Crown ether substituted cobalta bis(dicarbollide) ions as selective extraction agents for removal of Cs^+ and Sr^{2+} from nuclear waste

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Received (in Montpellier, France) 9th November 2001, Accepted 5th February 2002

A series of crown ether derivatives of the cobalta bis(dicarbollide) *closo*-$[(1,2\text{-}C_2B_9H_{11})_2\text{-}3,3'\text{-Co}]^-$ (**1**) anion was prepared using two synthetic strategies. The first method employs dioxane ring cleavage of the *closo*-$[\{8\text{-}(C_4H_8O_2)\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})]^0$ zwitterionic species with sodium oxymethyl crowns, producing a series of anions with spacer bonded crown ether moieties varying in crown ether ring size. Three compounds of this group; *closo*-$[\{8\text{-}(15\text{-crown-}5\text{-}CH_2O)\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})]^-$ (**2**), *closo*-$[\{8\text{-}(18\text{-crown-}6\text{-}CH_2O)\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})]^-$ (**3**) and $[\{8\text{-}(21\text{-crown-}7\text{-}CH_2O)\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})]^-$ (**4**) were prepared in high yields. The second approach involved reaction of deprotonated *closo*-$[8,8'\text{-}(OH\text{-}1,2\text{-}C_2B_9H_{12})_2\text{-}3,3'\text{-Co}]^-$ with *p*-toluenesulfonyl esters derived from hydroxymethyl crown ethers. Only compounds bearing one crown ether ring resulted in preparative amount from this reaction, the $[(8\text{-}\{(15\text{-crown-}5\text{-}CH_2O)\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}\{8'\text{-}(HO)\text{-}1',2'\text{-}C_2B_9H_{10}\}]^-$ (**5**) and $[\{8\text{-}(21\text{-crown-}7\text{-}CH_2O)\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}(8'\text{-HO-}1',2'\text{-}C_2B_9H_{10})]^-$ (**6**). All compounds were characterized by high field ^1H and ^{11}B NMR methods, HPLC and MS, with electrospray ionization, and the molecular structure of the Cs^+ complex of species **5** was determined by single crystal X-ray diffraction analysis. These compounds represent the first examples where oxygen crown ethers were successfully bonded to the cage of anion **1**. The scope and limitations of the use of these compounds in the liquid–liquid extraction of Cs^+ and Sr^{2+} from nuclear waste were studied, including comparison of extraction efficiency and selectivity of the covalently bonded species under study with synergistic mixtures of hexabrominated anion **1** with crown ethers. As a rule, crown ethers linked to the cobalta bis(dicarbollide) cage display distribution coefficients for Cs^+ and Sr^{2+} comparable to the crown ethers mixed with the hexabromoderivative of **1**, however, they were found to exhibit better selectivity with respect to Na^+ cation.

Nuclear fuel reprocessing operations produce both high and medium activity liquid wastes (HLW/MLW). Two alternatives are proposed to manage HLWs arising from spent fuel reprocessing: (1) disposal or long-term interim storage of waste after vitrification and (2) separation of long-lived elements in view of their destruction by transmutation or immobilization in very stable matrices for the radionuclides that cannot be transmuted. Medium activity waste can be disposed of in surface repositories provided that the activity of long-lived elements is removed. Much effort in past years has been devoted to the development of reliable liquid–liquid extraction processes for the selective separation of long-lived radioactive elements such as Cs^+, Sr^{2+}, lanthanides and actinides from HLW and MLW in order to decrease noticeably the volume or residual nocivity of waste to be disposed of in subsurface facilities.[1]

Removal of strontium and cesium from nuclear wastes needs efficient, chemically selective and radiochemically resistant extractants.[2] Since the end of the 60s, crown ethers, and from the mid-70s, cobalta bis(dicarbollide) removal of strontium and cesium from radioactive liquid waste has been extensively studied by means of crown ethers and cobalta bis(dicarbollides), synthesized for the first time by Pedersen[3] and Hawthorne *et al.*,[4] respectively. The potential of the *closo*-$[(C_2B_9H_{11})_23,3\text{-Co}']^-$ cobalta bis(dicarbollide) anion (COSAN, **1**) and its chloro- and bromo- derivatives (Cl_6^- and Br_6-COSAN) for liquid–liquid extraction recovery of strontium and cesium from HLW was recognized first by Czech scientists from this group. The hexachlorinated derivative of **1** was later synthesized on a large scale (200 kg) in Czechoslovakia, and used in the former USSR on the industrial scale to remove strontium and cesium from HLW.[5] This process is now called UNEX.[6]

In the dicarbollide process,[5] Cs^+ is extracted due to tight ion pair formation with the hexachlorinated cobalta bis(dicarbollide) anion **1**, and then Sr^{2+} can be effectively extracted with

DOI: 10.1039/b109956f

a synergistic mixture of dicarbollide and polyethylene glycols or crown ethers. The main drawback of this process based on the chlorinated derivative of **1** (Cl_6-COSAN) is the solubility, dissolution requiring the use of solvents of higher polarity, such as nitrobenzene, or chlorinated solvents.

Extraction of cesium and strontium by crown ethers has been extensively studied.[7] However, without adding synergistic agents, extraction of cesium from acidic high activity liquid waste was not possible. According to Horwitz *et al.*, the electrostatic interaction between the lipophilic cation-crown ether inclusion complex and the anion must be strong enough to strip the anion from its hydration shell and allow its transfer into the organic phase.[8] The low distribution coefficients obtained with crown ethers for the extraction of strontium and cesium are explained by an interaction between the cation and the hydrophilic nitrate, the major anion present in nuclear liquid waste. To overcome this drawback, McDowell *et al.* proposed to add large anions, such as di-dodecylnaphthalene sulfonic acid, versatic acid or bis(2-ethylhexylphosphoric acid) into the organic phase containing the crown ethers. These organophilic acids act as cation exchangers, allowing the metal cation to be transferred into the organic phase without the nitrate anion.[9] However, in the acidic HLW and MLW solutions, these lipophilic anions derived from relatively weak organic acids are easily protonated. From this viewpoint, the use of a cobalta bis(dicarbollide) anion, which is dissociated even at high acidity values, seems more promising. Vanura *et al.* investigated the extraction of strontium and cesium by a nitrobenzene solution of cobalta bis(dicarbollides) in the presence of different crown ethers and evidenced an increase of efficiency. They noticed also an important increase of the selectivity in the series of rare earth elements.[10]

More recently, calixarenes were proposed for the removal of these cations from nuclear liquid waste. Adding a polyethylene glycol chain (a crown ether is constituted by a cyclic polyethylene glycol chain) on the benzene units constituting the calixarene cavity led to much more efficient and selective extractant: in nitro phenyl hexyl ether (NPHE) diluent, the efficiency towards cesium and the cesium-over-sodium selectivity were increased a hundredfold in comparison with the most efficient crown ethers.[11] Similarly, one can consider improving the extracting abilities of the synergistic dicarbollide and crown ether mixture by synthesizing an extractant with these two moieties covalently bonded. The aim of this study has been to reduce the complexity of the extraction system and to find selective extraction agents (SEA) soluble in less polar solvents. The solution could be based on the development of SEA that combine in one molecule both hydrophobic cobalta bis(dicarbollide) anions and crown ether groups known as selective complexing agents for Cs^+ or Sr^{2+}. Such species with covalently bonded selective groups could increase the selectivity of the extractant and decrease the number of components in the extraction system, and would, in turn, minimize the amount of generated secondary waste due to the limited need to replenish the system with the SEA components in the process.

