Synthesis of Some New *p-tert*-octyl calix[4]Arene Derivatives for Metal Sequestration

ALINA SAPONAR[1]*, ELISABETH-JEANNE POPOVICI[1], RALUCA SEPTELEAN[2], ECATERINA BICA[1], IOANA PERHAITA[1], GABRIELA NEMES[2]

[1] Babes Bolyai University, Raluca Ripan Institute for Research in Chemistry, 30 Fantanele Str., 400294, Cluj-Napoca, Romania
[2] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Str., 400028, , Cluj-Napoca, Romania

*New p-tert-octyl calix[4]arene derivatives i.e. 5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)-25,27-bis-(but-2-enyloxy)- 26,28-dihydroxy calix[4]arene (**2**), 5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)-25,27-bis-[(ethoxycarbonyl)methoxy]-26,28-dihydroxy calix[4]arene (**3**) and 5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,27-bis-[(ethoxycarbonyl)methoxy]-26,28-(but-2-enyloxy) calix[4]arene (**4**) have been synthetised by reaction of the parent p-tert-octyl calix[4]arene with E-2-butenyl bromide and/or ethyl bromoacetate in the presence of K_2CO_3 or NaH as a base in organic solvents (CH_3CN). The new calixarenes derivatives have been characterized by elemental analysis, ^1H and ^{13}C NMR, FTIR and UV-Vis spectroscopy, mass spectrometry and were tested for the extraction of rare earth and precious metals from aqueous solutions.*

Keywords: p-tert-octyl calix[4]arenes, synthesis, functionalization, metal extraction

The calixarenes, an interesting class of cyclophanes, has received much attention in the last decades. There are cyclic oligomers produced by condensation of *p*-substituted phenols with formaldehyde under alkaline conditions [1, 2]. Owing to their cavity-shaped architecture, they are useful building blocks in the synthesis of receptors for ionic or neutral species [3, 4]. The calixarenes and their derivatives can be used as ionophores or complexing reagents for metal ions of analytic or technological interest [5, 6].

Calixarene derivatives can be prepared by functionalization at the phenolic OH groups (narrow rim), e.g. esterification, etherification, and/or in the *para*-position of the phenyl rings (wide rim), e.g. sulfonation, nitration, alkylation [7-17].

It is well known that calixarene derivatives containing oxygen donor groups such as acid, ester or kcetone linked at the phenolic oxygen at the "narrow rim", exhibit excellent properties as neutral receptors for metallic ions [18-34]. These chemically modified calixarenes form stabile complexes and show high selectivity because of their well pre-organized ionophoric groups.

Owing to their special properties regarding extraction or coordination of metallic ions, the finding of new calix[n]arene derivatives for use in the recovery of precious and rare earth metals from waste waters is of interest. Synthesis and properties of some new alkenyl- and/or ethylester derivatives of *p-tert*-butyl calix[4]arene was already reported by us [9]. The present paper reports about some similar functionalized derivatives of *p-tert*-octyl calix[4]arene, as shown in the general scheme depicted in figure 1. This work is focused on the synthesis and characterization of *p-tert*-octyl calix[4]arene with two alkenyl- groups (**2**), *p-tert*-octyl calix[4]arene with two ethylester groups (**3**) and mixed functionalized *p-tert*-octyl calix[4]arene derivative with two alkenyl- and two ethylester groups (**4**). Due to the presence of the *p*-electrons from the functional groups, these compounds could be of practical interest for metal sequestration.

