

NEW MATERIALS BASED ON PHOSPHORILATED CALIX[n]ARENE

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The paper refers to the synthesis and characterisation of some new materials based on phosphorilated calix[n]arene that could act as extracting agent for rare earths ions. The synthesis is based on the reaction between dichlorophenylphosphin oxide and p-tertbutylcalix [n]arene (n=4, 6, 8). FT-IR, UV-Vis, ¹H-NMR, ³¹P-NMR confirm the purity of the synthesised compounds.

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1. Introduction

Calix[n]arene are a class of compounds with three-dimensional cavity that can host cations¹, anions² and neutral molecules³ (Fig. 1).

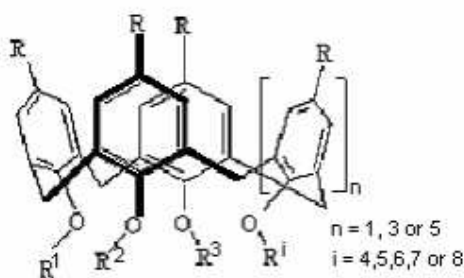


Fig. 1. Spatial representation of substituted calix[n]arene.

In order to achieve selectivity for such guest molecules, calix[n]arene must be functionalised with organic groups, both at “wide rim” (formerly “upper rim”) and “narrow rim” (formerly “lower rim”)⁴.

In the parent calix[n]arene, the “narrow rim” consists from hydroxyl groups forming a very stable cyclic H-bond network. The hydroxyl groups can be functionalised by organic groups such as alkyls, esters and amides. The “wide rim” is located above the aromatic rings. “Wide rim” substituted calix[n]arene are synthesised by replacing the *para*-alkyl groups (t-butyl, t-pentyl, t-octyl) of the parent calix[n]arene with groups that generally are less bulky and more branched than *para*-alkyl substitutes.

An important class of calix[n]arene derivatives are the organo-phosphorus functionalised compounds.⁴ The functionalisation of the calix[n]arene at the “narrow rim” can be performed directly,

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by the reaction with organo-phosphorus halide in strong alkaline medium (NEt_3 , NaOH , CsF , KH or pyridine).⁵⁻¹³

To obtain "wide rim" functionalised calixarene, after replacing the p-alkyl-substituted groups with halogen, followed by lithiation and reaction with organo-phosphorus has to be performed.¹⁴⁻²²

The organo-phosphorus functionalised calix[n]arene ($n = 4, 6, 8$) are very important for their high chelating ability towards different transition metals²³⁻²⁵, alkaline and alkaline-earth metals²⁶⁻²⁸ and lanthanide series.²⁹ For instance, the calixarene functionalised with organo-phosphorus groups are among the best know extracting agents for lanthanide series.³⁰⁻³³

Taking into account the high utilisation potential, the synthesis of new materials based on phosphorilated calix[n]arene was attempted. The paper reports our results referring to the preparation of some (P-phenyldioxaphenylphosphocin)-p-alkyl(R) calix[n]arene derivatives.

2. Experimental

The synthesis of bis, tris and tetra- (P-phenyldioxaphenylphosphocin)-p-alkyl(R) calix[n]arene ($R = t\text{-Butyl}$ or $t\text{-Octyl}$ and $n=4, 6, 8$) was performed using calix[n]arene and dichlorophenylphosphinoyl, in the presence of sodium hydride (NaH), in an appropriate solvent. All the syntheses were performed under inert atmosphere.

In one necked flask were introduced 1.15-1.54 mmoles of p-alkyl-calix[n]arene ($R = t\text{-Butyl}$ or $t\text{-Octyl}$ and $n=4, 6, 8$) and 4.59-6.16 mmoles of NaH dissolved in 100-150 ml of acetonitril, toluene or tetrahydrofuran. After the suspension was stirred for 24 hours at room temperature, 2,3-15 mmoles of dichlorophenylphosphinoyl (PhPOCl_2) were added. The mixture was refluxed 24 hours and, after cooling, the solvent was evaporated at low pressure. The residue was treated with chloroform. The chloroform solution was washed with water and brine successively and dried 24 hours on anhydrous Na_2SO_4 . After filtration, the chloroform layer was concentrated at low pressure and then kept in a cool place until the complete compound crystallisation. The compounds were re-crystallised from chloroform/ethanol. The new calix[n]arene derivatives were obtained with 44-54% yield.

