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# Cobalt bis(dicarbollide) ions functionalized by CMPO-like groups attached to boron by short bonds; efficient extraction agents for separation of trivalent f-block elements from highly acidic nuclear waste

Bohumír Grüner [a,*], Magdaléna Kvíčalová [a], Jaromír Plešek [a], Václav Šícha [a], Ivana Císařová [b], Mária Lučaníková [c], Pavel Selucký [c]

[a] Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež near Prague, Czech Republic
[b] Department of Chemistry, Faculty of Natural Sciences of the Charles University, Hlavova 2030, Prague 2, Czech Republic
[c] Nuclear Research Institute plc., 250 68 Řež near Prague, Czech Republic

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ABSTRACT

New boron substituted cobalta bis(dicarbollide)(1-) ion (**1**) derivatives of formula [(8,8′-(RPhP(O)($CH_2$)*n*-C(O)N) < (1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]$^-$ (R = Ph or $C_8H_{17}$, *n* = 1, **3a**, **3b;** R = Ph, *n* = 2, **3c**), [(8-($Ph_2P$(O)$CH_2$-C(O)NR)(1,2-$C_2B_9H_{10}$))(1′,2′-$C_2B_9H_{11}$)-3,3′-Co]$^-$ (R = H, $C_2H_5$, $CH_2C_6H_5$, **5a–c**) and [(8-($^2$RPhP(O)$CH_2$C(O)-N($^1$R)$CH_2$-1,2-$C_2B_9H_{10}$))(8′-$CH_3$O-1′,2′-$C_2B_9H_{10}$)-3,3′-Co]$^-$ ($^1$R = Benzyl, $^2$R = Ph or $C_8H_{17}$, **7a,b**) were prepared with the aim to develop a new class of efficient extraction agents for partitioning of polyvalent f-block elements, i.e. lanthanides and actinides from high-level activity nuclear waste. The anionic ligands were characterized by multinuclear NMR spectroscopy and MS, the structures of Cs**3a** and the calcium complex of **7a** were determined by X-ray diffraction analysis. The crystallographic study of the Cs**3a** proved a formation of linear chains in the structure, where the metal cation is coordinated by oxygen atoms of the CMPO terminal groups. The X-ray structure of the $Ca^{2+}$ complex of the ionic ligand **7a** proved a 1:3 metal to ligand ratio. Presented also is the X-ray structure of the starting ammonium compound **6** used in the synthesis of **7a** and **7b**. With exception of **5c**, these anionic ligands are of high extraction efficiency, the highest being found for **7a** in low polar solvent mixture hexyl methyl ketone–dodecane 1:1. These properties qualify some of these derivatives for possible technological applications.



## 1. Introduction

Nuclear fuel reprocessing operations produce both high and medium activity liquid waste (HLLW/MLLW). These contain major long lived nuclides $^{90}$Sr (β, 29 years), $^{137}$Cs (γ, 30 years) and α emitters such as uranium, plutonium and minor actinides (Am, Cm). The problem of handling and storing these wastes has to be solved. Assumed possibility is to separate the most harmful radionuclides by hydrometallurgical process, i.e. by liquid–liquid extraction [1–8].

Between other promising systems, CMPO (dialkyl amides of the carbamoylmethyl dialkyl phosphine oxides) and derivatives of the cobalt bis(dicarbollide)(1-) ion [9], *closo*-[(1,2-$C_2B_9H_{11}$)$_2$-3-Co]$^-$ (**1**) were designed as selective extraction agents for the recovery of radionuclides from HLLW and MLLW from the PUREX and UREX feed. The method based on the chloroderivative of anion **1,** originally developed in the Czech Republic has been utilized for the recovery of $Cs^+$ and $Sr^{2+}$ in the industrial processes in Russia [10].

The CMPO derivatives have been designed as efficient extractants for the class of lanthanides and actinides in the TRUEX process, studied in the USA and Russia [6,7,11–15]. Demonstration tests on the use of synergic mixtures of CMPO and chloroderivatives of **1** for lanthanide/actinide extraction have been carried out in the developments of the UNEX process [16–19].

Over the past years we have been interested in the synthesis of compounds combining favourable properties of these two efficient extraction agents within a single molecule. Such derivatives are expected to preserve the high complexation ability of CMPO for trivalent lanthanides and actinides (as the bidentate ligands forming strong chelate complexes with a six atom ring) together with ion-pairing and charge compensating power of the hydrophobic cobalt bis(1,2-dicarbollide) anion.

Indeed, the first successful venture into this field of the compounds has been represented by bonding of "classical" CMPO moiety to cage of the anion **1** by a diethylene glycol spacer [20]. This was followed by a series of calixarenes with mixed substitutions by CMPO groups and anion **1** at the lower rim of the platform [21,22]. These species exhibited exceptionally high extraction efficiency even in the high acidity range. However, such a high effi-

* Corresponding author. Tel.: +420 2 6617 3120; fax: +420 2 209 40 157.
*E-mail addresses:* gruner@iic.cas.cz (B. Grüner), cisarova@natur.cuni.cz (I. Císařová), sel@main.nri.cz (P. Selucký).

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ciency consequently requires a special procedure for the re-extraction step, e.g. use of DTPA (diethylene triamine pentaacetic acid) as a strong complexing agent. The effect of modifications of CMPO function in the long-chain series on extraction efficiency has been overviewed recently along with a detailed study of extraction properties [24].

On the other hand, there has not yet been sufficient knowledge and data sets relating to the influence of deeper structural variations in the structure of this type of compounds on extraction. Here we present the synthesis and extraction properties of three different families of such compounds, where the amidic nitrogen is directly attached to the boron cage, or bonded *via* a short methylene spacer. Presented are synthetic details for these families of compounds along with structural characterization of some new ligands by X-ray crystallography. Extraction properties are outlined and compared to the series of compounds already published.

## 2. Results and discussion

The synthesis of all new compounds is based on reaction of ammonium derivatives of cobalt bis(dicarbollide), which after deprotonation reacts with nitrophenyl esters of alkyl phenyl phosphoryl acetic acid (active esters, **ae1–3**, see Scheme 1). This reaction designed formerly for modifications of organic calixarenes [23], has been already used in the synthesis of previously reported family of cobalt bis(dicarbollide) extractants [20,24] and lower rim calixarenes with mixed substitutions by cobalt bis(dicarbollide) and CMPO groups [21,22]. This method proved as a very reliable, high yield and clean procedure, particularly suitable in combinations with cobalt bis(dicarbollide) where the rather high price of the starting material should be also considered.

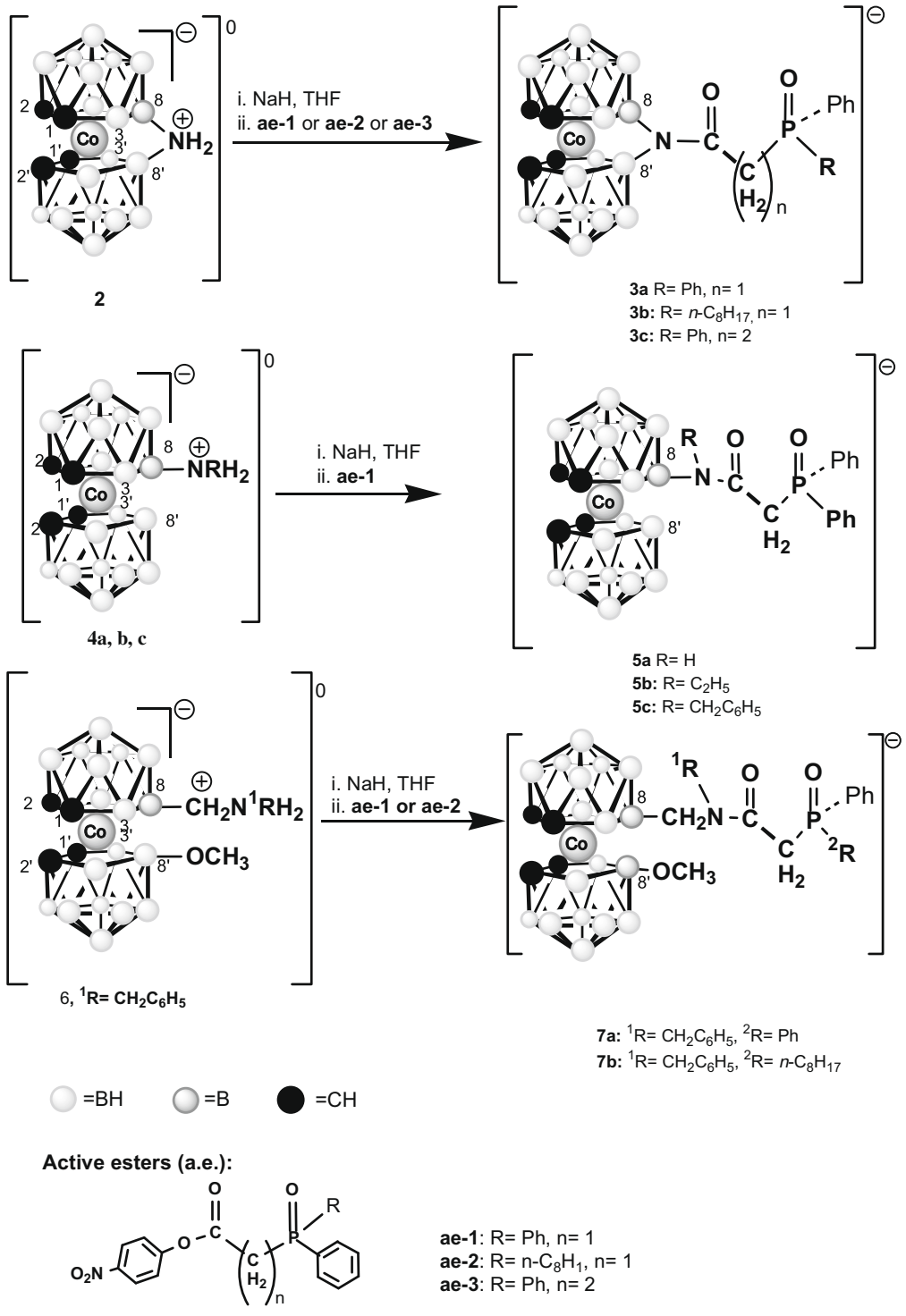
The synthesis of the first type of new compounds is based on employment of a long known bridged zwitterionic ammonium derivative, $[(8,8'\text{-}(H_2N) < (1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-}Co]^0$ (**2**), as the useful reactive building block. Bridging $>NH_2$ groups of this (or that of similar series of compounds from *meta*-cobalt bis(dicarbollide) series are prone to easy substitution by a variety of organic groups [25–27]. It should be mentioned in this context that the parent derivative **2** and its alkyl derivatives are bi-polar compounds and therefore unsuitable for extraction.

