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In memoriam prof. dr. Ioan A. Silberg

CALIX[n]ARENE DERIVATIVES WITH BINDING PROPERTIES TOWARD Eu^{3+}

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ABSTRACT. Narrow rim functionalized calix[6]arene with 2-Butenyl, ethylacetate and N,N-diethylacetamide were synthesized and investigated by Elemental Analysis (EA) and various spectroscopic methods such as: UV-VIS, FT-IR and ^{1}H and ^{13}C NMR. These derivatives were tested for the extraction of Eu^{3+} ions from the aqueous phase.

Keywords: *synthesis, calix[n]arene, functionalisation, Eu extraction;*

INTRODUCTION

The coordination as well as extraction properties of calix[n]arenes is very well known for a long time [1]. Calixarene derivatives incorporating ionophoric functional such as amine, amide, organophosphoric and ester or acid groups at the “narrow rim” exhibit selective extraction/complexation properties [2, 3].

The high ability of these calixarenes to form coordination compounds offers large utilization possibilities in the manufacture of sensitive membrane for electrical and optical sensors [4-6], elaboration of extraction methods for various cations [7], utilization in modern recovery procedures [8] and for the environmental protection [9].

Many preparation procedures have been developed for specific synthesis of calix[n]arene derivatives with oxygen or/and nitrogen and oxygen or/and organo-phosphorous functional groups because of their extraction / coordination properties toward metallic ions. Calixarene derivatives with ester, acid, amide and organo-phosphorous moieties are effective for extraction/ complexation of alkaline[10], alkaline earth[11], as well as lanthanide [12, 13] and transition metals [14].

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Our earlier work on extraction of precious metallic ions revealed that acylated calix[6] and calix[4]arene derivatives show a good extraction ability toward platinum(II) and palladium(II) ions but not for rhodium(III)ion [15]. This results encouraged us to extend our works on the synthesis of other calix[n]arene derivatives (n = 4, 6, 8) with possible extraction abilities [16-19].

The aim of this study is to present our works referring to synthesis of calix[n]arene derivatives with alkenyl, ester and/or amide groups and to test their extraction properties.

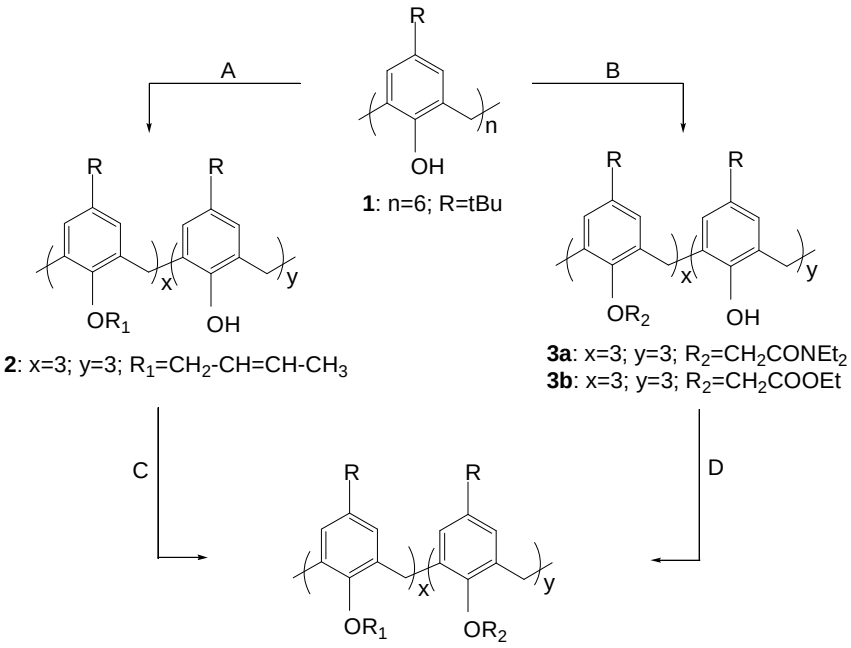
RESULTS AND DISCUSSIONS

The parent calix[6]arene was treated in the first stage with crotyl bromide in order to obtain calixarene derivative which contains three crotyl groups: 5,11,17,23,29,35-hexa-*t*Butyl-37,38,39-tris[(but-2-enyloxy]-40,41,42-trihydroxy-calix[6] arene (**2**) (scheme 1, pathway A).