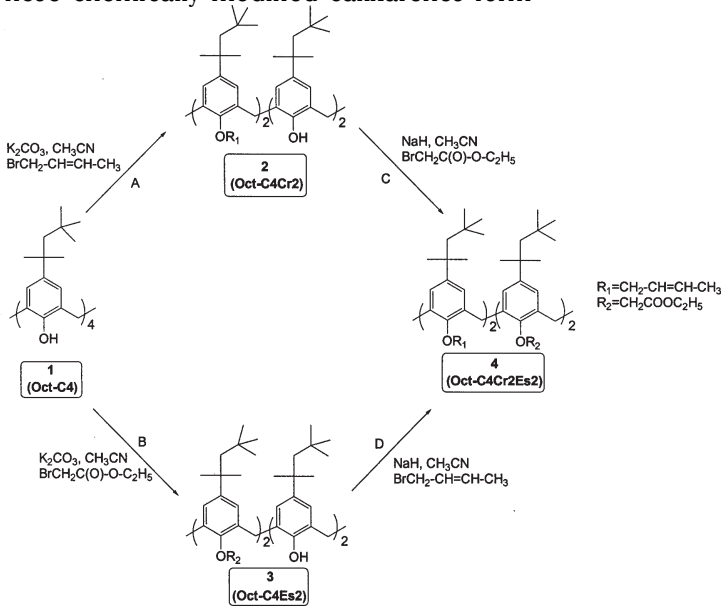

Fig. 1. Synthesis route of *p-tert*-octyl calix[4]arene derivatives

* *email: salina@chem.ubbcluj.ro; Tel.: 0727360184*

Experimental part

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 use. Reaction time was monitored by TLC on Kiselgell 60 F_{254} plates with detection by UV or iodine. Melting points (M.P.) were determined with POINT METER KSP II apparatus in a sealed capillary and are uncorrected values. ^{1}H and ^{13}C NMR spectra were recorded on VARIAN GEMINI 300S (300 MHz) spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent, and tetramethylsilane (TMS) as reference. Infrared absorption spectra were recorded on Thermo Scientific Nicolet 6700 FT-IR spectrometer, using KBr pellet technique. UV-Vis spectra in $CHCl_3$ solution ($1x10^{-4}$ mol/L) were recorded on UNICAM UV 4 spectrometer. Elemental analysis (E.A.) was performed with Vario EL analyser. Mass spectra (M.S.) were recorded on a Thermo Fisher Scientific Mass Spectrometer (DSQ) by chemical ionization method (NH_3).

The ability of the calixarene derivatives to extract rare earth and precious metals from aqueous solution was determined by liquid-liquid extraction from $1x10^{-3}$ mol/L $Eu(NO_3)_3.5H_2O$, $1x10^{-3}$ mol/L $PdCl_2$ and $1x10^{-3}$ mol/L $HAuCl_4.4H_2O$, using $1x10^{-3}$ mol/L solution of calixarene in $CHCl_3$. The metal concentration was determined in the aqueous medium, before and after extraction, using a Perkin Elmer ICP-OES spectrometer (OPTIMA 2100 DV). The extraction ability was estimated on the basis of the extraction yield (%) or by the ratio between the mol numbers of metal to calixarene (mol/mol).

The starting calixarene 5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,26,27,28-tetol (compound **1**) was prepared according to the procedures described in the literature [35]. The synthesis of the new derivatives of *p-tert*-octyl calix[4]arene and their characteristics are presented bellow.

5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)-25,27-bis-(but-2-enyloxy)-26,28-dihydroxy calix[4]arene (compound **2**)

To a mixture of 2.29 mmol *p-tert*-octyl calix[4]arene (**1**) in acetonitrile (200 mL), 9.40 mmols of K_2CO_3 were added. The mixture was stirred 30 min at 40°C. After cooling to room temperature, 9.92 mmols of crotyl bromide in acetonitrile (20 mL) were added dropwise and the mixture was refluxed for 20 h. The reaction mixture was mixed with ice and then concentrated HCl was added. The compound has been extracted in chloroform and successively washed with water and brine, and dried over anhydrous $MgSO_4$. After filtration, the chloroform solution was concentrated and methanol was added. The suspension was allowed to cool in refrigerator (24 h). The precipitated solid material was filtered and recrystallized from chloroform-methanol mixture yielding 0.91 g (~41 %) of compound **2** as white crystals.

M.P.: 104°C.

M.W. calculated for $C_{68}H_{100}O_4$: 982.

M.S. [m/z]: 982 (M^+).

