. The silver coordination in **5a** resembles that found in deltaphane–silver complex **8**, in paracyclophane–silver complex **9**, and in cofacial stilbene–silver complex **10**: in all these complexes the silver atom is attached to one or more oxygen atoms of the counteranion and lies on the rim of a cavity defined by electron-rich phenyl rings to which it is linked by between three and six Ag–C π-bonds. Thus, in **8** the Ag atom lies just outside the deltaphane cavity and is π-bonded to each phenyl ring through a single carbon atom;[20] in **9** the Ag–phenyl π-bonds involve ring edges rather tips;[19,20] in **10** both arrangements occur, one ring being bonded to silver through a single carbon atom and the other through a pair of adjacent carbon atoms.[18] The Ag–C distances of 2.50–2.64 Å in **5a** are fairly similar to those of 2.55–2.67 Å found in the perchlorate salt of (paracyclophane)Ag^+;[19] a rather wider range of Ag–C bond lengths, 2.40–2.69 Å, was observed in (deltaphane)silver(I) triflate.[20] In species such **8** and **10**, the Ag coordination is completed by one or two strong Ag–O bonds of 2.36–2.51 Å, similar in length to the shorter Ag–O bonds in **5a**. The partial cone conformation of the methoxycalix[4]arene in **5a** thus provides a particularly favorable environment for formation of a π-cryptand complex, since the silver can readily interact with a C_4O–calix[4]arene donor set. Ag^+ evidently prefers to lie on the rim rather than to occupy fully the cavity in such species. So far as we are aware, Cs^+ is the only metal cation whose presence in a calixarene cavity, stabilized by π-interaction with the calixarene phenyl rings, has been demonstrated by a diffraction study.[23]

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in 5a

(a) Bond Lengths			
Ag–O(2)	2.389(6)	Ag–O(3)	2.705(8)
Ag–O(31)	2.517(3)	Ag–C(23)	2.643(5)
Ag–C(24)	2.504(5)	Ag–C(44)	2.527(5)
Ag–O(45)	2.549(5)	O(1)–N	1.174(6)
O(2)–N	1.209(7)	O(3)–N	1.157(7)
Range, Mean			
C_{Ar}–C_{Ar}	1.351(9)–1.410(6), 1.387(3)	O–C_{Ar}	1.383(5)–1.394(5), 1.389(3)
C_{Ar}–CH_2	1.501(7)–1.530(7), 1.514(3)	O–CH_3	1.418(6)–1.451(6), 1.435(7)
Bond Angles			
O(2)–Ag–O(3)	44.0(2)	O(2)–Ag–O(31)	124.0(2)
O(2)–Ag–C(23)	103.5(3)	O(2)–Ag–C(24)	89.8(3)
O(2)–Ag–C(44)	88.1(3)	O(2)–Ag–C(45)	102.6(3)
O(3)–Ag–C(31)	80.7(2)	O(3)–Ag–C(23)	83.1(3)
O(3)–Ag–C(24)	92.0(3)	O(3)–Ag–C(44)	109.7(3)
O(3)–Ag–C(45)	101.1(3)	O(31)–Ag–C(23)	71.6(2)
O(31)–Ag–C(24)	102.5(2)	O(31)–Ag–C(44)	107.1(2)
O(31)–Ag–C(45)	75.7(2)	C(23)–Ag–C(24)	31.2(2)
C(23)–Ag–C(44)	166.9(2)	C(23)–Ag–C(45)	145.9(2)
C(24)–Ag–C(44)	145.5(2)	C(24)–Ag–C(45)	166.2(2)
C(44)–Ag–C(45)	31.6(2)	Ag–O(2)–N	110.9(4)
Ag–O(3)–N	95.3(5)	Ag–O(31)–C(31)	123.0(3)
Ag–O(31)–C(37)	123.1(3)	O(1)–N–O(2)	127.6(3)
O(1)–N–O(3)	122.4(6)	O(2)–N–O(3)	109.4(7)

Bond lengths and angles (Table 3) within the calix[4]arene residue are internally consistent and are in

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(22) Ugozzoli, F.; Andreetti, G. D. *J. Inclusion Phenom.* **1992**, *13*, 337.

(23) Harrowfield, J. M.; Ogden, M. I.; Richmond, W. R.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1159.

