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Functionalized cobalt bis(dicarbollide) ions as selective extraction reagents for removal of M^{2+} and M^{3+} cations from nuclear waste, crystal and molecular structures of the [8,8′-μ-ClP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]HN(C_2H_5)$_3$ and [8,8′-μ-Et_2NP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co](HN(CH_3)$_3$)

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Abstract

New reliable synthetic methods leading to derivatives of the *closo*-[(1,2-$C_2B_9H_{11}$)$_2$-3,3′-Co]$^-$ (**1**) anion **1** with phosphorus containing substituents on the cage boron atoms have been successfully developed, starting from its 8-OH (**2**) and 8,8′-(OH)$_2$ (**3**) hydroxyderivatives. Reactions of **2** with either Cl_3PO or $PhCl_2PO$ followed by hydrolysis gave 8-(HO)$_2$PO–O– (**4**) and [(8-PhPO(OH)–O)-1,2-$C_2B_9H_{10}$)(1,2-$C_2B_9H_{11}$)-3,3′-Co]$^-$ (**5**) phosphorylated species, respectively. Analogous reactions of Cl_3PO with **3** provided a chlorine bearing bridged product [8,8′-μ-ClP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]$^-$ (**6**) with surprisingly high hydrolytic stability. The anticipated anion [8,8′-μ-(HO)(O)-P(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]$^-$ (**7**) with phosphoric acid as the bridging substituent was obtained after alkaline hydrolysis of compound **6**. The related [8,8′-μ-Ph(O)P(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]$^-$ (**8**) derivative was prepared by similar reaction of **3** with $PhCl_2PO$ and subsequent hydrolysis. Further developments starting from versatile precursor **6** led to synthesis of a derivative containing an asymmetric bridging diethylphosporamide moiety [8,8′-μ-(Et_2N)P(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]$^-$ (**9**). A crystal of the compound **9** containing a pure enantiomer was selected, and its absolute configuration was determined by X-ray diffraction. Molecular structure of the compound **6** was also determined by X-ray diffraction analysis and the crystallographic results for both compounds are presented. Compounds **6** and **7** represent efficient Eu^{3+} extractants, enabling metal extraction even from highly acidic solutions (up to 1 M HNO_3) to aromatic solvents. The novel compounds thus amalgamate in the single molecule good extraction properties of cobalta bis(dicarbollide) anion and the complexation ability of alkylphosphates. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carboranes; Metallaboranes; Liquid–liquid extraction; Chirality; Chiral metal complexes; X-ray crystallography; Phosphorus

1. Introduction

During past years, a lot of effort has been devoted to the development of a robust and reliable process for the selective separation of medium- and long-lived radionuclides from high and medium level liquid waste (**HLW** and **MLW**). Such process would permit to decrease noticeably the volume of the waste to be buried in deep geological repositories (e.g. $^{137}Cs^+$, $^{90}Sr^{2+}$) or to be eventually transmuted (actinides) to short-lived nuclides in advanced nuclear reactors based on so-called ‘partition and transmutation’ technology concept (P&T) [1–3].

A variety of separation methods has been proposed based predominantly on hydrometallurgical processes, i.e. on liquid–liquid extraction. The most extraction

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methods exploit uncharged organic species as specific sequestrates for the target nuclides (e.g. crown ethers, malonamides, modified calixarenes, tri-*n*-butyl phosphine oxide, octyl phenyl (*N*,*N*-diisobutylcarbamoyl)methyl dialkyl phosphine oxide (**CMPO**), etc.). Such compounds act as uncharged ligands able to complex the target ion tightly in the aqueous phase and facilitating thus its transport to an immiscible organic phase. In this case, adequate number of anionic counter-ions (mainly the nitrate in practice) has to follow [4–7] cation into the organic phase.

A principally different approach in the development of the Selective Extraction Agents (**SEA**) emerged 25 years ago [8–16] from the application of various derivatives of the cobalt bis(dicarbollide) anion (1-) (for review of their synthesis and chemical properties see [17]), *closo*-$[(1,2\text{-}C_2B_9H_{11})_2\text{-}3,3'\text{-Co}]^-$ (**1**) (Fig. 1). In this case, the extremely hydrophobic anion enters the organic phase of a moderate polarity, followed with the least hydrated, large diameter, M^+ cations. This is due to electrostatic attraction between these ions and low hydratation of the resulting ion pair. In order to increase the chemical stability of **1** in nitric acid, the most reactive terminal hydrogen atoms at positions $B_{(8,8')}$ and $B_{(9,12,9',12')}$ are usually substituted for other groups, typically for halogens. The dicarbollide process based on the 'chlorine protected' **1** was designed many years ago for removal of $^{137}Cs^+$ and $^{90}Sr^{2+}$ [8–16] and from the beginning of 1990s, it became used in truly engineering scale. Slightly modified procedure is now called 'UNEX' [10–12]. The main advantages of the **1**-derivatives lie in their exceptional chemical and radiation stability, extreme acidity of their conjugate acids and high specificity for Cs^+ ions without other additives. Their main disadvantage lies in a virtual insolubility in low polar solvents (e.g. hydrocarbons). Consequently, less desirable moderately polar solvents are required (e.g. aromatic nitro compounds, halogenated ethers and esters, etc.). However, the **1**-based **SEA** can effectively extract multivalent cations only if synergic additives (e.g. mono alkyl polyethylene glycol for M^{2+} and, e.g. CMPO for M^{3+}) are simultaneously present in the extraction system. This fact further complicates the extraction mechanism and may create technological difficulties. Various aspects of these problems were discussed in several articles and reviews [8–16]. The problem of the synergists could be solved by chemical attachment of the selective moiety directly to the **1**-skeleton. Due to chemical versatility of the parent **1**, this approach has proven to be conceivable but until recently, it remained almost unexplored.

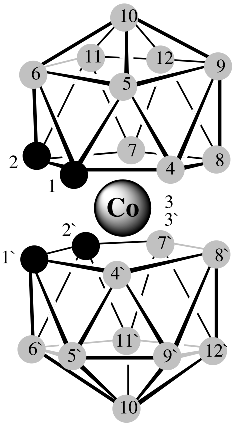


Fig. 1. Schematic drawing of the molecular structure of the parent anion *closo*-$[(1,2\text{-}C_2B_9H_{11})_2\text{-}3,3'\text{-Co}]^-$ (**1**).

This article summarizes one part of the continuing development of **SEA** suitable for transfer of lanthanides and actinides from acidic HLW into low polar organic phases without use of extra additives. In fact, we have been investigating several feasible synthetic ways how to link in one molecule the hydrophobic cluster anion together with the selective cation ligating groups. Later group should contain suitable electron donor atoms (e.g. oxygen, nitrogen, phosphorus, etc.) in geometric arrangement suitable for complexation. Especially the phosphorus based groups, like phosphine oxides, trialkyl phosphates or CMPO are known to be powerful sequestering agents for actinides [4,18,19]. Therefore, it could be expected, new effective extraction agents can emerge from combination of such groups with hydrophobic anion **1**.