The structure and purity of new calixarene derivatives was determined by FT-IR, $^1\text{H-NMR}$, $^{31}\text{P-NMR}$ spectroscopy.

Melting points were determined with MEL-TEMP apparatus in a sealed capillary and are uncorrected. $^1\text{H-NMR}$ spectra were recorded with a Bruker spectrometer (80MHz and 300 MHz) in CDCl_3 (tetramethylsilane as reference). $^{31}\text{P-NMR}$ spectra were registered from CDCl_3 , with a 200 MHz Bruker spectrometer (phosphoric acid as reference). FT-IR spectra were recorded with JASCO-615 Spectrometer, in KBr pellet technique.

3. Results

Main characteristics of the new compound are as follows:

bis-(P-phenyldioxaphosphocin)-p-tertbutylcalix[4]arene (I)

Melting point = 90-92 °C.

FT-IR: (KBr , cm^{-1}): ν_{OH} : – absent; $\nu_{\text{P=O}}$: 1189,38 cm^{-1} ; $\nu_{\text{P-O-C}}$: 970,02 cm^{-1} ; $\nu_{\text{P-C}}$: 687,98 cm^{-1} ;

$^1\text{H-NMR}$ (400MHz, δ_{ppm} , CDCl_3): 6.70-7.29(m, 18H, C_6H_2 and C_6H_5); 3.49-5.45(6d, 12H, ArCH_2Ar ,

$^2J_{\text{HH}} = 14\text{Hz}$); 0.68-1.43(m, 36H, tButyl).

$^{31}\text{P-NMR}$ (200MHz, δ_{ppm} , CDCl_3 , ppm): 22.43; and 12.42 (2 s, 2P) .

bis-(P-phenyldioxaphosphocin)-p-tertoctylcalix[4]arene (II)

Melting point = 170-173 °C.

FT-IR: (KBr , cm^{-1}): ν_{OH} : – absent; $\nu_{\text{P=O}}$: 1203,85 cm^{-1} ; $\nu_{\text{P-O-C}}$: 971,21 cm^{-1} ; $\nu_{\text{P-C}}$: 696,18 cm^{-1} ;

$^1\text{H-NMR}$ (300MHz, δ_{ppm} , CDCl_3): 6.62-7.20(m, 18H, C_6H_2 and C_6H_5); 3.50 and 4.3(2m, 8H, ArCH_2Ar); 0.58-1.26(m, 68H, tOctyl)

$^{31}\text{P-NMR}$ (200MHz, δ_{ppm} , CDCl_3 , ppm): 23.06 and 6.36(2 s, 2P) .

tris-(P-phenyldioxaphosphocin)-p-tertbutylcalix[6]arene (III)

Melting point = 105-108 °C.

FT-IR:(KBr, cm^{-1}): ν_{OH} : – absent; $\nu_{\text{P=O}}$: 1203,40 cm^{-1} ; $\nu_{\text{P-O-C}}$: 954,59 cm^{-1} ; $\nu_{\text{P-C}}$: 694,25 cm^{-1} ;

$^1\text{H-NMR}$ (300MHz, δ_{ppm} , CDCl_3): 6.35-7.82(m, 27H, C_6H_2 and C_6H_5); 3.40-4.7(3m, 12H, ArCH_2Ar); 1.03-1.35(m, 54H, tButyl)

$^{31}\text{P-NMR}$ (200MHz, δ_{ppm} , CDCl_3 , ppm): 21.32; 13.87; 12.39; 11.05 and 9.44 (5s, 3P)

tris-(P-phenyldioxaphosphocin)-p-tertoctylcalix[6]arene (IV)

Melting point = 140-143 °C.

FT-IR:(KBr, cm^{-1}): ν_{OH} : – absent; $\nu_{\text{P=O}}$: 1206,54 cm^{-1} ; $\nu_{\text{P-O-C}}$: 955,72 cm^{-1} ; $\nu_{\text{P-C}}$: 694,76 cm^{-1} ;

$^1\text{H-NMR}$ (80MHz, δ_{ppm} , CDCl_3): 6.30-7.70(m, 27H, C_6H_2 and C_6H_5); 3.50-4.40(m, 12H, ArCH_2Ar); 1.66(s, 12H, CH_2); 1.24(s, 36H, $\text{C}(\text{CH}_3)_2$); 0.69(s, 54H, $\text{C}(\text{CH}_3)_3$).

