



Crystal Structure and Complexing Properties of *p*-*tert*-butylcalix[6]-1,4-2,5-*bis*(crown-4)

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Abstract

The X-ray structure of the already published *p*-*tert*-butylcalix[6]-1,4-2,5-*bis*(crown-4) **1** is reported. Extraction of solid ammonium picrate in chloroform-*d* indicates the cation to be located outside of the calixcrown and forming a 1:2 (metal-ligand) complex.

Introduction

The introduction of polyether chains into the macrocyclic structure of calixarenes has provided a family of ligands [1] of considerable interest as selective ion transport agents [2] and in particular as materials of possible practical importance in the treatment of nuclear wastes [3]. These “calixcrowns” differ significantly from simple crown ethers in that metal ion binding is not solely determined by ether-oxygen donor interactions but appears also to involve the π -electrons of the phenyl groups of the calixarene moiety [1]. For the alkali metal cations, such interactions with π -donor centres are well characterized [4], though the role they may play in determining the selectivity of alkali metal ion binding by calixcrowns is as yet not fully understood. In singly bridged calixcrowns, structural studies have shown that the importance of these interactions may exceed that of ether lone pair donation but, in conformationally more restricted calix-*bis*(crowns), the question remains open. All these findings have been made on calixcrowns derived from calix[4]arenes [5] and recent work has been devoted to extend them to corresponding calix[6]crown type ligands. Thus, the synthesis of calix[6]-1,4-crown-5, *p*-*tert*-butylcalix[6]-1,4-crown-5 [6], and *p*-*tert*-butylcalix[6]-1,3-crown-3 [7] have been reported. It is only recently that the first calix[6]-*bis*(crown)s appeared [8–10]. The synthesis of the 2,5-diallyl derivative of calix[6]-1,3-4,6-*bis*(crown-4), obtained in the 1,2,3-*alternate* and *cone* conformations, has been described [8]. The cone conformation provides a more suitable cavity for selective binding of cesium with a Cs⁺/Na⁺ selectivity factor of 1500 while the selectivity factor decreases to 140 for the 1,2,3-*alternate* conformation.

π -Metal interactions were assumed to stabilize the complex [9].

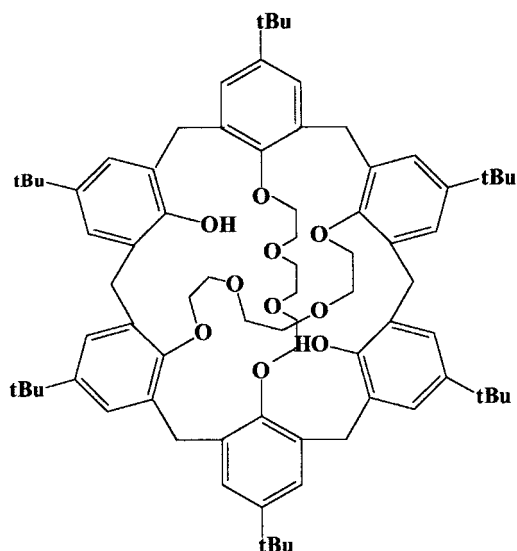
We report herein the crystal structure and NH₄⁺ complexation properties of *p*-*tert*-butylcalix[6]-1,4-2,5-*bis*(crown-4) **1** (Scheme 1), the synthesis of which has been previously published [9]. Previous extraction experiments with picrate salts of alkali and ammonium compounds have shown a high complexation selectivity of these ligands towards *n*-PrNH₃⁺ [9]. The present results allow the location of the cation in the complex.