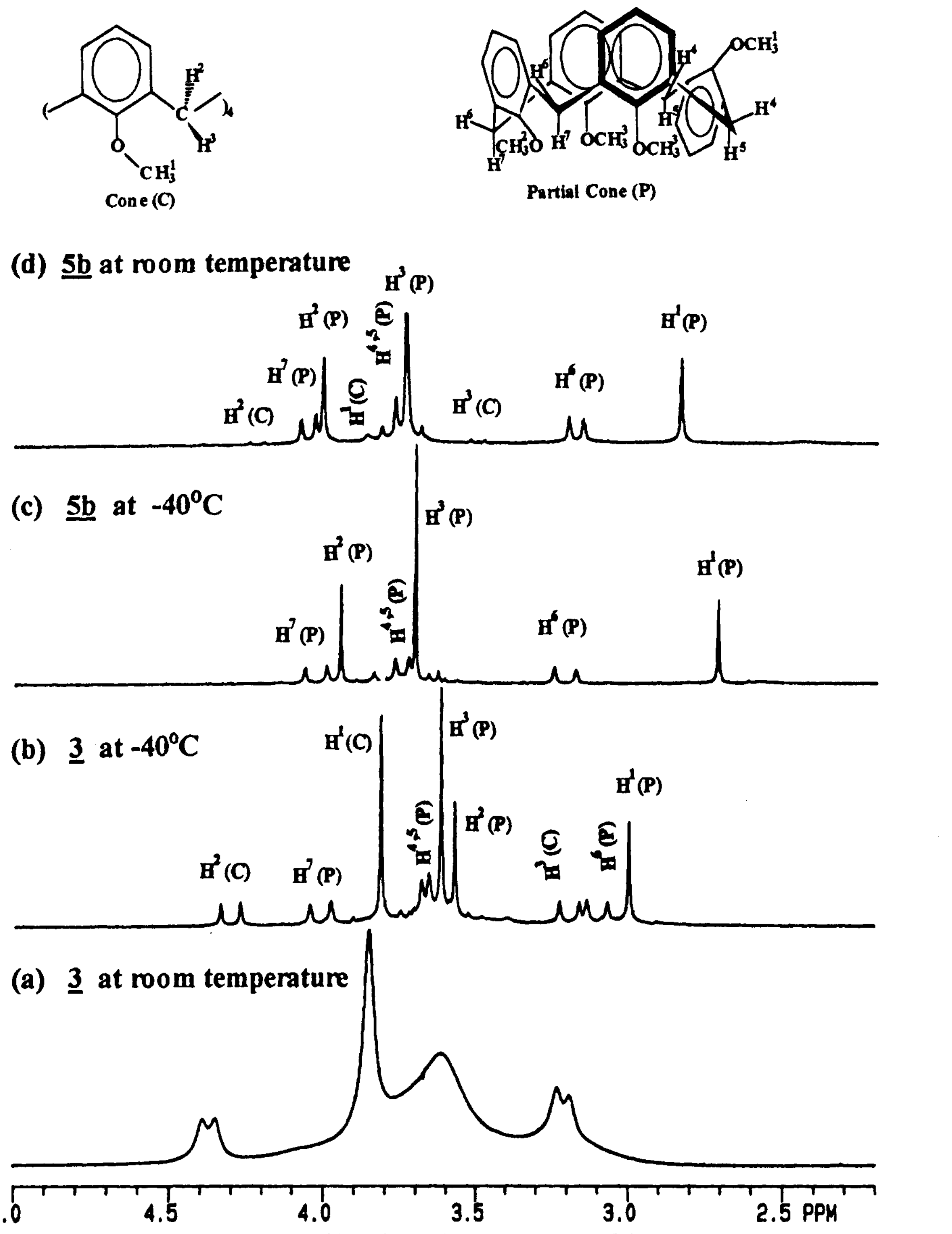

Figure 2. ^{1}H NMR spectra of **3** and **5b** in CD_2Cl_2. The aryl parts are omitted for clarity. P = partial cone; C = cone.

