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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, ^{1}H-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^+, Sr^{2+}, Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}). It has been observed that bisazocalix[4]arene shows high affinity to Hg^+ and Hg^{2+} 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 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^+, Hg^{2+} 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^+, Sr^{2+}, Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}) have been investigated by liquid–liquid extraction of corresponding metal

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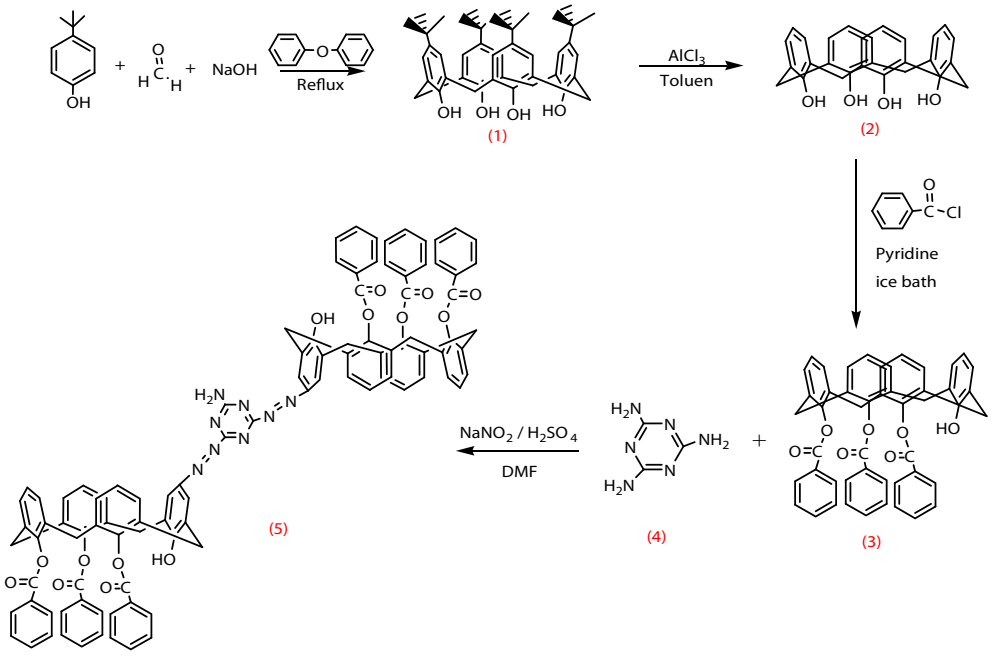

Scheme 1. Synthesis of bisazocalix[4]arene.

picrates from water into chloroform. The results have been compared to those previously obtained with the azocalix[4]arene [18], which is re-synthesized 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. ^{1}H-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).

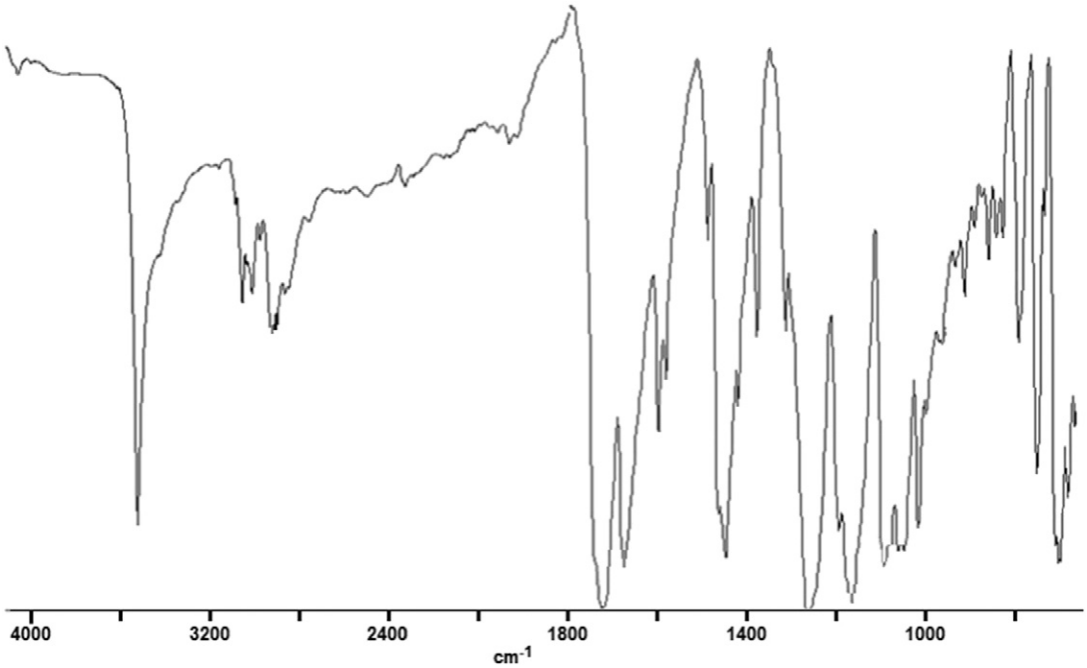

Fig. 1. The IR spectrum of bisazocalix[4]arene (**5**).

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