

Silver Tetrafluoroborate Complex of a Lower Rim Phosphorylated Calix[4]arene; Preparation and Characterization

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ABSTRACT: Silver tetrafluoroborate complex of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinomethoxy)calix[4]arene (**L**) has been synthesized by reaction of silver tetrafluoroborate and **L** in dichloromethane at room temperature. The complex formed has a 1:1 metal/ligand ratio. ^1H and ^{31}P NMR data support an encapsulated structure of the complex in which silver ion is located inside the hydrophilic cavity of the ligand.

KEY WORDS: Calix[4]arene, Phosphoryl, Silver(I) complex

INTRODUCTION

Calixarenes [1] (Fig. 1) are a class of readily accessible macrocyclic compounds which have played an important role on the developments of the selective ion recognition in recent years. The parent calixarenes can be modified at the lower or upper rim to produce a wide variety of ion receptors [2]. Calix[4]-arenes functionalized at the lower rim by neutral substituents such as amides, esters, ketones and phosphoryls have been shown to exhibit interesting complexation, extraction and mobile carrier properties towards metal ions [2-6].

Despite using calixarenes as ligands for transition metals [5], few investigations have been concerned with the complexation of silver (I) ions. Shinkai *et al.*

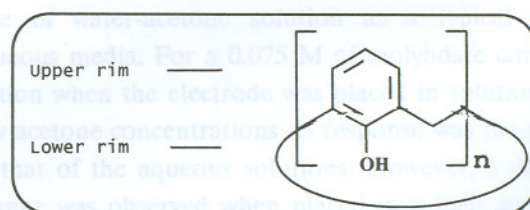


Fig. 1: Calix[n]arene ($n=4-8$)

[7] and Puddephatt *et al.* [8] have shown that tetra *O*-alkylated calix[4]arenes are able to complex a silver cation inside the cavity formed by the four aromatic rings via Ag-C π -bonding. In these structures, the metal ion is located between two *p*-carbon atoms of distal aryl rings. This situation contrasts with the

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complexation of silver ions by the calix-spherands reported by Reinhoudt *et al.* [9] where binding involves the methoxy oxygen atoms of the lower rim. Ohto *et al.* [10] described the extraction of Ag(I) ions in the presence of Pd(II) by a tetra-ketone-calix[4]-arene. Recently, we have reported [11] the extractive and mobile carrier properties of the calix[4]arenes substituted at the lower rim by amide, phosphoryl and ester groups towards silver (I) ions in the presence of copper nitrate. The results reveal a very high selectivity of the ligands for silver ions.

In the present paper the preparation and characterization of silver tetrafluoroborate complex of 5, 11,17,23- tetra- *tert*- butyl- 25,26,27,28-tetrakis (diphenylphosphinoylmethoxy)calix[4]arene (L) (Fig. 2) is described. Analysis of NMR data supports the conclusion that the silver ion is included within the cavity formed by the functional groups at the lower rim of the calixarene. Tetrafluoroborate salt of silver has been selected because of its lipophilic nature which facilitates its solubility in dichloromethane.

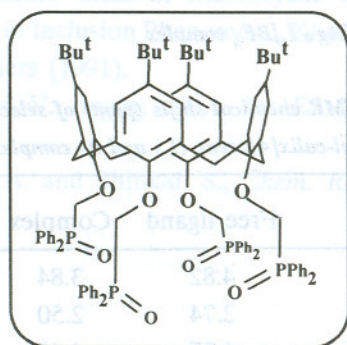


Fig. 2: 5,11,17,23- Tetra- *tert*- butyl- 25,26,27,28- tetrakis (diphenylphosphinoylmethoxy)calix[4]arene (L)

EXPERIMENTAL

Reagents and physical measurements

5,11,17,23-Tetra-*tert*-butyl-25, 26, 27, 28-tetra-kis (diphenylphosphinoylmethoxy)calix[4]arene (L) has been synthesized according to a published procedure [12]. Dichloromethane was dried [13] and distilled prior to use. Deuteriochloroform was passed through a 5 cm thick alumina column and stored under argon over molecular sieves (0.4 nm). The ^1H and ^{31}P - $\{^1\text{H}\}$ -NMR spectra were recorded by Bruker WP-200 SY instrument. The ^1H NMR data (Fig. 3)

were referenced to residual protiated solvent (7.25 ppm for CDCl_3) and ^{31}P NMR data are given relative to external H_3PO_4 . The mass spectrum was recorded on a ZAB HF VG Analytical, using tetraglyme as a matrix.