agreement with accepted values.[24] In particular, the C(23)–C(24) and C(44)–C(45) bond lengths [1.391(7) and 1.383(7) Å] do not differ significantly from the mean C_{Ar}–C_{Ar} bond length; nor are the C(31)–O(31) and O(31)–C(37) distances of 1.394(5) and 1.451(6) Å exceptional. Other authors, noting that arene ligands are little changed geometrically by complexation to a silver ion, have concluded that the metal–ligand interaction in **5a** must be relatively weak.[18,19] The interaction of the silver cation with the nitrate group also appears normal: the Ag–O(2) and Ag–O(3) distances [2.39 and 2.71 Å] may be compared with the Ag–O bond lengths of 2.384(5)–2.702(8) Å in solid silver nitrate.[25]

Spectral Properties of Calix[4]arene–Silver Complexes 5. It is known that the conformations of calix[4]arenes can be determined by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^{1}H NMR spectra and by the number of peaks in the ^{13}C NMR spectra, as shown schematically in Figure 4. Gutsche has shown that the tetramethyl ethers of **1** and **2** are conformationally flexible molecules. The ^{1}H NMR spectra of **3** and **4** recorded at room temperature at 100 MHz showed

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[24] Gallagher, J. F.; Ferguson, G.; Bohmer, V.; Kraft, D. *Acta Crystallogr.* **1994**, *C50*, 77.

[25] Meyer, P. P.; Rimsky, A.; Chevalier, R. *Acta Crystallogr.* **1978**, *B34*, 1457.

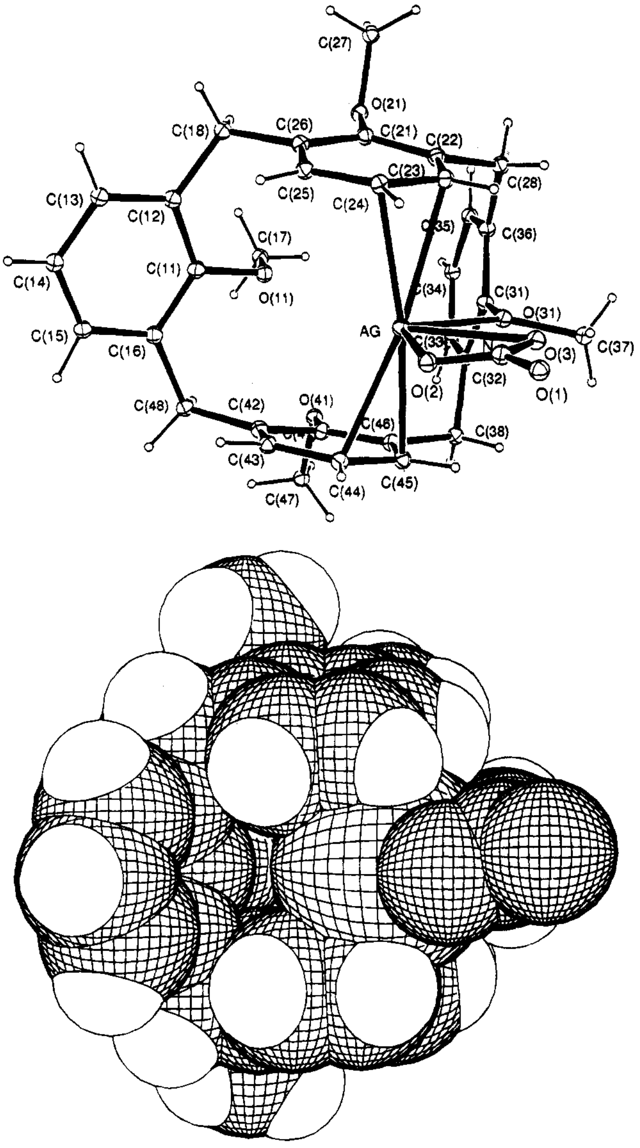

Figure 3. (a) View of (tetra-*O*-methylcalix[4]arene)silver nitrate (**5a**) showing the atom-numbering scheme. Atoms are represented as spheres of arbitrary radius. (b) View of a space-filling model of **5a**. The view direction is approximately the same as in Figure 3a.

broad signals that became sharp at lower temperature (−30 °C). The spectra were originally interpreted in terms of two partial cone configurations, with a methoxy group pointed toward the center or outside of the cavity, respectively, although reinvestigation revealed a more complex picture.[3] From our 300-MHz ^{1}H NMR spectrum of **3** (Figure 2a,b), the molecule is fluxional at room temperature but, at −40 °C, sharp spectra due to molecules in both cone and partial cone conformations are observed, with the ratio partial cone:cone = 4:1. In contrast, the ^{1}H NMR spectrum of **5b** (Figure 2c) at −40 °C contains resonances due to the partial cone conformation only. There are major coordination shifts of the partial cone resonances as a result of the coordination to silver(I), as can be seen by comparing spectra in Figure 2b,c and the data in Table 4.