Recently, new reliable high yield synthetic methods for bonding a variety of phosphorus containing moieties to the cage boron atoms of the anion **1** have been successfully developed and are subjects of this article. The starting synthons were the $[(8\text{-(HO)-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-Co}]^-$ (**2**) and $[8,8'\text{-(HO)}_2(1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-Co}]^-$ (**3**) ions. Adequate routes to large-scale preparation of these species from **1** had to be found before. These include procedure based on revision of reductive acetoxylation reaction [20] and/or the novel method of direct hydroxylation of **1**. This part of research has been published in a separate paper [21]. Here, we focus on derivatization of the anions **2** and **3** which led to several new phosphorus-containing compounds which might be promising as potential **SEA** tailored mainly for lanthanides and actinides. Syntheses and characterization of this class of species, including molecular structures of two compounds by X-ray crystallography are presented here along with their preliminary solvent extraction properties.

2. Experimental

2.1. General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by

Shriver [22], although some operations, such as column chromatography, were carried out in air. The starting compounds **2** and **3** were prepared for this study according to the procedures that have been described in the preceding paper [21]. Chloroform was dried over P_2O_5 and freshly distilled before use; Et_3N was dried over NaOH and distilled.

Other chemicals were reagent or analytical grade, starting cobalt bis(dicarbollide) Cs^+**1** was supplied by Katchem Ltd., Prague and used as received; $POCl_3$ and $PhPOCl_2$ from Fluka A.G., Germany; other chemicals from Lachema Brno, and were used as purchased. Column chromatography was carried out on silica gel (Aldrich 200–400 mesh) and the purity of the individual compounds and chromatographic fractions was monitored by analytical TLC on Silufol (Kavalier Votice, Czech Republic) (silica gel on aluminium foil with starch as the binder; orange or yellow spots, or detection by iodine vapors) and HPLC method (see details bellow).

The main physicochemical and analytical data (TLC, HPLC, MS, etc.) of the new species **4**–**9** are presented in Table 1.

2.2. *Physical measurements*

2.2.1. *NMR spectroscopy and mass spectrometry*

Proton (^1H)- and boron (^{11}B)-NMR and phosphorus (^{31}P) spectroscopy was performed at 11.75 T on Varian Unity-500 instruments and the samples were measured in deuterioacetone as the solvent. The procedure for [^{11}B–^{11}B]-COSY [23–25] and ^1H-{^{11}B(selective)} [26] NMR experiments were essentially as described in other papers from our laboratory [27]. NMR chemical shifts are given in ppm, the positive values being downfield. 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 digital resolution 2 Hz and are given in Hz. NMR data are summarized in Tables 2 and 3. High Resolution Mass spectra of ionic species were measured on Bruker Esquire-LC Ion Trap instrument using Electro spray Ionization. Negative ions were detected. Samples dissolved in acetonitrile (concentrations 1 ng l^{-1}) were introduced to ion source by infusion of 3 μl min^{-1}, drying temperature was 300 °C, drying gas flow 5 l min^{-1}, nebulizing gas pressure 10 psi.

2.2.2. *Analytical HPLC*

Equipment: 1. Analytical system: Merck–Hitachi, 6200 Intelligent pump, D-6000 Interface, Rheodyne 7125 Injection valve with 20 μl sample loop, L 7450 Diode Array detector with 7000 MANAGER SOFTWARE 2.1. Chromatographic procedure: The Ion-Pair RP chromatographic method for separation of hydrophobic borate anions [28] with DAD detection was used under modified conditions described earlier in the literature [29] by authors from this laboratory. Column: RP Separon C8 7 μm (silica with chemically bonded octyl groups) Tessek Prague, Mobile phase: 3 mmol hexylamine acetate in 58% aqueous acetonitrile, Flow rate 1 ml min^{-1}, detection DAD, fixed wavelengths 295, 308, 312 and 325 nm, Sensitivity range: 0.2 A.U.F.S, Samples of concentration ca. 1 mg ml^{-1}, Injection volume 5 μl.

2.2.3. *X-Ray crystallography*

The orange crystal of the compound **6** was mounted on glass fibre with epoxy cement and measured on four-circle diffractometer CAD4-MACHIII at 293(2) K using $\theta-2\theta$ scans. The crystallographic details are summarized in Tables 4 and 5. The crystals of **6** suffered by non-merohedral twinning, where only part of diffractions were overlapped exactly (diffractions with indexes fulfilling condition: mod(l,10) = 0). These diffractions were corrected for contribution of second part during refinement (SHELXL-97) yielding fractional contribution of two components as 0.443:0.557. Although this correction improve R-factor from 0.11 to 0.07, there are number of uncorrected reflections, which intensities are affected by vicinity of second spot due to unfavorable orientation of crystal during data collection and, there-

Table 1

TLC and HPLC k' values of the functionalized derivatives of the anion **1** of the general formulae $[(8\text{-}X\text{-}2\text{-}C_2B_9H_{10})(1,2\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ and $[8,8'\text{-}\mu\text{-}X<(1,2\text{-}C_2B_9H_{10})\text{-}3,3'\text{-}Co]^-$

Functional group X	Number	TLC R_f [a]	HPLC k' [b]	M.p. (°C)	m/z_{max}
$(OH)_2P(O)O-$	4	0.05	0.54	292–293 [d]	423.1 (420.2, 100%)
$Ph(OH)P(O)O-$	5	0.25	3.6		483.2 (480.2, 100%)
$ClP(O)(O)_2<$	6	0.39	1.80	259–261 [c]	441.1(436.1, 100%)
$HOP(O)(O)_2<$	7	0.08	0.53	> 380 [e]	421.1 (418.1, 100%)
$PhP(O)(O)_2<$	8	0.12	4.95	> 380 [e]	481.1 (478.1, 100%)
$EtNP(O)(O)_2<$	9	0.38	2.28	236–239 [d]	476.1(473.2, 100%)

[a] $CHCl_3:CH_3CN$ 3:1.

[b] $k' = 3.47$ for parent compound **1** under these chromatographic conditions.

[c] Et_3NH^+ salt, salt.

[d] Me_3NH^+ salt.

[e] K^+ salt.

Table 2
^{1}H chemical shifts $\delta(^1H)$ of the series of the salts of the anions of the general formulae $[(8\text{-X-2-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-3,3}'\text{-Co}]^-$ and $[8,8'\text{-}\mu\text{-X} < (1,2\text{-}C_2B_9H_{10})\text{-3,3}'\text{-Co}]^-$ measured in deuterioacetone at 294–297 K

Functional group	Number	δ ^{1}H (ppm)	δ ^{31}P[d] (ppm)
$(OH)_2P(O)O-$	4 [a]	10.09 br s (1H, OH), 5.99 br s (NH, $(HN(CH_3)_3)^+$), 4.27s (2H, Ch_{carb}), 4.133s (2H, Ch_{carb}), 3.00 (9H, $HN(CH_3)_3$)	−5.99
$Ph(OH)P(O)O-$	5 [a]	10.10 br s (1H, OH), 8.44 br s (NH), 7.94m (2H, Ar–P), 7.52m (1H, Ar), 7.44m (2H, Ar), 4.20s (2H, Ch_{carb}), 4.07s (2H, Ch_{carb}), 3.988 (9H, $HN(CH_3)_3$)	10.70
$ClP(O)(O)_2<$	6 [b]	8.54 br s (1H, $HNCH_2$), 3.96s (4H, Ch_{carb}), 3.42m (6H, NCH_2), 1.41 t (9H, CH_3)	−3.50
$HOP(O)(O)_2<$	7 [a]	7.23 br s (1H, OH), 3.99s (4H, CH_{carb}), 3.00m (9H, $(HN(CH_3)_3)^+$)	−4,14
$PhP(O)(O)_2<$	8 [c]	7.93m (2H, Ar–P), 7.48m (1H, Ar), 7.41d (2H, Ar), 3.88s (4H, CH_{carb})	8.15
$EtNP(O)(O)_2<$	9 [c]	3.89s (4H, Ch_{carb}), 3.10m (4H, NCH_2), 2.96 (9H, $HN(CH_3)_3^+$), 1.08t (9H, CH_3–CH_2)	3.27