Experimental

Crystallography

The data were collected at 110(2) K on a Nonius Kappa-CCD area detector diffractometer [11] using graphite-monochromated Mo-*K* α radiation ($\lambda = 0.71073$ Å). The crystal was introduced in a Lindemann glass capillary with a protecting “Paratone” oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from the reflections collected on ten frames and were then refined on all data. The data were processed with DENZO-SMN [12]. The structures were solved by direct methods with SHELXS-97 [13] and subsequent Fourier-difference synthesis and refined with SHELXL-97 [14]. No correction of absorption effects was done. All non-hydrogen atoms were refined with anisotropic displacement parameters. The phenolic protons have been found on the Fourier-difference map and all other hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, CH, CH₂) or 1.5 (CH₃) times that of the parent atom. Refinement of

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Scheme 1. *p*-*tert*-Butylcalix[6]-1,4-2,5-bis(crown-4), **1**.

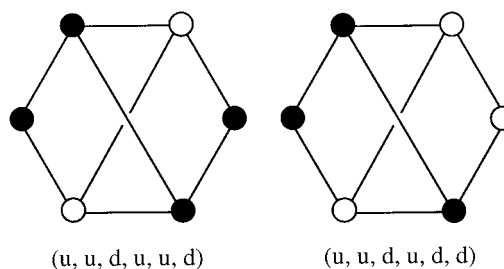
883 parameters by full-matrix least-squares on F^2 on 13289 independent reflections ($R_{\text{int}} = 0.095$) led to $R_1 = 0.102$, $wR_2 = 0.189$, $S = 1.007$, $\Delta\rho_{\text{max}} = 0.448$. The molecular plot was drawn with SHELXTL [15]. All calculations were performed on a Silicon Graphics R5000 workstation.

Crystal data for **1**·2CHCl₃: C₈₀H₁₀₆Cl₆O₁₀, $M = 1440.35$, triclinic, space group $P-1$, $a = 16.773(2)$, $b = 17.200(2)$, $c = 17.485(5)$ Å, $\alpha = 90.678(8)$, $\beta = 113.782(9)$, $\gamma = 118.848(9)^\circ$, $V = 3906.9(8)$ Å³, $Z = 2$, $D_c = 1.224$ g cm⁻³, $\mu = 0.275$ mm⁻¹, $F(000) = 1536$.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Results and discussion

Single crystals of **1**·2CHCl₃ were obtained by recrystallization from chloroform. The calixarene molecule, represented in Figure 1, lacks any symmetry element. The two crown ether loops are located on each side of the molecule. The six methylene carbon atoms define a mean plane with a rather large rms deviation of 0.94 Å, which will be taken as a reference plane in the absence of any better choice. The four oxygen atoms of each crown ether loop define a plane (with rms deviations of 0.014 and 0.099 Å, respectively); these planes cross the reference plane with dihedral angles of 83.0(2) and 82.3(1)°, i.e. they are not far from being perpendicular to it. These two O₄ planes are roughly parallel to each other, with a dihedral angle of 27.3(1)°. It may be noted that not all the oxygen atom lone pairs are directed towards the cavity centre, which indicates that conformation changes would be needed for a cation to be complexed by all donor atoms. The two crown loops define a large cavity surrounded by the eight ether oxygen atoms. The distances of these atoms to the O₈ centroid are in the range 3.316–



Scheme 2. Possible conformations of **1**.

4.259 Å: these values are larger than the ideal O-centroid distance of 3.1–3.2 Å convenient for complexation of a Cs⁺ ion [16]. The planes defined by the six aromatic rings make dihedral angles of 49.4(2), 60.5(2), 43.4(3), 41.4(3), 36.2(3) and 54.5(2)° with the reference plane. With the two ideally equivalent ether loops on both sides of the molecule, two ideal conformations only can be observed (and not three as in the 1,2,3-*alternate* form of calix[6]-1,3-4,6-*bis*(crown-4) derivatives [8]), which are represented in Scheme 2 and can be denoted as (u, u, d, u, u, d) and (u, u, d, u, d, d) in the notation of Kanamathareddy and Gutsche [17]. The conformation observed in **1** is (u, u, d, u, u, d), the chains being bound to (u, u) and (d, d) rings, and the two remaining rings being blocked on the same side than one of the loops by hydrogen bonds involving its two terminal oxygen atoms O(1) and O(4).