It is interesting to note that when silver(I) was added to the solution of **3**, the calix[4]arene−silver complexes **5** showed sharp signals even at room temperature and the ratio of partial cone to cone conformers increased from 4:1 in **3** to 99.9:1 in **5** (on the basis of ^{1}H NMR integration). Additional evidence for the existence of the two conformations and conformational distribution changes was obtained from the ^{13}C NMR spectra (Figure 5). The conformational abundances of these compounds are listed in Table 5. It is obvious that the P:C ratio is greatly increased upon silver ion complex formation.

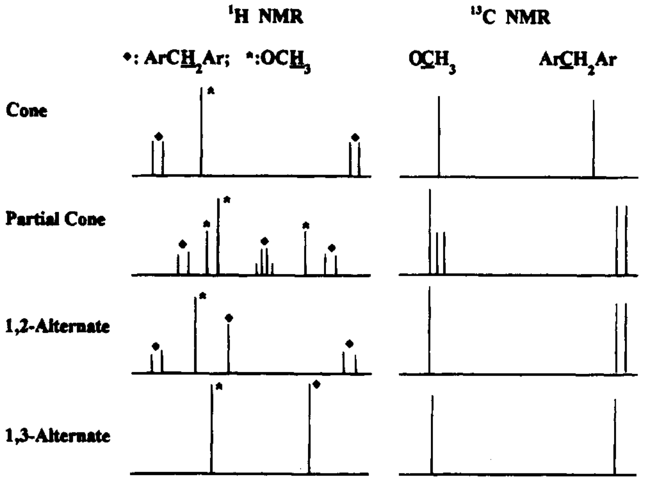

Figure 4. ^{1}H NMR and ^{13}C NMR spectral patterns of the four conformers of calix[4]arene ethers which would be expected to be observed.

Table 4. Comparison of ^{1}H NMR Chemical Shifts of 3 and 5b in Partial Cone Conformation in CD_2Cl_2 at −40 °C

	CH_3O-			$Ar-CH_2-Ar$		
δ(**3**), ppm	2.99	3.56	3.61	3.10 (d)	4.00 (d)	3.66 (dd)
δ(**5b**), ppm	2.70	3.69	3.94	3.20 (d)	4.02 (d)	3.75 (dd)
Δδ, Hz	−87	39	99	30	6	27

Table 5. Ratios of Abundances of Conformers 3, 4, 5, and 7[a]

	3	4	5a	5b	5c	7a	7b	7c
P:C (room temp)			99:1	99:1	95:5			98:1
P:C (−40 °C)	80:20	92:8[b]	>99:1	>99:1	98:2	99:1	99:1	98:2

[a] P = partial cone; C = cone conformation. The data were obtained from integration of ^{1}H NMR spectra and ^{13}C NMR spectra. [b] Literature[3] reported value.

The above spectra were reproducible, and so it is clear that the coordination of silver(I) to calix[4]arene **3** has a marked effect on both the ratio of the conformers in solution and the rate of interconversion of the conformers. In particular, silver(I) stabilizes the partial cone conformation (although a small amount of calixarene−silver complex does exist in the cone conformation) and reduces the rate of interconversion of the conformers. It seems clear that the silver(I) ion must dissociate before the conformational equilibration can occur.

Thermal Properties of Calix[4]arene−Silver Complexes 5. The thermal properties of the new complexes **5a−c** have been studied by TGA and DSC. TGA of **5** shows that its decomposition temperature is lower than that of either of its precursors (see Figure 6). For example, compound **5b** was half-decomposed at ~280 °C whereas ligand **3** and AgO_2CCF_3 decomposed at ~330 °C and 360 (mp of **3** 234−235[3]) °C respectively.

