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Preparation and Crystal Structure of the Sodium Iodide Complex of 5,11,17,23-tetra(*tert*-butyl)-25,27-di(ethoxymethoxy)-26,28-(diethylacetamido) Calix[4]arene in the Cone Conformation

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Abstract

The direct preparation of the sodium complex of 5,11,17,23-tetra(*tert*-butyl)-25,27-di(ethoxymethoxy)-26,28- (diethylacetamido) calix[4]arene **1.NaI** is reported. The crystal structure of **1.NaI** shows the calix unit to be in a cone conformation with the sodium located in the cavity delineated by the oxygen atoms.

Introduction

The calixarenes prepared by base-catalyzed condensations of *p*-substituted phenols with formaldehyde are attractive matrices, their phenol hydroxy groups being ordered in well shaped cyclic arrays which may be functionalized to give rise to selective metal cation receptors [1, 2]. Introduction of chosen functionalities on the phenolic OH groups of *p-tert*-butyl calix[4]arene produces derivatives with different shapes and subsequent selectivities. The amide derivatives of calix[4]arenes and their complexes with alkali metal, transition metal and lanthanide ions have been extensively investigated [3–5]. At the same time, some interest has arisen for the study of *p-tert*-butyl calix[4]arene derivatives with mixed functionalities with the general objective of examining structure-receptor relationships [6]. In the 1,3-diamide series, the diethylacetamido diethylester derivative of *p-tert*-butyl calix[4]arene has been shown to be selective in the order $Na^+ > K^+ > Li^+$ during extraction of picrates from water to dichloromethane [7]. The related diethylacetamido dibenzyl derivative of *p-tert*-butyl calix[4]arene showed selectivities in the order $Na^+ > K^+ > Rb^+$ in similar experiments [8].

Continuing our work in this direction, the reaction carried out to sythesize the 5,11,17,23-tetra(*tert*-butyl)-25,27-di(ethoxymethoxy)-26,28-(diethylacetamido) calix[4]arene, **1**, shown in Scheme 1, lead to the sodium complex **1.NaI**. The crystal structure of this complex is also described.

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Experimental

Instrumentation and analysis

The melting point (mp) was taken on a Büchi 500 apparatus in a capillary sealed under nitrogen. Thin layer chromatography (TLC) was carried out on Merck TLC plates (silica gel 60 F_{254} Merck Art 6484). The ^{1}H-NMR spectrum was recorded at 200 MHz in $CDCl_3$ on a Bruker SY200 spectrometer. Chemical shifts δ are given in ppm from $CHCl_3$ at 7.26 ppm. Coupling constants J are given in Hz. FAB(+)MS was obtained on a VG-Analytical ZAB HF. Elemental analysis was performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg.

Synthesis

2-Chloro-*N*,*N*-diethylacetamide, potassium carbonate, sodium iodide and the solvents were commercial reagents and used without further purification. 1,3-Diethoxymethoxy-*p-tert*-butyl calix[4]arene **2** was prepared according to the literature [9].

Synthesis of **1.NaI**

1,3-Diethoxymethoxy-*p-tert*-butyl calix[4]arene (**2**) (1.923 g; 2.5 mmol), K_2CO_3 (3.870 g; 28.0 mmol), 2-chloro-*N*,*N*-diethylacetamide (1.503 g; 10.0 mmol) and acetonitrile (60 mL) were refluxed for 24 h. After removal of the solvents, the crude residue was dissolved in CH_2Cl_2 and water. The mixture was acidified with 1N HCl-H_2O to pH 2. The organic layer was dried over Na_2SO_4. After filtration, the solvents were evaporated to dryness and the residue was precipitated with methanol to give