E.A. Calcd. (%): C = 83.21; H = 10.27; O = 6.52; Found (%): C = 83.15; H = 10.45; O = 6.40.

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε ($M^{-1}cm^{-1}$)]: 284 / 5080; 292 / 3980.

FTIR (KBr, $\nu_{max.}$, cm^{-1}): ν_{OH} = 3398 cm^{-1}; $\nu_{=C-H}$ = 965 cm^{-1}.

5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)-25,27-*bis*-[(ethoxycarbonyl)methoxy]-26,28-dihydroxy calix[4]arene (compound **3**)

To a mixture of 2.29 mmol *p-tert*-octyl calix[4]arene (**1**) in acetonitrile (200 mL), 9.40 mmols of K_2CO_3 were added. The mixture was stirred 30 min at 40°C. After cooling to room temperature, 9.88 mmols of ethyl bromoacetate in acetonitrile (20 mL) was added dropwise and the mixture was refluxed for 20 h. The reaction mixture was mixed with ice and then concentrated HCl was added. The reaction product has been extracted in chloroform and successively washed with water and brine and dried over anhydrous $MgSO_4$. After filtration, the chloroform solution was concentrated and methanol was added. The suspension was allowed to cool in refrigerator (24 h) and the precipitated solid material was filtered and recrystallized from chloroform-methanol mixture yielding 2.28 g (~95 %) of compound **3** as white crystals**.**

M.P.: 153°C.

M.W. calculated for $C_{68}H_{100}O_8$: 1046.

M.S. [m/z]: 1046 (M^+).

E.A. Calcd. (%): C = 78.12; H = 9.64; O = 12.24; Found (%): C = 78.25; H = 9.50; O = 12.25.

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε ($M^{-1}cm^{-1}$)]: 284 / 5550; 291 / 4510.

FTIR (KBr, $\nu_{max.}$, cm^{-1}): ν_{OH} = 3435 cm^{-1}; $\nu_{C=O}$ = 1740, 1760 cm^{-1}.

5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,27-bis-[(ethoxycarbonyl)methoxy]-26,28-(but-2-enyloxy) calix[4]arene **(**compound **4)**

To a mixture of 0.95 mmol compound **3** in acetonitrile (200 mL), 10 mmols of NaH were added. The mixture was stirred 30 min at 40°C. After cooling to room temperature, 6 mmols of crotyl bromide in acetonitrile (20 mL) were added dropwise and the mixture was refluxed for 20 h. The reaction mixture was mixed with ice and then concentrated HCl was added. The reaction product has been extracted in chloroform and successively washed with water and brine and dried over anhydrous $MgSO_4$. After filtration, the chloroform solution was concentrated and ethanol was added. The suspension was allowed to cool in refrigerator (24 h) and the precipitated solid material was filtered and recrystallized from chloroform-ethanol mixture yielding 0.22 g (~20 %) of compound **4** as white crystals**.**

M.P.: 100°C.

M.W. calculated for $C_{76}H_{112}O_8$: 1154.

M.S. [m/z]: 1154 (M^+).

E.A. Calcd. (%): C = 79.12; H = 9.78; O = 11.10; Found (%): C = 79.30; H = 9.80; O = 10.90.

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε ($M^{-1}cm^{-1}$)]: 276 / 3480; 283 / 3410.

FTIR (KBr, $\nu_{max.}$, cm^{-1}): $\nu_{C=O}$ = 1738, 1762 cm^{-1}; $\nu_{=C-H}$ = 969 cm^{-1}.

Results and discussions

The synthesis route for *p-tert*-octyl calix[4]arene derivatives with ethoxycarboxylmethyleneoxy and/or but-2-enyloxy functionalities grafted at the "narrow rim" is depicted in figure 1. Reaction of *p-tert*-octyl calix[4]arene (**1**) with two equivalents of 2-butenyl bromide (crotyl bromide) - *pathway A* - yields the crotyl *p-tert*-octyl calix[4]arene derivative (**2**). In the next step, this intermediate is treated with ethyl bromoacetate - *pathway C* - in order to obtain the new *p-tert*-octyl calix[4]arene derivative with mixed functionalities at the "narrow rim" (compound **4**).

