



# Halogen protected cobalt bis(dicarbollide) ions with covalently bonded CMPO functions as anionic extractants for trivalent lanthanide/actinide partitioning

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## ABSTRACT

Halogen protected CMPO derivatives of the cobalt bis(dicarbollide) ion ( $\mathbf{1}^-$ ) were synthesized with the aim to develop efficient extraction agents with increased stability for liquid–liquid extraction of lanthanides and actinides from high-level activity nuclear waste. New halogen protected compounds of the general formulation  $[3,3'-\text{Co(III)}-(8\text{-CMPO}-(\text{CH}_2\text{-CH}_2\text{O})_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(8'\text{-X-}1',2'\text{-C}_2\text{B}_9\text{H}_{10})]^-$  (where X = Cl, Br, I; CMPO =  $\text{Ph}_2\text{P}(\text{O})\text{-CH}_2\text{C}(\text{O})(t\text{-C}_8\text{H}_{17})\text{N-}$ ) ( $\mathbf{4a-c}$ ), were prepared and studied for Ln(III)/An(III) group extraction. These compounds were accessible via halogenated zwitterionic amino derivatives  $[3,3'-\text{Co(III)}-(8\text{-}t\text{-C}_8\text{H}_{17}\text{NH}_2\text{-(CH}_2\text{-CH}_2\text{O})_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(8'\text{-X-}1',2'\text{-C}_2\text{B}_9\text{H}_{10})]$  ( $\mathbf{3a-c}$ ), prepared by several different synthetic methods. All the compounds were characterized by a combination of  $^{11}\text{B}$  NMR,  $^1\text{H}$  high field NMR, ESI-MS, HPLC and other methods. The effect of the halogen in the structures of  $\mathbf{4a-c}$  on the extraction properties is outlined. In general, these compounds preserve good extraction efficiency and exhibit a better stability. On the other hand, the character of the halogenated ion  $\mathbf{1}^-$  seems to prevail in these compounds and their best extraction efficiency was achieved in more polar auxiliary solvents such as nitro-, chloro-solvents or a laurylonitrile–dodecane mixture than in mixtures of hexyl methyl ketone (HMK) and dodecane (D) applied as the optimum solution for extraction with the parent compound  $\mathbf{4}$ , which contains no halogen in the structure. The reason for this behaviour can be seen in the substitution of the polarized  $\text{B}(8')\text{-H}^{\delta-}$  bond, which may contribute to complexation or protonation at the  $\text{B}(8)\text{-O}$ -site, smoothing thus the solubility of  $\mathbf{4}$  in low polar solvents.

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## 1. Introduction

Nuclear power plants over the world produce thousands of tons of radioactive waste every year. This dangerous waste has to be stored in repositories for more than 100 000 years before the radioactivity drops to a level comparable to natural uranium. If the long-lived minor actinides(III) remaining in the waste after the PUREX process are separated from the spent fuel and eventually transmuted, the time necessary for storage can be significantly shortened, as estimated, to only about 1000 years [1,2]. However, a necessary condition to attain this target is selective separation of  $\alpha$ -emitters from the waste [3].

In the currently most studied methods for the extraction of trivalent radionuclides either substituted malonamides (DIAMEX process) [1,4–8] or (*N,N*-dialkyl-carbamoylmethyl)-dialkyl phosphine oxides (CMPO) (TRUEX process) [3,6,9–12] are used. Recently, also TODGA [7,13,14], CMPO substituted calixarenes [15] and several other promising compounds have been studied for this

purpose [16,17]. These organic ionophores are able to tightly complex the  $\text{M}^{3+}$  cations in a chelate by  $\text{C}=\text{O}$  and  $\text{P}=\text{O}$  donor atoms of the uncharged ligands. The TRUEX process uses (*N,N*-di-*iso*-butyl-carbamoylmethyl) octyl phenyl phosphine oxide (abb. *n*-Octyl-Ph-CMPO) [6,12]. The presence of one *n*-octyl and one phenyl ring on the phosphorus atom is important for solubility in less polar solvents, and has some effect on the selectivity for particular lanthanide ions [9,18]. A bit later, another compound, (*N,N*-di-*iso*-butyl-carbamoylmethyl) diphenyl phosphine oxide ( $\text{Ph}$ )<sub>2</sub>CMPO, was extensively studied in Russia [11,19,20]. The character of the amidic nitrogen substituent seems not be decisive in these organic series, but increases the extraction efficiency in the highly acidic range [19].