As shown in Scheme 1, synthesis proceeds *via* a smooth one step procedure starting from **2** whose reactions with active esters **ae-1** and **ae-2** (see Section 6 and Scheme 1) gave high yields of the expected products $[(8,8'\text{-}(C_6H_5)_2P(O)CH_2C(O)N < (1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-}Co]^-$ and $[(8,8'\text{-}(C_8H_{17})(C_6H_5)P(O)\text{-}CH_2C(O)N < (1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-}Co]^-$ (**3a, 3b**). A compound with a longer ethylene unit interconnecting the phosphine oxide and amide ends of the functional groups (carbamoyl ethyl diphenyl phosphine oxide, CEPO), $[(C_6H_5)_2P(O)(CH_2)_2C(O)N < (1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-}Co]^-$ (**3c**) was prepared for comparison, starting from corresponding active ester **ae-3** (see Section 6 and Scheme 1), to see the effect of the binding of the targed Ln/An ions in a chelate complex containing a larger seven atom ring. The compounds **3a–3c** were isolated in the anionic form, but can be easily reverted to the neutral protonated forms upon washing of their $CH_2Cl_2$ solutions with 1 M HCl. Interesting feature of these molecules is that the boron cage forms inherent part of the CMPO (CEPO) functional group by notional replacement of both N-alkyl substituents present in the organic series. Bridge substituent in the family of ligands of type **3** gives rise to a rigid arrangement around the bridge nitrogen atom, what is reflected in easy crystallization and purification of such compounds. On the other hand, this structure is at the expense of more complex $^{11}B$ NMR spectral pattern of the new species. The arrangement of the substituent around the bridge in **3a** is rigid and asymmetric, as the function group can point towards one or the other side of the boron cluster. The asymmetry is even more pronounced for **3b** with asymmetric phosphorus end substitution. Consequently, the presence of diastereoisomeric pairs in a mixture can be thus expected for all these compounds, which is reflected in the splitting of three lower field $^{11}B$ NMR signals in the spectra of $Me_4N^+$ salts (corresponding to B(8,8′), B(10,10′) and B(4,7,4′,7′)) into two sets of peaks of equal intensity when compared to the spectrum of the starting compound. This effect of the bridge substituent has been already observed and discussed in case of a simpler propargyl derivative [28]. Peaks in the spectrum of the $Me_4N^+$ salt of **3a–c** are comparatively sharper as those in the parent ammonium derivative **2**. In contrast, peaks of BH signals in the $^{11}B$ NMR spectra of the protonated forms, $Na^+$ and $Cs^+$ salts of **3a** and **3c** are extensively broadened. This peak broadening is temperature dependent, but is still notable at 50 °C. The boron resonances at this temperature are still more diffuse than in the spectrum of the $Me_4N^+$ salts (see Fig. 1). This effect can be consistent either with a slow intramolecular exchange of the cation or the formation of aggregates in the solution comprising several ionic clusters bound *via* protons or alkali metal ions into several different geometric orientations, which are sufficiently fixed and stable on the NMR time scale.

Indeed, the solid state structure of Cs**3a** shows the presence of endless linear chains (see crystallographic part below) in the crystal. Noteworthy is also a noticeable downfield shift of the $^{31}P$ signal (ca. 5 ppm) observed for the neutral protonated form of **3a**. However, these effects are not observed in the $^1H$ and $^{13}C$ NMR spectra of compounds **3a–c,** where expected $^1H$ and $^{13}C$ NMR patterns can be seen. The compounds also exhibit the expected $[M]^-$ cut-off peak in ESI-MS. The X-ray crystallography unambiguously confirmed the nature and the arrangement of the substituent sitting on the nitrogen atom. The solid state structure of the $Cs^+$**3a** proved the formation of almost linear chains of cesium atoms surrounded by the anionic ligands forming walls of a channel structure. $Cs^+$ cations are coordinated to P(O) and C(O) groups. For interatomic distances and angles see Fig. 2 captions. An interesting feature is the almost perpendicular position of the two phenyl rings of the diphenyl phosphine oxide moiety. This may account for a repulsion of the water molecules out of the metal coordination sphere.

From the viewpoint of extraction chemistry, more interesting seems the crystal structure of the $Eu^{3+}$ complex of **3a**. Unfortunately, the structure could not be fully anisotropically refined and therefore is not reported here. The disorder in the structure is mainly a consequence of the asymmetry of the nitrogen substitution and presence of both, dextrorotary and levorotary arrangement of terminal phenyl phosphine oxide ends in the crystal. This effect cannot be surpassed without separation of the two diastereoisomers. Only the arrangement around the central Eu(III) atom could be clearly resolved. Schematic Fig. 2 is based on the crystallographic evidence and reflects a 3:1 ratio of ligands to metal complex formation. As in the structure of the previously reported Ln(III) complex with flexible diethylene glycol arms between the CMPO group and the cage [20], even the bridged anionic ligand is able to fully displace the nitrate ions from the primary Eu(III) coordination sphere. This effect, not observed for purely organic CMPO ligands, is apparently caused by tight complexation and inherent charge compensation by three cobalt bis(dicarbollide)(1-) anions present in the proximity of the cation.

The second class of compounds is based on the use of 8-ammonium derivatives of cobalt bis(dicarbollide) $[(8\text{-}RH_2N\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ (R = H **4a; R =** $C_2H_5$**-4b; R =** $C_6H_5CH_2$**-4c**) in the reaction pathways (see Scheme 1). These compounds, accessible in preparative yields by reduction of 8-nitrilio derivatives of **1,** have been reported just recently [29]. The synthesis of CMPO derivatives starts either from the parent compound with bare ammonium group or from the N-ethyl and benzylammonium




**Scheme 1.** Reaction pathways and conditions used in the synthesis of the three new families of CMPO derivatives of cobalt bis(1,2-dicarbollide) ion.

derivatives, which upon reaction with **ae-1** gave a series of compounds **5a**, **5b** and **5c** (see Scheme 1). The compounds were characterized by NMR and MS. A possibility of free rotation of the functional group around the nitrogen centre can be expected in the series of compounds of type **5,** which would lead to no stereochemistry complications reflected in NMR spectra. This is, however, not true for alkali metal salts, where $^{11}B$ NMR peak broadening can be again observed, even in deuterioacetone solvent, while the corresponding $Me_4N^+$ salts exhibit sharp peaks and typical pattern for B(8)–N substitution of the cage, i.e. 12 boron signals of intensities corresponding to two different dicarbollide subunits in the molecule [29].

The third type of CMPO derivatives of ion **1** is based on the use of ammonium derivative **6**, which has benzyl ammonium group N-attached to the cage B(8) atom *via* methylene spacer and $CH_3O$ moiety bonded at B(8′) position of the cage. This compound is accessible from the ring opening reaction of the zwitterionic $[8,8'\text{-}\mu\text{-}(O^{(+)}(CH_3)\text{–}CH_2)\text{-}(1,2\text{-}C_2B_9H_{10})_2^{(-)}\text{-}3,3'\text{-}Co(III)]$ derivative [30] by benzyl amine as a nucleophile. Full details on the synthesis and use of this synthetically versatile building block will be

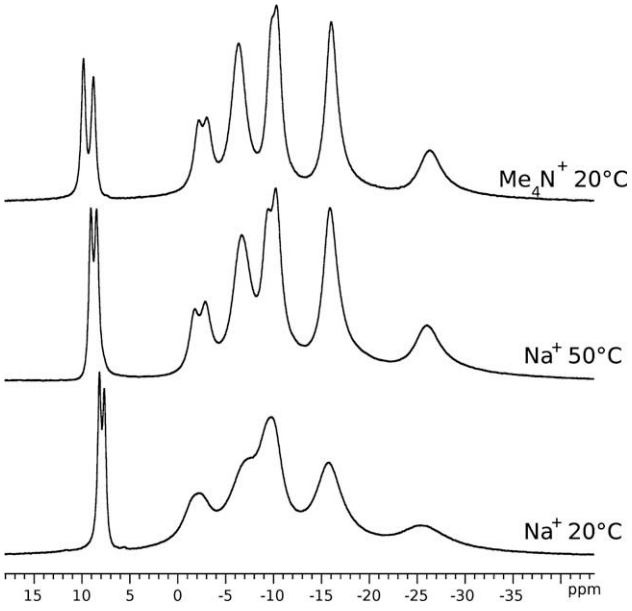



**Fig. 1.** An example of peak broadening in the $^{11}B\{^1H\}$ NMR spectra (128 MHz) of the sodium salt Na**3a** measured in deuterioacetone at 20 °C and 50 °C compared to the spectrum of the $Me_4N^+$ salt.

published elsewhere together with an overview of the scope and limitations of its ring opening reactions. Here we present the data necessary for characterization of **6,** along with crystallographic data for this compound and details on the synthesis of the ionic CMPO ligand **7a** prepared from **6** in a good yield *via* reaction with the active ester **ae-1**. Molecular structure of $Ca^{2+}$ complex of **7a** determined by crystallography proved the substitution of one dicarbollide ligand of the ion **1** by CMPO group bonded to B(8) atom *via* methylene spacer, the second dicarbollide being modified by the B(8′)–$OCH_3$ substitution. An interplay with the different phosphorus end group substitution was also performed, compound **7b**, an analogue of **7a**, but with *n*-octyl phenyl group was prepared for comparison starting from **ae-2**.

In this series, presence of the two substituents at both $\{C_2B_3\}$ pentagonal ligand planes, adjacent to the cage cobalt atom, contributes to a sterical strain which can to some extent restrict free rotation of dicarbollide ligands in the cluster around the central cobalt atom. This has been already discussed in context of asymmetry and sterochemistry in the cobalt bis(dicarbollide) series [31–33]. Here, this effect can, in principle, contribute to the observed broadening of signals by freezing out the rotation in several conformations. However, as in the two series discussed above, the main factor responsible for diffusion shape of the $^{11}B$ NMR signals is probably again fixing of the ligands into several discrete positions by $Na^+$ ions accompanied by presence of a larger molecular assemblies in the solution or a slow intra-molecular exchange of cations. In contrast, the $^{11}B$ NMR spectra of $Me_4N^+$ salts again exhibit quite sharp peaks. It seems obvious, that the $Me_4N^+$ cation is not able to interact with CMPO groups present in the ionic ligands. As further evidence may be the fact that the boron spectrum of the starting ammonium derivative bearing bulky benzyl substituent, also exhibits no peak broadening.