1.NaI (1.762 g; 71%). Mp 278–279 °C. Mass spectrum (FAB+, NBA) m/z = 1013.8 (M + Na^+; 100%). ^{1}H-NMR (200 MHz; $CDCl_3$) δ 7.13 (4H, s, Ar**H**); 7.07 (4H, s, Ar**H**); 4.57 (4H, s, $ArOC\mathbf{H}_2CONEt_2$); 4.36 (4H, d, J = 12.2, $ArC\mathbf{H}_2Ar$); 4.12–4.08 (4H, m, $ArOC\mathbf{H}_2CH_2OCH_3$); 3.74–3.67 (4H, m, $ArOCH_2C\mathbf{H}_2OCH_3$); 3.63 (4H, q, J = 7.0, $ArOCH_2CON(C\mathbf{H}_2CH_3)_2$); 3.37 (4H, d, J = 12.2, $ArC\mathbf{H}_2Ar$); 3.36 (6H, s, $ArOCH_2CH_2OC\mathbf{H}_3$); 3.32 (4H, q, J = 7.0, $ArOCH_2CON(C\mathbf{H}_2CH_3)_2$); 1.34–1.19 (12H, m, $ArOCH_2CON(CH_2C\mathbf{H}_3)_2$); 1.16 (18H, s, **tBu**Ar); 1.12 (18H, s, **tBu**Ar). FAB (positive) MS : m/z = 1013.8 (M + Na^+). Analysis calcd for $C_{62}H_{90}O_8N_2{\cdot}NaI{\cdot}CH_3OH$: C, 64.49; H, 8.07. Found C, 63.53; H, 7.78.

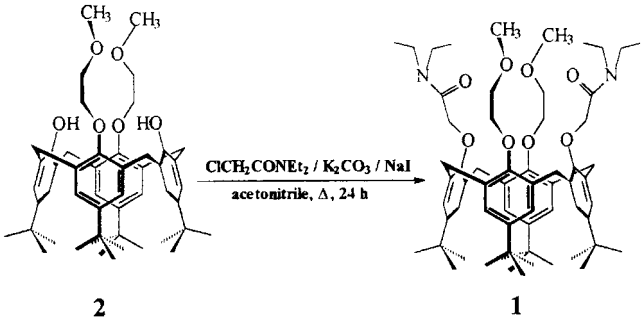
Crystal structure determination

Crystal data for $[Na^+\mathbf{1}]I^-{\cdot}2CH_2Cl_2$ (**3**), $C_{64}H_{94}Cl_4IN_2NaO_8$: M = 1311.10, triclinic, space group $P-1$, a = 13.064(2), b = 14.840(2), c = 20.025(2) Å, α = 108.779(7), β = 92.818(7), γ = 114.175(5)ø°, V = 3278.7(7) Å^3, Z = 2, D_c = 1.328 g cm^{-3}, μ = 0.711 mm^{-1}, $F(000)$ = 1376. The data were collected at 100 K on a Nonius Kappa-CCD area detector diffractometer [10] using graphite-monochromated Mo-K_α radiation (0.71073 Å). The crystal was introduced in a Lindemann glass capillary with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The data were processed with DENZO-SMN [11]. The structure was solved by direct methods with SHELXS-97 [12] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97 [13]. Absorption effects were corrected empirically with the program MULABS from PLATON [14]. One *tert*-butyl group was found disordered over two positions which were refined with occupation factors constrained to sum to unity. Hydrogen atoms were introduced at calculated positions (except in the disordered parts) and treated as riding atoms with a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. All non-hydrogen atoms were refined anisotropically, except the disordered ones, leading to a final $R1$ factor of 0.103 for 11118 unique reflections and 735 parameters. The molecular plot was done with SHELXTL [15].

Results and discussion

The synthesis is illustrated in Scheme 1.

1,3-Diethoxymethoxy-*p*-*tert*-butyl calix[4]arene (**2**) was reacted with 4 equivs of 2-chloro-*N*, *N*-diethylacetamide in the presence of K_2CO_3 (acetonitrile, 24 h reflux) to produce calixarene **1.NaI** (mp 278–279 °C from methanol) in 71% yield. The ^{1}H-NMR of **1.NaI** showed the molecule to be in the cone conformation as indicated by the presence of an AB system at 3.37 ppm and 4.36 ppm with J = 12.2 Hz for the $ArC\mathbf{H}_2Ar$ of the macroring. The FAB MS spectrum and elemental analysis indicated that **1** contained a complexed NaI moiety. It is well known that tetra *O*-alkyl derivatives of *p*-*tert*-butyl calix[4]arene are good complexants for alkali cations with a preference for Na^+ when the receptor is in the cone conformation [3]. We therefore assumed the sodium to be symmetrically included in the cavity delineated by the four phenolic oxygens and the two oxygens of the carbonyl functions with a possible involvment of the glycolic OCH_3 oxygens.