[a] Measured as: Me_3NH^+ salt.
[b] Measured as: Et_3NH^+ salt.
[c] Measured as: K^+ salt, ^{1}H decoupled spectra.

fore, the resulting R-factor is higher than was expected. However, the resulting structure determination is suitable to supply main geometric features of the compound. The structure of **6** was solved by the direct method (SIR-97) [30] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [31]. The absorption was neglected. Hydrogen atoms were localized on a difference Fourier map and refined isotropically, except those of ethyl, which were calculated into theoretical positions, riding during refinement on the respective pivot atom. The final difference map had no peaks of chemical significance.

The orange crystal of compound **9** was mounted on glass fibre with epoxy cement and measured on four-circle diffractometer κCCD with CCD area detector at 293(2) K using Φ and ω scan mode. The crystallographic details are summarized in Table 5. The same methods for solution and refinement as for **6** were employed. The absorption was neglected. Hydrogen atoms were localized on a difference Fourier map, however, some of them behaved erroneously during refinement, therefore, all hydrogen 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. Hydrogen of N–H group was refined without any constrains. The carbon atoms of trimethylammonium cation are disordered into several positions, which cannot be distinguished on difference Fourier map. This disorder was described by using two positions for one carbon atom and allowing all carbon atoms to obtain large anisotropic temperature parameters. The absolute structure was determined unambiguously, chiral parameter is

Table 3
^{11}B and ^{1}H (B–H) chemical shifts $\delta(^{11}B)$ [a], $^1J(^{11}B–^1H)$ in parentheses, $\delta(^1H)$ [a] [B–H] in square brackets for the series of derivatives of functionalized anion **1** of the of the general formulae $[(8\text{-X-2-}C_2B_9H_{10})(1,2\text{-}C_2B_9H_{11})\text{-3,3}'\text{-Co}]^-$ and $[8,8'\text{-}\mu\text{-X}<(1,2\text{-}C_2B_9H_{10})\text{-3,3}'\text{-Co}]^-$ measured in deuterioacetone at 294–297 K

Functional group	Number	$\delta(^{11}B)$, $^1J(^{11}B–^1H)$, [^{1}H-{^{11}B(selective)}] (ppm)
$(OH)_2P(O)O-$	4	19.36s (B 8), 6.58 (B 8′) (138) [3.148], 1.63 (B10′) (139) [2.902], −2.38 (B 10) (146) [2.694], −3.86 (B 4′,7′) (146) [2.777], −6.45 (136) [2.157], −6.90, (138) [1.863] (B 9,12, 9′,12′), −8.06 (B 4, 7) (151) [2.90], −16.68 (B 5′, 11′) (150) [1.653], −19.87 (B 5, 11) (157) [1.562], −21.72 (B 6′) (1.69) [1.719], −27.79 (B 6) (167) [1.462]
$Ph(OH)P(O)O-$	5	20.23s (B 8), 7.61 (B 8′) (142) [3.059], 1.56 (B10′) (142) [2.7], −2.61 (B10) (144) [2.695], −4.13 (B 4′,7′) (146) [2.841], −6.095 (138) [2.262], −6.478 (142) [2.053] (B 9,12, 9′,12′), −8.254 (B 4, 7) (150) [2.90], −16.68 (B 5′, 11′) (154) [1.664], −19.65 (B 5, 11) (157) [1.587], −22.07 (B 6′) (1173)[1.706], −28.12 (B 6) (173) [1.463]
$ClP(O)(O)2<$	6	23.18s (B 8,8′), −2.51 (B 10,10′) (142) [2.692], −5.54 (B 9, 9′,12,12′) (142) [2.259, 2.203], −8.23 (B 4, 4′,7, 7′) (146) [3.339, 3.097], −18.74 (B 5, 5′,11, 11′) (154) [1.61], −27.64 (B 6,6′) (161) [1.480]
$HOP(O)(O)2<$	7	23.16s (B 8,8′), −2.32 (B 10,10′) (142) [2.7], −5.59 (B 9, 9′,12,12′) (139) [2.095], −8.15 (B 4, 4′,7, 7′) (142) [3.098], −18.57 (B 5, 5′,11, 11′) (154) [1.61], −27.52 (B 6,6′) (142) [1.48]
$PhP(O)(O)2<$	8	23.44s (B 8,8′), −3.31 (B 10,10′) (142) [2.61], −5.50 (B 9, 9′,12,12′) (146) [2.216, 2.106], −8.54 (B 4, 4′,7, 7′) (149) [3.119, 3.053], −19.20 (B 5, 5′,11, 11′) (157) [1.574], −28.15 (B 6,6′) (153) [1.457]
$EtNP(O)(O)2<$	9	23.70s (B 8,8′), −3.35 (B 10,10′) (138) [2.64], −5.47 (B 9, 9′,12,12′) (127) [2.213], −8.88 (B 4, 4′,7, 7′) (140) [3.008], −19.22 (B 5, 5′,11, 11′) (143) [1.587, 1.561], −28.33 (B 6,6′) (153) [1.443]

[a] Assignment by relative intensities, [^{11}B–^{11}B]-COSY (measured for all the compounds; typically observed crosspeaks and ^{1}H-{^{11}B(selective)} experiments (for ^{1}H).

equal zero within it is estimated S.D. The final difference map had no peaks of chemical significance.

Table 4
Crystal data and structure refinement **6** and **9**

Empirical formula	$C_4H_{20}B_{18}ClCoPO_3$ $^{-}C_6H_{16}N^{+}$ (**6**)	$C_8H_{30}B_{18}CoNPO_3$ $^{-}C_3H_{10}N^{+}$ (**9**)
Habit and size, mm	Bar, 0.6 × 0.25 × 0.21	Prism, 0.45 × 0.35 × 0.25
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (Number 14)	$P2_1$ (Number 4)
a (Å)	15.421(2)	10.8110(2)
b (Å)	13.289(2)	10.0170(2)
c (Å)	13.582(2)	13.0660(3)
β (°)	107.73(1)	98.132(2)
Z	4	2
μ (mm^{-1})	0.826	0.689
θ Range (°); completeness (%)	1.4–24.5; 99.5	3.0–27.5; 99.7
Number of reflections measured	4556	18 634
Number of unique reflections; R_{int}	4556	6355; 0.035
Number of observed reference [$I > 2\sigma(I)$]	3910	5911
Number of parameters	401	343
Goodness-of-fit (all data) [a]	1.237	1.058
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.071$, $wR_2 = 0.28$	$R_1 = 0.034$, $wR_2 = 0.088$
R indices (all data) [a]	$R_1 = 0.081$, $wR_2 = 0.29$	$R_1 = 0.039$, $wR_2 = 0.092$
w_1/w_2 [b]	0.098/16.03	0.052/0.2617
Absolute structure parameter		−0.011(11)
$\Delta\rho$, max/min (e Å^{-3})	1.00, −0.641	0.306, −0.352

[a] Definitions: $R(F) = \Sigma||F_o| - ||F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2]^{1/2}$, goodness-of-fit $= [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$.