The structure of **6** (see Fig. 4) confirmed skeletal substitution by the benzylammonium group, attached by methylene spacer to B(8) atom of the cage, and the presence of the methoxy group at the exohedral site B(8′). As the bond distances and angles of **6** are unexceptional, only interesting feature of the structure is formation of two types of hydrogen bonds, intramolecular N–H···O–$CH_3$ and intermolecular –N–H···N with the solvating molecule of acetonitrile (see Fig. 4). The structure of the calcium complex of **7a** depicted in Figs. 5 and 6 revealed the highly symmetric (cubic space group $Pa\bar{3}$) octahedral arrangement of three ligands in **7a** around the $Ca^{2+}$ central atom. Each ligand is bonded by calcium

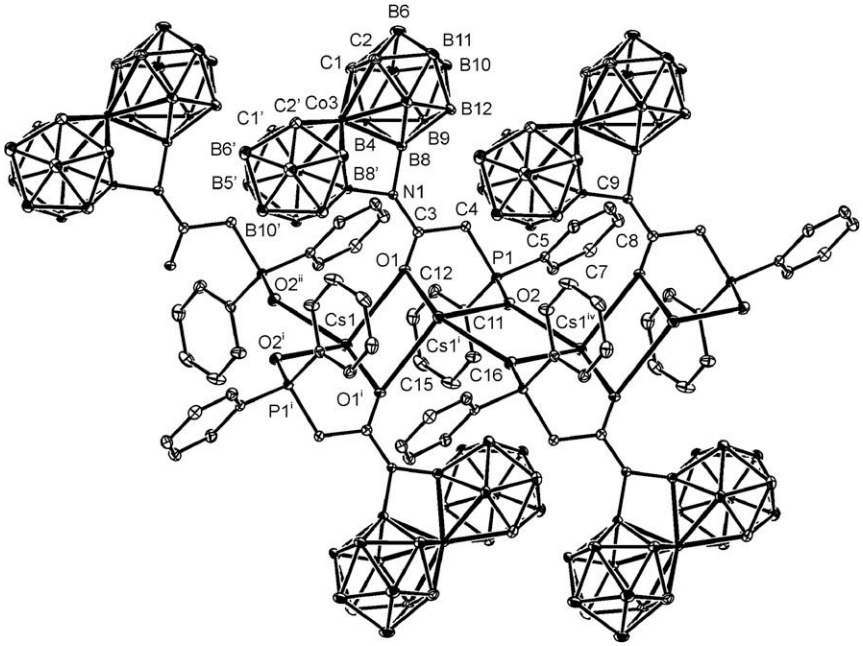



**Fig. 2.** View on the infinite chain of $Cs^+$**3a**. Displacement ellipsoids are drawn on 30% probability level, hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Cs1–O1 3.0091(14), Cs1–$O1^i$ 3.0412(14), Cs1–$O2^{ii}$ 3.0772(14), Cs1–$O2^i$ 3.2680(15), N1–C3 1.337 (3), N1–B8′ 1.505(3), N1–B8 1.515(3), O1–C3 1.242(3), C3–C4 1.519 (3), P1–C4 1.808(2), O2–P1 1.4916(15), P1–C5 1.812 (2), P1–C11 1.804(2); O1–Cs1–$O1^i$ 82.54(4), O1–Cs1–$O2^{ii}$ 106.17(4), $O1^i$–Cs1–$O2^{ii}$ 155.05(4), O1–Cs1–$O2^i$ 101.43(4), $O1^i$–Cs1–$O2^i$ 61.85(3), $O2^{ii}$–Cs1–$O2^i$ 93.29(4), Cs1–O1–$Cs1^i$ 97.47(4), B8′–N1–B8 97.79(15), C3–N1–B8 133.75(17), C3–N1–B8′ 128.14(17), O1–C3–N1 123.67(18), O1–C3–C4 120.49(17), N1–C3–C4 115.83(17), C3–C4–P1 115.59(14), O2–P1–C4 115.01(9), C11–P1–C5 104.92(9), C4–P1–C5 100.97(9), O2–P1–C11 113.55(9), O2–P1–C5 113.49(9). Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x-1, y, z$; (iii) $-x, -y, -z+1$; (iv) $x+1, y, z$.

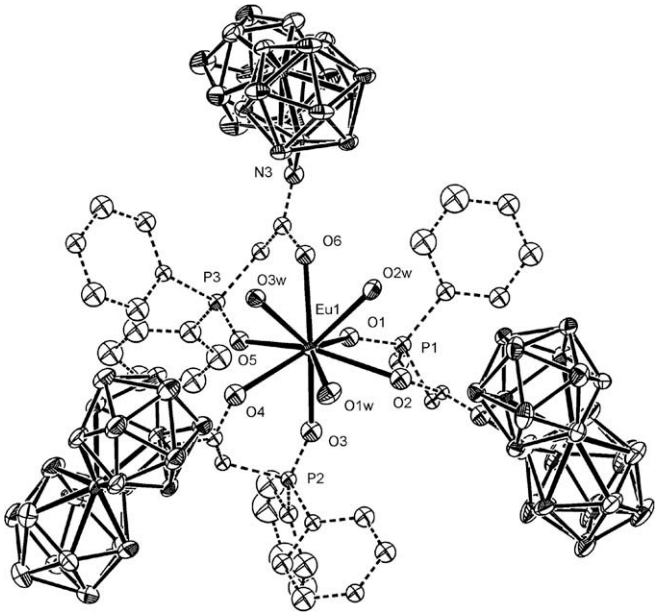



**Fig. 3.** View on one orientation of the $Eu^{3+}$ complex with three ligands of **3a**. Displacement ellipsoids are drawn on 30% probability level. The disordered atoms are connected with dashed lines. Hydrogen atoms and one phenyl moiety on P1 are omitted for clarity. The oxygen atoms of second orientation are overlapped with positions of oxygen of the first orientation and can be therefore treated as not disordered atoms during interpretation of the structure. Selected bond distances [Å] and angles [°], see also Ref. [39]: Eu1–O1 2.393(5), Eu1–O2 2.440(7), Eu1–O3 2.343(5), Eu1–O4 2.484(7), Eu1–O5 2.367(5), Eu1–O6 2.444(6), Eu1–O1W 2.495(6), Eu1–O2W 2.513(6), Eu1 O3W 2.491(6); O1–Eu1–O2 73.4(2), O3–Eu1–O1 74.23(18), O1–Eu1–O4 138.0(2), O5–Eu1–O1 74.35(17), O1–Eu1–O6 73.27(18), O1–Eu1–O1W 139.0(2), O1–Eu1–O2W 97.6(2), O1–Eu1–O3W 139.54(18), O3–Eu1–O2 74.0(2), O2–Eu1–O4 122.9(2), O5–Eu1–O2 142.5(2), O2–Eu1–O6 112.7(2), O2–Eu1–O1W 66.8(2), O2–Eu1–O2W 64.4(2), O2–Eu1–O3W 130.4(2), O3–Eu1–O4 74.5(2), O3–Eu1–O5 79.25(18), O3–Eu1–O6 142.83(19), O3–Eu1–O1W 85.9(2), O3–Eu1–O2W 138.08(18), O3–Eu1–O3W 137.67(19), O5–Eu1–O4 72.7(2), O6–Eu1–O4 121.2(2), O4–Eu1–O1W 64.6(2), O4–Eu1–O2W 124.4(2), O4–Eu1–O3W 63.1(2), O5–Eu1–O6 75.06(18), O5–Eu1–O1W 137.1(2), O5–Eu1–O2W 139.21(18), O5–Eu1–O3W 86.92(19), O6–Eu1–O1W 131.0(2), O6–Eu1–O2W 64.5(2), O6–Eu1–O3W 67.3(2), O1W–Eu1–O2W 73.7(2), O3W–Eu1–O1W 77.5(2), O3W–Eu1–O2W 73.6(2).

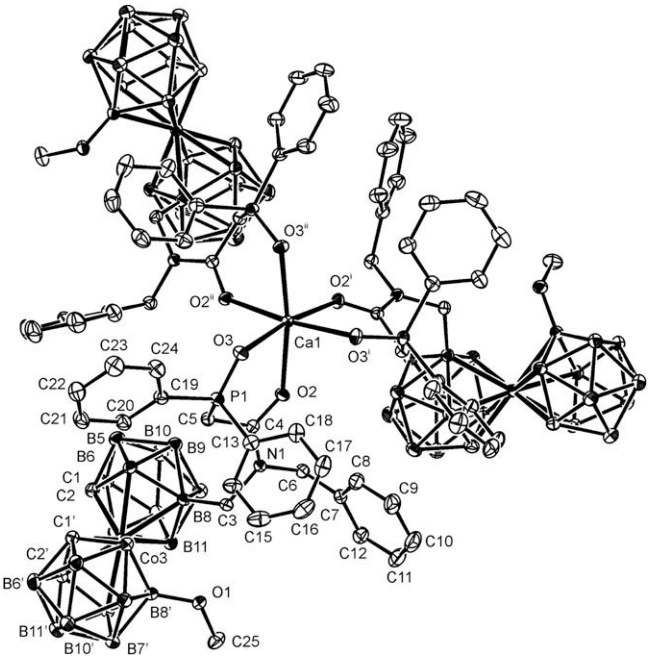



**Fig. 5.** View on the structure of the $Ca^{2+}$ complex with three ligands of **7a**. Displacement ellipsoids at the 30% probability level. Hydrogen atoms and the solvating molecules are omitted for clarity. High symmetry of the coordination sphere of $Ca^{2+}$ follows from position of calcium on three fold axis in the unit cell. Selected bond distances [Å] and angles. [°]: Ca1–O2 2.2987(14), Ca1–O3 2.3081(14), Ca1–$O2^{i}$ 2.2985(14), Ca1–$O2^{ii}$ 2.2987(14), Ca1–$O3^{i}$ 2.3079(14), Ca1–$O3^{ii}$ 2.3079(14), B8–C3 1.617(3), C3–N1 1.489(2), C4–N1 1.329(3), C6–N1 1.467(3), C4–O2 1.254(2), C4–C5 1.511(3), P1–C5 1.818(2), P1–O3 1.4983(15), P1–C13 1.799(2), P1–C19 1.797(2); O2–Ca1–O3 82.02(5), $O2^{i}$–Ca1–O2 90.06(5), O2–Ca1–$O3^{i}$ 93.50(5), O2–Ca1–$O3^{ii}$ 171.30(5), $O2^{i}$–Ca1–O3 171.30 (5), $O3^{i}$–Ca1–O3 94.83(5), N1–C3–B8 115.61(16), C4–N1–C3 124.07(17), C4–N1–C6 118.82(17), O2–C4–N1 121.78(19), N1–C4–C5 119.42(18), O2–C4–C5 118.80(18), C4–C5–P1 111.83(14), O3–P1–C5 113.27(9), C13–P1–C5 106.71(10), C19–P1–C5 106.04(10), C19–P1–C13 108.38(10), C4–O2–Ca1 136.30(14), P1–O3–Ca1 125.98(8). Symmetry codes: (i) *z*, *x*, *y*; (ii) *y*, *z*, *x*.

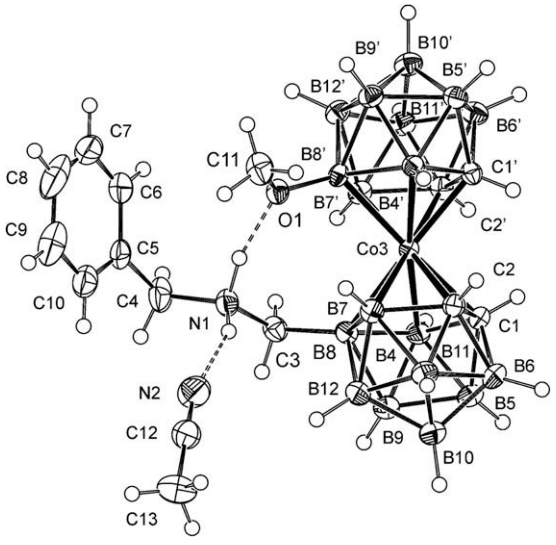



**Fig. 4.** View on the molecular structure of **6** with incorporated acetonitrile solvent. Displacement ellipsoids are drawn on 30% probability level. Selected bond distances [Å] and angles [°]: B8–C3 1.601(3), C3–N1 1.507(3), C4–N1 1.498(3), C4–C5 1.508(4), B8′–O1 1.424(3), C11–O1 1.419(3), N2–C12 1.123(3), C12–C13 1.454(4); N1–C3–B8 112.78(19), C4–N1–C3 114.73(19), N1–C4–C5 110.5(2). Hydrogen bonds: N1···O1 2.623(3), N1–H1A···O1 164(3); N1···N2 2.961(3), N1–H1B···N2 156(2).

