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The Synthesis of Sodium and Potassium Complexes of Two Calix[4]arene Derivatives

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Abstract

Two compounds (**1** and **2**) which have calix[4]arene units and their Na^+ and K^+-complexes were prepared. All the complexes have a metal-ligand ratio of 1 : 1. The newly prepared compounds were characterized on the basis of their ^1H NMR, IR, UV-visible as well as elemental analysis.

Introduction

Calix[*n*]arenes are macrocyclic molecules composed of *n* phenol rings linked by methylene groups. The chemistry of calix[4], [6], and [8]arenes is well reviewed by Gutsche [1]. Calix[4]arenes are not planar and can adopt four different stable conformations [(cone, partial cone (paco), 1,2-alternate (1,2-alt), and 1,3-alternate (1,3-alt)] when bulky groups are substituted for the phenolic protons ('lower rim') to prevent free rotation of the aromatic rings [1, 2]. These compounds are increasingly used as building blocks for the construction of more elaborate structures used for the complexation of cations and neutral substrates [1, 3].

The host–guest chemistry of the calixarenes is of great interest, since the calixarenes exhibit complexing abilities towards alkali, alkaline-earth and some transition metal cations by means of functional group modification at the phenolic groups [4–10]. In particular, the easy accessibility of *p*-tert-butyl calix[4]arene has made this member of the series increasingly popular with ligating side-arms or podands for the reception of guest species, notably alkali, alkaline-earth and some transition metal cations [11–15]. For example, in ion-selective electrodes a tetraester is sufficiently selective for Na^+ to enable its exploitation [16, 17]. This fact is attributable to the size of the ionophoric cavity composed of four $OCH_2C{=}O$ groups which is comparable with the ion size of Na^+, and also to the cone conformation which is firmly constructed on the rigid calix[4]arene platform.

It was found by Chang *et al.* [5], McKervey *et al.* [11], Ungaro *et al.* [12], and Shinkai *et al.* [18], that calix[*n*]arenes can be converted into neutral ligands by introducing ester or amide groups at the OH positions. They demonstrated that the metal selectivity is dependent on the calix[4]arene ring size, and in particular, calix[4]aryl acetates and acetamides with a cone conformation show remarkably high Na^+ selectivity. Arnaud-Neu *et al.* have synthesized various substituted calix[*n*]arenes and examined the complexes of the tetramethyl ketone, tetra-tert-butyl ketone, tetra-adamantyl ketone and tetra-ethyl ester of the calix[4]arene with NaSCN, KSCN and LiSCN [11].

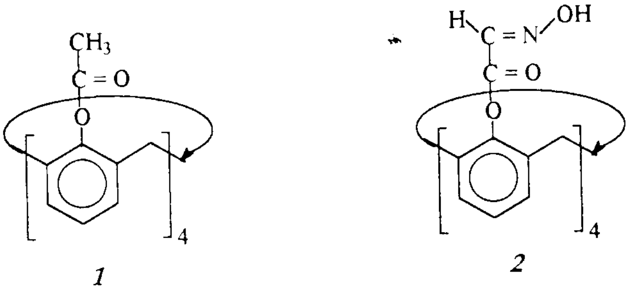
Until now, the complexation studies have been conducted with monomeric calixarenes. Polymeric calixarenes have been the subject of most recent innovation. In our recent work [19, 20], the preparation of two new polymeric calix[4]arenes were described, which were synthesized by reacting an oligomer or polyacryloylchloride with tetra-ethyl calix[4]arene tetraacetate. These polymers exhibited high selectivity to Na^+ similar to that of the parent calixarene.

The aim of the present paper is to synthesise the NaSCN and KSCN complexes of 25,26,27,28-tetraacetyl calix[4]arene (**1**) and 25,26,27,28-tetraisonitrosoaceto calix[4]arene (**2**).

Experimental

25,26,27,28-Tetraacetyl calix[4]arene (**1**) was synthesized according to the method described previously [21]. The preparation of the 25,26,27,28-tetraisonitrosoaceto calix[4]arene (**2**) was synthesized by treating (**1**) with *n*-butyl nitrite as described elsewhere [22].

Melting points were determined on a Electrothermal IA 9100 digital melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on a Mattson 1000 FTIR spectrometer as KBr pellets. Uv-Vis spectra were obtained on a Shimadzu 1601 UV-Visible recording spectrophotometer. The elemental analyses were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).



1 *2*

Figure 1. The structures of **1** and **2**.