[b] Weighting scheme $w = [s^2(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$. $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

Table 5
Selected bond lengths (Å) and angles (°) for **6** and **9**

Compound	**6**	**9**
Bond lengths		
Co(1)–C(1′)	2.039(10)	2.044(2)
Co(1)–C(2′)	2.040(9)	2.045(2)
Co(1)–C(2)	2.044(9)	2.046(2)
Co(1)–C(1)	2.048(8)	2.060(2)
Co(1)–B(8)	2.082(10)	2.105(3)
Co(1)–B(7)	2.085(11)	2.099(2)
Co(1)–B(7′)	2.085(10)	2.096(3)
Co(1)–B(8′)	2.092(9)	2.113(3)
Co(1)–B(4)	2.092(10)	2.106(3)
Co(1)–B(4′)	2.099(10)	2.090(3)
P(1)–O(3)	1.462(7)	1.476(2)
P(1)–O(2)	1.541(6)	1.553(2)
P(1)–O(1)	1.545(6)	1.549(2)
P(1)–Cl(1)	1.999(3)	
P(1)–N(1)		1.626(2)
O(1)–B(8)	1.465(11)	1.452(3)
O(2)–B(8′)	1.445(11)	1.436(3)
C(1)–C(2)	1.610(13)	1.626(4)
C(1)–B(4)	1.700(14)	1.702(4)
C(2)–B(7)	1.682(14)	1.698(4)
B(4)–B(8)	1.781(14)	1.817(4)
B(7)–B(8)	1.795(14)	1.797(4)
C(1′)–C(2′)	1.613(14)	1.620(4)
C(1′)–B(4′)	1.683(14)	1.695(4)
C(2′)–B(7′)	1.681(15)	1.705(4)
B(4′)–B(8′)	1.808(14)	1.817(4)
B(7′)–B(8′)	1.793(13)	1.806(4)
Bond angles		
O(3)–P(1)–O(2)	111.7(4)	115.05(12)
O(3)–P(1)–O(1)	116.6(4)	108.62(11)
O(2)–P(1)–O(1)	109.3(3)	106.91(9)
O(3)–P(1)–Cl(1)	110.6(3)	
O(2)–P(1)–Cl(1)	106.2(3)	
O(1)–P(1)–Cl(1)	101.4(3)	
O(3)–P(1)–N(1)		110.36(13)
O(2)–P(1)–N(1)		112.00(12)
O(1)–P(1)–N(1)		103.87(11)
B(8)–O(1)–P(1)	125.6(6)	126.45(16)
B(8′)–O(2)–P(1)	129.0(6)	133.00(16)

2.2.4. Extraction tests

All extraction experiments were performed in glass test tubes with polyethylene stoppers at laboratory temperature (23±1 °C). Phase volume ratio was 1:1 (2 ml of each phase). The samples were shaken for 1 h (10 min sufficient for attaining extraction equilibrium) on horizontal shaker. After shaking, the test tubes were centrifuged and 1 ml samples of each phase were taken for radioactivity measurement. All reagents used were of A.R. quality, the same is valid for solvents used. The distribution of Eu was investigated using carrier-free ^{152,154}Eu (radiochemical purity). The radioactivity of samples was measured using single-channel γ analyzer with NaI (Tl) well detector. Solvent extraction properties of the anions **4**–**9** are summarized in Table 7.

2.3. Synthetic part

2.3.1. Synthesis of the [(8-O-P(O)(OH)O-1,2-$C_2B_9H_{10}$) (1′,2′-$C_2B_9H_{11}$)-3,3′-Co][$HNMe_3$]$_2$ (4)

To a stirred suspension of the Et_3NH^+ salt of **2** (3.0 g, 6.75 mmol) in 20 ml of $CHCl_3$ $POCl_3$ (20 ml) was added, followed by dropwise addition of triethylamine (2 ml) during 30 min. The reaction mixture was stirred for 20 h at room temperature (r.t.), then water (50 ml) was dropwise added and stirring was continued for 3 h. The orange organic layer was separated; after stripping off in vacuum a viscous oil was obtained. It was treated for 1 h with a solution of 3.0 g of NaOH in 20 ml of water under stirring. Traces of the unreacted **2** were removed by extraction into diethylether, whereas the product remained in the aqueous phase; 50 ml of 4 M HCl was added and the precipitated acid was extracted with three

30 ml portions of ether–toluene mixture 2:1 (v/v). Solvents were stripped off in vacuum, the oily residue was dissolved in water (30 ml) and the product was precipitated with an excess of $Me_3N \cdot HCl$ as a microcrystalline salt containing two Me_3NH^+ cations per one borate anion, i.e. dianion was generated. The crystals were filtered and treated with 50% aqueous ethanol in a 60 °C warm water bath; final dissolution was achieved by addition of a small volume of acetone. Yellow leaflets separated after slow cooling down. Yield: 2.13 g, 59.3%.

2.3.2. Synthesis of the [(8-PhP(O)(OH)-O)-1,2-$C_2B_9H_{10}$) (1′,2′-$C_2B_9H_{11}$)–3,3′-Co][$HNMe_3$]$_2$ (5)

To a stirred suspension of the Et_3NH^+ salt of **2** (4.45 g, 10 mmol) in 20 ml of $CHCl_3$ was added $PhPOCl_2$ (4.96 g, 25.4 mmol) and the reaction mixture was stirred for 15 min (gaseous HCl evolution). During this period the starting salt completely dissolved. The reaction mixture was stirred for 15 h, and then ca. 10 ml of the solvent was evaporated in vacuum together with HCl. A new portion of $CHCl_3$ (20 ml) was added to the residue followed by dropwise addition of Et_3N (during 30 min). Then the slurry was stirred for additional 30 min; water (60 ml) was added dropwise and the content of the flask was stirred for 1 h. The chloroform layer was separated and the solvent evaporated leaving a viscous brown residue. A cold solution of 4.0 g of NaOH in 60 ml of water was added to the residue under stirring and the volatiles were stripped off in vacuum until a clear orange–brown solution resulted with a total volume of ca. 40 ml. This solution was heated for 1 h in a water bath to 80 °C. After cooling down, the solution was diluted with water (30 ml) and extracted with two 30 ml portions of diethylether. The aqueous layer was separated, evaporated shortly in vacuum to remove the dissolved ether, and acidified by 5 ml of glacial acetic acid. The product was precipitated by addition of 3.0 g of $Me_3N \cdot HCl$ in water (15 ml). The precipitate was filtered, treated with 50% aqueous ethanol (80 ml) in a water bath (60 °C), and a final dissolution was achieved by addition of a small volume of acetone. Crystals of the product separated upon slow cooling and standing overnight. Yield 1.43 g (24%).

