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Synthesis and structural characterization of bisazocalix[4]arene with melamine: Metal ion extraction studies



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ABSTRACT

In this study, the synthesis and characterization of novel bisazocalix[4]arene [2-amino-4,6-bis(5-azo-25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene)-1,3,5-triazine] (**5**), symmetrically derived from the diazo coupling of 2,4,6-triamino-1,3,5-triazine (melamine), were carried out. This compound was prepared by reacting 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (**3**) and melamine (**4**) in nitrosyl sulfuric acid and DMF. Purified product was characterized by elemental analyses, FT-IR, ¹H-NMR, MS and thermogravimetric analysis (TGA) techniques. Complexation properties of synthesized compound were studied by the liquid–liquid extraction of selected metal cations (Na⁺, K⁺, Sr²⁺, Ag⁺, Hg⁺, Hg²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺, Al³⁺). It has been observed that bisazocalix[4]arene shows high affinity to Hg⁺ and Hg²⁺ ions, whereas almost less affinity to other metals. This sensor therefore present a very significant advantage in that it allows for determination of mercury ion in environmental and industrial wastewater.

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1. Introduction

Calix[4]arenes belong to the class of compounds known as metacyclophanes and are synthetic cyclic tetramers composed of four phenolic and four methylene moieties [1]. They have long been of interest both as complexation hosts for ions and molecules, and as frameworks for elaborating more complex structures. Functional groups and calix core cavity system of calix[4]arenes, constrained to the *1,3-alternate* conformation, have received more attention due to possible applications as receptors for ions and neutral molecules [2]. This kind of compounds was found to be exceptionally selective for various metal cations in possible applications such as nuclear-waste remediation [3].

Nowadays, specific consideration is given to the control of toxic heavy metal-ion content, like lead, cadmium, copper, silver, mercury, chromium or arsenic in natural waters, which may cause great risk to human health [4–6]. This study aimed to design bis and/or tris azocalix[4]arene compounds possessing the ability of binding these metal cations.

Previous studies have shown that versatile ionophoric properties of chemically modified azocalixarenes depend greatly on the nature of the different substituents attached to the calixarene scaffold [7–10]. The introduction of soft donor atoms such as phosphorus or sulfur atoms into calix[4]arene substituents has been shown to

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promote their complexation ability toward transition and heavy metal ions such as the replacement of the amide carbonyl oxygen atoms of amide groups by sulfur atoms leading to thioamides [11]. The X-ray crystal structure of *p-tert*-butylcalix[4]arene diethylthioamide's lead complex showed that Pb^{2+} was bound to all four ethereal oxygens and four thiocarbonyl sulfur atoms of the ligand in the *cone* conformation [12].

Various studies on the syntheses of azocalix[*n*]arenes for related applications have been published previously [13–15]. In our laboratory, azocalix[4]arene derivatives have been synthesized and used as extractants in liquid–liquid extraction of transition metal ions (Ag⁺, Hg²⁺ and Hg⁺) [16–18]. Lu et al. [19] have obtained calix[4]arene carboxyphenylazo derivative to detect lead cation. Potassium and cesium selective azocalix[4]crown derivatives have been reported by Kim et al. [20] and Chawla et al. [21] while a nickel selective azocalix[4] arene derivative has been reported by Ma and coworkers [22].

The first study, using calixarenes to build dendrimers has been reported by Lhotak and Shinkai in 1995 which introduces a series of oligo-calixarenes linked through the phenolic oxygen with the help of aliphatic chains (*lower rim-lower rim* connections) [23].

This study reports the synthesis and the characterization of a novel azocalix[4]arene appended with melamine (Scheme 1). The structural characterization of dendrimeric azocalix [4]arene and its liquid–liquid extraction results are also presented as follows. The binding properties of this novel compound toward a selection of metal ions (Na⁺, K⁺, Sr²⁺, Ag⁺, Hg⁺, Hg²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺, Al³⁺) have been investigated by liquid–liquid extraction of corresponding metal



Scheme 1. Synthesis of bisazocalix[4]arene.

picrates from water into chloroform. The results have been compared to those previously obtained with the azocalix[4]arene [18], which is resynthesized in this study.