In the next stage **2** was treated with α-Chloro-N,N-diethylacetamide or Ethyl bromoacetate (scheme 1, pathway C) in order to obtain a calix[n]arene derivatives: 5,11,17,23,29,35–hexa-tButyl-37,38,39-tris[(N,N-diethylamino-carbonyl)methoxy]-40,41,42-tris-(But-2-enyloxy)-calix[6]arene(**4a**) and 5,11,17, 23,29,35 – hexa- *t*Butyl-37,38,39-tris[(carbonyl ethoxy)methoxy]- 40,41,42-tris-(But-2-enyloxy)-calix[6] arene (**4b**), with mixed functional groups at the narrow rim. On the other hand calix[6]arene was treated in the first stage with α-Chloro-N,N-diethylacetamide or Ethyl bromoaacetate (scheme 1, pathway B) to obtain calix[6]arene with amide, 5,11,17,23,29,35-hexa-*t*Butyl-37,38,39-tris[(N,N-diethylamino carbonyl) methoxy]-40,41,42-trihydroxy-calix[6] arene (**3a**), or ester functionality, 5,11,17,23,29,35-hexa-*t*Butyl-37,38,39-tris-[(ethoxycarbonyl)metoxy]-40,41,42-trihydroxy-calix[6]arene (**3b**), which reacts in the next stage with crotyl bromide to yield the same calixarene derivatives **4a** and **4b,** respectively.

The narrow rim functionalization is well illustrated by ^{1}H-NMR spectra which show the expected differences in the chemical shifts, between **1** and **3a**, **3b**. The chemical shift of the proton from the phenolic OH group appears at 10.55 ppm for compound **1** and between 7.09– 7.14 ppm for compounds **3a** and **3b.**

Infrared absorption spectra show that the band corresponding to OH stretching vibration of calixarene **1** appear at 3172 cm^{-1}, while for the intermediates **2**, **3a** and **3b** it is at: 3387(**2**) , 3248 (**3a**) and 3399 cm^{-1} **(3b**). In the FTIR spectrum of **3a** and **3b,** the band corresponding to the stretching vibration of carbonyl groups appears at 1644 (**3a**) and 1741 (**3b**) cm^{-1} , respectively (Fig. 1).



Scheme 1. Two pathways for the synthesis of calixarene compounds **2,3a,3b,4a, 4b.**

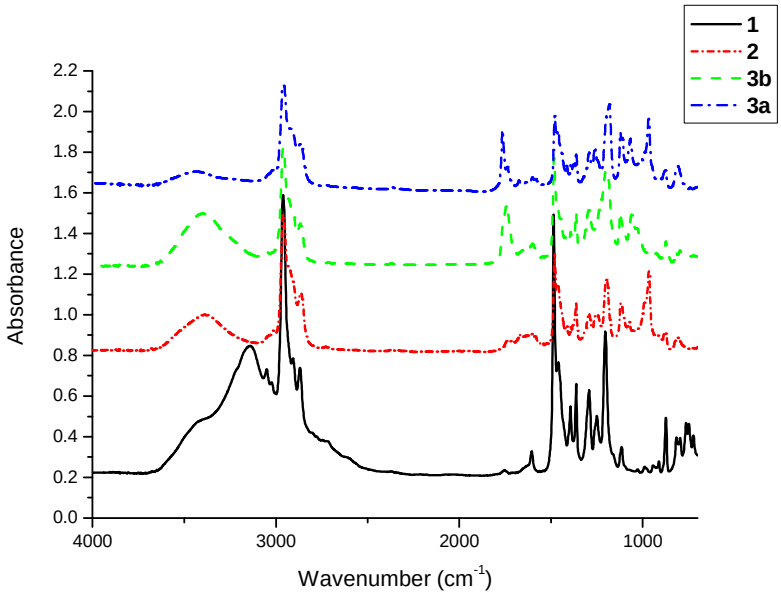


Figure 1. FTIR spectral characterization of compounds **1, 2, 3a** and **3b**.