Complexation of silver by L

AgBF_4 (0.017 g, 0.088 mmol) was added to a solution of L (0.120 g, 0.08 mmol) in CH_2Cl_2 (10 mL) and the solution was stirred at room temperature for 24 h. The solution was filtered, concentrated and pentane was added, affording the product as a precipitate (yield $\approx 75\%$). *Anal. Calcd.* for $\text{C}_{96}\text{H}_{100}\text{AgBF}_4\text{O}_8\text{P}_4 \cdot 0.5 \text{CH}_2\text{Cl}_2$ ($M_r = 1700.4 + 42.5$): C, 66.50; H, 5.84. Found: C, 66.3; H, 5.76. ^1H NMR(CDCl_3 , 298 K): δ 7.69- 7.59 and 7.47-7.38 (40H, $\text{P}(\text{O})\text{Ph}_2$); 6.65 (s, 8H, *m*-ArH); 5.04(s, 8H, $\text{OCH}_2\text{P}(\text{O})\text{Ph}_2$); 3.84 and 2.50 (AB spin system, 8H, ArCH_2Ar , $^2J(\text{AB}) = 13 \text{ Hz}$); 1.00 (s, 36H, Bu^t). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 , 298 K): δ 32.9 (s, $\text{P}(\text{O})\text{Ph}_2$). MS(FAB), $m/z(\%)$: 1613.2 (73) $[\text{M}-\text{BF}_4]^+$.

RESULTS AND DISCUSSION

The elemental analysis shows that the complex has a 1:1 metal/ligand ratio. This stoichiometry is in agreement with that found for the extracted species in two phase extraction of silver nitrate by L in 1,2-dichloroethane [11]. The elemental analysis has also shown the presence of solvent (dichloromethane) in the product which was confirmed by measuring the ^1H -NMR spectrum. The spectrum contains a signal at 5.30 ppm corresponding to the signal of dichloromethane. The ^1H NMR data indicates an apparent C_4 -symmetrical structure for the complex, as found for the free ligand [12].

Table 1, contains some selected ^1H NMR signals of the free ligand and its complex (see also Fig. 3) with AgBF_4 . The involvement of the phenolic oxygens in complexation is indicated by the downfield shift experienced by the aromatic protons (*m*-ArH of the calixarene matrix) in the ^1H NMR spectrum of the complex. The results are consistent with those reported by Ungaro *et al.* [14] for the complexation of potassium by tetra-amide-calix[4]arene and those reported by us [11,15] for sodium, potassium and silver complexation by diamide-diphosphoryl-calix[4]arene.