A significant advantage of the anion **1** lies in its amazing potential for possible substitution modifications by selective groups.[12] On the other hand, no examples of the combination of purely oxygen containing crown ethers with cobalta bis(dicarbollide) anion **1** can be found in the literature. Only compounds with long bridge substituents between carbon atoms have been reported.[13] A short list of anions containing bridges longer than three atoms includes cobalta bis(dicarbollides) bridged *via* alkyl chains[13] and one example of a mixed thiaoxa crown moiety containing a polyethylene chain with two sulfur and three oxygen atoms,[14] all synthesized by tedious procedures based on bonding two carborane units to carbon atoms *via* a chain, followed by deboronation and cobalt insertion reactions.

Recently, novel synthons enabling direct bonding of selective groups onto the cage anion **1** were prepared by the I.I.C. group, and opened thus new gates for the development of procedures for bonding various groups, among them also crown ether rings of variable size on the cobalta bis(dicarbollide) anions. The starting boron compounds now available on the preparative scale include: 8-dioxanate[15] of **1** and mono- and dihydroxy derivatives[16] of **1** obtained upon revision of an older procedure[17] and development of a simple new process. The high yield syntheses of cobalta bis(dicarbollide) crown ether derivatives were based on commercially available hydroxy methyl crown ethers as the second reagent. This approach led to the synthesis of the five crown ether anionic compounds described in this article. Their extraction properties are also provided and discussed.

Experimental

General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdon,[18] although some operations, such as column chromatography, were carried out in air. The starting compound **1** was provided by Katchem, Ltd. Prague. The solvents (Lachema, Brno, Czech Republic) were dried over Na metal and freshly distilled before use. High surface sodium hydride, made at I.I.C. and with a BET surface area of about 1 m^2 g^{-1}, was used.

The crown ether chemicals, hydroxymethyl-15-crown-5, hydroxymethyl-18-crown-6 and hydroxymethyl-21-crown-7, were obtained from the Institute of Organic Chemistry and Biochemistry, AS CR Prague (eventually, also commercially available from Aldrich) and were used for introduction of the crown ether ring moieties. Dioxanate[15] (**2**) of anion **1** and the dihydroxy derivative[16] were prepared according to procedures developed in the I.I.C. laboratory. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out on silica gel (Aldrich, 200–400 mesh) and the purity of the individual chromatographic fractions was monitored by analytical TLC on Silufol (silica gel on aluminium foil; orange spots, eventually detection by diiodine vapor, followed by 2% aqueous $AgNO_3$ spray). The oxymethyl crown *p*-toluenesulfonates were prepared according to published procedures.[19]

The chemicals for the preparation of synergic mixtures for the extraction tests were supplied as follows: benzo-15-crown-5 (Acros Chimica), 18-crown-6 (Janssen Chimica), decyl-18-crown-6 (Merck), benzo-18-crown-6 and dicyclohexano-18-crown-6 by Fluka. *t*-Butyl-benzo-21-crown-7 was synthesized by Chimie Plus (Marseilles, France) and bromo-protected cobalta bis(dicarbollide) (Br_6-COSAN) was from Katchem, Ltd. Prague. All these compounds were used without further purification.

Physical measurements

Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 11.75 T on Varian Unity-500 instruments. The procedure for [^{11}B-^{11}B]-COSY[20] and ^1H-{^{11}B(selective)} NMR experiments[21] were essentially as described in other recent papers from the I.I.C. laboratory. NMR chemical shifts are given in ppm to the high-frequency side (low field) of $\Xi = 160.380$ MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm) and $\Xi = 499.877$ MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in the literature.[21] Residual solvent ^1H resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B\text{-}^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution 2 Hz and are given in Hz.

Mass spectrometry measurements were performed on a Bruker Esquire-LC Ion Trap instrument using electrospray ionization. Negative ions were detected. Samples dissolved in acetonitrile (concentration 1ng μl^{-1}) were introduced into the ion source by infusion at 3 μl min^{-1}, drying temperature was 300 °C, drying gas flow 5 L min^{-1} and nebulizing gas pressure 10 psi.

Analytical HPLC

The analytical system was comprised by a 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. The ion-pair RP chromatographic method for the separation of hydrophobic borate anions[22] with DAD detection was used under modified conditions mentioned in the literature[22b] by authors from the I.I.C. laboratory. The column was a RP Separon C8, 7 μm (silica with chemically bonded octyl groups) from Tessek Ltd., Prague. The mobile phase was 3 mmol hexylamine acetate in 58% aqueous acetonitrile, flow rate 1 ml min^{-1}, DAD detection at the fixed wavelengths 295, 302, 308 and 325 nm, sensitivity range 0.2 a.u.f.s. Sample concentration was approx. 1 mg ml^{-1} and the injection volume 5 μl. $k' = 3.18$ for parent anion **1** under these chromatographic conditions. Samples taken from reaction mixtures were, prior to analysis, treated with water, evaporated in vacuum, dissolved in the mobile phase, the pH was adjusted by addition of acetic acid to 7.0, and the solutions were filtered through 0.45 μm nylon microfilters (Tessek Ltd., Prague).

X-Ray crystallography

The orange crystal of compound **5** of dimensions $0.27 \times 0.2 \times 0.17$ mm was mounted on glass fibers with glue and measured on a four-circle Kappa CCD diffractometer with CCD area detector at 150(2) K with graphite monochromated MoK$_\alpha$ radiation. For the selected interatomic distances and angles see Fig. 1 caption. The structure of compound **5** was solved by direct methods (SIR92) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97).[23] The data were corrected for absorption by the multi-scan method SORTAV.[24] Hydrogen atoms were calculated into theoretical positions and refined with restricted temperature factors, except for the hydrogen of the hydroxyl group, which was found on the difference map and refined isotropically. Reliability of atom positions of the crown ether ring is hampered by vast disorder of a majority of the ring, leading to large R factors and residual peaks on the final difference map. Efforts to find other position of atoms was unsuccessful; the remaining maxima of the difference Fourier map do not form any logical chain. Therefore, only dominant position of atoms were included into model with partial occupancy and restricted bond distances to prevent splitting of the chain during refinement. Scattering factors were those implemented in the SHELX programs.[23]

Crystallographic details for **5**: $C_{15}H_{42}B_{18}CoCsO_7$; $M = 720.9$; monoclinic; $C2/c$ (No 15); $a = 29.7050(7)$, $b = 11.1510(2)$, $c = 22.1100(2)$ Å; $\beta = 111.246(1)°$; $Z = 8$; $\mu = 1.595$ mm^{-1}; $\lambda = 0.71073$ Å; 45830 reflections measured; 6704 unique reflections ($R_{int} = 0.041$); 5784 observed reflections with $I > 2\sigma(I)$. Final R indices $[I > 2\sigma(I)]$: $R_I = 0.074$, $wR_2 = 0.200$; R indices (all data): $R_I = 0.084$, $wR_2 = 0.209$.

CCDC reference number 174006. See http://www.rsc.org/suppdata/nj/b1/b109956f/ for crystallographic data in CIF or other electronic format.