The UV-Vis spectra show the shift of the two specific absorption bands of the parent calix[n]arene towards shorter wavelengths. For **2, 3b** and **4b** the specific absorption bands appear at 272, 280 nm; 272, 279 nm and 271, 280 nm respectively in comparison with 284 and ~291 nm in the parent calixarene (Fig. 2).

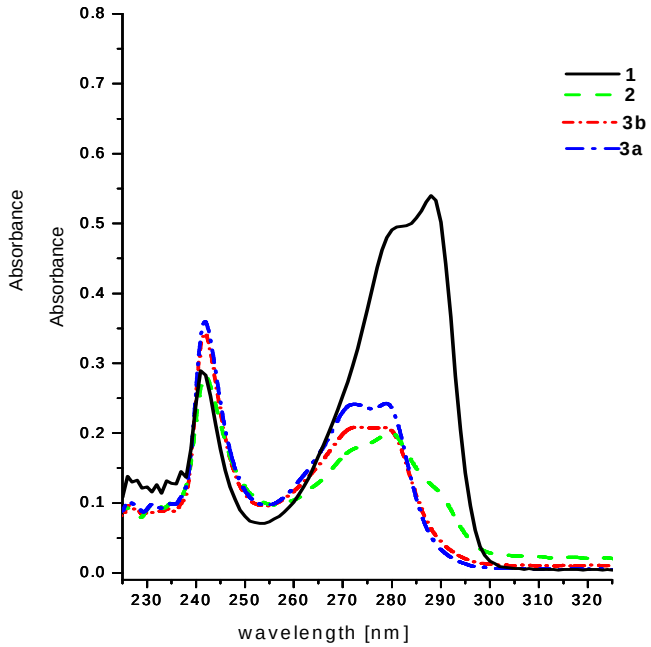


Figure 2. UV-vis absorption spectra of compounds **1,2,3a** and **3b**.

Extraction experiments were performed using $1x10^{-3}$ mol/l solution of calixarene in chloroform. The calixarene: metal ratio was varied between 2:1 to 1:2 and the pH of the medium was kept constant at 2.8. Extraction yield was determined by comparing the metal content from the aqueous phase before and after extraction. The concentration of the metal was determined with an ICP-OES Spectrometer (Spectroflame).

The ability of calixarene **3a**, **3b, 4a** and **4b** to extract rare earth ions from the aqueous medium was estimated from the extraction yield values (Table 1).

The extraction yield is influenced by the ratio between calixarene and metallic ions (Cx:Eu). Best results were obtained with **3b** derivative, for Eu^{3+} ions.

Table 1.

Extraction yield of Eu^{3+} using calixarene **1, 2, 3a-b, 4a-b**.

Calixarene derivatives	Extraction yield (%)		
	Ratio Cx :Eu **1:1**	Ratio Cx :Eu **2:1**	Ratio Cx :Eu **1:2**
1	23.85	26.14	13.16
2	18.70	42.62	23.79
3a	38.67	13.45	25.01
3b	57.06	58.33	44.59
4a	29.89	16.76	20.28
4b	34.22	55.21	61.13

EXPERIMENTAL PART

The parent tert-butyl-calix[6]arene (compound **1**) was prepared and purified by using the Gutsche technique [20].

Calixarene derivatives have been obtained from *tert*-butyl-calix[6]arene and 2-butenyl (crotyl) bromide, α-Chloro-N,N-diethyl acetamide or ethylbromoacetate, in acetonitrile or dimetylformamide-tetrahydrofuran mixture as solvent and K_2CO_3 or NaH as base.

All reactions were performed under nitrogen atmosphere using oven-dried glassware. Reagents were obtained from commercial suppliers and were used without further purification. All solvents were dried over standard drying agents and distilled prior to use. The complete conversion of the parent calix[n]arenes was checked up by thin layer chromatography on Kieselgell $60F_{254}$ plates with detection by UV or iodine. Melting points (m. p.) were determined with KSP II apparatus in a sealed capillary and are uncorrected values.