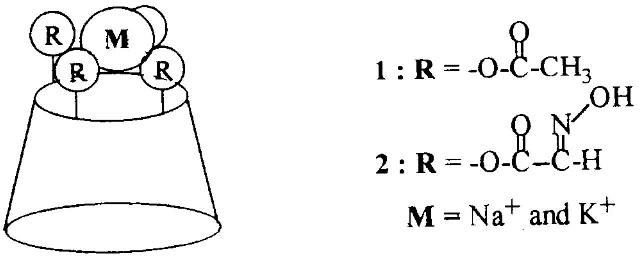


Figure 2. Complexation of a metal cation by **1** and **2**.

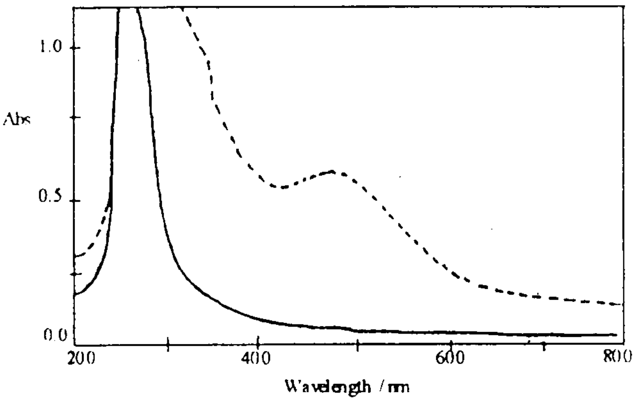


Figure 3. UV-Visible absorption of a mixture of ligand and metal salts. (—) 1×10^{-2} M of **1** in DMF; (- - - -) a mixture of **1** 1×10^{-2} M) and NaSCN (1×10^{-2} M) in DMF.

Synthesis of NaSCN and KSCN complexes of ***1*** *and* ***2***

0.02 mmol of ligand (11.8 mg **1**, or 14.2 mg **2**) was dissolved in 20 mL CH_2Cl_2. 20 mL of an aqueous solution containing 0.10 mmol (8.1 mg) of NaSCN was added to this solution. The mixture was shaken at room temperature for one hour and the solution was then set aside for phase separation. The organic phase was separated and dichloromethane was evaporated under reduced pressure, and a pale yellow powder formed (crystalline complex was precipitated for **1** and **2**). The product was precipitated by the addition of hexane, filtered under reduced pressure, washed several times with hexane and dried under vacuum. The yield, m.p., elemental analyses results, and spectral data of the complexes are given in Tables 1–3.

Results and discussion

The ionophores exist in the cone conformation either in solution or in the solid state. The oxygenated pendant groups serve to fix the cone conformation, which thus confers a high degree of primary preorganization: the ligating groups of the four ester carbonyl groups are mutually *syn*. In this arrangement, only a slight rotation of the carbonyl toward the inside of the cavity is needed to present a total of eight binding sites for the guest cation.

The selectivity in transport property of 25,26,27,28-tetraethyl calix[4]arene tetraacetate for alkali metal cations, and particularly Na^+, has been reported in the literature [11]. This experimental evidence enabled us to prepare the structures containing oxime groups (—C=N—OH). The structure of **2** has been described elsewhere [22].

In this study, the Na^+ and K^+ complexes of **1** and **2** were prepared and compared with the calix[4]arene tetraester complexes. The elemental analyses results, the characteristics of UV, IR and ^1H NMR absorptions are given in Tables 1, 2, and 3. The metal-ligand ratio in all complexes is 1 : 1.

The structure of the Na^+-complex of 25,26,27,28-tetraethyl calix[4]arene tetraacetate was investigated with X-ray diffraction analysis by Arnaud-Neu *et al.* [11]. The structure of the Na^+ and K^+ complexes of **1** and **2** was assumed to be similar as shown in Figure 2.

The ^1H NMR spectra of both compounds (**1** and **2**) exhibited rather broad signals for all protons. Complexation brings about a chemical shift of all protons in the ligands. The two largest changes were observed in the axial proton H_A of the bridging methylene groups (about 0.6 ppm upfield for **1** and **2**). The downfield shift observed for the aromatic protons suggests that the phenoxy oxygen atoms could be involved in complexation. These chemical shift changes on complexation are very similar to those observed with the calix[4]arene tetraethyl ester on complexation with sodium thiocyanate. The results are in agreement with the work of Arnaud-Neu [11] and our recent paper [20].

In order to determine whether these acetyl (**1**) and oxime (**2**) calix[4]arenes form a complex with Na^+ and K^+ similar to the calix[4]arene tetraester, a solution of these compounds (**1** or **2**) in DMF were mixed with aqueous solutions of the metal salts. When this mixture was shaken thoroughly, a color change of the organic phase was observed. Figure 3 shows the UV spectra of the Na^+ free solution compared with that of the Na^+ containing solution. It was observed that a new absorption maximum appeared at 485 nm for **1** and at 481 nm for **2** (Figure 3). The appearance of these absorption maxima is indicative of complex formation.