*2.3.3. Synthesis of the [8,8′-μ-ClP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co][$HNEt_3$] (**6**)*

To a suspension of the Et_3NH^+ salt of **3** (8.0 g, 17.4 mmol) in chloroform (30 ml) $POCl_3$ was added (5.03 g, 33 mmol) and the slurry was stirred 2 h at ambient temperature. An evolution of gaseous HCl occurred along with temporary dissolution of solids and precipitation at the end of this period. Then triethylamine (6 ml, 41.1 mmol) was dropwise added during 20 min. and the mixture was stirred for additional 2 h during which period solids dissolved again. An addition of $P(O)Cl_3$ (1.51 g, 10 mmol) and 2.0 ml (13.7 mmol) of Et_3N was repeated again and the reaction mixture was stirred for additional 2 h. The reaction was quenched by a careful addition of water (50 ml) and the bi-layer system was stirred for 12 h. During this period the main portion of the product precipitated. Solids were filtered, washed with two portions of chloroform (10 ml) and dried; 6.1 g (65%) of the essentially pure product were obtained. An additional quantity (0.3 g) was obtained from the combined chloroform extracts and washings by evaporation of the solvent and repeated recrystallization of the solid residue from hot 60% aqueous ethanol. Overall yield of **6**: 6.4 g, 68%.

2.3.4. Synthesis of the [8,8′-μ-HOP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co][$HNMe_3$] (7)

The Et_3NH^+ salt of the above derivative **6** (6.1 g) was treated with NaOH solution (4 g in 30 ml) at 80 °C (water bath temperature). Triethylamine was distilled off during ca. 20 min. period, then the solids were dissolved by addition of water (ca. 20 ml) and the solution was kept at this temperature for an additional 1 h. After cooling down, the resulting orange solution was extracted with diethyl ether (50 ml). Only traces of the unreacted starting compound were extracted. The water phase containing the desired anion was acidified with 4 M HCl (30 ml) and the product was extracted to a solvent mixture ether–toluene 1:1 (60 ml). The organic layer was separated, filtered and evaporated in vacuum to dryness leaving a solid orange residue. This residue was treated twice with 20 ml portions of toluene–ether mixture (9:1 v/v), the extracts were filtered, evaporated to dryness and washed two times with 20 ml of hexane. After drying in vacuum 4.72 g of an orange solid resulted, which was found to be the pure conjugate acid of **7** containing three equivalent of crystal water (according to ^{1}H-NMR). The acid is very soluble in water but precipitates upon acidification by HCl to pH value below ca. 1.0. The acid was dissolved in water and precipitated by addition of $Me_3N \cdot HCl$ in water. The resulting orange solid was filtered, washed two times with 30 ml of water and recrystallized from hot aqueous ethanol. Yield: 4.75 g, 88%.

*2.3.5. Synthesis of the [8,8′-μ-PhP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]K (**8**)*

To a solution of Et_3N (5.0 ml, 33 mmol) in chloroform (30 ml) cooled in an ice bath $PhPOCl_2$ (2.11 g, 10.8 mmol) was dropwise added. A suspension of the Me_3NH^+ salt of **3** (4.1 g, 10 mmol) in chloroform (15 ml) was added and the reaction mixture was warmed up to 80 °C and stirred for 1 h. The solids gradually dissolved and a yellow solution resulted at the end of this period. A second portion of $PhPOCl_2$ (0.8 ml) was added and stirring at 80 °C was continued for additional 1 h, when 1 ml of Et_3N was added. The reaction mixture was cooled down after additional 30 min. and carefully decomposed with water (50 ml). The slurry was stirred for 4 h at ambient temperature, chloroform layer was separated and evaporated to dryness leaving a glassy orange residue. This residue was dissolved in warm solution of KOH (2 g) in 50% aqueous ethanol (50 ml) and ethanol together with E_3N was stripped off in vacuum. The solid was dissolved in ethanol (20 ml) in an 80 °C water bath, and the crude product was allowed to crystallize for 3 days. The resulting yellow powder was filtered, washed with water and vacuum dried at 80 °C; 3.73 g (70.3%) of the pure **8**-potassium salt was obtained. Partial evaporation of mother liquors provided additional 1.4 g (27.2%) of the pure product.

2.3.6. Synthesis of the [8,8′-μ-$(CH_3CH_2)_2NP(O)(O)_2<(1,2\text{-}C_2B_9H_{10})_2$-3,3′-Co][K] (**9**)

The dry Et_3NH^+ salt of ($ClP(O)(O)_2<$) bridged compound **6** (6.18 g, 11.5 mmol) prepared as described above, was dissolved in 1,2-dimethoxy ethane (20 ml), $(CH_3CH_2)_2NH$ (10 ml) was added to this solution and the reaction mixture was stirred at 80 °C for 6 h. After cooling down, the volatiles were stripped off in vacuum leaving a viscous residue; water (15 ml) was added and then evaporated in vacuum to dryness. Then a solution of 2.0 g KOH in 30 ml of water was added; a vacuum evaporation of the volatiles afforded a mixture of the potassium salts of the product and of the starting species. Water (30 ml) was added to this orange solid mass followed by diethyl ether (30 ml) and the product, nearly insoluble in the water, was extracted to diethyl ether using two additional portions of the solvent. From the combined organic extracts the solvent was stripped off in vacuum and the residue was treated with three 50 ml portions of toluene; 2.45 g of potassium salt of the starting anion **6** was recovered as the insoluble solid. Slow vacuum evaporation of the toluene from combined toluene extracts from a hot water bath, leading to volume reduction to ca. 20 ml, provided an orange powder upon slow cooling down to r.t.; Yield 1.4 g, 23%. One third of the product was transformed to Me_3NH^+ by dissolution in aqueous ethanol (60%), precipitation by excess of $Me_3N \cdot HCl$, filtration and drying of the solid. Recrystallization of this salt from hot aqueous ethanol produced small prismatic crystals suited for X-ray diffraction analysis.

3. Results and discussion

3.1. Synthesis and properties of compounds with phosphorus containing selective groups

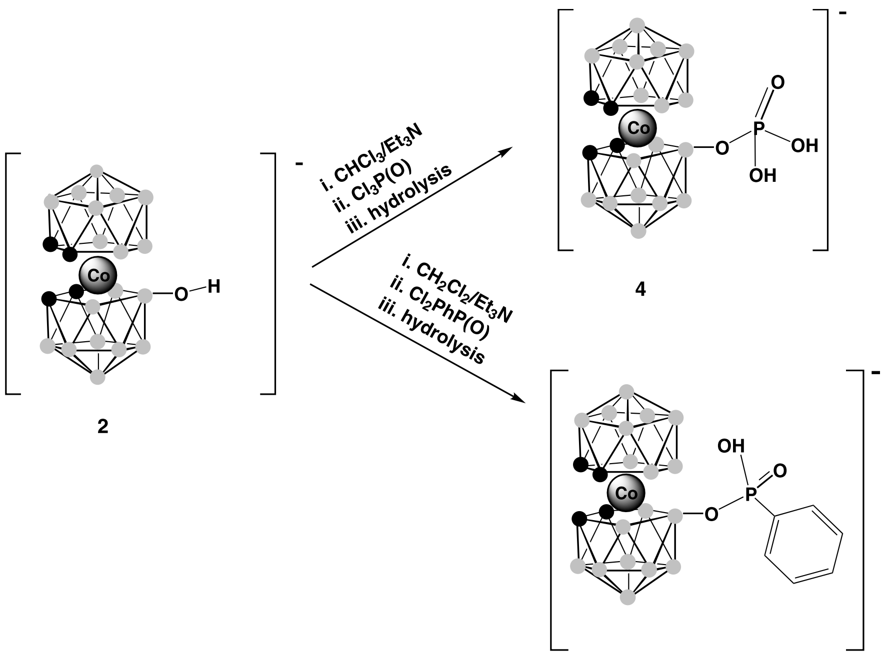
Hydroxy derivatives **2** and **3** were found to act as an useful synthons for bonding a variety of phosphorus containing moieties to the cage of **1**. The 8-mono hydroxy derivative **2** was used for convenient syntheses of deltahedral anions substituted with phosphinic and phosphoric groups.