Extraction tests

The γ emitters (^{22}Na, ^{85}Sr simulating long-lived β emitter ^{90}Sr, ^{137}Cs) used for spiking the simulated waste were obtained from Amersham. The solvent nitro phenyl hexyl ether (NPHE), synthesized by Eras Labo, was used without any further purification. Extractants were dissolved in NPHE at a concentration of 10^{-2} M. Liquid–liquid experiments were performed by contacting, for one hour, the same volume of organic and aqueous phases inside agitated tight tubes placed inside a constant temperature enclosure (25 ± 0.2 °C). Placing the tubes into a centrifuge for 5 min ensured complete separation of phases. Then aliquots of aqueous and organic phases were removed for analysis by γ spectrometry (Eurysis Mesures). The measurement duration was adapted to obtain reproducibilities of ±5%.

The distribution coefficients D_M were determined as the ratio of cation γ activity in the organic phase to γ cation activity in the aqueous phase. The selectivity $S_{2/1}$ of the cation M(1+) over M(2+) is expressed as the ratio of distribution coefficients of these cations.

$$D_M = \frac{\sum[M_{org}]}{\sum[M_{aq}]} \qquad (1)$$

$$S_{2/1} = \frac{D_{M_2}}{DM_1} \qquad (2)$$

Synthesis of cobalta bis(dicarbollide) ions with crown ether substitute bonded *via* diethylene glycol spacer: general procedure

The respective hydroxymethyl crown ethers were dried in vacuum over P_2O_5 for 2 days at room temperature, then 8 h at 80 °C. This reagent (3.0 mmol) was dissolved in toluene (30 ml), NaH (4.0 mmol) was added and the suspension was stirred 1 h at room temperature. Then a suspension of [(8-($C_4H_8O_2$)-($C_2B_9H_{10}$)-3-Co-($C_2B_9H_{11}$)] zwitterionic species (2.8 mmol) in 30 ml of toluene was added and the reaction mixture was stirred 1 h at room temperature and then at 60 °C for 3 h. The course of the reaction was monitored by TLC, and the reaction was stopped when the spot of the starting zwitterion disappeared (R_F 0.6 in CH_2Cl_2). After cooling down to room temperature, water (20 ml) was carefully added, followed with 0.5 ml of 3 M HCl, and the solvents were evaporated in vacuum. The orange semi-solid residue was treated with 3 M HCl and toluene (30 ml). The toluene layer was separated and discarded. The product was extracted into diethyl ether (3 × 50 ml). Water (30 ml) was added to the combined ether extracts and ether was evaporated in vacuum together with a small portion of the water (10 ml). Then MeOH was added until complete dissolution of the orange mass, and the pH was adjusted to 7.0 with 1 M NaOH (pH metric titration). Water was evaporated on a vacuum evaporator and the semi-solid residue was then dried in vacuum for 8 h at room temperature. The product was dissolved in acetone (50 ml) and the resulting solution filtered and evaporated to dryness after addition of water (20 ml). The product was then dissolved in a CH_3CN–$CHCl_3$ 1 : 2 solvent mixture, poured on top of a silica gel chromatographic column (2 × 25 cm) and purified by flash chromatography using the same eluent composition as above. Purity of the eluting fraction was checked by HPLC with DAD detection. Pure fractions containing the products were combined, evaporated and dried in vacuum at 40 °C. Samples for tests of extraction properties were used in this form of sodium salts. For characterization, the compounds were dissolved in aqueous ethanol, precipitated by CsCl, filtered and recrystallized from aqueous methanol at 0 °C. Yields of sodium salts based on the starting boron compound: **2**: 58%, **3**: 48% **4**: 71%; orange powders.

[{8-(15-Crown-5-CH_2O)-(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$}-3,3′-Co-(1′,2′-$C_2B_9H_{11}$)]Cs (2). TLC R_F ($CHCl_3$–CH_3CN 3 : 1): 0.35; HPLC k': 4.95; m/z_{max} 663.4 (660.4, 100%); m.p. 193–194 °C;

^{1}H NMR (acetone-d$_6$) δ: 4.24 s (2H, CH$_{carb}$), 4.12 s (2H, CH$_{carb}$), 3.92 m (1H, CHO), 3.82 m (2H, CH$_2$–O), 3.77–3.61 m (18H, CH$_2$–O), 3.61 m (6H, CH$_2$–O), 3.52 m (4H, 2CH$_2$–O); ^{11}B NMR (acetone-d$_6$) δ (B$_{assign}$) ($J_{B\text{-}H}$/Hz) [^{1}H-{^{11}B} selectively decoupled in square brackets]: 23.18 s (B8), 4.44 (B8′) (139) [2.576], 0.38 (B10′) (139) [2.930], −2.45 (B10) (139) [2.696], −4.40 (B4′, 7′) (135) [2.743], −7.25 (B9′, 12′) (131) [2.85, 1.804], −8.01 (B4, 7, 9, 12) (127) [2.902, 2.002], −17.28 (B5′, 11′) (150) [1.637], −20.37 (B5, 11) (154) [1.559], −22.1 (B6′) (overlap) [1.689], −28.43 (B6) (142) [1.471].

[{8-(18-Crown-6-CH$_2$O)-(CH$_2$CH$_2$O)$_2$-1,2-C$_2$B$_9$H$_{10}$}-3,3′-Co-(1′,2′-C$_2$B$_9$H$_{11}$)]Cs (3). TLC R_F (CHCl$_3$–CH$_3$CN 3 : 1): 0.48; HPLC *k*′: 13.0 (Na$^+$ salt); m/z_{max}: 707.4 (704.4, 100%); m.p. 202–206 °C; ^{1}H NMR (acetone-d$_6$) δ: 4.445 s (4H, CH$_{carb}$), 3.91 m (1H, CH–O), 3.74–3.60 m (22 H, CH$_2$–O crown), 3.59 m (6H, CH$_2$–O), 3.51 m (2H, CH$_2$–O), 2.85 s (2H, CH$_2$–O); ^{11}B NMR (acetone-d$_6$) δ ($J_{B\text{-}H}$/Hz) (B$_{assign}$) [^{1}H-{^{11}B} selectively decoupled in square brackets]: 22.96 s (B8), 3.98 (B8′) (142) [2.854], 0.38 (B10′) (142) [2.935], −2.42 (B10) (142) [2.699], −4.22 (B4′, 7′) (154) [2.760], −7.36 (B9′, 12′) (142) [2.81, 1.792], −8.20 (B4, 7, 9, 12) (146) [2.901, 1.98], −17.27 (B5′, 11′) (146) [1.65], −20.37 (B5, 11) (157) [1.563], −21.98 (B6′) (150) [1.698], −28.43 (B6) (159) [1.476].