On the other hand, *p-tert*-octyl calix[4]arene (**1**) was treated with ethyl bromoacetate - *pathway B* - to obtain derivatives which contain two substituting groups namely ethyl acetate *p-tert*-octyl calix[4]arene derivative (**3**). In

	Oct-C4 (1)	Oct-C4Cr2 (2)	Oct-C4Es2 (3)	Oct-C4Es2Cr2 (4)
C(C<u>H</u>$_3$)$_3$	0.54, s	0.73, s	0.68, s	0.68, s
C(C<u>H</u>$_3$)$_2$	1.24, s	1.08, s	1.08, s	1.08, s
C-C<u>H</u>$_2$-C	1.58, s	1.31, s	1.31, s	1.26, s
Ar-C<u>H</u>$_2$-Ar (exo)	3.48, brs	3.25 - 3.29, d	3.15 - 3.19, d	3.15 - 3.19, d
Ar-C<u>H</u>$_2$-Ar (endo)	4.23, brs	4.27 - 4.31, d	4.41 - 4.45, d	4.17 - 4.19, d
HC=CH-C<u>H</u>$_3$	-	1.77 - 1.79, d	-	1.65 - 1.67, d
O-C<u>H</u>$_2$-CH=	-	4.43 - 4.45, d	-	4.49 - 4.51, d
-C<u>H</u>=C<u>H</u>-	-	5.53 - 6.05, m	-	5.49 - 5.65, m
O-CH$_2$-C<u>H</u>$_3$	-	-	1.24 - 1.29, t	1.47 - 1.57, t
O-C<u>H</u>$_2$-CH$_3$	-	-	4.14 - 4.21, q	4.14 - 4.21, q
O-C<u>H</u>$_2$-CO	-	-	4.78, s	4.78, s
Ar<u>H</u>	7.00, s	6.81, s 7.00, s	6.74, s 6.89, s	6.73, s 6.79, s
ArO<u>H</u>	9.98, s	7.69, s	7.04, s	-

Table 1
^{1}H-NMR DATA OF *P-TERT*-OCTYL CALIX[4]ARENE DERIVATIVES

	Oct-C4 (1)	Oct-C4Cr2 (2)	Oct-C4Es2 (3)	Oct-C4Es2Cr2 (4)
-<u>C</u>(CH$_3$)$_3$	32.3	27.4	30.9	31.7
(<u>C</u>H$_3$)$_3$	31.6	30.9	31.2	31.9
-<u>C</u>(CH$_3$)$_2$	31.3	32.0	32.3	32.2
-C(<u>C</u>H$_3$)$_2$	32.4	31.8	31.5	31.8
Ar-<u>C</u>H$_2$-Ar	37.8	32.4	38.1	38.0
C-<u>C</u>H$_2$-C	57.2	58.8	57.1	57.2
HC=CH-<u>C</u>H$_3$	-	14.9	-	17.8
O-<u>C</u>H$_2$-CH=	-	60.8	-	60.3
HC=<u>C</u>H-CH$_3$	-	126.5	-	126.4
CH$_2$-<u>C</u>H=CH-CH$_3$	-	132.2	-	132.7
O-CH$_2$-<u>C</u>H$_3$	-	-	14.3	14.2
O-<u>C</u>H$_2$-CH$_3$	-	-	60.4	66.4
O-<u>C</u>H$_2$-CO	-	-	71.2	71.4
-<u>C</u>=O	-	-	170.5	170.5
Ar<u>C</u>-H	126.4 127.6	121.8 127.0	126.3 132.8	126.1 128.4
Ar<u>C</u>-C(CH$_3$)$_2$	143.0	137.7	141.5	144.3
Ar<u>C</u>-O	146.2	150.0	144.3	153.0

Table 2
^{13}C-NMR DATA OF *P-TERT*-OCTYL CALIX[4]ARENE DERIVATIVES

the second step- *pathway D* - the intermediate **3** was treated with crotyl bromide to yield the new *p-tert*-octyl calix[4]arene derivative (compound **4**).