Reactions of **2** in $CHCl_3$ with either Cl_3PO or $PhCl_2PO$ using triethylamine as base (for abstraction of HCl) proceeded smoothly and after aqueous hydrolysis gave (8-$(HO)_2PO$-O)-(**4**) and [(8-PhP(O)(OH)-O)-1,2-$C_2B_9H_{10}$)(1,2-$C_2B_9H_{11}$)-3,3′-Co]$^-$ (**5**) phosphorylated species in good and moderate yields, respectively (see Scheme 1).

Reactions of **3** with Cl_3PO or $PhCl_2PO$ in $CHCl_3$ using one equivalent of Et_3N as the base led to bridged products. Former reaction provided an interesting compound with chlorine bearing bridge, the [8,8′-μ-$ClP(O)(O)_2<(1,2\text{-}C_2B_9H_{10})_2$-3,3′-Co]$^-$ (**6**). This species proved amazingly high hydrolytic stability. The compound withstood 2 h reflux in water without hydrolysis. Molecular structure of compound **6** was determined by X-ray diffraction analysis.

The anticipated anion [8,8′-μ-$HO(O)P(O)_2<(1,2\text{-}C_2B_9H_{10})_2$-3,3′-Co]$^-$ (**7**) with phosphoric acid as the bridging substituent was obtained upon alkaline hydrolysis of compound **6.** Complete hydrolysis can be reached in few minutes in 10% ethanolic solution of NaOH (Scheme 2). The compound with phenyl substituted bridge [8,8′-μ-$Ph(O)P(O)_{2-}<(1,2\text{-}C_2B_9H_{10})_2$-3,3′-Co]$^-$ **8** was prepared by similar reaction of **3** with $PhCl_2PO$ and subsequent hydrolysis. All reactions proceeded smoothly giving good yields of the respective bridge products. Compounds **6** and **7** exhibited good transfer of Eu^{3+} from acidic aqueous phase to aromatic solvents (for illustration see extraction coefficients summarized in Table 7 and the discussion of extraction properties below) up to 1 M concentration of HNO_3 in the extraction system. It can be expected, that the compound **6** should be hydrolyzed upon contact with nitric acid present in the extraction system, providing the derivative **7**. This assumption is supported by the fact that the extraction coefficients obtained for anions **6** and **7** are almost equal. The values of the extraction coefficients for anion **8** bearing phenyl substituent on the bridge phosphorus atom are significantly lower in comparison with the anion **7**. This argues for assumption that the presence of the second acidic center in SEA **7** plays favorable role in the extraction mechanism.

The usefulness of the anion **6** for further synthetic purposes is exemplified in its reaction with diethylamine (see Scheme 3). This reaction under anhydrous conditions led to easy substitution of the bridge chlorine atom for the diethylamine moiety generating μ-Et_2N-$P(O)(O)_2<$ bridged derivative **9**. Despite this compound was not effective as extractant for trivalent cations, the reaction shows the versatility of reagent **6** for synthesis of similar compounds for other purposes, e.g. for Boron Neutron Capture Therapy and for possible modifications of solid supports and membranes with such

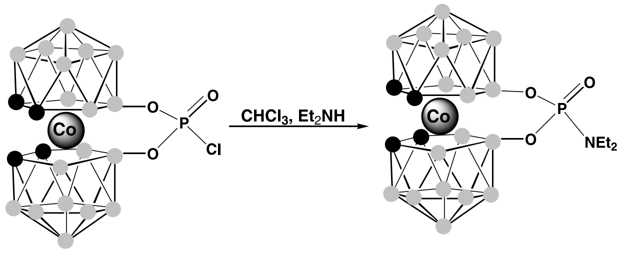


2

4

5

Scheme 1. Reaction path leading to B(8) phosphorylated species **4** and **5**.



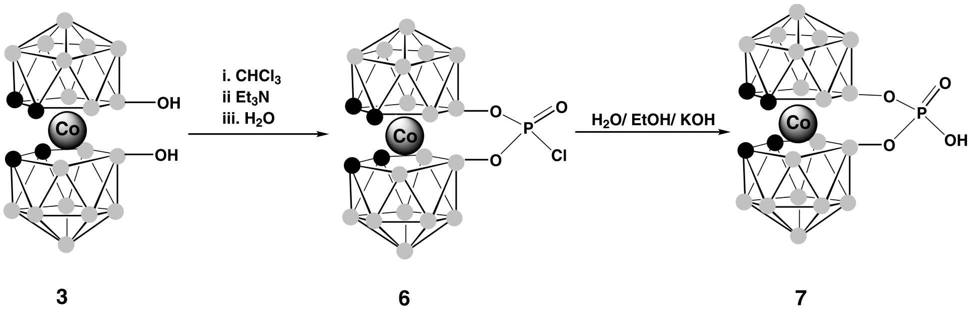
6

9

Scheme 3. Reaction leading to bridge diethyphosphoramide derivative **9**.

anionic moiety. Rich chemistry based on the precursor **6** chlorine atom replacements can be thus anticipated.

An interesting stereochemical feature of anions **6**, **7**, **8** and **9** consists in the trend of the X(O)P(O)$_2$ bridging moiety to preserve its tetrahedral arrangement. This, in turn, led to twisted structure with staggered *anti*-prismatic conformation of carborane ligands around the central cobalt atom. As the result, asymmetric chiral structure is created. Furthermore the inclination of (P= O) bond towards one carborane ligand and P–X (X = Cl, Ph, OH, Et$_2$N) bonds to other side of the molecule would lead, in principle, also to asymmetry of the anion. Apparently only one set of enantiomeric pairs would be created for all compound in the series, taking into account that the orientation of the starting Cl$_3$PO or PhCl$_2$PO moiety towards hydroxy groups proceeds on a statistic basis. On the other hand, the bridge arrangement should be sufficiently rigid and the energy barrier for bending the phosphorus atom by ‘umbrella effect’ on the other mirror side should be sufficiently high if an enantiomeric resolution can be accomplished. ^{11}B-NMR patterns 2:2:4:4:4:2 of all bridged compounds **6**–**9** did not bring any evidence about the asymmetric structures, or at least, argued for a fast tautomerism in the solution. On the other hand, the determination of the absolute configuration of one enantiomer of **9** in solid state by single X-ray diffraction analysis (performed on a



3

6

7

Scheme 2. Reaction path used in the synthesis of phosphoric acid bridged anion **7** proceeding via hydrolytically stable intermediate **6**.

incidentally selected crystal containing pure enantiomer, see crystallographic discussion bellow) brought evidence that the energy barrier for racemization should be sufficiently high. Also the recent resolution of the anion **7** into enantiomers by electrophoretic methods using β-cyclodextrin as a chiral selector [32] confirmed the chirality of this class of species and the possibility to resolve enantiomers in solution. The compound **7** and **9** represent the first known proven examples of chiral species in the series of cobaltacarboranes with polyatomic bridges between carborane ligands. These species form counterpart to the longer time known families of similar chiral compounds with monoatomic bridges [33–35].