[{8-(21-Crown-7-CH$_2$O)-(CH$_2$CH$_2$O)$_2$-1,2-C$_2$B$_9$H$_{10}$}-3,3′-Co-(1′,2′-C$_2$B$_9$H$_{11}$)]Cs (4). TLC R_F (CHCl$_3$–CH$_3$CN 3 : 1): 0.30; HPLC *k*′: 15.0 (Na$^+$ salt); m/z_{max}: 751.4 (748.4, 100%); m.p. 74–76 °C (Na$^+$ salt); ^{1}H NMR (acetone-d$_6$) δ: 4.25 s (2H, CH$_{carb}$), 4.23 s (2H, CH$_{carb}$), 3.87 m (1H, CH–O), 3.82–3.60 m (24H, CH$_2$–O crown), 3.75 m (2H, CH$_2$–O), 3.65 m (2H, CH$_2$–O), 3.61 m (4H, CH$_2$–O), 3.55 m (2H, CH$_2$–O), 2.75 s (2H, CH$_2$–O); ^{11}B NMR (acetone-d$_6$) δ ($J_{B\text{-}H}$/Hz) (B$_{assign}$) [^{1}H{^{11}B} selectively decoupled in square brackets]: 23.15 s (B8), 4.22 (B8′) (127) [2.542], 0.31 (B10′) (130) [2.932], −2.51 (B10) (142) [2.699], −4.42 (B4′, 7′) (137) [2.749], −7.31 (B9′, 12′) (139) [2.79, 1.804], −8.23 (B4, 7, 9, 12) (131) [2.901, 1.95], −17.34 (B5′, 11′) (150) [1.645], −20.44 (B5, 11) (154) [1.563], −22.12 (B6′) (overlap) [1.694], −28.55 (B6) (142) [1.466].

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

Anions 5 and 6 with crown ether functionalities attached *via* B–O–CH$_2$– moiety in position 8: general procedure

Me$_3$NH[(8,8′-(OH)$_2$-1,2-C$_2$B$_9$H$_{10}$)$_2$-3,3′-Co] (0.8 g, 1.92 mmol; dried in vacuum at 80 °C over P$_2$O$_5$ for 12 h) was dissolved in THF (20 ml) and added *via* canula to NaH (0.16 g, 6.7 mmol). The reaction mixture was stirred 2 h at ambient temperature and then refluxed for 1 h. After cooling down to room temperature, the respective crown tosylate (4.0 mmol) dissolved in THF (30 ml) was added dropwise over 2 h while stirring. The temperature was increased to 55 °C and the reaction mixture was stirred until no further changes were observed by TLC and HPLC (approx. 5 h). After cooling down, ethanol (10 ml) was carefully added dropwise from a syringe through a septum, followed by water (30 ml) and 5 drops of 3 M HCl. Organic solvents were evaporated on a vacuum evaporator and the aqueous slurry was extracted with 4 portions of diethyl ether (25 ml). Water (15 ml) was added to the combined organic extracts and ether was evaporated in vacuum. The orange semi-solid material was dissolved in an acetonitrile–chloroform solvent mixture (1 : 3), poured on top of a silica gel chromatographic column (2.5 × 20 cm) and the product was purified by flash chromatography using the same mobile phase, later increasing the content of CH$_3$CN to 1 : 2. The purity of the fractions was monitored by TLC and HPLC. Fractions containing the pure products **5** and **6**, respectively, were combined. Samples for tests of extraction properties were used in the form of sodium salts resulting from the above procedure. For crystallization, compounds were transformed into Cs$^+$ salts by dissolution in aqueous ethanol, precipitation by CsCl, filtration and recrystallization from aqueous methanol or aqueous acetone at 0 °C. Yields: **5**: 75%; **6**: 56%.

{[8-(15-Crown-5-CH$_2$O)-1,2-C$_2$B$_9$H$_{10}$]-3,3′-Co-(8′-HO-1′,2′-C$_2$B$_9$H$_{11}$)}Cs (5). TLC R_F (CHCl$_3$–CH$_3$CN 3 : 1): 0.34; HPLC *k*′: 6.85; m/z_{max} 591.3 (588.3, 100%); m.p. > 240 °C; ^{1}H NMR (acetone-d$_6$) δ: 4.04 m (1H, CH–O), 3.84–3.70 m (18 H, CH$_2$–O), 3.60 s (4H, CH$_{carb}$), 3.55 (2H, CH$_2$–O); ^{11}B NMR (acetone-d$_6$) δ ($J_{B\text{-}H}$/Hz) (B$_{assign}$) [^{1}H-{^{11}B} selectively decoupled in square brackets]: 26.99 s and 24.95 s (B8, 8′), −4.22 d (B10, 10′) (overlap) [2.491], −5.14 d (2B), −7.91 d (2B), −8.64 d (4B) (B4, 7, 4′, 7, 9, 12, 9′, 12′) (overlap) [2.85, 2.13], −20.18 (B5, 11, 5′, 11′) (154) [1.501], −29.75 (B6, 6′) [1.367, 1.324].

{[8-(21-Crown-7-CH$_2$O)-1,2-C$_2$B$_9$H$_{10}$]-3,3′-Co-8′-HO-1′,2′-C$_2$B$_9$H$_{11}$}Cs (6). TLC R_F (CHCl$_3$–CH$_3$CN 3 : 1): 0.41; HPLC *k*′: 11.9; m/z_{max} 679.3 (676.3, 100%); m.p. 108–114 °C; ^{1}H NMR (acetone-d$_6$) δ: 3.76 m (1H, CH–O), 3.85–3.50 m (26 H, CH$_2$–O crown), 3.62 s (4H, CH$_{carb}$), 3.55 m (2H, CH$_2$–O); ^{11}B NMR (acetone-d$_6$) δ ($J_{B\text{-}H}$/Hz) (B$_{assign}$) [^{1}H-{^{11}B} selectively decoupled in square brackets]: 26.35 s, 24.91 s (B8, 8′), −4.25 (B10, 10′) (overlap) [2.507, 2.477], −5.54 d (2B), −8.64 d (4B) (B4, 7, 4′, 7′, 9, 12, 9′, 12′) (overlap) [2.896, 2.846, 2.103, 1.804], −20.16 (B5, 11, 5′, 11′) (154) [1.473], −29.87 (B6, 6′) (167) [1.41, 1.323].

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). For compounds **5** and **6** signals for boron atoms in positions B(10, 10′, 4, 7, 4′, 7′, 9, 12, 9′, 12′) could be assigned, due to incidental overlaps, only based on analogy with the 8,8′-**1** dihydroxy derivative.[16] Mutual assignment of signals B(8) and B(8′) in **5** and **6** could not be succesfully made, due to peak overlap.

Results and discussion

Synthesis and characterization of compounds

Synthetic routes to SEA, combining in one molecule a hydrophobic cobalta bis(dicarbollide) anion with a metal selective crown ether moiety, or at least containing any cyclic substituents, have been searched for many years by several authors working in this area. It has been assumed that such anionic species can be a step forward in metalladicarbollide chemistry with respect to the anticipated improvement in metal binding properties.[13b,14,25] However, up to now, only a limited number of derivatives of **1**, containing larger rings in the molecule, have been synthesized.[13,14] Synthetic ways to the known compounds, substituted with polyatomic bridges between two dicarbollide ligands, rather than with a regular cyclic moiety, proceeded *via* several difficult steps including: (1) bonding of two *closo*-1,2-C$_2$B$_{10}$H$_{12}$ *via* a polyatomic chain; (2) degradation of the resulting adduct to the [*nido*-7,8-C$_2$B$_9$H$_{11}$-R-7,8-C$_2$B$_9$H$_{11}$]$^{2-}$ [R = (CH$_2$)$_n$, -S-(CH$_2$CH$_2$)$_3$-S-] dianion;[25] (3) metal insertion reaction. The first two steps would lead, in principle, to stereochemical difficulties. Due to the presence of two available binding carbon sites in the starting *o*-carborane and two possible sites for degradation, B(3) and B(6), *meso* and *racemic* diastereoisomers may be generated. This inevitably complicates the characterization and physicochemical properties of the resulting sandwich complexes, if the diastereoisomers are not separated before metallacarborane sandwich synthesis. If the preparative scale separation could be performed, then serious separation problems arise. The presence of the chain in *nido*-