Halogen derivatives of the cobalt bis(dicarbollide)( $\mathbf{1}^-$ ) ion  $[3\text{-Co(III)}-(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  ( $\mathbf{1}^-$ ) [21] proved to serve as efficient extraction agents for the partitioning of  $^{137}\text{Cs}^+$  and  $^{90}\text{Sr}^{2+}$  (in the presence of synergist polyethylene glycol) from highly acidic nuclear waste. The gradual development of the original idea into an industrial process over four decades is outlined in two recent reviews [22,23]. Considering this process, difficulties still persist in the extraction of trivalent  $\alpha$ -emitters, although some synergist mixtures of halogen-protected cobalt bis(dicarbollide) with

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polydentate ligands have been proposed and tested [23,24]. The latest version of this process is currently called “UNEX” [24].

A different approach consists of the design of ionic extraction agents, cobalt bis(dicarbollides) with covalently bound lipophilic or selective functions [22,23]. Early examples of such ligands for Cs<sup>+</sup> complexation and extractions consisted of B(4,8',8,4') bis(arylene) bridged cobalt bis(dicarbollide), that proved to have extraordinary high efficiency [25], and *ortho* and *meta* cobalt bis(dicarbollides) substituted with two or four phenyl groups at carbon atoms [26] or by alkylether groups [27]. The latter type was also tested as a carrier for trivalent radionuclides in studies on supporting liquid membranes [28].

Over the past few years we have developed several families of extraction agents based on covalent combinations of cobalt bis(dicarbollide) with CMPO functions in one single molecule [23,29–31]. Especially, the class of calix[4]arenes modified with two 1<sup>−</sup> ions and two CMPO groups at the lower rim proved to have exceptionally high efficiency, several orders higher than their organic analogues [23,32,33]. From various types of recently prepared simpler compounds, CMPO derivatives of the general formulation [3,3'-Co(III)-(8-<sup>1</sup>R<sup>2</sup>R-P(O)-CH<sub>2</sub>-C(O)-(<sup>3</sup>R)NH-(CH<sub>2</sub>-CH<sub>2</sub>O)<sub>2</sub>-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>)]<sup>−</sup> proved to have the highest extraction efficiency [23,30,31]. These compounds are accessible in good yields via the ring opening reaction of the dioxane cobalt bis(dicarbollide) derivative [34,35] by amines, and subsequent reaction of the resulting ammonium derivatives (**2**) with various active esters [29,31]. In particular, the ionic CMPO derivative where <sup>1</sup>R = <sup>2</sup>R = C<sub>6</sub>H<sub>5</sub> and <sup>3</sup>R = *tert*-C<sub>8</sub>H<sub>17</sub> was selected for further studies due to its sufficient solubility in lower polarity solvents and reasonably high stability towards nitric acid. Extractions of Am<sup>3+</sup> and Eu<sup>3+</sup> (in macroquantities) and interfering fission products using this compound were recently studied and have shown promising results [31], but the tests revealed a continuing need to seek for further possible improvements in the extractant stability.

From published extraction studies, it follows that two halogen atoms attached to the most electron rich skeletal boron positions, B(8,8'), can effectively stabilize the whole molecule towards attack of highly concentrated nitric acid and high irradiation doses [22,36,37]. Indeed, these skeletal positions are electron rich and can be easily affected by acid catalyzed reactions, proceeding by an EINS mechanism (Electrophile Induced Nucleophilic Substitution) [38], or they can undergo other types of reactions (degradation, oxidation). From this point, the other boron sites are comparatively less reactive. In this paper we report on synthetic ways to prepare compounds based on merging the properties of halogen protected cobalt bis(dicarbollides) with substitution by the *tert*-octyl-CMPO function, efficient in extraction of trivalent  $\alpha$ -emitters. We present here the results of extraction and stability tests for this series of compounds, indicating that the effect of substitution by a halogen is not only the simple addition of two favourable properties, but has also an inherent influence on the extraction efficiency in the several systems under study.

## 2. Material and methods

### 2.1. General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdon [39], although some operations, such as column chromatography, were carried out in air.