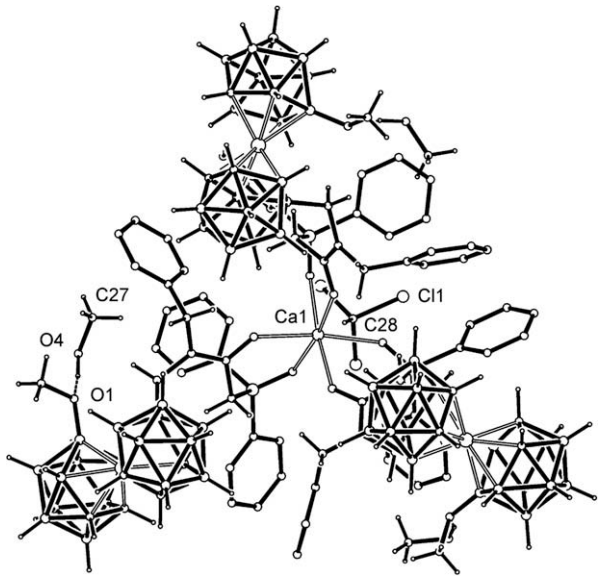



**Fig. 6.** View on of the calcium complex Ca**7a** drawn with solvating molecules of $CH_3OH$ and $CHCl_3$. Displacement ellipsoids are drawn on 20% probability level. Hydrogen atoms of phenyl moieties are omitted for clarity. Whereas trichlormethane molecule is placed on three fold axis without apparent contact with the complex, the three methanol moieties are attached via O–H···O hydrogen bonds to methoxy groups: O4···$O1^{i}$ 2.738(3), O4–H4M···$O1^{i}$ 162. Symmetry codes: (i) *z*, *x*, *y*.

cation by both C(O) and P(O) functions. To preserve condition of electroneutrality, the charge of the resulting complex should be compensated by presence of an extra proton located at oxygen or nitrogen sites of the molecule close to cobalt bis(dicarbollide) cage or sodium cations hidden in the voids (see Section 6). The mutual position of the two sets of the cage carbon atoms is close to *cisoid* with angle and thus the methoxy substituent points towards the same side of the cage as the CMPO group. The methoxy group in B(8′) is on a distance far away from the metal cation centre. Hydrogen bond interactions of the oxygen atoms from the methoxy group with methanol present in the structure as the residual solvent were found. This indicates that the second substituent can contribute not only to higher rigidity of the molecule by sterical effect, but can provide additional interactions with polar solvents. For selected interatomic distances see Fig. 5 captions.

## 3. Extraction properties

A comparison of the extraction properties can be seen from Table 2. Tests of individual extractants were carried out in two solvents differing in polarity, toluene and HMK/TPH (hexyl methyl ketone and hydrogenated tetrapropylene, i.e. branched dodecane which was replaced by *n*-dodecane in some experiments) mixture. Table 2 presents the extraction data for all new extractants together with data for the most promising member of the previously reported family, compound **8** [(8-($Ph_2P(O)CH_2C(O)N(i$-$C_8H_{17})(C_2H_4O)_2$-1,2-$C_2B_9H_{10}$) (1′,2′-$C_2B_9H_{11}$)-3,3′-Co]$^-$ used here as the reference. For reliable comparison of properties of all the derivatives, all extractants were diluted to $1.10^{-3}$ M concentrations in the respective solvents. Practically all the extractants at this concentration exhibited very efficient Eu(III) extraction up to 0.1 M nitric acid, then a steep decrease of distribution ratios occurs. An exception exists for compounds **5a** and **5c**, from the second family. These derivatives show high distribution ratios even at 1 M acid provided that toluene is used as the solvent. In less polar solvent HMK/TPH (or dodecane), distribution ratios decrease rather steeply from 0.1 to 1.0 M nitric acid. This decrease is similar as for the reference compound **8** and its already published congeners**.** On the other hand, the dependence of $D_{Eu}$ on the acidity for **8** shows a maximum occurring close to 0.1 M $HNO_3$ concentration, whereas the other extractants show a monotonous decrease in the extraction efficiency starting from rather high $D_{Eu}$ values at pH 3.

Considering effects of structural factors on the extraction, compounds of the bridged family **3** showed the lowest efficiency. In principle, there can be two effects responsible for decrease in the extraction properties with respect to the previous series. One can result from the higher steric strain or ligand rigidity, second from easier protonation of the amidic nitrogen atom due to the presence of strongly acidic ion **1**$^-$ in the proximity of the functional group, or combination of both factors. Attention was focussed on the latter effect. The diphenyl-CMPO derivative **3a** was prepared in defined anionic and protonated forms. These two forms exhibit distinct differences in $^1$H and $^{31}$P NMR spectra. We found, extraction properties of the anionic and the protonated form of this compound in toluene are almost identical in the higher acidity range (see the second row in the Table 2). At pH 3, the protonated form of **3a** extracts even better. This probably indicates an equilibrium between anionic and protonated forms in solutions, or the protonated form easily looses the proton upon contact with the $M^{3+}$ cation due to formation of a far more strong complex.

The preparative methods leading to type **3** of the compounds allowed for easy interplay with any CMPO moiety of choice, especially with respect of the $^1R^2R$-P(O) end group. The tests with compound bearing different phosphine oxide end substitution in **3b** revealed only slightly improved solubility, but coming at the expense of decrease of the extraction efficiency. The substitution of the methylene moiety in the central alkyl connector in the CMPO group by ethylene in **3c** (CEPO) led to marked decrease in extraction properties disqualifying this compound from considerations about possible use. Assumed advantage of the bridge substitution in the structural type **3** is that this blocks both the most reactive sites B(8,8′) sites of the cobalt bis(dicarbollide) cage, which are

**Table 1**
Crystallographic data and refinement parameters of Cs**3a, 6** and the complex Ca**7a**.

| | **Cs3a** | **6** | Ca**7a** |
|---|---|---|---|
| Empirical formula | $C_{18}H_{32}B_{18}CoCsNO_2P$ | $C_{13}H_{34}B_{18}CoN_1O \cdot C_2H_3N$ | $C_{169}H_{289}B_{108}Ca_2Cl_3Co_6N_6O_{24}P_6$ |
| $M_r$ | 711.84 | 514.98 | 4682.45 |
| Crystal system | Monoclinic | Orthorhombic | Cubic |
| Space group | $P2_1/c$ | *Pbca* | $P\bar{a}3$ |
| *a* (Å) | 7.5047(1) | 13.6846 (2) | 30.51500 (10) |
| *b* (Å) | 33.1324 (3) | 12.2663 (2) | |
| *c* (Å) | 12.5495 (2) | 32.7260 (5) | |
| *β* (°) | 102.4880 (6) | | |
| *Z* | 4 | 8 | 4 |
| $\mu$ ($mm^{-1}$) | 1.82 | 0.64 | 0.49 |
| $D_x$ ($mg\,m^{-3}$) | 1.552 | 1.245 | 1.095 |
| Crystal size (mm) | 0.5 × 0.1 × 0.03 | 0.3 × 0.25 × 0.2 | 0.5 × 0.4 × 0.4 |
| Crystal shape | Plate | Plate | Octahedron |
| $T_{min}$, $T_{max}$ | 0.585, 0.908 | | |
| Color | Red | Red | Red |
| Temperature (K) | 150 | 150 | 150 |
| *θ* range (°) | 2.5–27.5 | 1–27.5 | 3.0–27.5 |
| No. of reflections measured | 42 495 | 44 239 | 361 644 |
| No. of unique reflections; [$R_{(int)}$] | 6963, 0.057 | 6291, 0.063 | 10854, 0.053 |
| No. of observed reflections [$I > 2\sigma(I)$] | 5999 | 4134 | 8675 |
| No. of parameters | 411 | 366 | 493 |
| $S$[a] all data | 1.05 | 1.02 | 1.04 |
| Final $R$[a] indices [$I > 2\sigma(I)$] | 0.026 | 0.041 | 0.050 |
| $wR_2$[a] indices (all data) | 0.069 | 0.114 | 0.170 |
| $w_1/w_2$[b] | 0.0313/1.8955 | 0.0506/2.4983 | 0.1152/16.680 |
| $\Delta\rho$ maximum, minimum (e Å $^{-3}$) | 0.62, −0.64 | 0.39, −0.34 | 1.14, −0.45 |

[a] Definitions: $R(F) = \sum ||F_o| - ||F_c|| / \sum |F_o|, wR_2 = [\sum(w(F_o^2 - F_c^2)2)/\sum(w(F_o^2)2]^{1/2}$, $S = [\sum(w(F_o^2 - F_c^2)2)/(N_{reflns} - N_{params})]^{1/2}$.
[b] Weighting scheme $w = [\sigma(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$. $R_{int} = \sum |F_o^2 - F_o^2(mean)| / \sum F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

otherwise prone to the attack by the nitric acid in the extraction process.

In the series **5** could be seen that the most efficient compound **5a** contains no alkyl at the amidic nitrogen atom. This effect was previously observed also in a long chain connector series [24]. On the other hand, presence of benzyl substituents in **5c** improves the solubility and the compound which still preserves a good extraction efficiency, comparatively better than the short-alkyl chain substitution in **5b**.

The most interesting feature within all the series is the rather high preference of **7a** for less polar solvent mixture. As compared to the first two families showing the highest efficiency in toluene, this new compound in HMK/TPH proved even much higher distribution ratios than compound **8** [24]. It should be pointed out that this solvent would be preferred in respect to better ecological acceptability and eventual better compatibility with other processes, which use organic extractants dissolved in higher alkanes.

To further test technological suitability, which assumes extractions from 3 M nitric acid, extractant concentrations in the HMK:dodecane mixture 1:1 were increased to 0.01 M. Such concentrations, or higher, are necessary to extract macroquantities of lanthanides and actinides present in the fission product mixture in concentrations ca. $10^{-2}$ M. The distribution ratios for selected compounds are summarized in Table 3. From this Table could be seen that with exception for **3b** (with octyl phenyl phosphine oxide end substitution), all these compounds at $10^{-2}$ M concentrations are very efficient extractants even in 3 M nitric acid. The distribution ratios at 3 M $HNO_3$ are still technologically acceptable for all the compounds and especially for **5c**, where the positive influence of benzyl substituent at the amidic nitrogen atom of the CMPO group can be seen. The best efficiency is again observed for **7a**. This compound is at $10^{-2}$ M concentration even three times more efficient than the reference compound **8** in the same solvent.

The results of the stability tests of two extractants **3a**, **5a** at $10^{-3}$ M and 5**b** at $10^{-2}$ M concentrations in HMK/TPH and comparison with data obtained for the reference compound **8** are presented in Table 4. It can be seen, that all new compounds are sufficiently stable towards 3 M $HNO_3$ for a period of 30 days.