$[7,8\text{-}C_2B_9H_{11}\text{-R-}7,8\text{-}C_2B_9H_{11}]^{2-}$ often has caused difficulties in metal binding in the course of the third reaction step. It is a known fact in metallaborane chemistry that dicarbollide species substituted even by alkyl or ethylene oxide chains require special treatment for the sandwich synthesis. Generally, anhydrous and more drastic conditions should be used, apparently owing to the steric effects of substituents and preferable metal complexation by donor atoms in the *exo*-skeletal substituent, provided O, S or N are present.[12–14] Yields are then, in general, more or less dramatically decreased. In summary, such procedures do not seem suitable for the production of pure products on a larger scale.

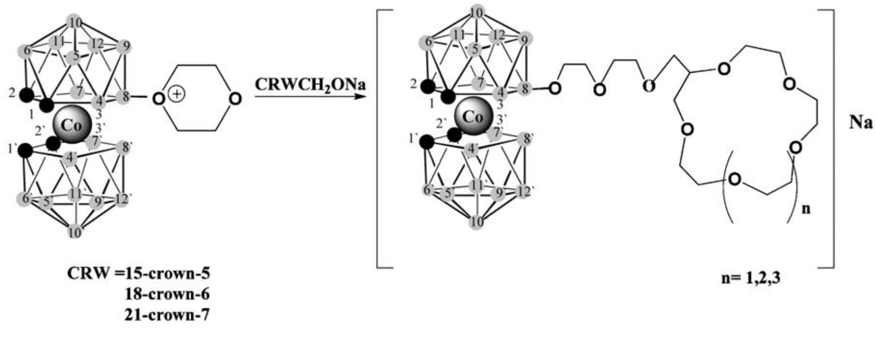
The two preparative methods described below are based on direct bonding of the crown ether ring to the boron atom in position B(8) of the cage of anion **1** *via* one-step procedures using commercially available crown ether derivatives. The advantage of this convenient approach lies in its reliability, simple reaction paths, high yields and stereospecific bonding of the crown onto the boron atom of the skeleton.

Synthesis of cobalta bis(dicarbollide) ions with a crown ether substituent bonded *via* a diethylene glycol spacer

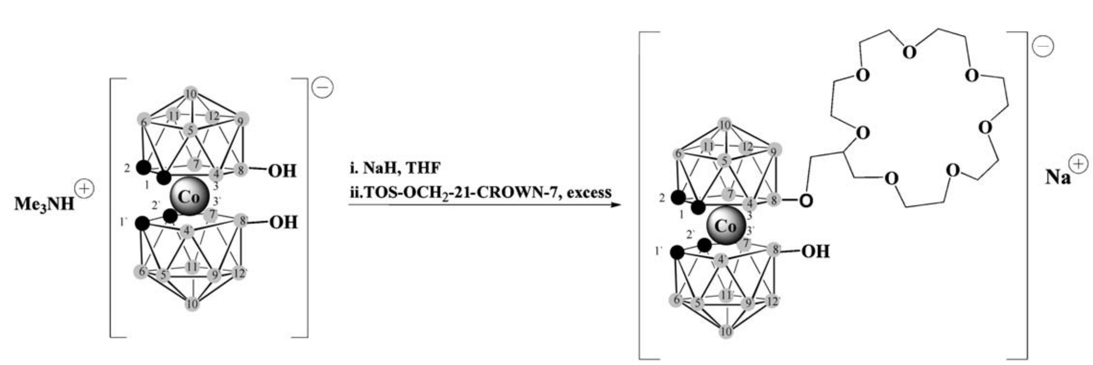
The cleavage reaction of the oxonium-oxygen-containing dioxane ring of $\{[8\text{-}(C_4H_8O_2)\text{-}1,2\text{-}C_2B_9H_{10}]\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})\}^0$ by hydroxymethyl crown ethers deprotonated *in situ* with NaH (see Scheme 1) was used. This method has recently proved[26] to be very efficient and a high-yield synthetic route to various anion **1** derivatives with simpler substituents, including phenolic groups and phosphorus containing moieties bonded to the cluster B(8) atom. The addition of the crown ether moieties also proceeded smoothly and gave single pure product in high yield after a relatively simple purification procedure. Three derivatives were synthesized: $\{[8\text{-}(15\text{-crown-}5\text{-}CH_2O)\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10}]\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})\}$ (**2**), *closo*-$\{[8\text{-}(18\text{-crown-}6\text{-}CH_2O)\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10}]\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})\}$ (**3**), *closo*-$\{[8\text{-}(21\text{-crown-}7\text{-}CH_2O)\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10}]\text{-}3,3'\text{-Co-}(1',2'\text{-}C_2B_9H_{11})\}$ (**4**). The yields ranged from 48% for **3** to 71% for compound **4**. The compounds were characterized by HPLC, electrospray MS and high field NMR techniques. As can be expected, ^{11}B NMR patterns of all three compounds are almost identical and closely related to previously reported series.[26] The chemical shift of the singlet of intensity one is in good agreement with the substitution of one dicarbollide ligand of parent compound **1** in position B(8). In the ^1H spectra, the presence of one crown ether moiety per cage can be clearly seen. The mass spectrometry measurements in negative ion mode also show the expected molecular mass cut-off for all three anionic species.

Anions with crown ether functionalities attached *via* B–O–CH_2– moiety in position 8

A one-step procedure to crown ether derivatives bonded in closer proximity to the cage was also successfully developed. The synthetic procedure was based on the reaction of the 8,8′-dihydroxy derivative of **1** deprotonated with NaH (for example see Scheme 2) with the methylcrown esters of *p*-toluenesulfonic acid. Two crown ether ring sizes were selected for this reaction, 15-crown-5 and 21-crown-7. Despite the use of 2 equiv of NaH and an excess of crown ether reagent, compounds with only one crown ether substituent per cage, $[(8\text{-}\{(15\text{-crown-}5\text{-}CH_2O)\text{-}1,2\text{-}C_2B_9H_{10}[\text{-}3,3'\text{-Co-}\}8'\text{-}\{(HO)\text{-}1',2'\text{-}C_2B_9H_{10}]^-$ (**5**) and $[\{8\text{-}(21\text{-crown-}7\text{-}CH_2O)\text{-}1,2\text{-}C_2B_9H_{10}\}\text{-}3,3'\text{-Co-}(8'\text{-HO-}1',2'\text{-}C_2B_9H_{10})]^-$ (**6**), were almost exclusively obtained, even if forcing conditions were applied. Only traces of disubstituted products were observed by HPLC and MS with electrospray ionization in the reaction mixtures. Tight chelating of the cation between the crown ether ring and the second OH group, as observed in the solid state structure (see below), and the steric effect of the bulky crown ether cycle probably prevent bonding of the second crown ether moiety to the remaining reaction site available on the anion.



