



# Anionic *tert*-butyl-calix[4]arenes substituted at the narrow and wide rim by cobalt bis(dicarbollide)(1<sup>−</sup>) ions and CMPO-groups. Effect of stereochemistry and ratios of the functional groups on the platform on the extraction efficiency for Ln(III)/An(III)

Bohumír Gruner<sup>a,\*</sup>, Volker Böhmer<sup>b</sup>, Crenguta Dordea<sup>b</sup>, Pavel Selucký<sup>c</sup>,  
Mária Bubeníková<sup>c</sup>

<sup>a</sup>Institute of Inorganic Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Husinec-Řež 1001, 25068 Řež, Czech Republic

<sup>b</sup>Abteilung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

<sup>c</sup>Nuclear Research Institute a. s., Husinec-Řež 130, 25068 Řež, Czech Republic

## ARTICLE INFO

### Article history:

Received 28 February 2013

Received in revised form

19 April 2013

Accepted 22 April 2013

This paper is dedicated to Professor Vladimir I. Bregadze on the occasion of his 75th birthday in recognition of his outstanding contributions to cage-boron chemistry.

### Keywords:

Calixarenes

Carboranes

Actinides

Lanthanides

Liquid–liquid extraction

## ABSTRACT

Two ionic calix[4]arenes substituted at the narrow rim with an unpaired number (*n*) of cobalt bis(dicarbollide)(1<sup>−</sup>) anions (**1<sup>−</sup>**) (*n* = 1 and 3) and (4 − *n*) CMPO groups (**3c**, **4c**) have been synthesized via a three-step procedure based on nitrile substituted calix[4]arene precursors. Conjointly with them, the compound with a paired ratio of the groups, where *n* = 2 and the same substituents are located in mutually adjacent 1,2-positions, is reported (**5c**). Another compound with the paired ratio, but from a wide rim series (**6c**) (*n* = 2) was successfully prepared starting from calix[4]arenes substituted with two nitro functions and two −OH sites available for further modifications. The reaction steps included, a) O-alkylation of the hydroxy functions present on the same rim by the 1-dioxane derivative [8-O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O<sup>(+)</sup>]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-3,3'-Co] (**2**) used as the reactive building block resulting in the respective ionic nitriles (**3a–5a**) or nitro compound (**6a**); b) Reduction of the nitrile or nitro function(s) to the respective amino/ammonio derivatives (**3b–6b**) using either a BH<sub>3</sub>SMe<sub>2</sub> or Pd catalyzed reaction with hydrazine hydrate (for **6b**); c) the ammonio functions in these derivatives were subsequently converted to CMPO group(s) by the reaction with nitrophenyl ester of diphenylphosphoric acid. Pure *cone* conformers were isolated in moderate to good yields. The extraction properties for the An(III)/Ln(III) group of elements have been studied. The new ionic calixarenes still proved highly efficient extraction properties for M<sup>3+</sup>, but lower than the previously reported lower rim calixarene with *n* = 2, used here as the reference compounds **R-7** and **R-8** for comparison. This observation further confirms that the preorganization of the two functions (ion **1<sup>−</sup>** and CMPO) in the paired ratios and in alternating fashion at calixarene low rim has the unique character for attaining the highest extraction efficiency.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