2. Experimental

The solvents, ethyl acetate (Sigma-Aldrich), hexane (Merck), DMF (Merck), benzene (Sigma-Aldrich), acetone (Sigma-Aldrich), chloroform (Sigma-Aldrich), ethanol (Sigma-Aldrich), DMSO (Merck), and benzene (Merck) were acquired commercially and used without further purification. The compounds, 2,4,6-triamino-1,3,5-triazine (Merck), sodium nitrite (Merck), sodium acetate (Merck), TLC (Merck), glacial acetic acid

(Merck), sulfuric acid (Sigma-Aldrich), acetic acid (Merck), HCl (Sigma-Aldrich), and NaOH (Merck), were acquired commercially and used without further purification. Melting points of the compounds were measured by Electrothermal IA9100 digital melting point apparatus in capillaries. ¹H-NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as internal standard and were recorded on a Bruker 400 MHz spectrometer at room temperature (25 ± 1 °C). Mass spectroscopy was performed on Bruker Daltonics of flight LC/MS. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer using KBr pellets. UV–Vis spectra were obtained on a Shimadzu 160A UV–Visible recording spectrophotometer. The elemental analyses were performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).



Fig. 1. The IR spectrum of bisazocalix[4]arene (5).



Fig. 2. The ¹H NMR spectrum of bisazocalix[4]arene (5).

2.1. Preparation of the calix[4]arenes

p-tert-Butylcalix[4]arene, calix[4]arene and 25,26,27-tribenzoyloxy-28-hydroxycalix [4]arene were synthesized as described by previously reported methods [24–27].

2.2. The synthesis of bisazocalix[4]arene [28]

2,4,6-Triamino-1,3,5-triazine (0.057 g, 0.45 mmol) was dissolved in hot glacial acetic acid (10 mL) and resulting solution was rapidly cooled in an ice-salt bath to 0 °C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulfuric acid [prepared from sodium nitrite (0.093 g, 1.35 mmol) and concentrated sulfuric acid (4 mL at 70 °C)]. The mixture was stirred for an additional hour at 0 °C. After the

completion of diazotization, diazo liquor was slowly added to a vigorously stirred solution of 25,26,27-tribenzoyloxy-28-hydroxy calix[4] arene (1.0 g, 1.36 mmol) in 20 mL DMF. The pH of the reaction mixture was maintained at 7–8 by simultaneous addition of solid sodium acetate in portions. The mixture was then stirred for 15 h at 0–5 °C. The progress of the reaction was followed by TLC using an ethyl acetate–hexane (4:6, v/v). The resulting solid was filtered, washed with cold water and dried consecutively. Recrystallization from DMF–H₂O mixture gave a pale yellow product (yield, 0.81 g (73.5%), m.p. 265–269 °C) [Found: C: 75.22%; H: 4.27%; N: 6.55%]; C₁₀₁H₇₂N₈O₁₄ requires C: 74.80%; H: 4.48%; N: 6.91%. IR (KBr) v: 3528 cm⁻¹ (–OH), 2924 cm⁻¹ (–C–H), 1724 cm⁻¹ (–C = O), 1451 cm⁻¹ (–N = N), 1270 cm⁻¹ (C–O). ¹H-NMR (CDCl₃, 25 °C) $\delta_{\rm H}$: 3.4–3.9 (16H, m, Ar–CH₂–Ar), 5.5 (2H, s, – NH₂), 6.6–7.2 (22H, m, Calix-H), 7.2–8.2 (30H, m, Bnz-H), 8.0 (2H, s, – OH).



Fig. 3. The mass spectrum of bisazocalix[4]arene (5).



Fig. 4. The most stable fragmentation structure of bisazocalix[4]arene (5).

Bisazocalix[4]arene is soluble in acetic acid, benzene, acetone, CHCl₃, DMF, and DMSO, but insoluble in water, EtOH, 10% HCl and 10% NaOH.

3. Results and discussion

The synthetic route was showed in Scheme 1. A novel bisazocalix[4] arene derivative, was prepared with melamine by using calix[4]arene tribenzoyl derivative as the new synthetic platform.

The structure and conformation of novel bisazocalix[4]arene (**5**) have been elucidated by spectroscopic methods (FR-IR, ¹H-NMR, ESI-MS) and elemental analyses. The absorption band observed at 1451 cm⁻¹ of FT-IR spectrum can be assigned to the azo group stretching $\nu_{(-N = N-)}$ of compound **5** (Fig. 1). The band appearing at 3528 cm⁻¹ can be ascribed to the presence of hydroxyl $\nu_{(OH)}$ group in compound **5**. The absorption peak at 1724 cm⁻¹ can be attributed to $\nu_{(C = 0)}$ ester carbonyl. The weak absorption bands appeared at 1584–1600 cm⁻¹, ascribed to $-NH_2$ group, also confirmed formation of compound **5**.

¹H-NMR data of bisazocalix[4]arene **(5)** includes a peak (δ 5.5 ppm), which can be attributed to the presence of amino protons (–NH₂). While the appearance of peak at δ 3.0 ppm can be ascribed to protons of recrystallization solvent DMF the appearance of peak at δ 7.2 ppm can also be attributed to the proton of dissolving solvent CHCl₃ (Fig. 2).

