



Calixcrowns and Related Supramolecular Systems

J. VICENS and S. ASFARI

ECPM, UMR 7512 du CNRS, 25 rue Becquerel, F-67087 Strasbourg, France (e-mail: vicens@chimie.u-strasbg.fr)

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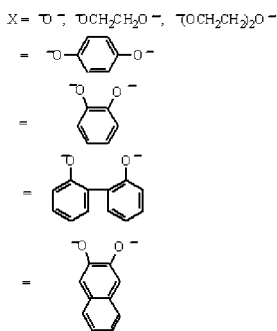
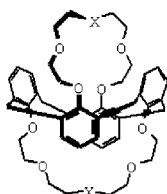
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Abstract

Our main results in the chemistry of 1,3-calix[4]-bis-crowns taken from recent literature are reported.

Introduction

Calix[4]arene-crown ethers or calixcrowns are one of the most widely investigated class of cation ligand based on calixarenes [1]. 1,3-Calix[4]-bis-crowns (see below) correspond to calixcrown ethers containing one calix[4]arene and two polyether chains [2]. We have prepared a series of calix[4]-bis-crowns by a one-pot procedure in ~50–80% yields by reacting calix[4]arene with various ditosylates in basic conditions. The reaction in the presence of potassium carbonate mainly produced 1,3-calix[4]-bis-crowns in the 1,3-alternate conformation [3].



The X-ray structures of 1,3-calix[4]-bis-crowns showed that 1,3-calix[4]-bis-crowns-n, noted **Bis-Cn**, have a globular arrangement in which two polyether chains are equivalent on each side of the calix unit in the 1,3-alternate conformation. They are potential ditopic receptors. Due to the presence of donor oxygen atoms *mononuclear and binuclear* complexes have been isolated during the complexation of alkali metals and their crystal structures have been determined. Mononuclear $\text{KBis-C6}(\text{NO}_3)$, $\text{CsBis-C6}(\text{NO}_3)$ and binuclear $\text{Na}_2\text{Bis-C6}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Cs}_2\text{Bis-C6}(\text{NO}_3)_2$, and $\text{Cs}_2\text{Bis-C6}(\text{SCN})_2$ have been characterized. The following conclusions were drawn:

1. The ligands containing **5 O** in the glycolic chains have a loop-size adapted to the complexation of potassium and

rubidium. The ligands containing **6 O** are convenient for complexation of cesium.

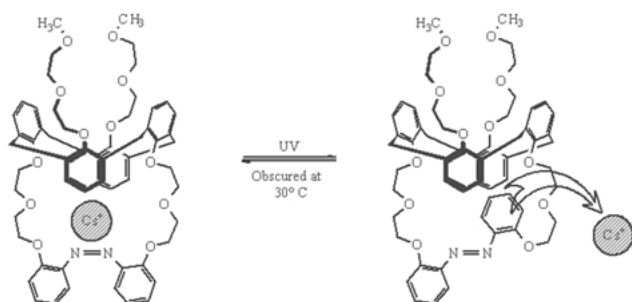
2. The complexation of cesium by **Bis-C6** occurred without changing the conformation of the glycolic chains showing the ligand to be highly preorganized for capturing this metal.
3. There are π -metal interactions in the complexes of **Bis-C6** with potassium and cesium.

Treatment of nuclear wastes (cesium and technetium)

Bis-Cn have been used to remove radioactive cesium from nuclear wastes [4]. The treatment involves selective extraction of cesium from aqueous solutions that are 1 M in HNO_3 and 4 M in NaNO_3 . A study of their extraction and transport properties has shown that 1,3-calix[4]-bis-crowns-6 were selective carriers in *supported liquid membranes* (SLM's). The procedure consisted of using *ortho*-NitroPhenylOctylEther as transport solvent with selectivities ~50000 (decontamination factor = 20; concentration factor >100; over 50 days of stability) for **Bis-2,3-Naphtho-C6**. This selectivity was demonstrated to occur in alkaline conditions [5]. In very similar conditions, simultaneous extraction of pertechnetate was demonstrated [6]. This co-extraction was made possible by the occurrence of electrostatic interactions between the complexed cation (Na^+ or Cs^+) and the pertechnetate anion. These interactions were visualized by the determination of the crystal structures of the model complexes of sodium and cesium perrhenates with calix[4]arene bis(crown-6) : $[(\text{Na}^+ \cdot \text{H}_2\text{O})_2\text{BisC6}](\text{ReO}_4^-)_2$, and cesium complexes $[(\text{Cs}^+)_2(\text{ReO}_4^-)\text{BisC6}](\text{ReO}_4^-) \cdot \text{H}_2\text{O}$, $[(\text{Cs}^+)_2(\text{ReO}_4^-)(\text{H}_2\text{O})\text{BisC6}](\text{ReO}_4^-)(\text{H}_2\text{O})_{0.5}$ which differ one from the other by the coordination mode of ions (monodentate, bidentate, bridging) and the position of the cesium in the crown [7].

Photoresponsive 1,3-azocalix[4]crowns

Subsequently, we have designed a series of photosensitive 1,3-calix[4]crowns containing a photoisomerizable (E) \leftrightarrow (Z) *azo* unit in the crown ether loop. (Z)-isomer of 1,3-azobenzenecalix[4]-crown-6 was shown to improve the transport of cesium and rubidium through supported liquid membranes (30% to 60%) when compared to (E)-isomer [8, 9].