^{1}H-NMR and ^{13}C-NMR were recorded on Varian Gemini 320S (300 MHz) spectrometer. Deuterated chloroform was used as solvent and TMS as internal standard. Infrared absorption spectra were recorded on FTIR (JASCO) 610 and UV-VIS spectra on UNICAM UV4 spectrometers.

The main characteristics of the compound **2** were already reported [16] while the compounds **3a**, **3b**, **4a**, **4b** are described below:

5,11,17,23,29,35-hexa-tButyl-37,38,39-tris[(N,N-diethylaminocarbonyl) methoxy] - 40,41,42-trihydroxy-calix[6] arene **(3a).**

M.p. = 272-3℃.

M.W. calculated for $C_{84}H_{117}N_3O_9$ = 1312.82

E.A.(%): Calcd:C = 76.85; H = 8.98; N = 3.20 / Found: C =75.57;H = 8.44; N = 3.03

UV-Vis: [$CHCl_3$; λ_{max} (nm): 281 ; 288.

FTIR : ($v_{max.}$, KBr , cm^{-1}): $v_{C=O}$ =1644 ; v_{OH} =3248 .

^{1}H-NMR(δ_{ppm},$CDCl_3$):0.92-0.97 (t,18H,N-CH_2-C*H*$_3$); 1.09 (s,27H,C(C*H*$_3$)$_3$); 1.26 (s,27H, C(C*H*$_3$)$_3$); 3.11 – 3.18 (q,12H, N-C*H*$_2$-CH_3) ; 3.62 (s,12H,Ar-C*H*$_2$-Ar); 4.33(s,6H,O-C*H*$_2$-CO); 6.72 (s,6H, Ar*H*) ;7.03 (s,6H, Ar*H*),]; 7.09 (s, 3H, OH).

^{13}C-NMR:(δ_{ppm} ,$CDCl_3$) :169.1, 151.8, 144.9, 1414.3, 125.9, 124.2, 69.7, 40.3, 39.8, 32.9, 31.9, 31.4, 30.5, 12.0.

5,11,17,23,29,35-hexa-tButyl-37,38,39-tris[(ethoxycarbonyl)methoxy]-40,41,42-trihydroxy-calix[6] arene **(3b).**

M.p. = 248-250℃.

M.W. calculated for $C_{78}H_{102}O_{12}$ = 1231,62

E.A.(%): Calcd: C = 76.06; H = 8.35; O =15.59 / Found: C =75.90; H = 8.21; O = 15.89

UV-Vis [$CHCl_3$; λ_{max} (nm): 272 ; 279.

FTIR ($\nu_{max.}$, KBr , cm^{-1}): $\nu_{C=O}$ =1741 ; ν_{OH} =3399.

^{1}H-NMR; (δ_{ppm} ,$CDCl_3$): 0.92 (t,9H,CH_2-C*H*$_3$) ; 1.10 (s,27H,C(C*H*$_3$)$_3$); 1.17 (s,27H, C(C*H*$_3$)$_3$); 3.84 (brs,12H,Ar-C*H*$_2$-Ar); 4.12 (q,6H,C*H*$_2$-CH_3); 4.47 (s,6H,O-C*H*$_2$-CO); 6.91 (s,6H, Ar*H*); 6.95 (s,6H, Ar*H*); 7.14 (s, 3H, OH).

^{13}C-NMR; (δ_{ppm} ,$CDCl_3$): 169.6; 151.8; 149.3; 147.7; 142.5; 132.9; 125.84; 70.9; 61.4; 34.25; 33.95; 32.55; 29.71; 14.0.