2 **1**

Scheme 1.

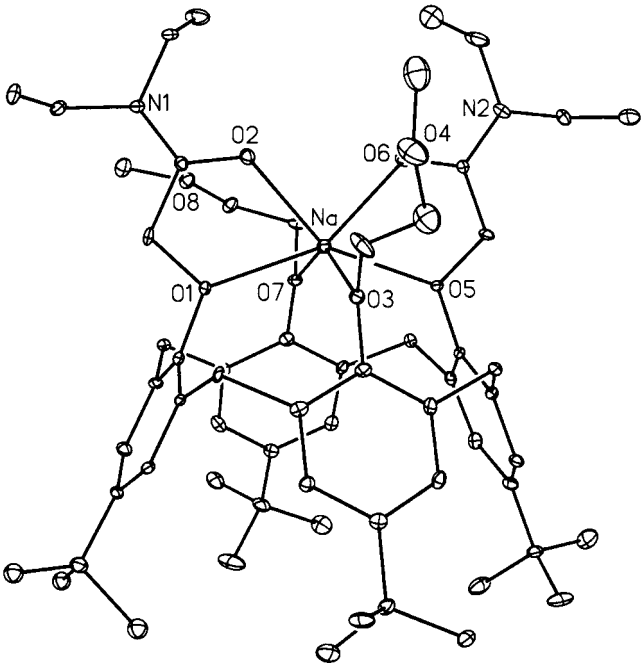


Figure 1. View of the molecular structure of complex **3**. Hydrogen atoms, counter-ion and solvent molecules omitted.

Crystal structure of **1.NaI**

$[Na^+\mathbf{1}]I^-{\cdot}2CH_2Cl_2$ (**3**) crystallizes with one complex molecule in the asymmetric unit (Figure 1).

The calixarene is in the *cone* conformation, with dihedral angles between the four aromatic rings and the mean plane defined by the four methylenic carbon atoms of 65.0(3), 66.1(3), 67.6(2) and 61.8(3)°, i.e. with a pseudo-fourfold symmetry. The sodium ion is located between the four substituent arms and bound to the four phenolic oxygen atoms (Na–O distances in the range 2.331(7)–2.397(7) Å) and to the two amide oxygen atoms (2.262(9) and 2.312(8) Å). These distances are in good agreement with those reported recently in the case of the sodium ion complex of a *p*-*tert*-butylcalix[4]arene bearing two amide functions similar to those in **1** and two phosphoryl arms [16]. The two oxygen atoms of the glycolic chains are not bonding to the cation

in **3**, which gives a coordination environment for the cation similar to that observed in the compound just cited, in which the two phosphine oxides are not bound to the cation. The overall geometries of these two complexes are very similar, since the common parts of the ligands only are involved in complexation. Another sodium ion complex involving a calix[4]arene bearing two amide functions has been reported [17], but in this case, the conformation of the calixarene and the coordination environment are quite different due to the replacement of the two other phenolic rings by quinone moieties. The counter-ion in **3** is non-bonding. One of the two dichloromethane molecules is included in the calixarene cavity.

Conclusion

Attempts to remove the sodium cation from the calixarene in acidic conditions were unsuccessul. Compound **1.NaI** was used for extraction of alkali metal picrates from water to dichloromethane according to a procedure already described ($C_{\mathbf{1.NaI}} = 2.5 \times 10^{-3}$ mol.L^{-1}, $C_{MPic} = 2.5 \times 10^{-3}$ mol.L^{-1}) [18]. The extraction values were 74, 85, 72, 76 and 70% for Li^+, Na^+, K^+, Rb^+ and Cs^+, respectively. The similarities in the %E values allows us to conclude that the extraction implies the replacement of the iodide ion by the picrate. This was confirmed by carrying out similar extractions of alkaline earth metal picrates. The extraction values were 49, 40, 39 and 35% for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} respectively. This property is currently being investigated in selective transport of anions and the results will be published in due course.

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