$^{31}\text{P-NMR}$ (200MHz, δ_{ppm} , CDCl_3 , ppm): 22.66; 13.54 and 8.89 (3s, 3P).

tetra-(P-phenyldioxaphosphocin)-p-tertbutylcalix[8]arene (V)

Melting point = 228-230 °C.

FT-IR:(KBr, cm^{-1}): ν_{OH} : – absent; $\nu_{\text{P=O}}$: 1202,40 cm^{-1} ; $\nu_{\text{P-O-C}}$: 946,88 cm^{-1} ; $\nu_{\text{P-C}}$: 692,80 cm^{-1} ;

$^1\text{H-NMR}$ (300MHz, δ_{ppm} , CDCl_3): 6.70-7.30(m, 36H, C_6H_2 and C_6H_5); 3.50 and 4.65(2d, 16H, ArCH_2Ar); 1.17-1.3(m, 72H tButyl).

$^{31}\text{P-NMR}$ (200MHz, δ_{ppm} , CDCl_3 , ppm): 22.79; 13.67; 12.01 and -1.75 (4s, 4P).

tetra-(P-phenyldioxaphosphocin)-p-tertoctylcalix[8]arene (VI)

Melting point = 285-287 °C.

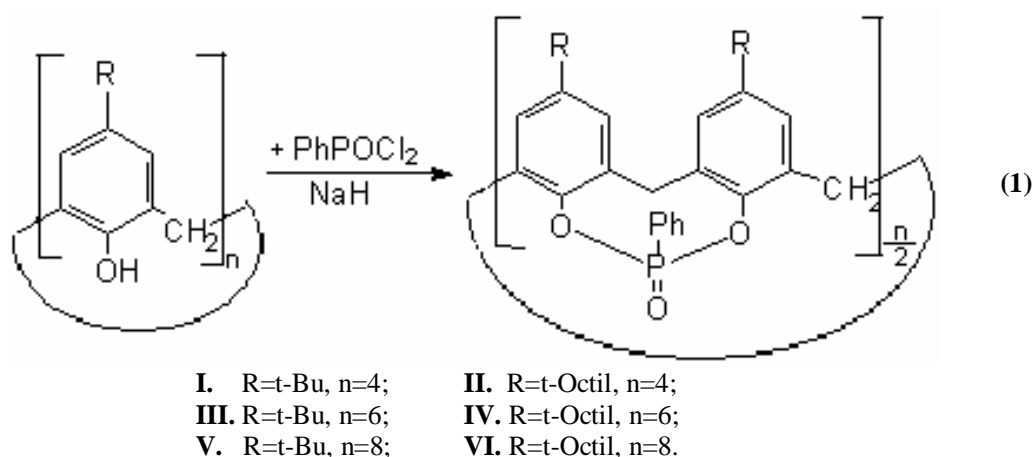
FT-IR:(KBr, cm^{-1}): ν_{OH} : – absent; $\nu_{\text{P=O}}$: 1190,35 cm^{-1} ; $\nu_{\text{P-O-C}}$: 966,16 cm^{-1} ; $\nu_{\text{P-C}}$: 695,21 cm^{-1} ;

$^1\text{H-NMR}$ (80MHz, δ_{ppm} , CDCl_3): 6.50-7.50(m, 36H, C_6H_2 and C_6H_5); 3.70 and 4.30(2d, 16H, ArCH_2Ar); 1.66(s, 16H, CH_2); 1.24(s, 48H, $\text{C}(\text{CH}_3)_2$); 0.69(s, 72H, $\text{C}(\text{CH}_3)_3$).

$^{31}\text{P-NMR}$ (200MHz, δ_{ppm} , CDCl_3 , ppm): 21.86; 15.99; 12.16 and 10.68 (4s, 4P).

4. Discussion

The synthesis of new calix[n]arene derivatives was attempted by selective alkylation with dichlorophenylphosphinoyl in the presence of sodium hydride (**reaction 1**).