The ¹H-NMR spectrum of novel bisazocalix[4]arene (**5**) in CDCl₃ revealed a multiplet at δ 6.6–8.2 ppm corresponding to all aromatic protons. The formation of this compound is confirmed by the sharp multiplet at δ 6.6–7.2, which can be ascribed to azocalix[4]arene

aromatic protons. The sharp multiplet signals of the phenyl protons appear in the region δ 7.2 to 8.2 ppm.

As it is seen in the mass spectrum (Fig. 3), synthesized bisazocalix[4] arene (**5**) compound has very weak molecular ion peaks (m/z = 1621). This indicates that melamine has been coupled to two triester molecules and melamine's molecular mass is calculated to be 1621 amu. Examination of mass spectrum refers to the breakdown and removal of some structures consecutively. Benzoyl and amine groups have been separated from the main structure during the analysis which can be attributed to m/z = 1501. Following, entire molecule has been broken down to give the structure shown in Fig. 4 with molecular weight of 748. This indicates the fragmentation of bisazocalix[4]arene (**5**) compound.

Thermal analysis methods are useful tools for the determination of thermal stability and inclusion behavior of calix[n]arenes with guest molecules such as toluene, xylene, chloroform, acetone and alkylammonium [29,30]. The TG and DTA curves of tribenzoyl calix[4]arene (**3**) and novel bisazocalix[4]arene (**5**) compounds are shown in Fig. 5.

Tribenzoyl calix[4]arene (**3**) is the starting material in synthesis of bisazocalix[4]arene (**5**) compound. Thermal behavior of bisazocalix[4] arene becomes similar to that of tribenzoyl calix[4]arene after removal of triazin group. Tribenzoyl calix[4]arene (**3**) decomposes in three stages. First decomposition stage corresponds to removal of 1.5 mol of methanol group. Theoretical mass loss is (6.130%) compatible with experimental mass loss (6.507%). Tribenzoyl groups leave the structure in the second decomposition stage. Finally the remaining structure decomposes between 460–620 °C. This reaction occurs exothermically like the decomposition reactions of other calixarene compounds [31].

Decomposition of novel bisazocalix[4]arene (5) molecule occurs in four stages. The first stage corresponds to removal of DMF, which has been bound to the structure during recrystallization. This initial decomposition reaction occurs endothermically and its peak temperature is 192.92 °C. Theoretical mass loss (4.282%) is compatible with experimental mass loss (4.650%). Triazin groups leave the structure in the second decomposition stage. After the second decomposition reaction occurs endothermically in 365–415 °C temperature range. Experimental mass loss value (36.379%) is very close to theoretical mass loss value (36.950) for this stage. Final decomposition stage, which breaks down the remaining structure, occurs exothermically. All of the thermal analysis results are summarized in Table 1.

Metal transportation experiments for picrate salts were carried out with a H_2O -CHCl₃ liquid-liquid phase transfer system using diazo calixarene compounds as cation carriers. The results of cation transportation experiments are compatible with those of two-phase extraction measurements.

The ionophoric properties of all **3**, **4** and **5** compounds toward the alkaline-earth and the transition metal cations were investigated by



Fig. 5. The TG and DTA curves of tribenzoyl calix[4]arene(a) and bisazocalix[4]arene(b).

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The thermoanalytical results obtained from TG and DTA curves. ^{exp}: Experimental, ^{theo}: theoretical.

Compounds	$T_i - T_f$	T _{peak} Mass loss% ^{exp}		Mass loss% ^{theo}	Removed groups		
Tribenzoyl calix[4]arene	175–205 305–460 357–535	188.49 413.46 579.46	6.141 40.240 52.684	6.130 40.230 54.151	1.5 mol CH₃OH Tribenzoyl groups Rest of structure decomposes		
Bisazocalix[4]arene	150-197192.92281-365275.15365-515427.29515-648561.96		4.650 9.959 36.379 49.506	4.282 9.501 36.950 49.267	1 mol DMF Triazin groups Tribenzoyl groups Rest of structure decomposes		

the picrate extraction method initially [18]. The results, expressed as a percentage of cation extracted (E%), are demonstrated in Table 2 and shown graphically in Fig. 6.

The extraction studies of cations $(Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Al^{3+})$ with ligand **3** had already been done [18] with same experimental conditions earlier. The ligand is selected due to its functional groups (tribenzoyl ester groups) which increases its solubility. This situation increases the efficiency of extraction. Extraction properties of compound **5** for Hg²⁺ (61.0%) and Hg⁺ (43.2%) are measured to be much higher than those of compound **3** for Hg²⁺ (17.0%) and Hg⁺ (15.5%).