**Table 2**
Influence of acidity on Eu extraction with different cobalt bis(dicarbollides) with covalently attached CMPO groups.

| Extractant | Solvent | Acidity (M) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.001 | 0.01 | 0.1 | 1.0 | 2.0 | 4.0 |
| Na**3a** | Toluene | 346 | 270 | 210 | 0.0489 | 0.00410 | 0.0005 |
| | HMK/TPH[a] | 303 | 142 | 0.130 | 0.00780 | 0.00231 | 0.00120 |
| $H^+$**3a** | Toluene | 651 | 271 | 80.5 | 0.0724 | 0.0230 | 0.0199 |
| Na**3b** | Toluene | 352 | 343 | 61.5 | 0.0608 | 0.0184 | 0.0105 |
| | HMK/TPH | – | 553 | 75.2 | 0.0516 | 0.0070 | 0.0012 |
| Na**3c** | Toluene | – | 22.0 | 0.699 | 0.0049 | 0.0012 | <0.001 |
| | HMK/TPH | – | >100 | 1.61 | 0.001 | <0.001 | <0.001 |
| Na**5a** | Toluene | 1555 | 1327 | 652 | 54.2 | 6.02 | 0.131 |
| | HMK/TPH | 628 | 619 | 333 | 0.257 | 0.0253 | 0.00330 |
| Na**5b** | Toluene | 1697 | 748 | 435 | 0.212 | 0.0254 | 0.00428 |
| | HMK/TPH | 442 | 372 | 334 | 0.268 | 0.0304 | 0.00321 |
| Na**5c** | Toluene | – | 1005 | 999 | 12.6 | 0.835 | 0.0326 |
| | HMK/TPH | – | 343 | 61.5 | 0.0608 | 0.0184 | 0.0105 |
| Na**7a** | Toluene | 1469 | 240 | 129 | 0.335 | 0.113 | 0.00468 |
| | HMK/TPH | 135 | 330 | 1616 | 67.9 | 3.79 | 0.0389 |
| Na**7b** | Toluene | 93.5 | 67.5 | 45.0 | 0.527 | 0.289 | 0.00420 |
| Na**8** | Toluene | 19.8 | 186 | 445 | 55.6 | 5.24 | 0.190 |
| | HMK/TPH | – | 347 | 183 | 0.243 | 0.0623 | 0.0173 |

$1 \times 10^{-3}$ M extractant in respective solvent; variable nitric acid concentration; HMK – hexyl methyl ketone, TPH – hydrogenated tetrapropylene.
[a] *n*-dodecane instead of TPH.

**Table 3**
Eu(III) extraction with cobalt bis(dicarbollide) derivatives with CMPO functional groups.

| Compound | $c_{HNO_3}$ | 1 M $HNO_3$ | 3 M $HNO_3$ |
|---|---|---|---|
| Na**3a** | $D_{Eu}$ | 77.2 | 1.31 |
| Na**3b** | | 10.9 | 0.136 |
| Na**5a** | | 172 | 2.58 |
| Na**5b** | | 123 | 2.80 |
| Na**5c** | | 147 | 7.58 |
| Na**7a** | | 753 | 79.4 |
| Na**8** | | 90.5 | 21.8 |

$1 \times 10^{-2}$ M extractants in HMK/*n*-dodecane mixture.

**Table 4**
Tests of chemical stability of the new extractants **3a** and **5a**.

| Compound | Solvent | Time of contact (days) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 5 | 15 | 20 | 30 |
| **3a** | HMK/TPH | 0.126 | 0.139 | 0.158 | 0.117 | 0.131 | 0.149 | 0.121 |
| **5a** | HMK/TPH | 0.423 | 0.436 | 0.456 | 0.409 | 0.395 | 0.436 | 0.380 |
| **5b**[a] | HMK/TPH | 4.34 | 3.96 | 3.65 | 3.19 | 4.16 | – | 3.40 |
| **8** | HMK/TPH | 1.85 | 1.81 | 1.77 | 1.71 | 2.02 | 2.08 | 2.01 |

0.001 M extractant in the solvent mixture 1:1.
[a] 0.01 M extractant.

## 4. Comments on the extractions with all cobalt bis dicarbollides functionalized with covalently bonded CMPO groups

Previously, the highest extraction coefficients were observed for compounds of type $[(8\text{-}^{1}RPh(PO)CH_2C(O)\text{-}N^{2}R\text{-}(CH_2CH_2O)_2\text{-}C_2B_9H_{10})(C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$, where the CMPO group is bonded *via* flexible diethyleneglycol chain [20,24] represented in this study by the most studied reference compound **8**. The long pendant group apparently allows the CMPO moiety to adopt optimal geometric orientation around the Ln/Ac cation. This has been also observed in the solid-state structure of the Ln(III) complex. Due to the larger distance of the CMPO function from the anion, these ligands are less prone to protonation and usually occur in their anionic forms in solution. Relatively significant effects on the extraction efficiency were observed when both, the nitrogen and phosphorus ends of CMPO moiety were modified [24].

Similar effects were observed also for the species with the short connectors presented here. Less efficient in the $M^{3+}$ extraction have proved the compounds of the series **3** and **5**, where the CMPO moiety is interconnected by direct B(8)–N bonding to the cluster of the cobalt bis(dicarbollide). Due to direct bonding of the amidic nitrogen on the CMPO group to the cage, these compounds are prone to be protonated. However this has no dramatic effect on the extraction. As for the reference compound, the highest efficiency can be seen in toluene solvent. Nevertheless, the extraction efficiency remains still high for $10^{-2}$ M concentration of reagents in HMK/TPH giving $D_{Eu}$ values in the order of tens from 1 M $HNO_3$ and still sufficiently high considering extraction from 3 M $HNO_3$.

The compound **7a** proved surprisingly high efficiency in a low polar solvent mixture, even higher then the reference compounds **8** and thus seems to be a good candidate for more detailed future studies. The efficiency of Eu(III) extraction with **7a** in HMK/TPH is approx. four orders of magnitude better than that of classical organic ionophore $(Ph)_2$CMPO and approx. two orders of magnitude better than that of synergic mixtures with chlorinated cobalt bis(dicarbollide) [10,20]. The reason for this behaviour is not understood enough, the main differences from a similar compound **5c** being the methylene spacer between the cage and CMPO group and presence of $CH_3O$- function on the second dicarbollide ligand. It seems, particularly a bit remote position of the functional group from the ionic boron cluster brings the main positive effect to the

extraction efficiency. As can be deduced from the effects observed in the solid state structure of Ca**7a**, the methoxy group may improve solvatation of the resulting complex *via* interactions with the polar solvent component (HMK). The more detailed studies are being now in the progress.

## 5. Conclusions

Three new families of cobalt bis(dicarbollide) compounds complementary to previously reported compounds with longer connectors [20,24] were prepared and their extraction properties were evaluated. A unique feature of compounds of type **3** and **5** is that the charged anionic boron cluster replaces alkyl substituents typically present in organic CMPOs and becomes inherent part of the functional group. These compounds thus represent a quite new family of CMPOs, in which the molecular structure has been modified by charged inorganic subgroups. A characteristics feature of the most of compounds is their good solubility in low polar solvents and good stability in nitric acid. The members of the whole series of the ionic CMPO ligands now available offer a wide range of extraction efficiencies which can cover a variety of potential applications in hydrometalurgical separations of f-group elements from high level waste to pre-concentration and analytical purposes.

## 6. Experimental

The caesium salt of cobalt bis(dicarbollide) (**1**) was obtained from Katchem Ltd., Czech Republic. The ammonium derivatives **2a,b**, **4a–c** were prepared according to published methods, the synthesis of **6** is described below. All the ammonium derivatives were dried in vacuum for 8–12 h over $P_2O_5$, at 80 °C prior to use. Solvents, i.e. tetrahydrofuran (THF), ethylene glycol dimethyl ether (DME) and toluene were dried with sodium diphenyl ketyl and distilled prior to use. Other chemicals and solvents were purchased from Aldrich, Lachema a.s. and Penta Ltd. Czech Republic, respectively, and used without purification. Analytical TLC was carried out on TLC plates RP-8-$F_{254}$ S, Merck (0.25 mm layer of octyl silica on glass formers 20 × 5 cm) in the reverse phase mode. Unless otherwise specified, column chromatography was performed on a high purity silica gel (Merck Grade, Type 7754, 70–230 mesh, 60 Å), using acetonitrile/dichloromethane 1:3 as the mobile phase.

All reactions were performed with the use of standard vacuum or inert-atmosphere techniques as described by Shriver [34], although some operations, such as flash chromatography and crystallization were carried out in air. Melting points were determined in sealed capillaries on BŰCHI Melting Point B-545 apparatus and are uncorrected. The identity of all the reported compounds has been unambiguosly proven by their spectral data and the purity was assessed by analytical HPLC with DAD detection, being better than 98% for all compounds.

### 6.1. Instrumental techniques

$^1H$, $^{13}C$, $^{31}F$ and $^{11}B$ NMR spectroscopy was performed on Varian Mercury 400$^{Plus}$ Instrument. The spectra of all compounds were measured immediately after dissolution. $^{11}B$ NMR (120 MHz) chemical shifts are given in ppm to high-frequency (low field) to $F_3B{\cdot}OEt_2$ as the external reference. Residual solvent $^1H$ resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B–^1H)$ are taken from resolution-enhanced $^{11}B$ spectra with a digital resolution of 2 Hz and are given in Hz. The NMR data are presented in the text as follows: $^{11}B$ NMR: $^{11}B$ chemical shifts $\delta$ ($^{11}B$) (ppm), multiplicity, coupling $J(^{11}B–^1H)$ constants are given in Hz. Peak assignment is based on [$^{11}B–^{11}B$] COSY NMR spectroscopy and the spectrum of the parent cluster used for assignment of the unsubstituted ligand (in series **3** and **5**). $^1H$ NMR (400 MHz) and $^{13}C$ (100 MHz): chemical shifts $\delta$ ($^1H$) are given in ppm relative to $Me_4Si$ (0 ppm) as the external standard, coupling constants J(*H*,*H*) in Hz, $\delta$ ($^1H$)–{$^{11}B$} data are also presented, assignment is based on selectively decoupled $\delta$ ($^1H$)–{$^{11}B$ selective} NMR experiments and analogies B-substituted cobalt bis(dicarbollide) compounds previously published [7]. $^{31}P\{^1H\}$ NMR (162 MHz): chemical shifts $\delta$ ($^1H$) are given in ppm relative to 85% $H_3PO_4$ (ppm) as the external standard.

### 6.2. 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$^{-1}$) were introduced to the ion source by infusion of 5 μL min$^{-1}$, source voltage −5.57 kV, tube lens voltage −49.8 V, capillary voltage −80.0 V, drying temperature was 188 °C, drying gas flow 8 L min$^{-1}$, auxiliary gas pressure 6 Bar. In most cases the negative ions corresponding to the molecular ion were observed with 100% abundance for the highest peak in the isotopic distribution plot. Molecular ions $[M]^-$ were detected for all univalent anions and $[M–H]^-$ for zwitterionic compounds as the base peaks in the spectra. Full agreement of the experimental and calculated isotopic distribution pattern was observed for all these 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.

### 6.3. Analytical HPLC

Was used to check the purity A Merck-Hitachi HPLC system LaChrom 7000 series equipped with DAD 7450 detector and an Intelligent Injector L7250 was used. Chromatographic procedure: An Ion-Pair RP chromatographic method with an isocratic elution was used, based on the methods previously reported [32] for the separation of hydrophobic borate anions. Column: RP Separon™ SGX C8, 7 μm (silica with chemically bonded octyl groups) Tessek Prague, Czech Rep. Chromatographic conditions: Solvent 4.5 mmol/L hexylamine acetate (adjusted to pH 5.5) in 58% aqueous acetonitrile, detection DAD (220–600 nm), fixed wavelengths 254, 265, 290 and 312 nm; sensitivity range 0.2 A.U.F.S; samples of concentration approx. 0.5 mg mL$^{-1}$ in the mobile phase or $CH_3CN$ were injected (1–5 μL); the method allowed for the resolution of most of the compounds from the real reaction mixtures and for the purity assay and control. Capacity factors $k' = (t_R - t_0)/t_0$ (where $t_R$ is retention time, $t_0$ is the void retention time of an non retained peak) are given for individual compounds; $k' = 3.53$ was observed for the parent ion $\mathbf{1}^-$ under the chromatographic conditions used for analysis. Purity assay was based on the peaks area on the chromatograms of the individual compounds.