In $^1\text{H-NMR}$ spectra of parent calix[n]arene the chemical shift of the free hydroxyl groups appears at 9.3-10.2 ppm. In the new compounds, no such signals was observed (Fig. 2 and 3), thus illustrating that all OH groups of the parent calixarene were functionalised with organo-phosphorus groups.

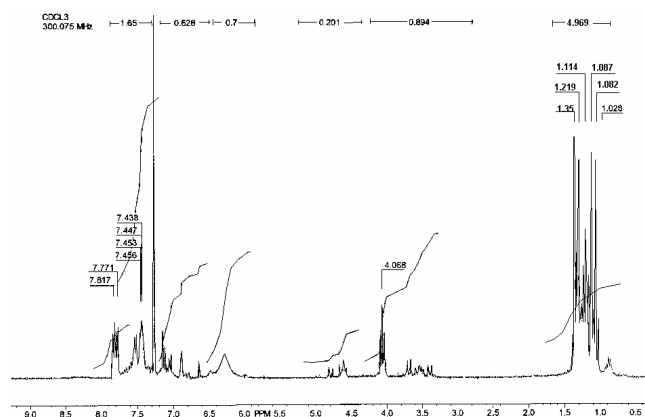


Fig. 2. ^1H -NMR spectra of the tris-(P-phenyldioxaphosphocin)-p-tertbutylcalix[6]arene (III).

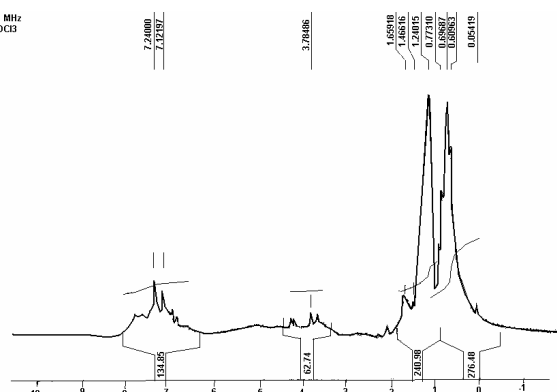


Fig. 3. ^1H -NMR spectra of the tetra-(P-phenyldioxaphosphocin)-p-tertoctylcalix[8]arene (VI).

The protons from the phenylphosphinoyl bridge give broad signals in the same aromatic region as the protons from the calix[n]arene skeleton ($\delta = 6.5\text{--}7.5$ ppm). The chemical shifts of p-alkyl groups and of methylene bridge from parent calix[n]arene and the new functionalized compounds appear at 0.6–1.5 ppm.

The presence of the phosphorus atoms in the new materials was confirmed by ^{31}P -NMR spectra. Two (Fig. 4), three (Fig. 5) or four signals could be noticed, thus illustrating the number of phosphorus atoms from the calix[n]arene bridge.

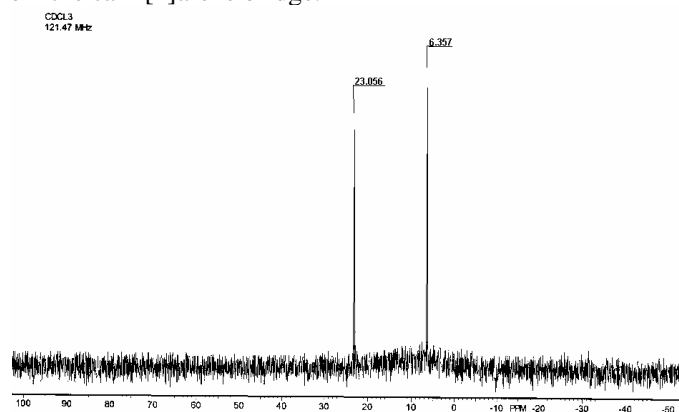


Fig. 4. ^{31}P -NMR spectra of the bis-(P-phenyldioxaphosphocin)-p-tertoctylcalix[4]arene (II).