3.2. NMR results

^{11}B-NMR patterns of both derivatives **4** and **5** with 8-O–X bonded substituent consist of 12 peaks, one singlet of relative intensity 1 which is the first downfield peak in the spectrum and 11 doublets of intensities 1:1:1:2:2:2:2:2:2:1:1. This is in agreement with the expected spectral pattern for the substitution in the position B(8) of the cage [21] leaving the existence of one plane in the each dicarbollide part of the molecule. Furthermore, the chemical shifts in the spectra are very close to parent compound **2**. The rather complex ^{11}B spectrum consists of two sets of signals for individual carborane ligand parts, one perturbed by B–O–X substitution and second almost untouched comparing to parent-unsubstituted anion **1**. Almost all signals corresponding to these two individual carborane parts can be clearly distinguished on the basis of crosspeaks in the ^{11}B–^{11}B-COSY experiments and assigned to respective boron positions. An exception forms uncertainty in the assignment of B(9, 12) and B(9′, 12′) positions, due to peak coincidence overlap. With this exception, all B–H signals could be assigned from the ^{1}H{^{11}B(selective)} experiments. Also ^{1}H and ^{31}P spectra of both derivatives **4** and **5** are in agreement with the proposed structures. ^{1}H spectrum of **4** consists of a singlet at 10.09 ppm, apparently corresponding to OH groups and two sets of CH resonances at 4.13 and 3.00 ppm, each of intensity 2. These peaks at the similar frequencies can be found also in the ^{1}H spectrum of **5** along with sets of three peaks corresponding to the aromatic ring. ^{31}P spectra of both derivatives **4** and **5** consist of one singlet.

^{11}B-NMR spectra of bridged derivatives **6**–**9** consist of six peaks, one singlet with relative intensity 2 which is the first downfield peak in the spectrum and five doublets of intensities 2:4:4:4:2. Both, the spectral pattern and chemical shifts very closely resemble these of the parent dihydroxyderivative **3** and seemingly reflect the same symmetry equivalence of the two carborane ligands, as in the parent compound. All signals corresponding to individual boron resonances can be unambiguously assigned to the respective boron positions from the ^{11}B–^{11}B-COSY experiments. Also, all ^{1}H B–H signals could be assigned from the ^{1}H{^{11}B(selective)} experiments. Two sets of B–H signals in the ^{1}H{^{11}B} and ^{1}H{^{11}B(selective)} spectra corresponding to B–H positions (H 9, 9′,12, 12′) and (H 4, 4′,7, 7′) in compounds **6**–**8** and B–H positions (H 4, 4′,7, 7′) and (H 5, 5′,11, 11′) in **9** are splitted into two singlets of equal intensity. In the parent compound **3** only one peak for each symmetrically equivalent atoms BH groups can be seen. The splitting of these signals may indicate non-equivalency of two carborane ligands in solution and seems to indicate better sensitivity of ^{1}H {^{11}B} signals to subtle changes in the stereochemistry of these metallaboranes. ^{1}H and ^{31}P spectra of the derivatives **6**–**9** are in agreement with their proposed structures. ^{1}H spectrum of all compounds in this series consists of one CH resonances of intensity 4 and peaks corresponding to presence of OH group in **7**, phenyl ring in **8** and $(CH_3CH_2)_2N$ substituent in **9**. ^{31}P spectra of all derivatives consist of one singlet. For NMR details see Tables 2 and 3.

3.3. X-Ray crystallography

The most interesting feature of molecular structure of **6** (Fig. 2) and **9** (Fig. 3) is the influence of three atoms –O–P–O– bridge on mutual position of carborane cages in the bis(dicarbollide) moiety. The least-square planes defined by ring (ri1) of atoms C(1), C(2), B(4), B(7), B(8) and ring (ri2): C(1)′, C(2)′, B(4)′, B(7)′, B(8)′ are almost parallel in both structures since their dihedral angles are 3.0(7) and 1.5(1)° for **6** and **9**, respectively. Also the position of Co atom with regard of dicarbollide ligands is unaffected by the bridge, the angles cg1–Co–cg2 (cg = centroid of ri) are very close to 180° (177.7° for **6** and 178.8° for **9**). However, the bridge moves the ligands from eclipsed conformation, the torsion angles φ: B(8)–cg1–cg2–B(8′) are −30.91 and 26.01° for **6** and **9**, respectively. The crystal of **6** is centrosymmetric and both molecules with φ equal −30.91 and 30.91 are present in one unit cell, whereas two enantiomers of **9** crystallized separately.

The bond distances and angles are within usual range of similar structures [35–38] (for selected ones see Table 5). The hydrogen bonds N–H···O, together with coulombic forces, form the most important intermolecular contacts in both structures (Table 6). From comparison of parameters in Table 5 those remarkable features appear: whereas angle O(2)–P(1)–O(3) is similar, the differences between angles B(8)–O1–P(1) and B(8′)–O(2)–P1 are almost two times larger for **9** than **6**. The flexibility in B–O–P angles facilitate the change in dihedral angle between least-square planes O(1), P(1), O(2) and ri1 equal 53.8(3) and 59.21(8)° for **6** and **9**, respectively.