Elemental analysis, mass spectrometry, infrared and UV-Vis spectroscopy, ^{1}H and ^{13}C NMR investigations confirmed the formation of the above mentioned *p-tert*-octyl calix[4]arene derivatives.

^{1}H- and ^{13}C NMR spectra

The "narrow rim" functionalization with alkenyl- and/or ethyl ester groups is well illustrated by ^{1}H and ^{13}C NMR spectra, which show the expected differences in the chemical shifts (table 1 and 2). For the parent calixarene (compound **1**), the chemical shifts of the phenolic OH groups (Ar-OH) appear at 9.98 ppm. The compounds **2** and **3** show this characteristic signal at 7.69 and 7.04 ppm while for the calixarene derivatives with mixed functional groups (compunds **4**), the chemical signal of the phenolic OH groups disappears due to total functionalization. In compound **2,** the chemical shifts of the alkenic moieties appear as multiplete at 5.53 - 6.05 ppm, while the signals corresponding to the protons appear as two doublets at 3.25-3.29 and 4.27-4.31 for the methylene bridge and as singlets at 6.81 and 7.00 ppm for the aromatic ring. In compound **3**, the chemical shifts appear at 3.15-3.19 and 4.41-4.45 ppm for the methylene protons and at 6.74 and 6.89 ppm for the aromatic protons. In the compound **4**, with mixed functional groups, the chemical shifts for methylene bridge protons appear at 3.15-3.19 and 4.17-4.19 ppm as doublets and for aromatic protons at 6.73 and 6.79 ppm as singlets.

^{1}H and ^{13}C NMR spectra show, in all cases, the specific signals for all the protons and carbon atoms present in the compounds **1-4**.

FTIR spectra

The grafting of a variable number of groups on the *p-tert*-octyl calix[4]arene can be monitored by infrared spectroscopy (fig.2).

The parent calixarene i.e. *p-tert*-octyl calix[4]arene (**1**) shows the characteristic absorption band assigned to the OH stretching vibration at 3181 cm^{-1}, while the intermediates **2** and **3** showed the OH vibrations at 3398 cm^{-1} (**2**) and 3435 cm^{-1}(**3**), respectively, due to the destroying of the circular strong hydrogen bonds. For the calixarene derivatives with mixed functional groups (compound **4**), the OH absorption band disappears, due to total functionalization. The alkenyl derivatives show the characteristic deformation vibrations of =C-H bonds at 965 cm^{-1} (**2**) and 969 cm^{-1}(**4**), respectively. The ethyl ester derivatives (compounds **3** and **4**) exhibit the strong absorption peaks assigned to the carbonyl stretching vibration at 1740, 1760 cm^{-1} (**3**) and 1738, 1762 cm^{-1} (**4**), respectively.

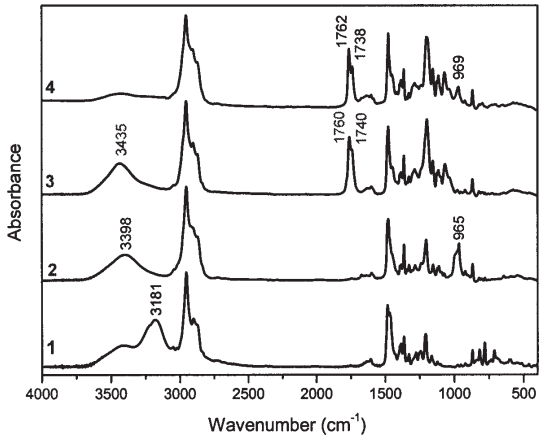

Fig. 2. FTIR spectra of compounds **1** (**Oct-C4**), **2** (**Oct-C4Cr2**), **3** (**Oct-C4Es2**) and **4** (**Oct-C4Es2Cr2**)

UV-VIS spectra

The UV-Vis absorption spectra of the *p-tert*-octyl calix[4]arene derivatives **2-4** illustrate the alkenyl- and/or ester functionalization of the parent *p-tert*-octyl calix[4]arene (**1**). Table 3 presents the characteristic UV-