### 6.4. X-ray Structure determinations

The single crystals of compounds of Cs**3a**, **6** and Ca**7a** were mounted onto a glass fibre with epoxy cement and measured on four-circle diffractometer KappaCCD with a CCD area detector by mono-chromatized Mo Kα radiation ($\lambda$ = 0.71073 Å) at 150(2) K. The crystallographic details are summarized in Table 1, the numerical absorption correction [35] was applied for structure Cs**3a**, (absorption was neglected in data reduction for **6** and Ca**7a,** $\mu$(Mo) = 0.64 and 0.49 mm$^{-1}$). The structures were solved by the direct method (SIR97) [36] and refined by a full matrix least squares procedure based on $F^2$ (SHELXL97) [37]. The hydrogen atoms were

fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom), for the methyl moiety multiple of 1.5 was chosen.

PLATON/SQUEEZE [38] was used to correct the data of **7a** for the presence of the disordered solvent. Four potential solvent volumes each of 1378 Å$^3$ were found at special position with the high site symmetry. Six hundred and thirty two electrons per unit cell worth of scattering were located in the voids, highest peak corresponds to electron density 4.6 e/A$^3$. The trichlormethane as well as methanol molecules were found as solvents in the crystal. However the high electron count suggests about the presence of additional disordered molecules of trichlormethane in majority of the voids. By using SQUEEZE procedure the precision of determination of $Ca^{2+}$ complex was improved, however the problem of additional compensating cations could not be resolved. Properly ordered part of the structure corresponds to the moiety of formulation: $2[(C_{81}H_{132}B_{54}CaCo_3N_3O_4P_3)^-]\cdot 6(CH_3O)\cdot CHCl_3$, where unit cell contains four such moieties. Consequently eight (+) charges are necessary for compensation. They can be either hidden in voids for example in the form of disordered $Na^+$ cation or attached to Ca-complex as disordered protons probably on methoxy groups. Neither of these ideas could be confirmed or excluded. This exceptional feature of the crystal probably issues from the high symmetry of Ca-complex (3-fold rotational axis), which enables high symmetry of the whole crystal (cubic $Pa3^-$ space group). However this symmetry is not followed by the rest of the content of the unit cell resulting in vast disorder.

The final difference maps of all the three structures presented here displayed no peaks of chemical significance.

The structure determination of complex $Eu^{3+}$ complex [34] afforded to create a model of the complex with low precision due to vast disorder of substation part of the molecule (see Fig. 3). Therefore we hereby present only geometric parameters of the coordination sphere around the $Eu^{3+}$ atom, as they are not affected with disorder [39].

### 6.5. Extraction tests

Extraction experiments were performed in glass test tubes with polyethylene stoppers at laboratory temperature (25 ± 1 °C). The phase volume ratio was 1:1 (1 ml of each phase). The samples of sodium salts were shaken for 1 h (10 min intervals were sufficient for attaining extraction equilibrium) on a horizontal shaker. After shaking, the test tubes were centrifuged and 0.5 ml samples of each phase were taken for radioactivity measurement. All used reagents were of A.R. quality, the same is valid for the solvents. The distribution of Eu and Am was investigated using $^{152,154}$Eu and $^{241}$Am tracers (radiochemical purity). The radioactivity of the samples was measured using single-channel γ analyser with NaI (Tl) well-type detector. The measurement duration was adapted to obtain reproducibility between ±5%.

### 6.6. Synthetic procedure for synthesis of the CMPO derivatives

These compounds were prepared by reaction of the corresponding zwitterionic ammonium derivatives **2** and **4a–c** reported previously and the newly prepared benzylammonium derivative **6** (for synthesis and characterization see part below) with the active nitrophenylesters of diphenyl (**ae-1**) octyl phenyl (**ae-2**) phosphoryl acetic and diphenyl phosphoryl propionic acid (**ae-3**) prepared accordingly to the reported procedures [20,23,24].

### 6.7. General synthetic procedure to compounds of the series 3, 5 and 7

The zwitterionic derivatives **2a,b, 4a–c and 6** (1.0 mmol) were dried in vacuum at 60 °C for 6 h, then dissolved in THF (15 ml). Solid NaH (105 mg, 95%, 2.05 mmol) was added and the resulting slurry was stirred at room temperature for 2 h. Then the solution of nitrophenyl ester of alkylphenyl phosphoryl acids (**ae-1, ae-2** or **ae-3**) (1.2 mmol) in THF (20 ml) was dropwise added from addition funnel during 60 min, the content of the reaction flask was heated at 60 °C (bath temperature) until the spot of starting species persisted on TLC (2–16 h). After cooling down and standing overnight, the solids were removed by filtration under nitrogen, washed with dry THF (2 × 5 ml) and discarded. Ethanol (1 ml) was carefully added to the supernatants followed by water (5 ml) and acetic acid (3 M, 0.2 ml). Solvents were removed in vacuum and the residue was dissolved in $CH_2Cl_2$ (20 ml) and washed with HCl (3 M, 15 ml) and cold 5% aqueous $Na_2CO_3$ (0 °C, 4 × 15 ml) followed with brine (4 × 15 ml). After addition of water (5 ml) $CH_2Cl_2$ was evaporated to dryness. The semi-crystalline materials were then dried in vacuum at ambient temperature for 10 h. The sodium salts were purified by crystallization from $CH_2Cl_2$ or benzene solutions (a drop of $CH_3OH$ was added to the solvent to effect the dissolution) layered carefully with hexane and left to stand for several days. Alternatively, part of the compounds was purified by liquid chromatography on a silica gel column (for chromatographic conditions for each particular compound see below). The sodium salts were used in the extraction tests. Tetramethyl ammonium or $Cs^+$ ($Eu^{3+}$, $Ca^{2+}$) salts for compounds characterizations were prepared by dissolution of the corresponding sodium salts (20 mg) in $CH_2Cl_2$ (2.5 ml) washed with HCl (3 M, 3 × 2.5 ml), water (3 × 2.5 ml), dissolved in aqueous MeOH (70%) and precipitated by an excess of aqueous solution of $Me_4NOH$ (or $Cs_2CO_3$, $Eu(NO_3)_3$, $CaCl_2$), filtered through a 45 μm syringe nylon filter, washed with $H_2O$ (3 × 1 ml) and dried in vacuo. Protonated forms were isolated by evaporation of the methylene chloride solutions washed with 1 M HCl and water (see above).

#### 6.7.1. Synthesis of *3a*

The compound was prepared starting from starting ammonium derivative **2** and the active ester **ae-1** and purified by crystallization from benzene–hexane and dried 12 h under reduced pressure at 50 °C. Single crystals of Cs**3a** and Eu(**3a**)$_3 \cdot 3H_2O$ for X-ray diffraction were grown by slow diffusion of hexane into benzene solutions containing 5% of aqueous ethanol. Na**3a:** a wine red powder, yield 575 mg (96%) m.p. 329–332 °C**,** HPLC $k'$ 3.74, purity assay 99.5%; $Me_4N$**3a**: m.p. 200–202 °C, TLC $R_F$ (80% aqueous $CH_3OH$) 0.47, $^{11}$B NMR (160 MHz, acetone-$d_6$) δ (ppm) ($J_{B-H}$, Hz) 7.85, 7.29 (2s, B8, 8′) (127), −1.63, −2.50 (2d, *J* 142 B10′,10) (142), −7.15 (d, *J* 157, B 9, 12, 9′,12′), −9.29, −10.15 (2d, *J* 150, B4, 4′,7, 7′), −15.79 (d, *J* 158, B5, 5′, 11, 11′), −25.53 (br. d, *J* 144, B6, 6′) (144). $^1$H NMR: (acetone-$d_6$) δ (ppm) 7.827 (m, 4H, Ar), 7.63 (m, 2H, Ar), 7.553 (m, 4H, Ar), 3.72 (d, *J*(P-H) = 17.6 Hz, 2H, $CH_2$-P), 3.575 (br. s, 4H, $CH_{carb.}$), 3.334 (s, 12H, $(CH_3)_4N^+$). B-H signals from $^1$H{$^{11}$Bselective} NMR (acetone-$d_6$) δ (ppm) 3.66 (H4, 7, 4′,7′), 2.82, 2.77 (H10, 10′), 2.11, 2.02 (H 9, 12, 9′,12′), 1.75 (H5, 5′, 11, 11′), 1.63 (H6, 6′); $^{13}$C NMR (acetone-$d_6$) δ (ppm) 166.35 (C=O), 136.38 (d, *J*P-H 99.5 Hz, ArC-P), 131.88, 131.79, 129.06, 128.95 (ArC) 55.80 ($Me_4N^+$), 42.83, 42.69 ($CH_{carb.}$), 38.275 (d, $J_{C-P}$ = 71.6 Hz, $CH_2$P); $Na^+$**3a:** $^{31}$P{$^1$H} NMR: 32.36 ppm, $H^+$**3a:** $^1$H NMR: (acetone-$d_6$) δ (ppm) 7.80 (m, 4H, Ar), 7.61 (m, 2H, Ar), 7.583 (m, 4H, Ar), 3.54 (br. s, 2H, $CH_2$-P), 3.42 (br. s, 4H, $CH_{carb.}$); $^{31}$P{$^1$H} NMR: 37.46 ppm; Mass. (ESI) 579.3 (100%), 582.31 (3%) calcd. 582.31 $[M]^-$; 1181.6 (15%), 1187.6 (1%) $[2M+Na]^-$.