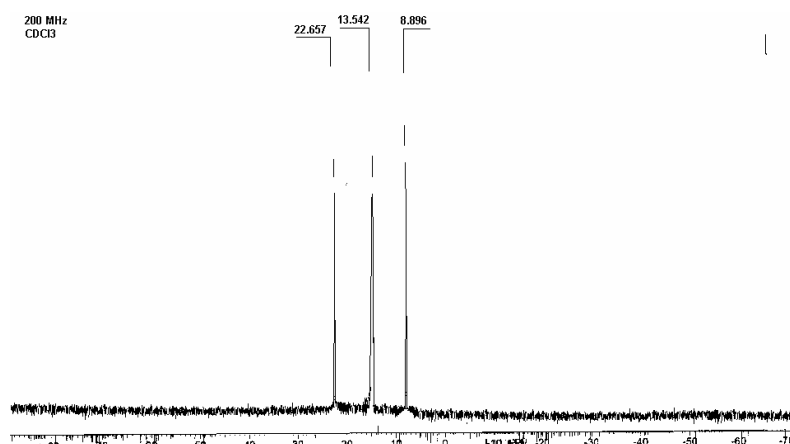


Fig. 5. ^{31}P -NMR spectra of the tris-(P-phenyldioxaphosphocin)-p-tertoctylcalix[6]arene (IV).

The FT-IR spectroscopy is a very good investigation method for characterization of calixarene derivatives. In the p-tertbutylcalix[4]arene and p-tertoctylcalix[4]arene spectra the OH group vibrations appears at 3172.81 cm^{-1} ; 3173.29 cm^{-1} respectively whereas in the spectra of all functionalised calix[4]arene, no vibration of this group were observed (Fig. 6).

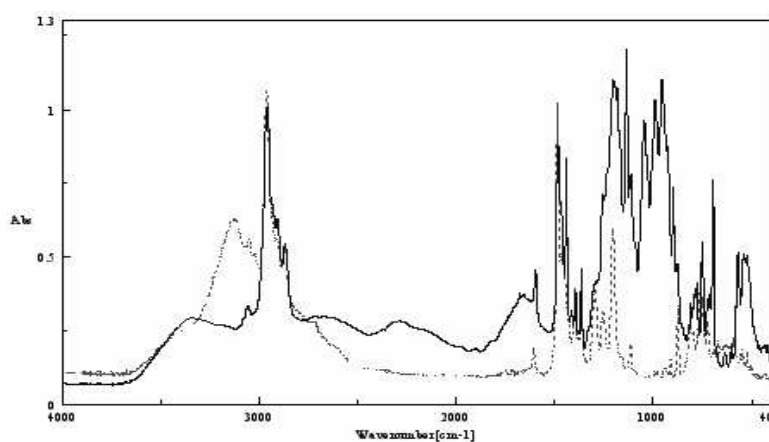


Fig. 6. Infrared spectra of the tris-(P-phenyldioxaphosphocin)-p-tertbutylcalix[6]arene (III) (straight line) as compared with the original p-tertbutylcalix[6]arene (dashed line).

Large bands at $1189\text{--}1203\text{ cm}^{-1}$ of the P=O groups and 970 cm^{-1} of P-O-C groups could be noticed. In the p-tertbutylcalix[6]arene and p-tertoctylcalix[6]arene spectra, the OH group vibrations appears at 3150 cm^{-1} and 3152 cm^{-1} , respectively. In the calix[6]arene derivatives (III and IV) spectra, neither of these vibration could be observed, whereas intensive bands at $1203\text{--}1206\text{ cm}^{-1}$ assigned to P=O groups and $954\text{--}955\text{ cm}^{-1}$ assigned P-O-C groups were noticed.

The structure of the new calix[n]arene derivative was proved by ^1H -NMR, ^{31}P -NMR and FT-IR spectroscopic methods. The structure was in good agreement with that wanted.

In order to obtain a first insight into the chelating properties of these new materials, the extraction of europium from water solutions with variable concentration was attempted. Promising results were obtained, thus proving that this class of compounds could behave as potent extractants of lanthanide from residual waters.

5. Conclusion

The spectroscopic investigation confirms the formation of six new calix[n]arene derivatives, functionalized with two, three or four phenylphosphin oxide bridges. The new compounds (not mentioned in the literature) could show high selectivity and extractability for lanthanide ions and could be used for rare-earth ions separation.

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