Factors Influencing the Complexing Ability of the Calix[4]arene Hosts. Both electronic effects and steric effects of substituents on the calix[4]arene derivatives on the formation of complexes **5** were investigated. Neither compound **1** nor compound **2** showed evidence

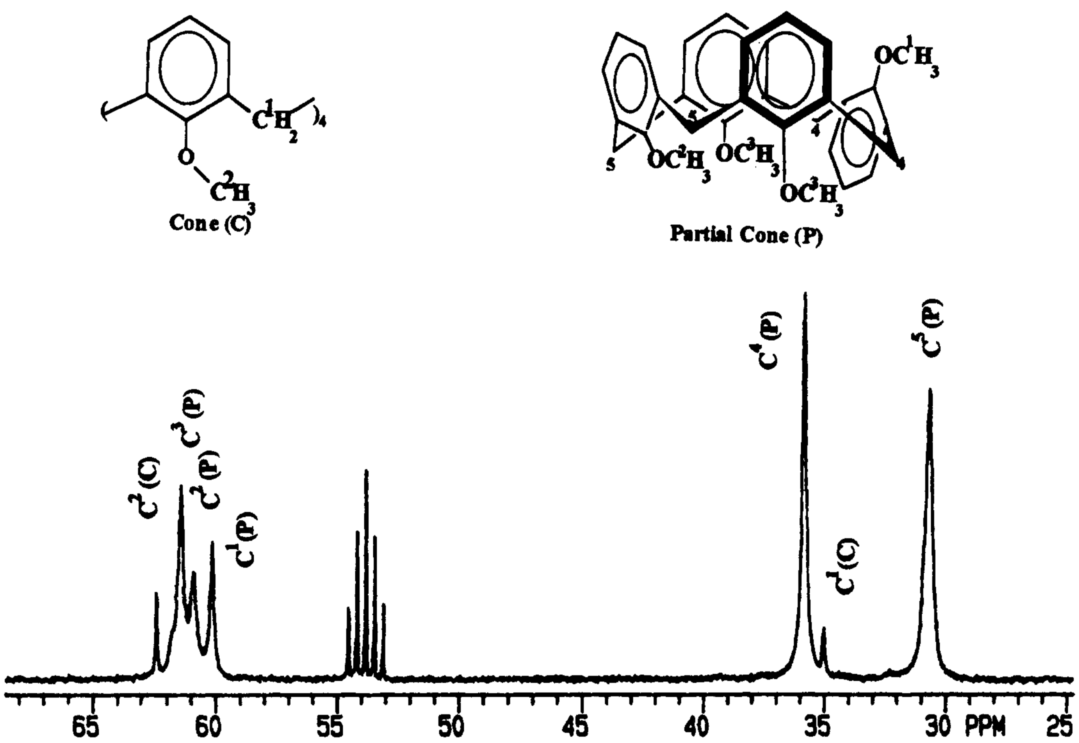

Figure 5. ^{13}C NMR spectra of **5b** in CD_2Cl_2 at room temperature. The aryl parts are omitted for clarity. P = partial cone; C = cone.