5,11,17,23,29,35–hexa-tButyl-37,38,39-tris[(N,N-diethylaminocarbonyl) metoxy]- 40,41,42-tris-(But-2-enyloxy)-calix[6] arene **(4a).**

M.W. calculated for: $C_{96}H_{135}O_9N_3$

M.p.:218-220ºC

E.A (%): Calcd.C =78.18; H = 9.22; N=2.85/ Found C =79.39; H = 8.94; N=2.56

UV-Vis [$CHCl_3$; λ_{max} (nm)/ε($M^{-1}cm^{-1}$)]: 272/ε; 279/ε

FTIR; ($\nu_{max.}$, KBr , cm^{-1}): $\nu_{C=O}$ =1649; $\nu_{CH=CH}$=966, 3016

^{1}H-NMR (δ_{ppm} ,$CDCl_3$) : 1.02 [t, 18H, -CH_2-$\underline{CH_3}$] ; 1.14 [s, 27H, C(C$\underline{H_3}$)$_3$]; 1.18 [s, 27H, C(C$\underline{H_3}$)$_3$]; 1.56 [d, 9H, =CH-$\underline{CH_3}$]; 3.32-3.39[brs, 12H, N-$\underline{CH_2}$-CH_3]; 3.87 [brs, 12H, Ar-$\underline{CH_2}$-Ar]; 3.99 [d, 6H, O-$\underline{CH_2}$-CH=]; 4.42 [s, 6H, O-$\underline{CH_2}$-CO-]; 5.45-5.67 [m, 6H, -$\underline{CH=CH}$-]; 6.88 [s, 6H, Ar$\underline{H}$]; 7.08 [s, 6H, Ar$\underline{H}$]

^{13}C-NMR (δ_{ppm} ,$CDCl_3$):168.2; 152.2; 151.8; 144.9; 141.4;132.6; 131.7; 126.6; 125.9; 75.7; 69.6; 40.3; 39.7; 31.5; 30.8; 17.7; 12.1.

5,11,17,23,29,35 – hexa- tButyl-37,38,39-tris[(carbonylethoxy) methoxy] - 40,41,42-tris-(But-2-enyloxy)-calix[6] arene **(4b).**

M.W. calculated for: $C_{90}H_{120}O_{12}$

M.p.:206-208ºC

E.A. (%): Calcd: C =77,55; H = 8,68; N=13,77/Found :C =78,18; H = 8,87; N=12,96.

UV-Vis[$CHCl_3$; λ_{max} (nm)/ε($M^{-1}cm^{-1}$)]: 271/ ε; 280/ ε.

FTIR; ($\nu_{max.}$, KBr , cm^{-1}): $\nu_{C=O}$ =1763, 1737; $\nu_{CH=CH}$=966.

^{1}H-NMR: (δ_{ppm} ,$CDCl_3$) : 0.90 [t, 9H, -CH_2-$\underline{CH_3}$] ; 1.01 [s, 27H, C($C\underline{H_3}$)$_3$]; 1.19 [s, 27H, C(CH_3)$_3$]; 1.65 [d, 9H, =CH-$\underline{CH_3}$]; 3.51[brs, 12H, Ar-$\underline{CH_2}$-Ar]; 4.13 [q, 6H, O-$\underline{CH_2}$-CH_3]; 4.57 [d, 6H, O-$\underline{CH_2}$-CH=]; 4.72 [s, 6H, O-$\underline{CH_2}$-CO-]; 5.57-5.86 [m, 6H, -$\underline{CH=CH-}$]; 7.04 [s, 6H, Ar$\underline{H}$]; 7.15 [s, 6H, Ar$\underline{H}$].

^{13}C-NMR :(δ_{ppm} ,$CDCl_3$):169.5; 153.1; 150.8; 149.3; 147.7; 132.8; 126.0; 125.1; 75.7; 70.9; 61.4; 34.2; 33.8; 32.5; 31,2; 29.7; 17.7; 14.1.

CONCLUSIONS

The spectroscopical investigations confirm the formation of calix[6]arene derivatives with three ethylester (**3b**), three N,N-diethylacetamido (**3a**), three crotyl and three N,N-diethylacetamido (**4a**), three crotyl and three ethylester (**4b**) groups. These calixarenes show ability for the extraction of europium ions from slightly acid aqueous phase.

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