#### 6.7.2. Synthesis of *3b*

The compound was prepared starting from the ammonium derivative **2** and the active ester **ae-2**. The compound was isolated by chromatography on silica gel using $CH_3CN$–$CH_2Cl_2$ 3:1 to 2:1 as the mobile phase. Na**3b:** a wine-red solid, yield 275 mg (43%)**,** HPLC $k'$ 10.6, purity assay 98.0%; $Me_4N$**3b:** m.p. 185–187 °C, TLC

$R_F$ (80% aqueous $CH_3OH$) 0.30; $^{11}B$ NMR (acetone-$d_6$) $\delta$ (ppm) ($J_{B-H}$, Hz) 9.98, 8.95 (2s, B8, 8′), −2.13, −3.22 (2d, $J$ = 143, B10′,10) (142), −6.41 (d, $J$ = 155, B 9, 12, 9′,12′), −9.69, −10.37 (2d, $J$ = 158, B4, 4′,7, 7′), −16.09 (d, $J$ = 158, B5, 5′, 11, 11′), −26.33 (br. d, $J$ = 150, B6, 6′); $^1H$ NMR: (acetone-$d_6$) $\delta$ (ppm) 7.762 (m, 4H, Ar), 7.45 (m, 6H, Ar), 3.34(br. s, 2H, $CH_{carb.}$), 3.29 (br. s, 2H, $CH_{carb.}$), 3.343 (s, 12H, $(CH_3)_4N^+$); 3.051 (dd, $J$(P-H) = 16.8 Hz, 2H, $CH_2$-P), 2.298 (m, 2H, $CH_2$-P), 2.032 (m, 2H, $CH_2$), 1.558 (m, 2H, $CH_2$), 1.244 (m, 8H, $CH_2$), 0.878 (t, 3H, $J$ 7.2 Hz, $CH_3$); B-H signals from $^1H\{^{11}B$selective} NMR (acetone-$d_6$) $\delta$ (ppm) 3.92, 3.42 (H4, 7, 4′,7′), 2.783, 2.673 (H10, 10′), 2.16, 2.07 (H 9, 12, 9′,12′), 1.72 (H5, 5′, 11, 11′), 1.59 (H6, 6′); $^{13}C$ NMR (acetone-$d_6$) $\delta$ (ppm) 166.94 (C═O), 135.91 (d, $J$ 45 Hz, ArC-P), 131.98, 131.49, 128.78 (ArC), 55.13 ($Me_4N^+$), 42.52, 42.40 ($CH_{carb.}$), 38.56 (d, $J_{C-P}$ = 63.1 Hz, $CH_2P$), 31.18(d, $J_{C-P}$ = 75.2 Hz, $CH_2P$), 30.21 ($CH_2$, Oct), 23.29 ($CH_2$, Oct), 22.18 ($CH_2$, Oct), 21.4 ($CH_2$, Oct), 14.36 ($CH_3$, Oct); $H^+$**3b**: $^{31}P\{^1H\}$ NMR 48.12 ppm, $Na^+$**3b**: $^{31}P\{^1H\}$ NMR 45.85 ppm, Mass. (ESI) 616.62 (100%) 618.52 (8%) calcd. 618.42 $[M]^-$; 1871.42 (20%), 1879.42 (1%) $[3M+Na+H]^-$.

### 6.7.3. Synthesis of **3c**

The compound was prepared starting from the ammonium derivative **2** and active ester **ae-3**. The compound was isolated by chromatography on silica gel using $CH_3CN$–$CH_2Cl_2$ 3:1 as the mobile phase. Na**3c**: yield 296 mg, 48%, HPLC $k'$ 1.54, purity assay 98.4%, $Me_4N$**3c**: m.p. 222–225 °C TLC $R_F$ (80% aqueous $CH_3OH$) 0.61, $^{11}B$ NMR (160 MHz, acetone-$d_6$) $\delta$ (ppm) ($J_{B-H}$, Hz) 10.19, 9.07 (2s, B8, 8′), −2.27, −3.74 (d, $J$ = 142, B10′,10), −6.26 (d, $J$ = 157, B 9, 12, 9′,12′), −9.61, −10.45 (2d, $J$ = 150, B4, 4′,7, 7′), −16.16 (d, $J$ = 158, B5, 5′, 11, 11′) (158), −27.05 (br. d, $J$ = 144, B6, 6′). $^1H$ NMR: (acetone-$d_6$) $\delta$ (ppm) 7.818 (m, 4H, Ar), 7.506 (m, 6H, Ar), 3.487 (s, 12H, $(CH_3)_4N^+$), 3.315 (br. s, 2H, $CH_{carb.}$), 3.28 (br. s, 4H, $CH_{carb.}$), 2.494 (m, 4H, $CH_2$-P, $CH_2$), B-H signals from $^1H\{^{11}B$selective} NMR (acetone-$d_6$) $\delta$ (ppm) 3.76 (H4, 7, 4′,7′), 2.75, 2.67 (H10, 10′), 2.13, 1.82 (H 9, 12, 9′,12′), 1.69 (H5, 5′, 11, 11′), 1.54 (H6, 6′); $^{13}C$ NMR (acetone-$d_6$) $\delta$ (ppm) 209.98 (C═O), 131.65, 132.62, (d, $J$P-H 93.3 Hz), 129.35, 129.3 (ArC), 54.65 ($Me_4N^+$), 69.17 ($CH_2CO$), 54.47 (m, $CH_2P$), 54.74, 42.32 ($CH_{carb.}$); $^{31}P\{^1H\}$ NMR: 32.69 ppm; Mass. (ESI) 593.2 (100%) 596.3 (18%) calcd. 596.33 $[M]^-$, 1824.9 (5%), 1834.9 (1%) $[3M+2Na]^-$.

### 6.7.4. Synthesis of **5a**

The compound was prepared starting from the ammonium derivative **4a** and the active ester **ae-1**. The compound was isolated by chromatography on silica gel using $CH_3CN$–$CH_2Cl_2$ 2:1 as the mobile phase to yield 375 mg (62%) of orange microcrystalline material. Found: HPLC $k'$ 3.13, purity assay >99.5%; $Me_4N$**5a** m.p. 185–187 °C; TLC $R_F$ (80% aqueous $CH_3OH$) 0.54, $\delta_B$ (128 MHz, $CD_3COCD_3$, $Et_2O \cdot BF_3$) 12.17 (1 B, s, B8), 5.44 (d, $J$ = 140, B8́), 1.30 (d, $J$ = 139, B10́), −0.30 (d, $J$ = 137, B10), −3.65 (d, $J$ = 156, B4́, 7́), −6.08 (d, $J$ = 135, B9′, 12′), −6.08 (d, $J$ = 132, B4, 7, 9, 12), −16.94 (d, $J$ = 156, B5́, 1́1), −20.18 (d, $J$ 159, B5, 11), −21.72 (d, $J$ 165, B6́), −24.96 (1 B, d, $J$ 151, B6); $\delta_H$ (400 MHz, $CD_3COCD_3$, $Me_4Si$) 7.818 (m, 4H, Ar), 7.53 (m, 2H, Ar), 7.509 (m, 4H, Ar), 6.831 (s, 1H, NH), 4.593 (br. s, 2H, $CH_{carb.}$), 4.327 (br. s, 2H, $CH_{carb.}$), 3.412 (s, 12H, $(CH_3)_4N^+$), 3.352 (d, $J$(P-H) = 13.6 Hz, 2H, $CH_2$-P); B-H signals from $^1H\{^{11}B$selective} NMR (acetone-$d_6$) $\delta$ (ppm) 2.94 (H10́), 2.85 (H10), 2.62 (H8́), 2.76 (H4, 7), 2.85 (H4́, 7́), 1.92 (H9′, 12′), 3.07, 1.80 (H9, 12), 1.57 (H5́, 1́1), 1.53 (H5, 11), 1.58 (H6), 1.49 (H6́), Na**5a:** $\delta_C$ (100 MHz, $CD_3COCD_3$, $Me_4Si$) $\delta$ (ppm) 168.34 (C═O), 133.47, 131.85, 129.76 (ArC) 53.09 ($CH_{carb.}$), 49.75 ($CH_{carb.}$), 40.03 (ArC-P); $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$) NMR: 32.55 ppm, $H^+$**4a** $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$): 36.64 ppm; M. S. $m/z$ ($ESI^-$) 582.46 (100), 584.40 (10) (calcd. 585.34) $[M]^-$.

### 6.7.5. Synthesis of **5b**

The compound was prepared starting from ammonium derivative **4b** and the active ester **ae-1**. The compound was isolated by chromatography on silica gel using methylene chloride to remove traces of the starting compound **4b** and then by $CH_3CN$–$CH_2Cl_2$ solvent mixture from 3:1 to 2:1 as the mobile phase to elute the product. An orange solid, yield 475 mg, (75%); HPLC $k'$ 5.20, purity assay >99.5%; $Me_4N$**5b**: m.p. 157–159 °C; TLC $R_F$ (80% aqueous $CH_3OH$) 0.42, $\delta_B$ (128 MHz, $CD_3COCD_3$, $Et_2O{\cdot}BF_3$) 17.40 (1 B, s, B8), 8.62 (d, $J$ = 150, B8́), 1.32 (d, $J$ = 141, B10́), −0.98 (d, $J$ = 140, B10), −4.79, −5.62 (d, B4,7,9, 12, 9′, 12′), −7.43 (d, $J$ = 140, B9, 12), −16.56 (d, $J$ = 150, B5́, 1́1), −19.80 (d, $J$ 153, B5, 11), −21.96 (d, $J$ 153, B6́), −25.31 (1 B, d, $J$ 150, B6); $\delta_H$ (400 MHz, $CD_3COCD_3$, $Me_4Si$) 7.832 (m, 4H, Ar), 7.482 (m, 6H, Ar), 4.17 (br. s, 4H, $CH_{carb.}$), 3.828 (m, 2H, $CH_2$-N), 3.433 (s, 12H, $(CH_3)_4N^+$), 3.456 (d, $J$(P-H) = 13.4 Hz, 2H, $CH_2$-P); 0.867 (t, 3H, $J$(H-H) = 6.8 Hz, $CH_3$); B-H signals from $^1H\{^{11}B$selective} NMR (acetone-$d_6$) $\delta$ (ppm) 3.43 (H8́), 2.97 (H10́), 2.91 (H10), 2.87 (H4, 7), 3.11 (H4́, 7́), 2.34, 1.93 (H4, 7, 9, 12, 9′, 12′), 1.62 (H5́, 1́1), 1.69 (H6), 1.60 (H5, 11), 1.55 (H6́); Na**5b:** $\delta_C$ (100 MHz, $CD_3COCD_3$, $Me_4Si$) $\delta$ (ppm) 174.91 (C═O), 137.36, 136.43, 134.23 (ArC) 57.07 ($CH_{carb.}$), 53.86 ($CH_{carb.}$), 51.99 ($CH_2N$), 45.31 (d, $J$ 69.9 Hz, $CH_2$-P), 18.74 ($CH_3$); Na**5b** $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$) NMR: 31.74 ppm, MS $m/z$ ($ESI^-$) 610.46 (100), 612.36 (38) (calcd. 612.36) $[M]^-$.

### 6.8. Synthesis of **5c**

This derivative was prepared starting from ammonium derivative **4c** and the active ester **ae-1**. The compound was isolated by chromatography on silica gel using methylene chloride to remove traces of the starting derivative **4c** and then by $CH_3CN$–$CH_2Cl_2$ solvent mixture from 3:1 to 2:1 as the mobile phase to yield 542 mg (78%) of an orange microcrystalline material. Found for Na**5c**: HPLC $k'$ 7.22, purity assay >99.5%; $Me_4N$**5c:** m.p. 197–199 °C; TLC $R_F$ (80% aqueous $CH_3OH$) 0.38, $\delta_B$ (128 MHz, $CD_3COCD_3$, $Et_2O \cdot BF_3$) 12.59 (1 B, s, B8), 7.69 (d, $J$ = 150, B8́), 1.51 (d, $J$ = 141, B10́), −0.89 (d, $J$ = 140, B10), −4.62 (d, $J$ = 122, B4́, 7́), −5.45 (d, $J$ = 130, B4, 7, 9′, 12′), −7.31 (d, $J$ = 140, B9, 12), −16.30 (d, $J$ = 150, B5́, 1́1), −19.56 (d, $J$ 153, B5, 11), −21.53 (d, $J$ 153, B6́), −25.01 (1 B, d, $J$ 150, B6); $\delta_H$ (400 MHz, $CD_3COCD_3$, $Me_4Si$) 7.847 (m, 4H, Ar), 7.482 (m, 6H, Ar), 7.207 (m, 1H, Ar), 7.068 (m, 2H, Ar), 7.028 (m, 2H, Ar), 4.474 (d, $J$(P-H) = 12.4 Hz, 2H, $CH_2$-P), 4.145 (br. s, 4H, $CH_{carb.}$), 3.268 (s, 12H, $(CH_3)_4N^+$), 2.877 (br. s, 2H, $CH_2N$); B-H signals from $^1H\{^{11}B$selective} NMR (acetone-$d_6$) $\delta$ (ppm) 3.46 (H8́), 3.01 (H10́), 2.88 (H10), 2.84 (H4, 7), 2.97 (H4́, 7́), 2.84, 1.87, 1.79 (H4, 7, 9, 12, 9′, 12′), 1.59 (H5́, 1́1), 1.59 (H5, 11), 1.57 (H6), 1.49 (H6́), Na**5c:** $\delta_C$ (100 MHz, $CD_3COCD_3$, $Me_4Si$) $\delta$ (ppm) 171.43 (C═O), 140.37, 133.34, 132.21, 131.30, 129.99, 128.38, 127.14, 126.07 (ArC) 53.09 ($CH_{carb.}$), 49.53 ($CH_{carb.}$), 52.85 ($CH_2N$), 38.86 (d, $J$ 69.4 Hz, ArC-P); $H^+$**5c** $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$): 36.98 ppm; $Na^+$**5c** $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$) NMR: 33.25 ppm; MS $m/z$ ($ESI^-$) 671.48 (100), 675.40 (4) (calcd. 675.38) $[M]^-$.