Compound	Peak # 1		Peak # 2	
	λ_{max} (nm)	ε (l x mol^{-1} x cm^{-1})	λ_{max} (nm)	ε (l x mol^{-1} x cm^{-1})
Oct-C4 (1)	280	12410	288	10240
Oct-C4Cr2 (2)	284	5080	292	3980
Oct-C4Es2 (3)	284	5550	291	4510
Oct-C4Es2Cr2 (4)	276	3480	283	3410

Table 3
UV-Vis DATA OF *P-TERT*-OCTYL CALIX[4]ARENE DERIVATIVES

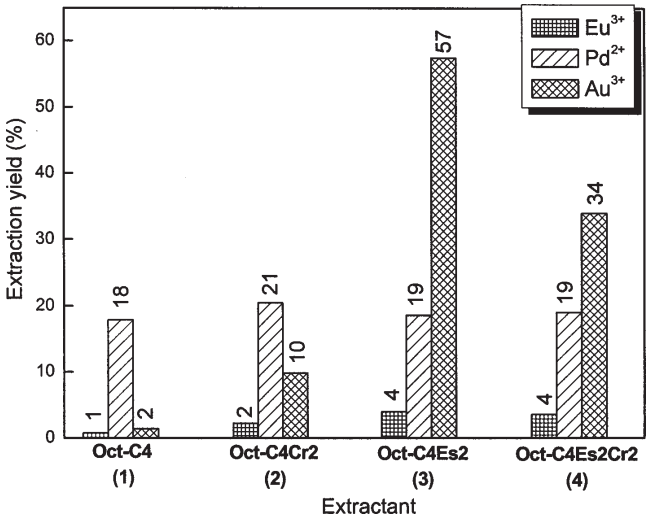

Fig.3. Extraction yield of Eu^{3+}, Pd^{2+} and Au^{3+} from aqueous solution, using $CHCl_3$ solution of compounds **1-4**

Vis absorption data i.e. peak position (λ_{max}) and molar absorption coefficient (**ε**) of the of calix[4]arene derivatives **1-4**.

The UV-Vis absorption spectra of the starting *p-tert*-octyl calix[4]arene (**1**) consist in two strong specific charge-transfer bands (peak #1 and peak #2), whose characteristics are influenced by the alkenyl- and ethylester functionalization.

According to UV-Vis spectra, the specific absorption bands appear at 280, 288 nm (**1**) for the parent calix[4]arene, and at 284, 292 nm (**2**), 284, 291 nm (**3**) and 276, 283 nm (**4**), for the *p-tert*-octyl calix[4]arene derivatives, respectively.

The functionalization brings about the shift of the characteristic bands towards higher energy and the decrease of the molar absorption coefficient, in parallel with the increase of the number of alkenyl- and/or ethylester groups graphted on the calix[4]arene skeleton.

Ability to extract rare earth and precious metals from aqueous solution

The capability of *p-tert*-octyl calix[4]arene functionalized at the "lower rim" with alkenyl- and/or ethylester groups to sequestrate *europium, palladium and gold ions* have been investigated by liquid-liquid extraction. The experiments were performed at *p*H = 2.9 (Eu^{3+}), *p*H = 3.3 (Pd^{2+}) and *p*H = 3.5 (Au^{3+}), using equal volumes of equal concentration of aqueous solution of metallic ion [$Eu(NO_3)_3$, $PdCl_2$ or $HAuCl_4$] and $CHCl_3$ solution of calixarene derivatives (compounds **1-4**). The extraction yield was monitored by ICP-OES spectrometry.

All *p-tert*-octyl calix[4]arene derivatives exhibit a better capability to extract precious mettalic ions, in comparison with the rare earth ions (fig.3). The extraction yield varies between 1 and 4% for europium ions, 18 and 21% for palladium ions and between 2 and 57% for gold ions.