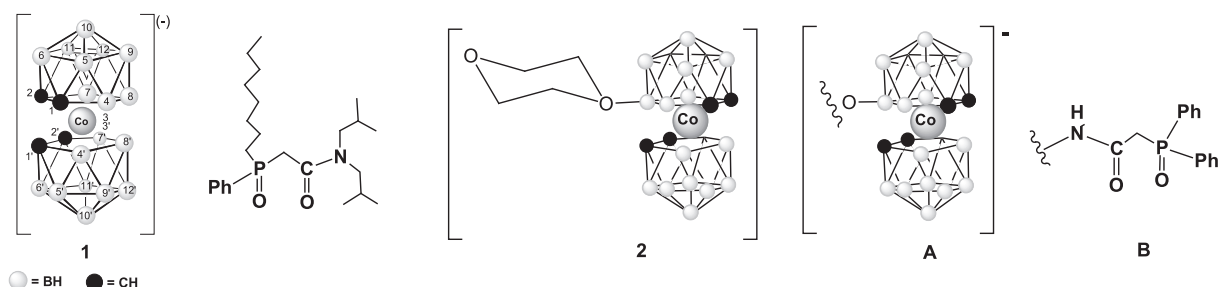
Calix[4]arenes [1–4] represent a versatile platform that can serve readily for the assembly of various functional groups in a pre-defined spatial arrangement. Several efficient extraction systems have been reported for the partitioning of the radionuclides [5] <sup>137</sup>Cs [6–9] and <sup>90</sup>Sr [10,11], as well as actinides and lanthanides An(III)/Ln(III) [12] from strongly acidic high level activity nuclear waste (HLW). Their efficiency and selectivity emerged upon the

incorporation of several (potentially different) chelating groups on the narrow and/or wide rim of the calixarene platform, where a pre-organized arrangement allows for their cooperative action. The calix[4]arenes functionalized by carbamoyl methyl diphenyl phosphine oxide (CMPO) (Fig. 1) groups at the wide [12–16] or narrow rim [12,17,18] belong to the most efficient compounds for An(III)/Ln(III) extraction. However, the use of calixarenes (and other organic ionophores) in the treatment of strongly acidic HLW, is often accompanied by the unwanted co-transport of nitrate ions into the organic phase.

The singly charged cobalt bis(dicarbollide)(1<sup>−</sup>), [(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>-3-Co]<sup>−</sup>, cluster ion (**1<sup>−</sup>**) (see Fig. 1) is known for its extraordinarily

\* Corresponding author. Fax: +420 220940161.

E-mail address: [gruner@iic.cas.cz](mailto:gruner@iic.cas.cz) (B. Gruner).



**Fig. 1.** Schematic presentations of cobalt bis(dicarbollide) ion (**1**), the technically used CMPO, cobalt bis(dicarbollide) ion dioxane derivative (**2**) used to introduce the anion on the platform and the structural elements **A**<sup>−</sup> and **B** corresponding to the functional groups.

high chemical and thermal stability, hydrophobicity and inorganic superacid behaviour [19,20]. When used in synergistic mixtures with various organic ionophores [21–23], this hydrophobic ion is capable to form tight ion pairs with target radionuclides and intermolecularly compensate their positive charge. This reduces or eliminates the nitrate co-transport into the organic phase. Another approach consists in covalent bonding of functional groups able to complex target nuclides directly to the cage of the ion **1**<sup>−</sup> [21,22]. Early examples of such ligands for Cs<sup>+</sup> complexation and extractions consisted of B(4,8',8,4') bis(arylene) bridged cobalt bis(dicarbollides) [24], that proved to have extraordinarily high efficiency, ortho and meta cobalt bis(dicarbollides) substituted with two or four phenyl groups at carbon atoms [25], crown ethers for Sr<sup>2+</sup> extraction [26] or by alkylether groups [27,28]. The latter type was also tested as an efficient carrier for trivalent radionuclides across supporting liquid membranes [28]. A significant positive synergistic effect of the covalent bond on extraction of trivalent radionuclides (Ln/An) has been observed for structurally simpler combinations of cobalt bis(dicarbollide) (**1**<sup>−</sup>) anion **1**<sup>−</sup> and CMPO group [29–33] or for ionic scaffolds comprising two anions attached to the diglycolic acid platform that served also as the chelating group [34–36]. In these cases, a tight intramolecular complexation and shielding of the ions towards hydrating water could be considered as the main factor for the enhanced extraction efficiency.

Some years ago, the possibility to covalently bind the ionic boron cluster to calix[4]arene and resorcin[4]arene platforms was also successfully addressed [37]. Later, we have shown that the regioselective mixed substitution of calixarene platform at the narrow rim by two CMPO functions and two cobalt bis(dicarbollide) ions resulted in extraordinarily high extraction efficiency for An(III)/Ln(III) group extraction even from strongly acidic solutions [38,39]. The effects of the length of the spacer for CMPO groups and the possible conformations *cone*/1,3-*alternate* were studied. The highest efficiency has been observed for ionic species in *cone* conformation containing both groups attached to the platform *via* flexible organic spacers of similar length [22,38,39].