The most significant difference in the IR spectra of the ligands and their complexes was the appearance of the SCN group vibration at 2050 cm^{-1} in all complexes and the shift of the C=O vibration from 1780 cm^{-1} (**1** and **2**) to lower frequencies in the complexes, due to metal complexation (Figure 4).

Conclusion

In conclusion, the new metal complexes of calix[4]arene derivatives were synthesized and their chemical structures were characterized. These compounds showed effective

Table 1. Elemental analytical results for the complexes

Complex (Formulas)	Color	m.p. (°C)	Yield (%)	Calcd. (Found) % C	H	N	S	M
1-NaSCN. H_2O	Pale	>300	86	64.24	4.96	2.03	4.63	3.33
($C_{37}H_{34}O_9NSNa$)	yellow			(64.05)	(5.09)	(1.87)	(4.51)	(3.52)
1-KSCN. H_2O	Pale	>300	88	62.79	4.85	1.98	4.52	5.51
($C_{37}H_{34}O_9NSK$)	yellow			(62.36)	(4.72)	(2.11)	(4.44)	(5.64)
2-NaSCN. H_2O	Yellow	>300	92	54.87	3.99	8.65	3.95	2.84
($C_{37}H_{32}O_{13}N_5SNa$)				(54.58)	(3.89)	(8.76)	(4.08)	(2.97)
2-KSCN.H_2O	Orange	>300	89	53.81	3.91	8.49	3.87	4.72
($C_{37}H_{32}O_{13}N_5SK$)				(53.46)	(3.77)	(8.63)	(3.69)	(4.81)

Table 2. ^1H NMR data for the complexes in $CDCl_3$, (ppm)

Complexes	Ar-H	Ar-CH_2-Ar	—CH_3	—CH
1-NaSCN.H_2O	7.10–7.20 (m)	4.00–4.40 (broad d)	1.80 (s)	–
1-KSCN.H_2O	7.00–7.30 (m)	4.20–4.60 (broad d)	1.90 (s)	–
2-NaSCN.H_2O	6.90–7.20 (m)	3.80–4.30 (broad d)	–	8.30 (s)
2-KSCN.H_2O	7.10–7.40 (m)	4.30–4.70 (broad d)	–	8.40 (s)

Table 3. Characteristic IR bands of the complexes as KBr pellets (cm^{-1})

Complexes	$\nu_{(S=C=N)}$	$\nu_{(C=O)}$
1-NaSCN.H_2O	2050	1740
1-KSCN.H_2O	2050	1740
2-NaSCN.H_2O	2050	1715
2-KSCN.H_2O	2050	1710

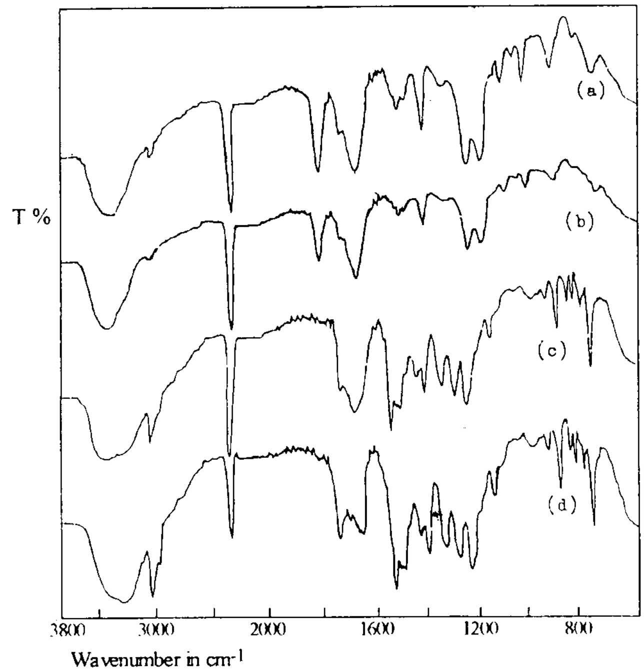


Figure 4. IR spectra (KBr pellets) of the complexes. (a) **1**-NaSCN.H_2O, (b) **1**-KSCN.H_2O, (c) **2**-NaSCN.H_2O, (d) **2**-KSCN.H_2O.

complex formation with Na^+ and K^+ alkali metal ions, and could be useful for further development of metal-ion selective materials or for phase transfer applications.

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