Extraction of solid picrates

Although the studies of heterogeneous reactions between solid metal picrates salts and a solution of the ligand do not give data interpretable in quantitative terms, the results are qualitatively interesting and provide a useful means for contrasting the behaviour of the ligand towards several cations. In addition, the direct reaction in a ¹H-NMR tube enables location of the cation in the molecular receptor. After a one month reaction between the solid picrates (alkali and ammonium) in excess and a deuterated chloroform solution of **1** (~10⁻³ M), the ratios of metal to ligand in solution was estimated by integration of the picrate proton resonances versus those for the aromatic protons of **1**. The only cation extracted was NH₄⁺ in a 1:2 ratio (metal:ligand). Surprisingly the ¹H-NMR [18] pattern of **1** remained unchanged while the picrate signal appeared. This was imputed to external interactions between the ligand and the ammonium cation to form an *exo* complex in which one ammonium is linked to two calixcrowns.

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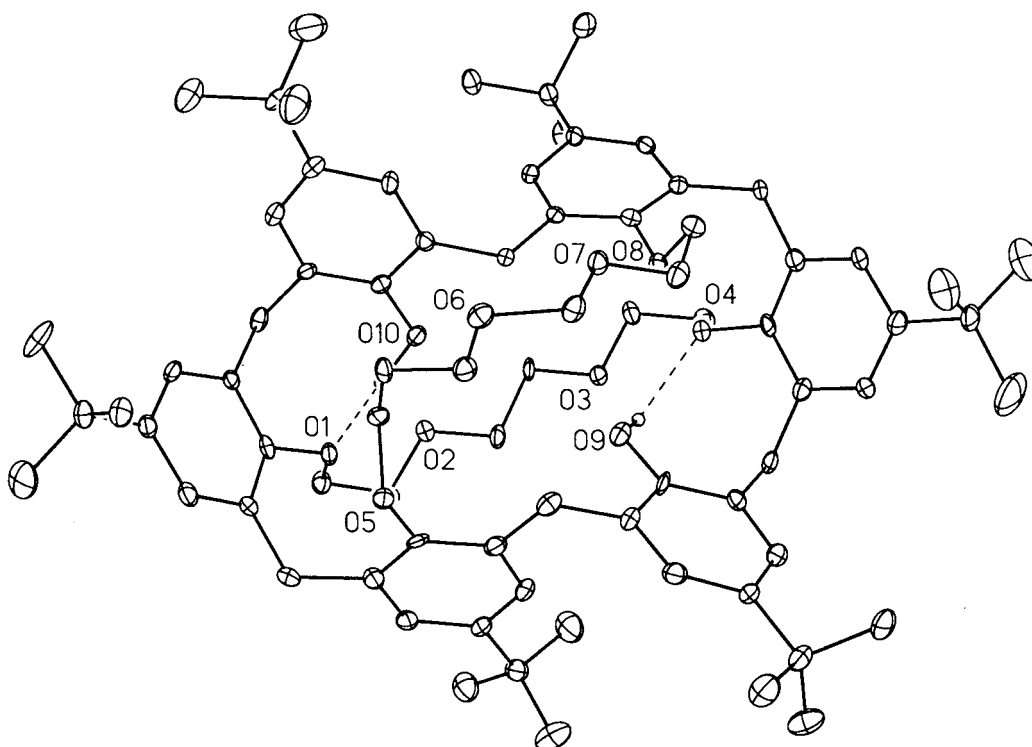


Figure 1. View of the molecular unit in 1-2CHCl₃. Hydrogen bonds are represented as dashed lines. Phenolic protons are represented as small spheres of arbitrary radii. All other hydrogen atoms and solvent molecules are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen bonding distances (Å) and angles (°): O(9)–H 1.11, H···O(4) 2.13, O(9)···O(4) 2.889(8), O(9)–H···O(4) 123; O(10)–H 1.24, H···O(1) 1.69, O(10)···O(1) 2.797(7), O(10)–H···O(1) 145.

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