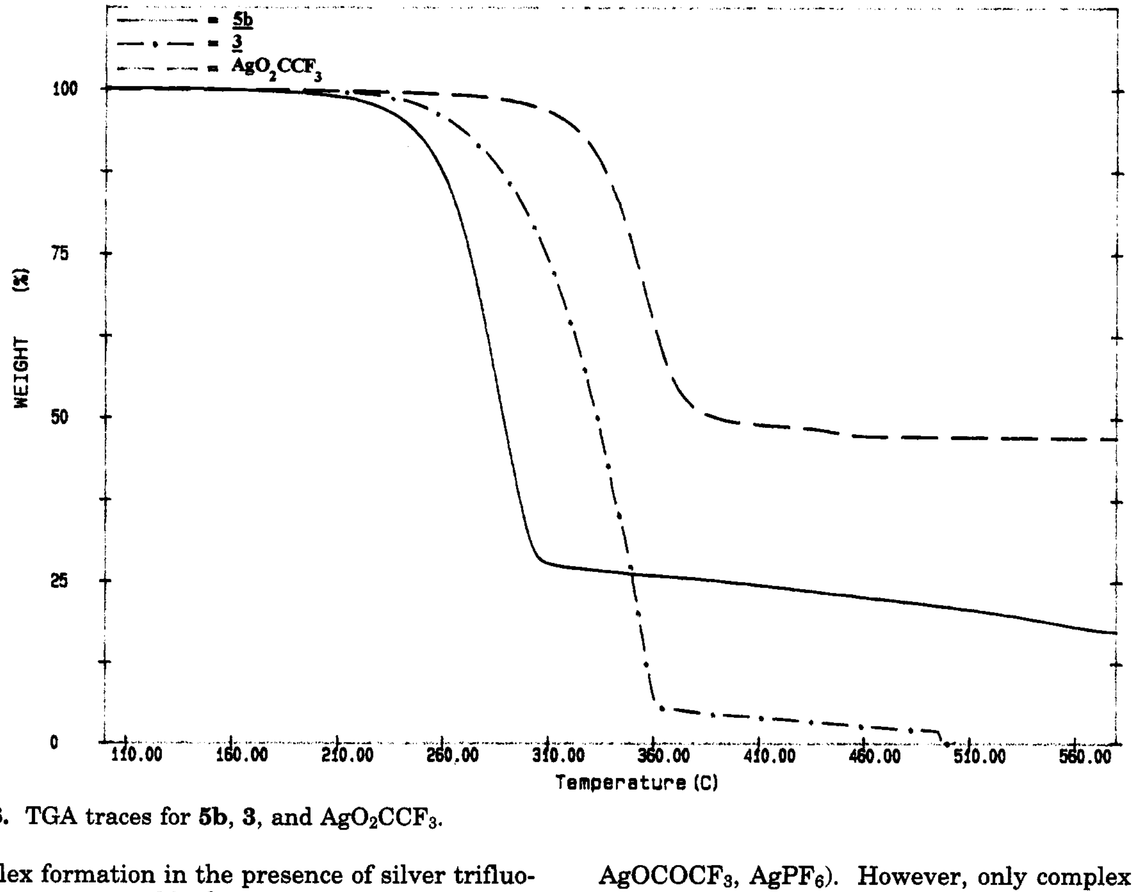

Figure 6. TGA traces for **5b**, **3**, and AgO_2CCF_3.

for complex formation in the presence of silver trifluoroacetate as monitored by ^1H NMR. The complexation os silver salts with the cavitand **7**, which has a rigid cone conformation, has also been tested, but no evidence for complex formation with silver salts was observed by ^1H NMR.

In spite of the presence of bulky *tert*-butyl substituents, compound **4** can interact with Ag(I) ($AgNO_3$, $AgOCOCF_3$, $AgPF_6$). However, only complexation between **4** and $AgPF_6$ leads to relatively sharp peaks in the ^1H NMR spectrum at room temperature. The peaks in the ^1H NMR spectra of the other complexes, **6b**,**c**, are broad, but obvious chemical shift changes can be observed by comparison with the spectra of the precursors **4**. It is known that, at −25 °C in $CDCl_3$, **4** consists of 2% cone, 92% partial cone, 5% 1,2-alternate, and 1%