The new calixarene derivatives containing ethylester groups (compounds **3** and **4**) show rather good capability to extract the precious metallic ions from aqueous medium, in opposition to the crotyl derivatives (compound **2**).

In our experimental conditions, the derivative with two ethylester groups exhibits the highest extraction yield, i.e. 57% corresponding to an ability to sequestrate 0.52 mol Au^{3+} per mol calixarene. As expected, the lowest extraction ability was shown by the parent calix[4]arene (**1**), i.e.0.07 mol Eu^{3+} per mol calixarene (1% extraction yield).

The performed tests show that the functionalization of the parent calixarenes increases their complexing abilities towards rare earth and precious metal ions from aqueous solutions.

Conclusions

P-tert-octyl calix[4]arene derivatives with two crotyl and/or two ethylester groups were synthesized and characterized by elemental analysis, mass spectrometry, infrared and UV-Vis spectroscopy as well as by ^1H and ^{13}C NMR investigations. Their ability to extract europium, palladium and gold ions from aqueous medium was also evaluated. The highest extraction ability was found for the calix[4]arene derivative containing two ethylester groups (compound **3**) in relation with gold ions (57% extraction yield; 0.52 mol Au^{3+}/mol calixarene sequestration ratio).

Additional experiments are to be performed in order to use the new derivatives of *p-tert*-octyl calix[4]arene for the sequestration/extraction of rare earth and precious metals from waste waters.

Acknowledgements

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References

1.ASFARI, Z., BOHMER, V., HARROWFIELD, J., VICENS, J., Calixarenes 2001, Kluwer Academic Publishers, Dordrecht, 2001
2.GUTSCHE, C.D., STODDART, J.F., Calixarenes Revisited, The Royal Society of Chemistry, England, Cambridge, 1998
3.ATANASSOVA, M., VASSILEV, N., DUKOV, I., Separation and Purification Technology, **78(2)**, 2011, p.214
4.KULESZA, J., GUZINSKI, M., HUBSCHER-BRUDER, V., ARNAUD-NEU, F., BOCHENSKA, M., Polyhedron, **30(1)**, 2011, p.98
5.ADHIKARI, B.B., GURUNG, M., KAWAKITA, H., OHTO, K., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **71(3-4)**, 2011, p.479
6.YANG, Y., LEE, E.K., ZHOU, H., SUROWIEC, K., BARTSCH, R.A., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **70(1-2)**, 2011, p.197
7.FAYZULLIN, D.A., VYLEGZHANINA, N.N., GNEZDILOV, O.I., SALNIKOV, V.V., GALUKHIN, A.V., STOIKOV, I. I., ANTIPIN, I.S., ZUEV, YU.F., Applied Magnetic Resonance, **40(2)**, 2011, p.231
8.MONNEREAU, C., REBILLY, J.-N., REINAUD, O., European Journal of Organic Chemistry, **2011(1)**, 2011, p.166
9.SAPONAR, A., SILAGHI-DUMITRESCU, I., POPOVICI, E.-J., POPOVICI, N., Rev. Chim. (Bucharest), **58,** no. 5, 2007, p.481