Although both compounds of **3** and **5** form complexes with Hg cations, extraction property of compound **5** toward Hg cations has been measured higher with respect to that of compound **3**. This difference can be attributed to conjugated chromophore azo (-N = N-) groups of compound **5**. π -interactions of these chromophore azo (-N = N-)

Table 2
Extraction of metal picrates with ligands.

groups may play a role in complexation with azocalix[n] arenes. The results have shown that compound **5** displays a strong affinity toward soft metal cations Hg²⁺ and Hg⁺. This phenomenon can be attributed to the soft nitrogen donor atoms of novel compound **5**.

These results suggest that the match between cation and azo group of calix[4]arene derivative is an evident factor in selectivity. As a part of research study, a novel azocalix[4]arene based sensor **5** has been synthesized and characterized. It has been revealed from the experimental evidences that **5** exhibits significant sensing behavior toward Hg⁺ and Hg²⁺ among a series of selected transition metals.

An ORTEP diagram for novel bisazocalix[4]arene (**5**) is shown in Fig. 7. Torsion angles and around Ar–CH₂–Ar bonds about the presence of two sets of characteristic AB spin systems at 3.40 and 3.90 ppm are consistent with *cone* conformation. The inter planar angles between rings and its distally positioned ring are about 25.0° theoretically, which suggest that these are almost parallel to each other. Phenyl rings of the benzoyl group are perpendicular to the respective calixaryl aromatic ring plane. The oxygen of the carbonyl group remains *exo* to the cavity. The dihedral angle between the phenylazo group plane and ring melamine is 9.0°, which corroborates that one phenylazo ring is parallel and the other phenylazo ring is perpendicular to the ring, which remains outward of the calixarene cavity. This brings the substituted phenylazo group much closer to the adjacent benzoyl ring. The molecular packing of bisazocalix[4]arene along the axis a is shown in Fig. 7.

4. Conclusion

This study demonstrated the synthesis of novel bisazocalix[4]arene (**5**) by using 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (**3**) and melamine (**4**). The mass spectrum of novel compound (**5**) was measured

Ligand	Picrate salt extracted (%)													
	Na ⁺	K^+	Sr ²⁺	Ag^+	Hg^+	${\rm Hg}^{2+}$	Co ²⁺	Ni ²⁺	Cu ²⁺	Cd^{2+}	Pb ²⁺	Zn ²⁺	Cr ³⁺	Al ³⁺
3	0.8	0.9	0.6	3.3	15.5	17.0	1.2	0.7	5.1	0.1	3.0	0.3	6.5	3.2
4	1.5	1.2	1.5	2.1	13.2	21.1	1.6	2.1	5.7	0.1	1.9	0.7	6.8	2.6
5	15.8	17.9	19.6	21.2	43.2	61.0	19.8	19.6	26.2	20.2	24.6	20.0	19.8	23.1

^a H₂O/CHCl₃ = 10/10 mL (v/v): [picric acid] = 2×10^{-5} M, [ligand] = 1×10^{-3} M, [metal nitrate] = 1×10^{-2} M; 298 K, 1 h contact time. Experimental error was ±2%.



Fig. 6. Extraction percentages of compounds 3, 4 and 5.



Fig. 7. (a) ORTEP diagram of bisazocalix[4]arene (hydrogens, solvent molecules, and disordered part have been omitted for clarity); (b) view of the molecular electron density.

as a significant peak corresponding to m/z = 1501.6. This product is measured to be thermally stable by TG and DTA methods. The results of extraction studies performed on ligands **3**, **4** and **5** suggest that the match between cation and ligand is an evident factor in their selectivity properties. It has been observed that novel bisazocalix[4]arene compound (5) shows high affinity to Hg^+ and Hg^{2+} ions, whereas almost no affinity to other metal cations. The results have also shown that compound 5 displays stronger affinity toward soft metal cations Hg²⁺ and Hg⁺. This phenomenon can be explained by the (hard-soft) acid-base (HSAB) principle whereby -N = N group which is a soft base shows a stronger affinity toward soft acidic cations like Hg^{2+} and Hg^+ . Bisazocalix[4]arene (5) showed a thermal behavior and a decomposition in four stages. These data are very important for the determination of potential application areas of azocalix[4]arenes. This study suggests that novel bisazocalix[4] arene compound (5) may have a potential application as a highly selective sensor toward Hg cations. Studies on the respect of research are underway in our laboratory.

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