In this paper, we focus on effects related to several other important structural factors that can influence the extraction properties. The structural changes address mainly the number of the functional groups, stereochemical aspects of the preorganization of groups at the platform and the ionic charge of the resulting ligands affecting the charge balance over the assumed complex with the target cations. The synthetic results currently complete the previous study [39] covering now the whole range of possible modifications: from these relating to paired and unpaired ratios of cobalt bis(dicarbollide) ion to CMPO functions over their mutual position at the calixarene narrow rim, to the compound substituted at the wide rim. Extraction properties are evaluated and compared here for all various types of compounds possessing a different stereochemistry. Extraction data are presented in connection with the reference compounds from the previous series, where  $n = 2$  [39].

## 2. Synthesis

### 2.1. Cobalt bis(dicarbollide)-CMPO *t*-Bu-calix[4]arenes substituted at a narrow low rim

One of the aims of the synthetic part of this study was to prove the feasibility of preparing and characterising compounds regioselectively substituted by unpaired ratios ( $n$ ) of the two groups **A** and **B** (see Fig. 1). As could be anticipated, variations in the number of charged cobalt bis(dicarbollide) ions (**A**) can, in principle, strongly influence several factors that play an important role in synthesis, i.e., conformational interconversions in the initial step, solvation and solubility of the transient species and their aggregations or assembly during reactions and isolations.

As has been reported previously [39], the clean alkylation of the calixarenes that were already substituted with two cobalt bis(dicarbollide) ions was difficult to carry out under anhydrous conditions (usually needed for deprotonation of the –OH groups) due to difficulties in removing water and residual solvents from the respective alkali metal salts. Thus, the reversal procedure was applied using calixarene intermediates (**III** and **IV**) that were already modified with three or one nitrile functions as the starting compounds (see Schemes 1 and 2). The length of the propyloxy (or butyloxy after subsequent reduction) spacer was selected in accord with the previous optimisation of the reaction conditions performed over series of compounds with paired ratios of the substituents **A** and **B**, where  $n = 2$  [39]. Similarly as in these reported syntheses, the reaction pathways consisted of three steps that were conducted in a step-wise manner including the isolation of the intermediates and their characterisation by <sup>1</sup>H, <sup>11</sup>B NMR spectroscopy and ESI MS after each reaction step. The first alkylation step using the ring cleavage of [8-O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O<sup>+</sup>-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-3,3'-Co] (**2**) and leading to the respective ionic nitrile species **3a** and **4a** proceeded under controlled conditions with the formation of *cone* conformers in high yields. These could be isolated in pure form by crystallisation and chromatography.

The most critical step of the whole synthesis consisted of purifications and characterisation of the amino derivatives (**3b** and **4b**), particularly with respect to **3b** after the second, pertinent reduction step by BH<sub>3</sub>·Me<sub>2</sub>S. This can probably be attributed to the formation of stable aggregates in the solution due to the presence of strong intermolecular hydrogen bonds NH<sub>2</sub>–H<sup>+</sup>–**1**<sup>−</sup>, or to the slow intramolecular exchange of an extra proton between three butylene amine groups present in the molecule and their interactions with ion **1**<sup>−</sup>. In fact, compound **3b** contains one anion **1**<sup>−</sup>, one NH<sub>3</sub><sup>+</sup> group and two NH<sub>2</sub> groups and the proton can probably exchange slowly between the three available positions. This results in a broadening of the resonances in the <sup>1</sup>H and <sup>11</sup>B NMR spectra, which may also seem to reflect the presence of several different stereochemical positions of the clusters within a larger molecular assembly. This

Download English Version:

<https://daneshyari.com/en/article/1323683>

Download Persian Version:

<https://daneshyari.com/article/1323683>

[Daneshyari.com](https://daneshyari.com)