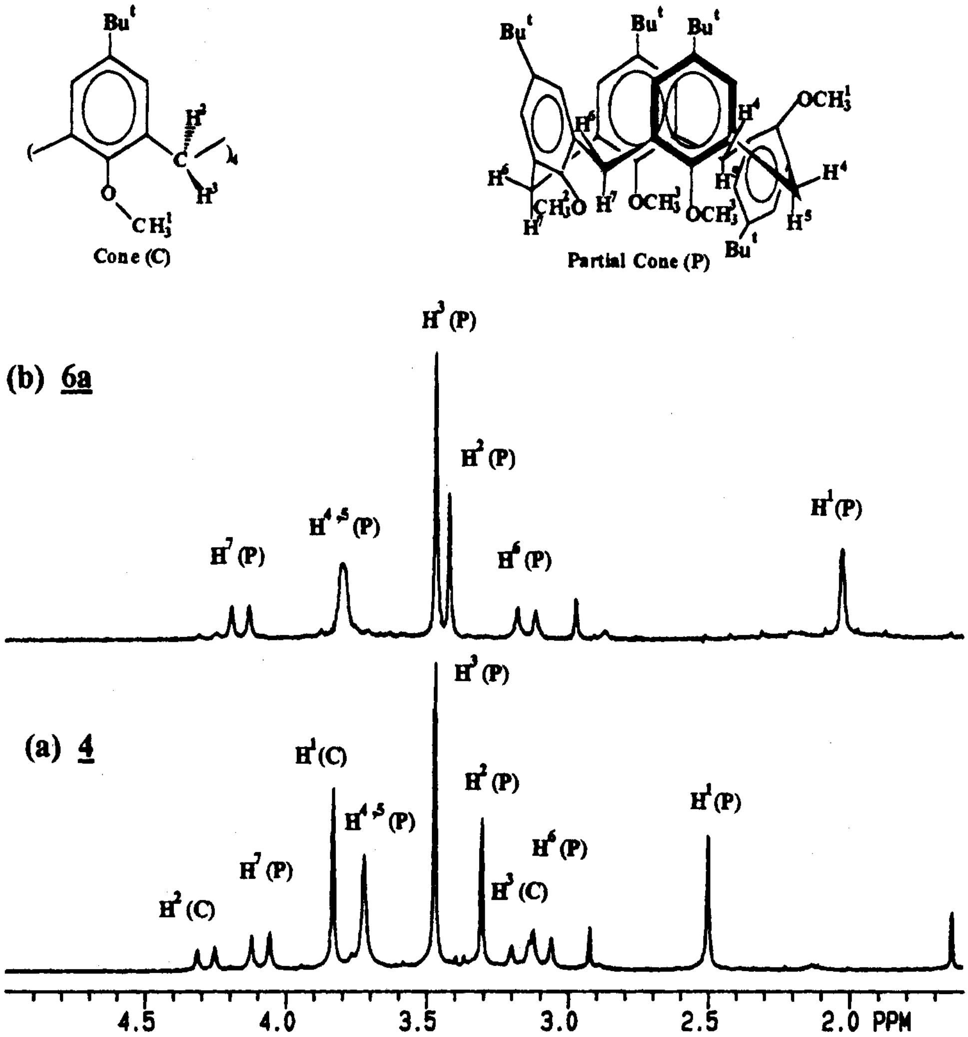

Figure 7. ^{1}H NMR spectra of **4** and **6a** in CD_2Cl_2 at −40 °C. The aryl parts are omitted for clarity. P = partial cone; C = cone.

1,3-alternate conformers, as determined by ^{1}H NMR (400 MHz) measurements.[3,26] The interconversion of these conformers of **4** at room temperature is not completely stopped upon addition of silver ion. Only complexation between **4** and $AgPF_6$ gives sharp ^{1}H NMR resonances. Thus, there is probably a competition between the calixarene and the anion for coordination to silver(I). Only with the most weakly coordinating anion PF_6^- is the dissociation of Ag^+ from the silver−calix[4]arene complex sufficiently slow that the conformational tumbling of **4** appears slow on the NMR time scale. The relatively weak binding of silver(I) to this calixarene is attributed to steric hindrance due to the bulky *tert*-butyl groups. If it is accepted that the calixarene fluxionality can only occur after dissociation of silver(I), the strength of the silver(I)−calixarene binding with respect to silver(I) anion binding will be important in determining the overall rate of interconversion of the calixarene conformers.

The ^{1}H NMR and ^{13}C NMR spectra of compounds **6** show that they prefer to stay in the partial cone conformation at low temperatures (−40 °C, Figure 7). Why is this so? Since coordination between the calix[4]arene and silver(I) will tend to draw two phenyl rings together and roughly parallel to each other, the resultant squeezing effect apparently decreases the relative thermodynamic stability of the cone conformation because of increased steric crowding at the lower rim. The proposed structure for the silver(I)−calix[4]arene complex in the cone conformation is shown in Figure 8; it can be described as a "pinched cone" conformation.[27] Both the steric hindrance and a related electrostatic repulsion can be reduced by inversion of a phenyl unit to give the preferred partial cone conformation.

Since only one set of resonances in the ^{1}H NMR and ^{13}C NMR spectra due to the cone conformation of **5** was observed, a fast equilibrium process in which the Ag^+ ion moves rapidly between the opposite pairs of phenyl rings must occur to give apparent 4-fold symmetry (Figure 8).