10.SAPONAR, A., SILAGHI-DUMITRESCU, I., POPOVICI, E.-J., POPOVICI, N., Studia Universitatis Babes-Bolyai, Chemia, **LII (4)**, 2007, p.67
11.SAPONAR, A., POPOVICI, E.-J., POPOVICI, N., BICA, E., NEMES, G., PETRONELA, P., SILAGHI-DUMITRESCU, I., Rev. Chim. (Bucharest), **60**, no. 3, 2009, p.278
12.SAPONAR, A., POPOVICI, E.-J., GRECU, R., SILAGHI-DUMITRESCU, I., POPOVICI, N., Studia Universitatis Babes-Bolyai, Chemia, **LIV (4)**, 2009, p.203
13.SAPONAR, A., POPOVICI, E.-J., NEMES, G., POPOVICI, N., PERHAITA, I., SILAGHI-DUMITRESCU, I., Rev. Chim. (Bucharest), **62**, no. 6, 2011, p.596
14.SAYIN, S., OZCAN, F., YILMAZ, M., Journal of Hazardous Materials, **178(1-3)**, 2010, p.312
15.SAYIN, S., YILMAZ, M., TAVASLI, M., Tetrahedron, **67(20)**, 2011, p.3743
16.TORGOV, V.G., KOSTIN, G.A., US, T.V., KORDA, T.M., KLIMCHUK, O.V., MIROSHNICHENKO, S.I., SUWINSKA, K., VARNEK, A.A., KALCHENKO, V.I., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **71(1-2)**, 2011, p.67
17.YANG, Y., ARORA, G., FERNANDEZ, F.A., CRAWFORD, J.D., SUROWIEC, K., LEE, E.K., BARTSCH, R.A., Tetrahedron, **67(7)**, 2011, p.1389
18.ADHIKARI, B.B., OHTO, K., GURUNG, M., KAWAKITA, H., Tetrahedron Letters, **51(27)**, 2010, p.3481
19.DUTU, G., CRISTEA, C., EDE, B., SIMA, V., SAPONAR, A., POPOVICI, E-J., SĂNDULESCU, R., Farmacia, **58(4)**, 2010, p.430
20.DUTU, G., CRISTEA, C., BODOKI, E., HARCEANGA, V., SAPONAR, A., POPOVICI, E.-J., SĂNDULESCU, R., Farmacia, **59(2)**, 2011, p.147
21.DINAKE, P., PROKHOROVA, P.E., TALANOV, V.S., BUTCHER, R.J., TALANOVA, G.G., Tetrahedron Letters, **51(38)**, 2010, p.5016
22.ENACHE, I.V., MUTIHAC, L., OTHMAN, A.B., VICENS, J., Journal of Inclusion Phenomena and Macrocyclic Chemistry. **71(3-4)**, 2011, p.537
23.HAJIPOUR, A.R., HABIBI, S., RUOHO, A.E., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **69(1-2)**, 2011, p.107
24.MAKRLIK, E., VANURA, P., Journal of Radioanalytical and Nuclear Chemistry, **289(3)**, 2011, p. 663
25.MAKRLIK, E., VANURA, P., SELUCKY, P., Journal of Radioanalytical and Nuclear Chemistry, **287**, 2011, p.899
26.MAKRLIK, E., VANURA, P., SELUCKY, P., Journal of Radioanalytical and Nuclear Chemistry, **287(1)**, 2011, p.277
27.MOKHTARI, B., POURABDOLLAH, K., DALALI, N., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **69(1-2)**, 2011, p.1
28.PODYACHEV, S.N., BURMAKINA, N.E., SYAKAEV, V.V., SUDAKOVA, S.N., HABICHER, W.D., KONOVALOV, A.I., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **71(1-2)**, 2011, p.161
29.QAZI, M.A., QURESHI, I., MEMON, S., Journal of Fluorescence, **21(4)**, 2011, p.1703
30.SAPONAR, A., POPOVICI, E.-J., PERHAIŢA, I., POPOVICI, N., SILAGHI-DUMITRESCU, I., Studia Universitatis Babes-Bolyai, Chemia, **XLV, 2, TOM I**, 2010, p. 133
31.TENKOVTSEV, A.V., DUDKINA, M.M., SCHERBINSKAYA, L.I., ASEYEV, V., TENHU, H., Polymer, **51(14)**, 2010, p.3108
32.TORGOV, V. G., US, V. V., KORDA, T. M., KOSTIN, G. A., KALCHENKO, V. I., Russian Journal of Inorganic Chemistry, **56(3)**, 2011, p.473
33.YANG, F., HUANG, Z., XIE, J., ZHANG, X., GUO, H., Journal of Inclusion Phenomena and Macrocyclic Chemistry, **70(1-2)**, 2011, p.11
34.YIN, R.H., WU, Q.S., CHEN, Y., Chemical Papers, **61(3)**, 2007, p.224
35.ARAKI, K., YANAGI, A., SHINKAI, S., Tetrahedon, **49(31)**, 1993, p.6763

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