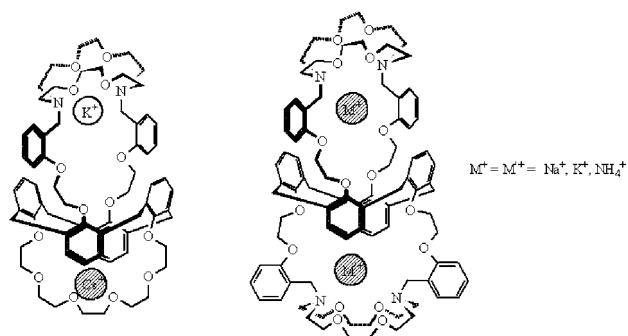
Metal-ligand exchanges

In order to obtain more information on the behaviour and structure of the alkali-complexes in solution we used NMR techniques. **Bis-C5** formed 1:1 and 1:2 complexes with alkali picrates in CDCl_3 [10] and $\text{CD}_2\text{Cl}_2\text{-DMF-}d_7$ [11]. 1:1. Complexes have been observed for K^+ , Rb^+ , Cs^+ and NH_4^+ . The highest association constant was observed for potassium cation in agreement with the crystal data of **Bis-C5**. 1:2 Complexes were observed for Na^+ and NH_4^+ . NMR Spectra of the 1:1 complexes with K^+ , Rb^+ , Cs^+ and NH_4^+ presented coalescence patterns. A study with temperature dependent $^1\text{H-NMR}$ showed the existence of two temperatures of coalescence corresponding to both *intra- and intermolecular exchanges* between the metal and the ligand. The intramolecular exchange was identified from the independence of the coalescence temperature on the concentration.

The replacement of the central O atoms in one or both of the crown-5 loops by NH (X = O or NH) groups stops the cation-ligand exchange in the case of ammonium picrate in CDCl_3 [12].

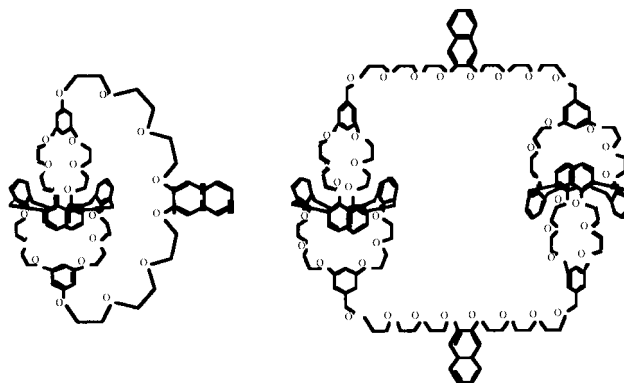
Calixcryptands

The obtention mixed receptors of [N,O] ligands with reactive N-H groups [1, 13] led to further cyclization into products we named 1,3-calix[4]cryptands and 1,3-calix[4]-*bis*-cryptands [14]. These ligands combine in their molecular structure the calix[4]arene unit in 1,3-alternate conformation and one or two oxa-aza [18]- N_2O_4 subunits. They are able to form 1:1 and 1:2 complexes 1:1:1 and heterobinuclear complexes with alkali cations and ammonium as detected by $^1\text{H-NMR}$ spectroscopy [14].

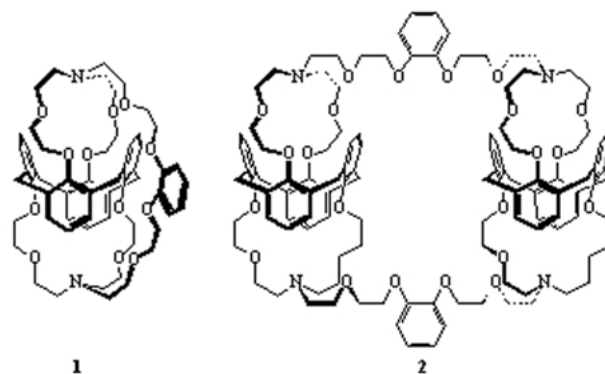


Molecular machines

The globular shape of calix[4]-*bis*-crowns suggested us to create molecular architectures looking like world globes [15] and mills [16].



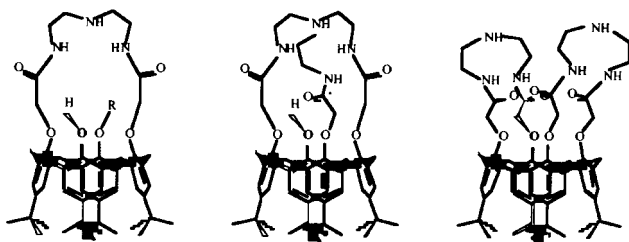
We have shown by NMR that the *globular* calix[4]-*bis*-crowns are spinning around its two poles. This was assumed on the observation of a well-resolved singlet for the methylene attached at both poles. Complexation of ammonium occurred more rapidly than with the unbranched calix[4]-*bis*-crown and globe spinning was lowered by complexation.



The replacement of the calix[4]-*bis*-crown by related calix[4]-*aza*-crowns lead to similar architectures but the rotation did not occur probably due to the way of anchoring by using nitrogen atoms [17].

Recent research

Recent work is devoted to the chemistry of calix[4](aza)crowns. *Calix[4](aza)crowns* refer to molecules combining calix[4]arene elements and aza crown units [18, 19]. They are constructed with NH-ethylene chains attached to the phenolic oxygen atoms of the calix via acetamido functions which may also serve as linking functions and chelating groups. We have prepared the following receptors:



Preliminary complexation studies of transition metal picrates showed that Co, Ni and Zn are complexed and that the absence of OH functions in the receptor is needed for the complexation to occur.

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