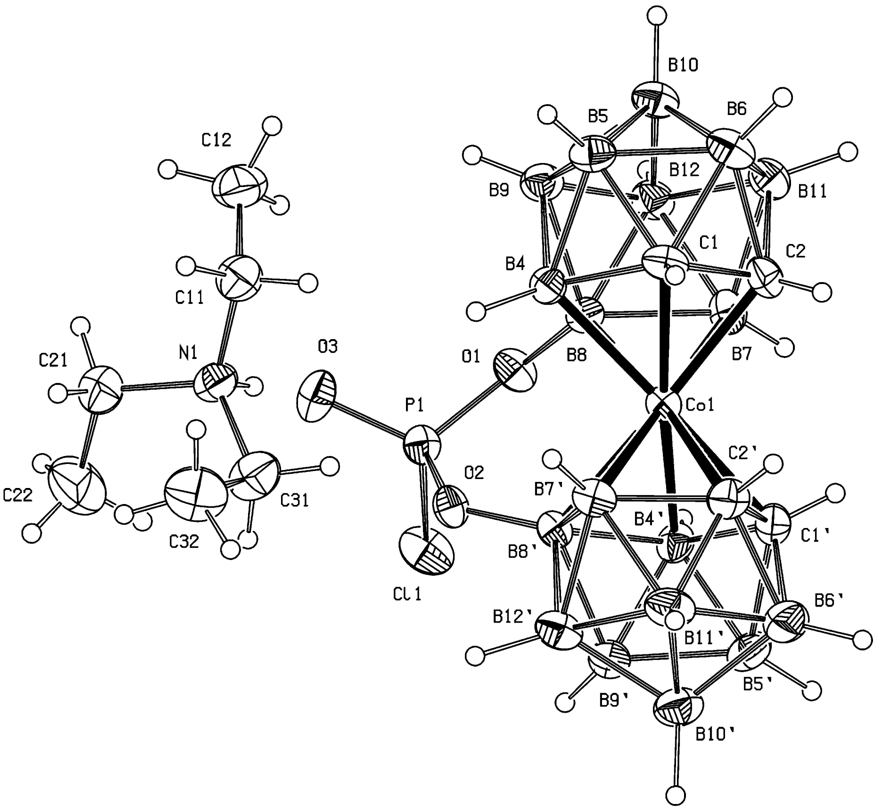


Fig. 2. Molecular structure of **6** showing the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

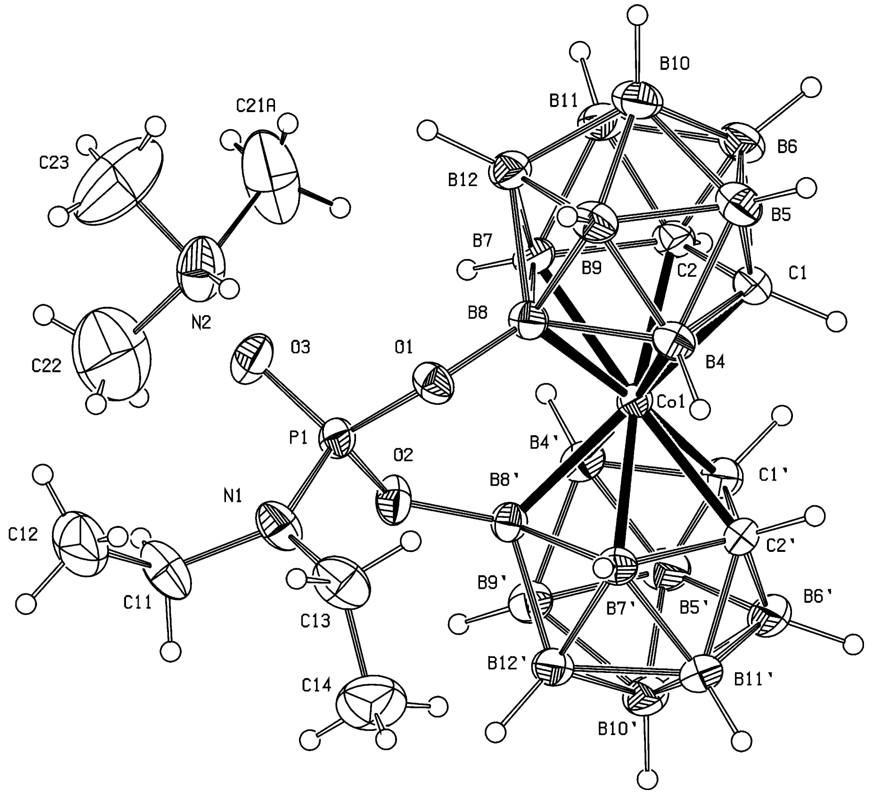


Fig. 3. Molecular structure of the σ, σ-enantiomer of the chiral anion **9** showing the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. The second position of disordered atom C21A was omitted for clarity.

Table 6
Hydrogen bonds for **6** and **9** (Å and °)

Compound	D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
6	N(1)–H(1N)···O(3)	0.92(9)	1.96(9)	2.872(12)	173(7)
9	N(2)–H(2N)···O(3)	0.94(5)	1.68(5)	2.591(4)	162(4)

3.4. Extraction tests of synthesized extractants

Extraction efficiency of prepared compounds was tested on extraction of trivalent europium as a representative of rare earths and actinides. Preliminary extraction tests were always carried out under standard testing conditions described in the Section 2. As supposed, both parent anions, i.e. mono- and dihydroxy derivatives of cobalt bis(dicarbollide) (compounds **2** and **3**), were ineffective in extraction of Eu ($D_{Eu} < 0.01$ under standard testing conditions of 0.01 M extractant solution in toluene or xylene and 1 M nitric acid). However, on the basis of our experience in extraction of the fission products, hydroxyderivatives of dicarbollide usually bring about an increased extraction of Zr^{4+}, thus decreasing the overall selectivity of the system. Slightly enhanced extraction efficiency for Eu^{3+} was observed for the derivatives containing phosphorus moiety bound to the skeleton *via* single oxygen bond, i.e. extractants **4** and **5**. On the other hand, sufficiently high distribution ratios were obtained only at low acidity (0.001 M nitric acid). At 1 M nitric acid concentration the extraction efficiency is far from being acceptable ($D_{Eu} < 0.005$).

Promising results were obtained with phosphorus-bridged extractants, i.e. compounds **6**, **7** and **8**. The dependence of Eu^{3+} extraction on acidity for mentioned extractants can be seen from the data summarized in Table 7. These indicate continuous decrease of distribution ratios with increasing nitric acid concentration; nonetheless, technologically acceptable distribution ratios can be obtained even at 1 M nitric acid. Distribution ratios below value 1 for higher acidities indicate the possibility to regenerate the extracting phase in a back-extraction step. As for compound **8** (phenyl substituted bridge), the decrease of Eu^{3+} distribution ratio is so important that it is not possible to use this extractant for the extraction from 1 M nitric acid. The explanation probably lies in sterical hindrance (shielding effect) of the phenyl group. Compound **9** proved to be ineffective for the extraction of Eu^{3+} again probably due to the steric hindrance of ethyl groups or probable protonization of amide nitrogen.

Interesting results were obtained in tests of chemical stability (contact of extracting organic phase with 1 M nitric acid) for extractant **6**. Due to the continuing hydrolysis of phosphate substituent (substitution of chlorine by hydroxy group), the extraction of Eu^{3+} increases with increasing time of contact.

Table 7
Dependence of Eu extraction with functionalized derivatives of cobalt bis(dicarbollide) on acidity

Extractant	c_{HNO_3}				SWS
	0.1	0.3	1.0	2.0	
D_{Eu}					
6	45.7	29.9	4.82	1.55	0.462
7	158	61.6	4.79	0.91	–
8	32.2	–	0.12	–	–
9	0.030 [a]	–	–	–	–

Extractant (0.01 M) in xylene.

[a] Solution in toluene, SWS—1 M HNO_3+4 M $NaNO_3$.

The short summary of above results obtained with newly prepared extractants indicates that a new type of efficient Eu^{3+} extractants was developed. New compounds amalgamate in the single molecule very good extraction properties of the cobalt bis(dicarbollide) anion and the complexation ability of alkylphosphates, before used only as synergists. In addition, good separation properties of mentioned compounds were observed also for cesium and strontium, with separation factors exceeding 100.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 169693 for compound **6** and CCDC no. 169694 for compound **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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