The starting *clos*-[3,3'-Co(III)-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sub>2</sub>.Cs (Cs1) was purchased from Katchem, Ltd., Prague. The active ester used for the final synthetic step, *para*-nitrophenyl (diphenylphosphoryl) acetate

(**ae**), was prepared according to a published procedure [40]. Toluene (Lachema, Brno, Czech Rep.) was dried over Na metal, THF was dried over Na metal and sodium diphenyl ketyl, CH<sub>2</sub>Cl<sub>2</sub> was dried over P<sub>2</sub>O<sub>5</sub>, and all the solvents were freshly distilled before use. High surface sodium hydride (96%) made at the Institute of Inorganic Chemistry was used with a BET surface area of about 1.5 m<sup>2</sup> per gram. Other chemicals were reagent or analytical grade and were used as purchased. Preparative column chromatography was carried out on silica gel (Aldrich 230–400 mesh). The purity of the individual chromatographic fractions was monitored by analytical TLC Silufol plates, Lachema, Czech Rep. or TLC on Merck RP-8 F<sub>254</sub> S pre-coated plates (yellow-orange spots, eventually detected by 2% aqueous AgNO<sub>3</sub> spray) and the purity was controlled by an Ion Pair Reverse Phase HPLC (IP-RP-HPLC) [41] method, being better than 98% for the compounds **4a–c** under study.

Melting points were determined in a Koeffler melting point apparatus in sealed capillaries and are uncorrected. The purity of the product was controlled by HPLC, <sup>11</sup>B, <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy, Elemental analysis, Melting points, TLC and other methods.

### 2.2. Instrumental techniques

<sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy was performed on a Varian Mercury 400<sup>Plus</sup> Instrument. The spectra of all the compounds were measured immediately after their dissolution. <sup>11</sup>B NMR (128 MHz) chemical shifts are given in ppm to high-frequency (low field) to F<sub>3</sub>B-OEt<sub>2</sub> as the external reference. Residual solvent <sup>1</sup>H resonances were used as internal secondary standards. Coupling constants <sup>1</sup>J(<sup>11</sup>B–<sup>1</sup>H) are taken from resolution-enhanced <sup>11</sup>B spectra with a digital resolution of 2 Hz. Signal assignments are based on [<sup>11</sup>B–<sup>1</sup>H] COSY NMR spectroscopy. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C (100 MHz): chemical shifts  $\delta$ (<sup>1</sup>H) are given in ppm relative to Me<sub>4</sub>Si (0 ppm) as the external standard, coupling constants <sup>1</sup>J(<sup>1</sup>H) in Hz,  $\delta$ (<sup>1</sup>H)–{<sup>11</sup>B} data are also presented, assignments are based on selectively decoupled  $\delta$ (<sup>1</sup>H)–{<sup>11</sup>B selective} NMR experiments.

The radioactivity of samples was measured using a single-channel  $\gamma$  analyser with a NaI (TI) well-type detector.

Mass spectrometry measurements were performed on a Thermo-Finnigan LCQ-Fleet Ion Trap instrument using electrospray (ESI) ionization with detection of negative ions. Samples dissolved in acetonitrile (concentrations approx. 100 ng mL<sup>−1</sup>) were introduced to the ion source by infusion of 5  $\mu$ L min<sup>−1</sup>, source voltage –5.57 kV, tube lens voltage –49.8 V, capillary voltage –80.0 V, drying temperature 188 °C, drying gas flow 8 L min<sup>−1</sup>, auxiliary gas pressure 6 Bar. In the case of the CMPO derivatives **4a–c**, negative ions corresponding to [M]<sup>−</sup> were observed with 100% abundance for the highest peak in the isotopic distribution plot. The zwitterionic compounds **3a–c** were measured with APCI ionization in both negative and positive modes, exhibiting correct [M–H]<sup>−</sup> or [M+H]<sup>+</sup> ions. Full agreement of the experimental and calculated isotopic distribution pattern was observed for all compounds. The isotopic distribution in the boron plot of all peaks is in perfect agreement with the calculated spectral pattern. The data are presented for the most abundant mass in the boron distribution plot (100%) and for the peak corresponding to the *m/z* value.

### 2.3. Synthesis

The ammonium derivative [3,3'-Co-(8-*t*-C<sub>8</sub>H<sub>17</sub>-NH<sub>2</sub>-(CH<sub>2</sub>CH<sub>2</sub>-O)<sub>2</sub>-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>)] **2a**, used as the starting compound for the majority of the derivatives, was prepared by a known alkylation reaction using the dioxane ring opening reaction of dioxane-**1** by the *tert*-C<sub>8</sub>H<sub>17</sub>NH<sub>2</sub> [31] in toluene/dimethoxyethane (DME) (3:1) solution. Isolation was performed analogously as described in the preceding paper [31].

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