Scheme 1 General synthetic procedure leading to crown ether moieties bonded onto the cage of anion **1** *via* a diethylene glycol chain.



Scheme 2 Reaction scheme leading to compound **6**.

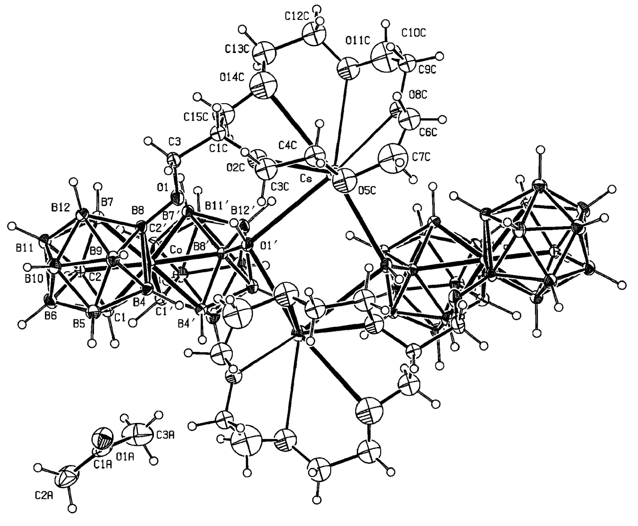


Fig. 1 Ortep presentation of the molecular structure of the {[8-(15-crown-5-CH_2O)-1,2-$C_2B_9H_{10}$}-3,3′-Co-(8′-HO-1′,2′-$C_2B_9H_{10}$)}Cs (**5**) containing a solvating acetone molecule. Thermal ellipsoids are drawn at the 30% probability level. Selected interatomic distances (Å) and angles (°): Cs–O(5C) 2.992(10), Cs–O(2C) 3.053(7), Cs–O(1′)^i 3.101(4), Cs–O(8C) 3.111(10), Cs–O(11C) 3.150(16), Cs–O(1′) 3.284(4), Cs–O(14C) 3.324(11), B(8′)–O(1′) 1.407(8), B(8)–O(1) 1.416(8); O(1′)–H(1O′) 0.97(9), O(1)–C(3) 1.396(8), O(5C)–Cs–O(2C) 54.8(2), O(5C)–Cs–O(1′)^i 81.0(2), O(2C)–Cs–O(1′)^i 116.53(15), O(5C)–Cs–O(8C) 56.6(3), O(2C)–Cs–O(8C) 90.3(2), O(1′)^i–Cs–O(8C) 101.3(2), O(5C)–Cs–O(11C) 105.7(3), O(2C)–Cs–O(11C) 96.5(3), O(1′)^i–Cs–O(11C)141.7(3), O(8C)–Cs–O(11C) 57.5(3), O(5C)–Cs–O(1′) 92.21(19), O(2C)–Cs–O(1′) 61.41(15), O(1′)^i–Cs–O(1′) 80.13(12), O(8C)–Cs–O(1′) 147.5(2), O(11C)–Cs–O(1′) 135.7(3), O(5C)–Cs–O(14C) 88.4(3), O(2C)–Cs–O(14C) 49.0(2), O(1′)^i–Cs–O(14C) 165.5(2), O(8C)–Cs–O(14C) 80.7(3), O(11C)–Cs–O(14C) 51.0(3), O(1′)–Cs–O(14C) 90.5(2), B(8′)–O(1′)–Csi 108.0(4), B(8′)–O(1′)–Cs 121.5(4), Cs′–O(1′)–Cs 98.71(11), B(8′)–O(1′)–H(1O′) 116(5), C(3)–O(1)-B(8) 124.9(5). Symmetry transformation used to generate equivalent atoms: $^{\mathrm{i}}$ $-x+2, y, -z+1/2$.

The molecular structure of compound **5** was confirmed by X-ray diffraction analysis of its Cs^+ salt (see Fig. 1). In the solid state, two cesium atoms are coordinated with two crown cobalta bis(dicarbollide) ligands. Each Cs^+ atom is coordinated to five oxygen atoms of one 15-crown-5 ring and to two O atoms of the second unreacted OH moiety in the B(8′) position of the two ligands, forming thus a distorted square planar arrangement of two Cs^+ cations and two O donor atoms. The cation is thus encapsulated inside a polar cavity formed by six inner polar oxygen atoms of each anion. The hydrophobic core of the resulting complex composed of the hydrophobic anions and crown ether CH_2 groups is directed away from the complexed metal. The oxygen atom included in the –CH_2–O–B spacer does not participate in the metal complexation but it's connection by intramolecular hydrogen bonds to the H–O–B moiety supports further the stability of this arrangement [parameters of the hydrogen bond: O1′···O1 2.664(4) Å; O1′–H1O′···O1 139(7)°]. For selected inter-atomic bond distances and angles see Fig. 1 caption.

The metal bonding observed in the solid state may also explain the solution behavior and the expected extraction mechanism, in which the metal encapsulated inside of the charge neutral complex with its hydrophobic outer shell is expelled from the aqueous phase to the organic solvent.

Both **5** and **6** were adequately characterized by a combination of HPLC, electrospray MS, and high field multinuclear NMR methods, for data see Experimental. ^{11}B NMR spectra of both compounds are almost identical. The spectra preserve more or less the pattern of the parent dihydroxy derivative,[16] except for the splitting of the B(8)–OH singlet of intensity at lowest field (−25.92) into two peaks of intensity one. These singlets are shifted about 1 ppm to higher and lower field, respectively, in comparison with the ppm for the parent compound of unsubstituted dihydroxy derivative. Other peaks, corresponding to the respective boron positions of the same symmetry in both dicarbollide subclusters, are mutually slightly shifted or broadened, which results in the occurrence of extensive coincidence overlaps in the spectra for resonances of boron atoms B(10, 10′, 9, 9′, 12, 12′, 4, 4′ and 7, 7′). On the other hand, the presence of two singlets differing by about 2 ppm, each of them of intensity one, clearly indicates substitution of only one oxygen atom in position B(8) with the crown ether substituent, which is in sound agreement with the above presented X-ray diffraction results. In the ^1H spectra, the presence of only one crown ether moiety per one cage can be seen. The mass spectrometry results showed clearly a highest mass peak corresponding to the mono-substituted product.

Extraction results

Used at a concentration of 10^{-2} M in NPHE, crown ethers alone, whatever the ring size, have not been found sufficiently efficient for the removal of the target cations Cs^+ and Sr^{2+} (See Tables 1 and 2). As expected, addition of hexabrominated anion **1** (Br_6-COSAN) at the same concentration as that of crown ether to the organic phase led to a marked enhancement of the cation extraction (see Tables 1 and 3). On the other

Table 1 Distribution coefficients of sodium, strontium and cesium and selectivity for benzo 15-crown-5, *tert*-butyl 21-crown-7, and their synergic mixtures with the hexabromo derivative of anion **1** (Br_6-COSAN) at a concentration of 10^{-2} M in NPHE

HNO_3/M^a	D_{Na}		D_{Sr}		D_{Cs}	
	10^{-1}	1	10^{-1}	1	10^{-1}	1
Br_6-COSAN	0.04	$< 10^{-3}$	0.03	$< 10^{-3}$	25	2.1
Benzo-15-crown-5	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
tert-Butyl-21-crown-7	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	0.05	0.25
Br_6-COSAN + benzo-15-crown-5	$> 10^2$	9.6	$> 10^2$	37	53	6.7
Br_6-COSAN + *tert*-butyl-21-crown-7	1.1	0.11	19	0.2	70	15

Selectivity HNO_3/M^a	$D_{Sr/Na}$		$D_{Cs/Na}$	
	10^{-1}	1	10^{-1}	1
Br_6-COSAN	0.75	1	625	$> 2.1 \times 10^3$
Br_6-COSAN + benzo-15-crown-5	1	< 0.5	3.8	0.7
Br_6-COSAN + *tert*-butyl-21-crown-7	17	1.8	63	135

[a] $^{22}Na + ^{85}Sr + ^{137}Cs$ at trace levels.