The inability of **1** or **2** to bind silver(I) may be due to the strong hydrogen bonding which locks the hosts into the cone conformation. Distortion to the "pinched cone" conformation, which is probably necessary to allow binding of silver(I), would lead to weakening of hydrogen bonding. The net result is that binding of silver(I) does not occur.

As well as these subtle variations in the binding abilities of the hosts, it must be emphasized that the

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[26] (a) Bocchi, V.; Foina, D.; Pochini, A.; Ungaro, R.; Andreetti, G. D. *Tetrahedron* **1982**, *38*, 373. (b) Nagasaki, T.; Sisido, K.; Arimura, T.; Shinkai, S. *Tetrahedron* **1992**, *48*, 797.

[27] Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 9670.

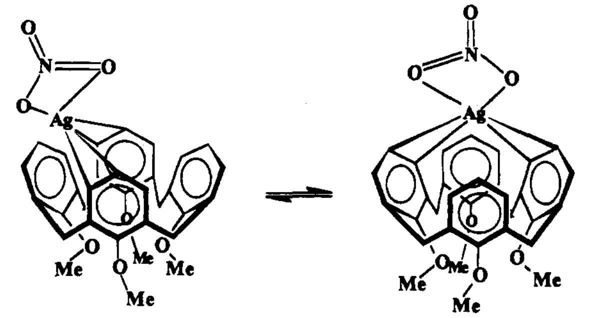

Figure 8. Molecular structure of the calix[4]arene–silver complex in the cone conformation.

Table 6. Reciprocal Recognition between Host Calix[4]arene or Calix[4]resorcinarene Ethers and Guest Ag(I) Species[a]

host	$AgPF_6$	AgO_2CCF_3	$AgNO_3$	Ag_2SO_4	AgO_2CCH_3
1	−	−	−	−	−
2	−	−	−	−	−
3	+	+	+	−	−
4	+	*	*	−	−
6	−	−	−	−	−

[a] Key: (+) obvious chemical shift changes can be observed by ^{1}H NMR; (−) no chemical shift changes can be observed by ^{1}H NMR; (*) obvious chemical shift changes can be observed by ^{1}H NMR, but all the peaks are still broad and the ^{1}H NMR spectra at room temperature and at −40 °C are different.

electrophilicity of silver(I) is strongly affected by its counterion, as summarized in Table 6. On the basis of the complexation with hosts **3** and **4**, the affinities of silver salts for ether calix[4]arenes fall in the series **$AgPF_6$ > AgO_2CCF_3 > $AgNO_3$ > Ag_2SO_4, AgO_2CCH_3**. Clearly, this series is the inverse of the coordinating ability of the anions.

Competition Experiments. Competitive complexation experiments were performed by comparing the relative stability of **5** with those of other known silver–arene complexes. Adding simple aromatic compounds, such as *o*-xylene, mesitylene, or bibenzyl, to the calix[4]arene–silver complexes **5** did not cause changes in the ^{1}H NMR spectra in CD_2Cl_2 solution. However, when phenylacetylene or cyclohexene was added to solutions of **5**, the silver ion was displaced and formed π-complexes with these more electron-rich triple or double bonds with release of the free ligand **3**. When other weakly coordinating ligands such as MeCN or EtCN were present, the calix[4]arene–silver complexes could not be formed. The silver ion could also be removed from calix[4]arene–silver complexes by washing the solids **5** or **6** with MeCN.

Conclusions

The electron-rich calix[4]arene ethers in the partial cone conformation provide a suitable cavity to host the silver ion. The ability of the calix[4]arene ether host to complex silver(I) is strongly influenced by both the steric and electronic effects of substituents on the calix[4]arene, and the electrophilicity of the silver ion determines its ability to act as the guest. The binding of silver(I) is relatively weak, and the silver can easily be removed by competition with stronger ligands. The silver–calix[4]arene complexation provides a method to stop the conformational tumbling of the calix[4]arene and to lock it in the partial cone conformation.

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Supplementary Material Available: Tables of hydrogen positional parameters, anisotropic displacement parameters, bond lengths, bond angles, and torsion angles (6 pages). Ordering information is given on any current masthead page.

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