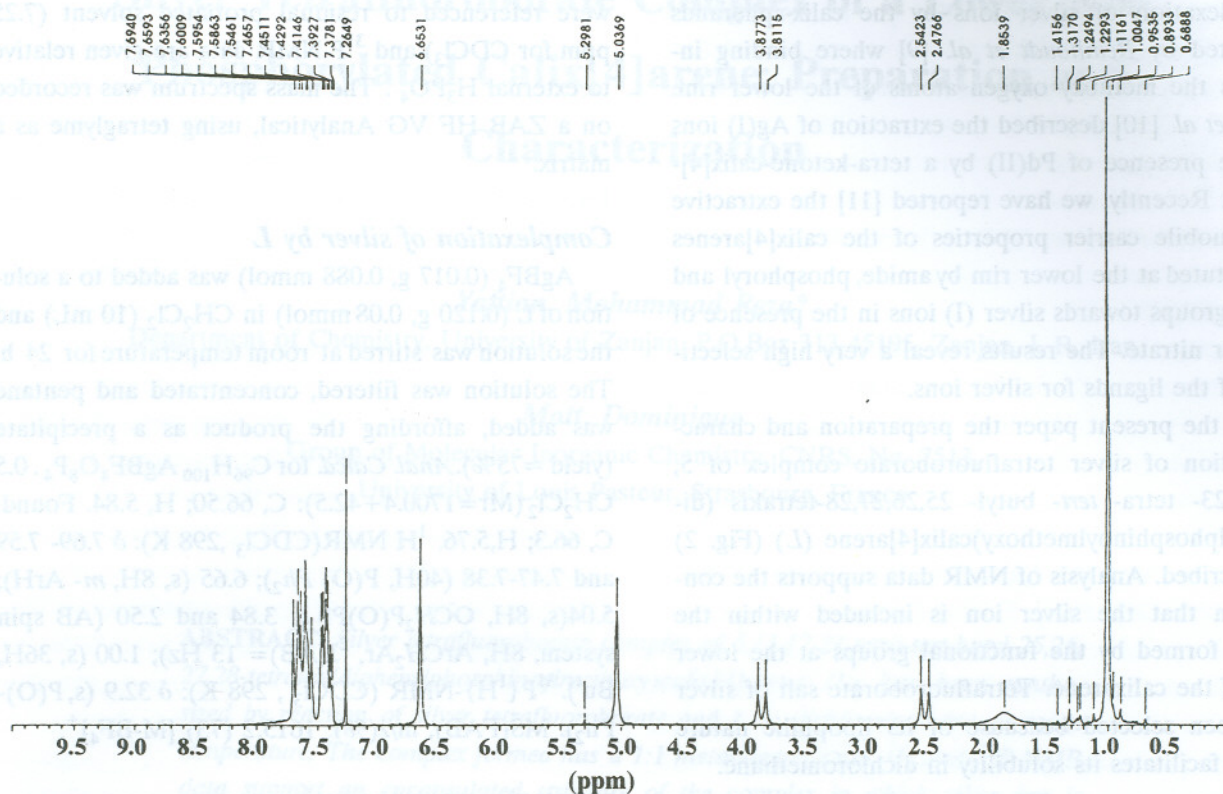


Fig. 3: ^1H NMR (200 MHz, CDCl_3) spectrum of the $[\text{Ag}\bullet\text{L}]\text{BF}_4$ complex

The upfield shift experienced by the methylene protons of the phosphoryl groups can be explained by assuming that upon complexation the $-\text{CH}_2-\text{P}=\text{O}$ fragment of the phosphoryl binding groups adopt a *trans* conformation. This conformation brings the PO towards the cation located in the interior of the hydrophilic cavity and the CH_2 groups experience the shielding effect of the aromatic rings of the calixarene matrix or of the diphenylphosphino groups. The phosphoryl moieties seem to participate in complexation via the $\text{P}=\text{O}$ groups. The ^{31}P NMR spectrum of the complex shows a single signal at 32.9 ppm, i.e. 7.3 ppm down field shift with respect to the phosphorus signal of the free ligand (25.6 ppm) [12].

The largest variation in chemical shift upon complexation is experienced by the axial proton of CH_2 bridges (H_A) which moves 0.98 ppm upfield. The upfield shift of the axial (0.98 ppm) and equatorial (0.28 ppm) proton of CH_2 bridges reveals that these protons are sensitive to the variation in the polar environment of the ether oxygens, which are in close

Table 1: ^1H NMR chemical shifts (ppm) of selected signals of tetra-phosphoryl-calix[4]arene (L) and its complex with AgBF_4

Proton	Free ligand	Complex	$\Delta\delta^a$
H_A^b	4.82	3.84	-0.98
H_B^c	2.74	2.50	-0.24
<i>m</i> -ArH	6.37	6.65	+0.28
$-\text{CH}_2\text{P}(\text{O})\text{Ph}_2$	5.25	5.04	-0.19

a) $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Free ligand}}$; b) Axial ArCH_2Ar hydrogen atoms; c) Equatorial ArCH_2Ar hydrogen atoms.

proximity and a probable shielding effect imposed by phenyl groups attached to the phosphorus of the phosphoryl groups.

The results suggest full encapsulation of the silver ion inside the cavity defined by the four lower rim phosphoryl substituents (Fig. 4) and is reminiscent of the results for the complexation of silver by tetra-ketone-calix[4]arene [10] and diamide-diphosphoryl-calix[4]arene [11].

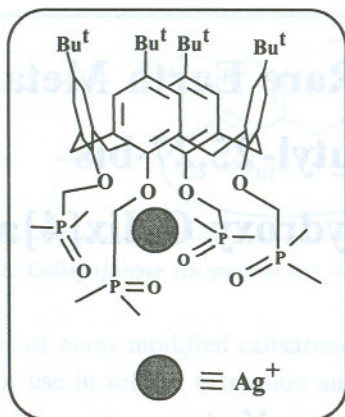


Fig. 4: Proposed structure for the $[Ag\bullet L]^+$ complex

Received: 8th February 1999 ; Accepted: 21th February 2000

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