Table 2 Sodium, strontium, cesium distribution coefficients for different derivatives of the 18-crown-6 series of crown ethers

	HNO_3/M^a			
	10^{-3}	10^{-2}	10^{-1}	1
D_{Na}				
18-Crown-6	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Decyl-18 crown-6	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	3×10^{-3}
Benzo-18-crown-6	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	2×10^{-3}
Dicyclohexano-18-crown-6	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	4×10^{-3}
D_{Sr}				
18-Crown-6	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	6×10^{-3}
Decyl-18 crown-6	$< 10^{-3}$	$< 10^{-3}$	2×10^{-3}	52×10^{-3}
Benzo-18-crown-6	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	10^{-3}
Dicyclohexano-18-crown-6	$< 10^{-3}$	$< 10^{-3}$	14×10^{-3}	0.20
D_{Cs}				
18-Crown-6	$< 10^{-3}$	$< 10^{-3}$	10^{-3}	4×10^{-3}
Decyl-18 crown-6	2×10^{-3}	2×10^{-3}	4×10^{-3}	32×10^{-3}
Benzo-18-crown-6	3×10^{-3}	4×10^{-3}	$< 10^{-2}$	0.14
Dicyclohexano-18-crown-6	2×10^{-3}	3×10^{-3}	2×10^{-2}	24×10^{-3}

[a] $^{22}Na + ^{85}Sr + ^{13}Cs$ at trace levels.

hand, insufficiently lipophilic compounds such as 18-crown-6, decyl-18-crown-6 or benzo-18-crown-6 displayed a lower solubility in NPHE upon addition of Br_6-COSAN.

Medium level radioactive liquid waste comprises radionuclides such as ^{90}Sr or ^{137}Cs at trace concentrations in a system with a large excess of other salts containing inactive cations, and, in particular, sodium nitrate. In order to remove the target cations from such high salinity solutions, extractants displaying an important selectivity for strontium or cesium *versus* sodium are required. The extracting ability of Br_6-COSAN (CoB_2), which behaves simply as a liquid cation exchanger, decreases with increase of the acidity. This effect is due to a competition of the target cations with protons present in a large excess [see eqn. (3)–(5):

$$M^{n+}_{aq} + nH^{+}_{org} + nCoB^{-}_{2org} \rightleftharpoons nH^{+}_{aq} + M^{n+}_{org} + nCoB^{-}_{2org} \qquad (3)$$

with an equilbrium extraction constant K_{ex} defined by the following relation:

$$\frac{\left[H^{+}_{aq}\right]^{n}\left[M^{n+}_{org}\right]}{\left[H^{+}_{org}\right]^{n}\left[M^{n+}_{aq}\right]} = K_{ex} \qquad (4)$$

From eqn. (1) and (4), we deduce the relation linking D_M and K_{ex}:

$$D_M = K_{ex} \cdot \frac{\left[H^{+}_{org}\right]^{n}}{\left[H^{+}_{aq}\right]^{n}} \qquad (5)$$

In contrast, the efficiency of crown ethers (CE), which are neutral solvating compounds, is increased by the presence of nitrate, as shown by eqns (6)–(8).

$$M^{n+}_{aq} + nNO^{-}_{3aq} + CE \rightleftharpoons M^{n+}(NO^{-}_{3})_{n}CE_{org} \qquad (6)$$

with an extraction equilibrium constant K^{CE}_{ex}

$$\frac{\left[M^{n+}\left(NO^{-}_{3}\right)_{n}CE\right]_{org}}{[M^{n+}]_{aq}\left[NO^{-}_{3}\right]_{aq}[CE]_{org}} = K^{CE}_{ex} \qquad (7)$$

Distribution coeficients are linked to extraction eqilibrium constant by the relation:

$$D_M = K^{CE}_{ex} \cdot [NO_3{}^{-}]^{n}_{aq}[CE]_{aq} \qquad (8)$$

In strongly acidic medium, the dicyclohexano-18-crown-6/Br_6-COSAN mixture has been found relatively efficient for both cesium and strontium; even higher cesium extraction has been achieved using synergistic mixtures of Br_6-COSAN with benzo-15-crown-5, and, especially with *t*-butyl-21-

Table 3 Sodium, strontium, cesium distribution coefficients and selectivity for mixtures of different 18-crown-6 derivatives and the hexabromo-derivative of the anion **1** (Br_6-COSAN) present in equimolar concentrations