### 6.8.1. Synthesis of 8-N-benzylammonium-8′-methoxy-3,3-cobalt bis(1,2-dicarbollide) (**6**)

The starting zwitterionic derivative [8,8′-μ-$CH_2O(CH_3)$-(1,2-$C_2B_9H_{10}$)2-3-Co] 1.0 g (2.73 mmol) was dried in vacuum, then dissolved in toluene–DME (9:1, 20 ml) and solution of the benzylamine in excess dissolved the same solvent (20 ml) was added. The reaction mixture was stirred for 12 h, then the solvents were evaporated under reduced pressure, the residue was dissolved in a $CH_2Cl_2$–hexane (1:1, 3 ml), injected on a top of a silica gel column (2.5 × 25 ml) and the orange band was eluted using the same solvent mixture as the mobile phase. The single crystal for X-ray

diffraction was grown by a slow evaporation of the acetonitrile solution of **6**. Data for **6**: yield 1.25 g, 96%, HPLC purity assay 99.8%; TLC $R_F$ 0.32 (TLC plate Silufol, silica gel, $CH_2Cl_2$–hexane 1:1); $\delta_B$ (128 MHz, $CD_3COCD_3$, $Et_2O{\cdot}BF_3$) 26.57 (1 B, s, B8′), 10.09 (s, B8), 0.31 (d, $J$ = 151, B10), −2.09 (d, $J$ = 150, B10′), −4.75 (d, $J$ = 152, B9, 12), −5.92 (d, $J$ = 162, B4, 7, 9′, 12′), −7.87 (d, overlap, B4′, 7′), −18.14, −18.91 (2d, $J$ 143, 147, B5, 5′, 11,11′), −22.83 (d, $J$ 180, B6), −27.79 (1 B, d, $J$ 179, B6′); $\delta_H$ (400 MHz, $CD_3COCD_3$, $Me_4Si$) 8.16 (br. s., 2H, NH), 7.455 (m, 2H, Ar), 7.36 (m, 3H, ArH), 4.292 (t, $J$ = 5.6 Hz, 2H, Ph-$CH_2NH_2CH_2$), 3.95 (br. s, 4H, $CH_{carb.}$), 3.188 (d, 3H, $CH_3O$; 2.894 (t, 2 H, $J$ = 4.9 Hz, B-$CH_2NH_2CH_2$); B-H signals from $^1H\{^{11}B$selective$\}$ NMR (acetone-$d_6$) $\delta$ (ppm) 2.90 (H10), 2.70 (H10′), 2.97 (H4́, 7́), 2.78 (H4, 7), 2.26 (H 9′, 12′), 1.87 (H 9, 12), 1.58, 1.56 (H5, 5́, 11,11′), 1.62 (H6), 1.41 (H6́); $\delta_C$ (100 MHz, $CD_3CN$, $Me_4Si$) 132.33, 130.87, 130.06, 129.79 (ArC) 57.53 ($CH_3O$), 54.06 ($CH_2N$), 51.47, 48.31 ($CH_{carb.}$); $m/z$ ($ESI^-$) 473.33 (100), 476.36 (4) (calcd. 476.36) $[M-H]^-$.

*6.8.2. Synthesis of **7a***

The compound was prepared starting from the above ammonium derivative **6** and the active ester **ae-1** and purified by crystallization from benzene–hexane and dried 12 h under reduced pressure at 50 °C. Single crystal of the calcium complex was grown by slow diffusion of hexane into chloroform solution of the compound to which few drops of MeOH were added to complete the dissolution. Na**7a**: an orange solid, yield 577 mg (78%), HPLC $k'$ 6.83, purity assay >99.5%; $Me_4N$**7a:** m.p. 135–137 °C; TLC $R_F$ (80% aqueous $CH_3OH$) 0.21, $\delta_B$ (128 MHz, $CD_3COCD_3$, $Et_2O \cdot BF_3$) 24.25 (1B, s, B8′), 9.86 (s, B8), −0.72 (d, $J$ = 150, B10), −2.29 (d, $J$ = 146, B10′), −5.12 (d, $J$ = 165, B9, 12), −7.79 (3d, $J$ = 140, 148, 147, B4, 7, 4′, 7′, 9′, 12′), −17.85, −19.92 (2d, $J$ 143, 147, B5, 5′, 11,11′), −23.88 (d, $J$ 156, B6), −28.19 (1 B, d, $J$ 179, B6′); $\delta_H$ (400 MHz, $CD_3COCD_3$, $Me_4Si$) 7.929 (m, 4H, Ar), 7.493 (m, 6H, Ar), 7.241 (m, 2H, ArH), 7.206 (m, 3H, ArH), 4.551 (s, 2H, Ph-$CH_2$-N), 4.212 (br. s, 2H, $CH_{carb.}$), 4.05 (br. s, 2H, $CH_{carb.}$), 3.804 (d, 2H, $J$ = 14.0 Hz, $CH_2$-P), 3.379 (s, 12H, $(CH_3)_4N^+$), 3.221 (s, 3H, $CH_3O$; 2.882 (br. s, 2H, B-$CH_2$N); B-H signals from $^1H\{^{11}B$selective$\}$ NMR (acetone-$d_6$) $\delta$ (ppm) 2.88 (H10), 2.66 (H10′), 2.82 (H9, 12), 2.78, 2.01, 1.88 (H4, 7, 4′, 7′, 9′, 12′), 1.68, 1.52 (H5, 5́, 11,11′), 1.63 (H6), 1.41 (H6́); $\delta_C$ (100 MHz, $CD_3COCD_3$, $Me_4Si$) $\delta$ (ppm) 165.70 (C=O), 139.72, 135.52 (d, $J$P-H 101.3 Hz), 132.19, 131.87, 129.21, 128.93, 128.35, 127.10 (ArC) 57.41 ($CH_3O$), 55.88 ($Me_4N^+$), 53.48 ($CH_{carb.}$), 50.35 ($CH_2$N), 48.02 ($CH_{carb.}$), 38.77 (d, $J$ 64.7 Hz, $CH_2$-P); Na**7a** $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$) NMR: 35.22 ppm, M. S. $m/z$ ($ESI^-$) 716.15 (100),719.41 (4) (calcd. 719.41) $[M]^-$.

*6.8.3. Synthesis of **7b***

This derivative was prepared starting from the ammonium derivative **6** and the active ester **ae-2**. The compound was isolated by chromatography on silica gel using methylene chloride to remove traces of the starting derivative **6** and then by $CH_3CN$–$CH_2Cl_2$ solvent mixture 2:1 as the mobile phase to yield an orange microcrystalline material. Na**7b**: yield 202 mg, 26%, HPLC $k'$ 21.5, purity assay >99.0%; $Me_4N$**7b:** m.p. 103–105 °C; TLC $R_F$ (80% aqueous $CH_3OH$) 0.13, $\delta_B$ (128 MHz, $CD_3COCD_3$, $Et_2O \cdot BF_3$) 24.15 (1 B, s, B8′), 9.76 (s, B8), −0.70 (d, $J$ = 153, B10), −2.32 (d, $J$ = 153, B10′), −5.20 (d, $J$ = 153, B9, 12), −7.76 (3d, $J$ = 153, 137, B4, 7, 4′, 7′, 9′, 12′), −17.82, −19.89 (2d, $J$ 144, B5, 5′, 11,11′), −23.79 (d, $J$ 156, B6), −28.05 (1 B, d, $J$ 156, B6′); $\delta_H$ (400 MHz, $CD_3COCD_3$, $Me_4Si$) 7.842 (m, 2H, Ar), 7.542 (m, 1H, Ar) 7.492 (m, 2H, Ar), 7.218 (m, 4H, ArH), 7.203 (m, 1H, ArH), 4.50 (m, 2H, Ph-$CH_2$-N), 4.197 (br. s, 2H, $CH_{carb.}$), 4.01 (br. s, 2H, $CH_{carb.}$), 3.14 (d, 2H, $J$ = 14.0 Hz, $CH_2$-P), 3.448 (s, 12H, $(CH_3)_4N^+$), 3.237 (s, 3H, $CH_3O$), 3.095 (d, 2H, $J$ = 27.6 Hz, $CH_2$-P), 2.845 (br. s, 2H, B-$CH_2$N), 2.363 (m, 2H, $CH_2$), 1.84 (m, 2H, $CH_2$), 1.617 (m, 2H, $CH_2$), 1.367 (m, 2H, $CH_2$), 1.253 (m, 4H, $CH_2$), 0.876 (t, 3H, $J$ = 6.8 Hz, $CH_3$); B-H signals from $^1H\{^{11}B$selective$\}$ NMR (acetone-$d_6$) $\delta$ (ppm) 2.75 (H10), 2.66 (H10′), 2.82 (H9, 12), 2.77, 2.04, 2.00 (H4, 7, 4′, 7′, 9′, 12′), 1.66, 1.52 (H5, 5́, 11,11′), 1.60 (H6), 1.36 (H6́); $\delta_C$ (100 MHz, $CD_3COCD_3$, $Me_4Si$) $\delta$ (ppm) 166.47 (C=O), 132.15, 131.69, 129.01, 128.64, 127.50, 127.25 (ArC) 57.42 ($CH_3O$), 55.95 ($Me_4N^+$), 53.33 ($CH_{carb.}$), 50.43 ($CH_2N$), 47.93 ($CH_{carb.}$), 31.1 (d, $J$ 65.5 Hz, $CH_2$-P); 24.36 (2C, $CH_2$), 23.28, 22,06, 20.35 ($CH_2$), 14.36 (2C, $CH_2$), 13.85 ($CH_3$); Na**7b** $\delta_P$ $^{31}P\{^1H\}$(161.91 MHz, $CD_3COCD_3$, $H_3PO_4$) NMR: 36.32 ppm, MS $m/z$ ($ESI^-$) 752.75 (100), 755.44 (2) (calcd. 755.51) $[M]^-$.

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## Appendix A. Supplementary material

CCDC 705521, 705652 and 705522 contain the supplementary crystallographic data for Cs**3a, 6** and Ca**7a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.056.

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