<table>
<tr><th></th><th></th><th colspan="8">HNO_3 M^a</th></tr>
<tr><th></th><th>Concentration in NPHE/M</th><th colspan="2">10^{-3}</th><th colspan="2">10^{-2}</th><th colspan="2">10^{-1}</th><th colspan="2">1</th></tr>
<tr><td>D_{Na}</td><td></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Br_6-COSAN + 18-Crown-6</td><td>5×10^{-3}</td><td colspan="2">21</td><td colspan="2">2.9</td><td colspan="2">0.37</td><td colspan="2">39×10^{-3}</td></tr>
<tr><td>Br_6-COSAN + decyl-18 crown-6</td><td>10^{-2}</td><td colspan="2">40</td><td colspan="2">10</td><td colspan="2">1.05</td><td colspan="2">0.13</td></tr>
<tr><td>Br_6-COSAN + benzo-18-crown-6</td><td>5×10^{-3}</td><td colspan="2">> 100</td><td colspan="2">23</td><td colspan="2">2.6</td><td colspan="2">21×10^{-3}</td></tr>
<tr><td>Br_6-COSAN + dicyclohexano-18-crown-6</td><td>10^{-3}</td><td colspan="2">0.57</td><td colspan="2">0.075</td><td colspan="2">10^{-2}</td><td colspan="2">$< 10^{-3}$</td></tr>
<tr><td>D_{Sr}</td><td></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Br_6-COSAN + 18-Crown-6</td><td>5×10^{-3}</td><td colspan="2">> 100</td><td colspan="2">> 100</td><td colspan="2">28</td><td colspan="2">0.2</td></tr>
<tr><td>Br_6-COSAN + decyl-18 crown-6</td><td>10^{-2}</td><td colspan="2">> 100</td><td colspan="2">> 100</td><td colspan="2">14</td><td colspan="2">1.2</td></tr>
<tr><td>Br_6-COSAN + benzo-18-crown-6</td><td>5×10^{-3}</td><td colspan="2">> 100</td><td colspan="2">25</td><td colspan="2">0.27</td><td colspan="2">$< 10^{-3}$</td></tr>
<tr><td>Br_6-COSAN + dicyclohexano-18-crown-6</td><td>10^{-3}</td><td colspan="2">0.59</td><td colspan="2">2×10^{-3}</td><td colspan="2">2×10^{-3}</td><td colspan="2">2×10^{-3}</td></tr>
<tr><td>D_{Cs}</td><td></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Br_6-COSAN + 18-Crown-6</td><td>5×10^{-3}</td><td colspan="2">> 100</td><td colspan="2">62</td><td colspan="2">8</td><td colspan="2">0.56</td></tr>
<tr><td>Br_6-COSAN + decyl-18 crown-6</td><td>10^{-2}</td><td colspan="2">> 100</td><td colspan="2">> 100</td><td colspan="2">12</td><td colspan="2">1.02</td></tr>
<tr><td>Br_6-COSAN + benzo-18-crown-6</td><td>5×10^{-3}</td><td colspan="2">> 100</td><td colspan="2">> 100</td><td colspan="2">26</td><td colspan="2">1.6</td></tr>
<tr><td>Br_6-COSAN + dicyclohexano- 18-crown-6</td><td>10^{-3}</td><td colspan="2">4.3</td><td colspan="2">0.54</td><td colspan="2">0.06</td><td colspan="2">5×10^{-3}</td></tr>
<tr><th>Selectivity</th><th></th><th>Sr/Na</th><th>Cs/Na</th><th>Sr/Na</th><th>Cs/Na</th><th>Sr/Na</th><th>Cs/Na</th><th>Sr/Na</th><th>Cs/Na</th></tr>
<tr><td>Br_6-COSAN + 18-crown-6</td><td>5×10^{-3}</td><td>> 5</td><td>> 5</td><td>> 35</td><td>20</td><td>75</td><td>22</td><td>5</td><td>14</td></tr>
<tr><td>Br_6-COSAN + decyl-18 crown-6</td><td>10^{-2}</td><td>> 25</td><td>> 2.5</td><td>> 10</td><td>> 10</td><td>1</td><td>12</td><td>9</td><td>8</td></tr>
<tr><td>Br_6-COSAN + benzo-18-crown-6</td><td>5×10^{-3}</td><td>1</td><td>1</td><td>1</td><td>> 4</td><td>< 1</td><td>1</td><td>< 1</td><td>80</td></tr>
<tr><td>Br_6-COSAN + dicyclohexano- 18-crown-6</td><td>10^{-3}</td><td>1</td><td>8</td><td>< 1</td><td>9</td><td>< 1</td><td>6</td><td>< 1</td><td>> 5</td></tr>
</table>

[a] $^{22}Na + ^{85}Sr + ^{137}Cs$ at trace levels.

Table 4 Sodium, strontium, cesium distribution coefficients and selectivity for the series of anionic species with covalently bonded crown ether rings, compounds **2**–**6** (10^{-2} M in NPHE), differing in the crown ether size and the spacer

	HNO_3/M[a]							
	10^{-3}		10^{-2}		10^{-1}		1	
D_{Na}								
2	46		64		9.3		0.77	
3	>100		12		1.2		0.11	
4	3.4		3.1		0.33		0.03	
5			0.24		0.3		$<10^{-3}$	
6			0.46		0.06		$<10^{-3}$	
D_{Sr}								
2	>100		>100		>100		1	
3	>100		18		2.4		0.34	
4	>100		>100		>100		1	
5			11		0.95		0.02	
6			50		0.64		0.01	
D_{Cs}								
2	>100		>100		11		0.6	
3	>100		>100		16		1.24	
4	>100		>100		47		3.8	
5			0.32		0.21		0.05	
6			>100		20		1.25	
Selectivity	Sr/Na	Cs/Na	Sr/Na	Cs/Na	Sr/Na	Cs/Na	Sr/Na	Cs/Na
2	>2.2	>2.2	>1.5	>1.5	>10	1.2	>1.2	<1
3	1	1	1.5	>8	2	13	3	>11
4	>30	>30	>32	>35	>300	140	33	125
5			45	1.3	3.2	<1	>20	>50
6			110	>200	11	>330	>10	>1250

[a] $^{22}Na + ^{85}Sr + ^{137}Cs$ at trace levels.

crown-7. With respect to Cs/Na selectivity, benzo-15-crown-5, whose crown cavity is best suited to the sodium cation, displayed no selectivity for cesium over sodium. In contrast, *tert*-butyl 21-crown-7 with a larger size ring has proved to be very selective for cesium.

In the case of crown ethers covalently linked to cobalta bis(-dicarbollide) anion (**2**–**6**) the overall extraction behavior has not been modified. The extraction of sodium decreases while that of cesium increases with increasing diameter of the crown ring (see Table 4). Best extraction coefficients for Cs^+ and Sr^{2+} were achieved using compound **4** with the 21-crown-7 selective group bonded *via* a longer spacer. However, an unexpected and disappointing decrease of efficiency of compound **3** for strontium was observed. Indeed, anion **3** contains an 18-crown-6 crown ether ring with a diameter that could be assumed to be optimum for Sr^{2+} cation binding, taking into account the parent crown ether series. Surprisingly, even for derivative **2** bearing the smaller 15-crown-5 ring as the substituent proved more efficient. The lower efficiency of the similar derivatives **5** and **6** with crowns attached *via* the shorter arm can be attributed to the steric hindrance of the bulky dicarbollide.

As a rule, crown ethers linked to dicarbollides (Table 4) display distribution coefficients comparable to that of the synergic mixture of the crown ethers mixed with the hexabromo derivative of anion **1** (see Tables 1, 3 and 4). On the other hand, covalently bonded compounds exhibit higher selectivities. It is known that the presence of units such as benzo or cyclohexano groups on the crown ether ring can play a key role in the affinity of a crown ether for a particular cation. In this study, only basic members of the crown ether series, linked to bis(dicarbollide), **2**–**6**, were prepared. The improvement in extraction properties should be compared to the unsubstituted crown ethers (15-crown-5, 18-crown-6, *etc.*). In this respect, an increase of the extraction properties can be clearly seen. Without any doubt, the presence of benzo groups on the crown ether would further improve both the extraction of the target radionuclides and the selectivity by rigidifying the crown and by making it more hydrophobic.

Conclusions

Two preparative methods for compounds **2**–**6** are based on direct bonding of the crown ether ring to the boron atom in position B(8) of the cage of anion **1** *via* one-step procedures using commercially available crown ether derivatives. The advantages of this convenient approach lie in its reliability, simple reaction paths, high yields and stereospecific bonding of the crown to a boron atom of the skeleton. Synthetic routes to such compounds remained undiscovered for a long time, since it has been difficult to prepare them by direct crown cyclization on the anionic cobalta bis(dicarbollide) moiety. The species **2**–**6** thus represent the first known examples of covalently bonded cobalta bis(dicarbollide) anion with regular oxygen crown ether moieties.

As expected, addition of the hydrophobic cobatta bis(dicarbollide) anion into the organic phase containing crown ethers strongly increases the extracting ability of the latter. The significant advantage of crown ethers covalently linked to cobalta bis(dicarbollide) as in **2**–**6** lies in their higher solubility in NPHE in comparison with simple mixtures of both components. Better selectivities were observed for covalently bonded compounds compared to that of the synergic mixtures. Most probably, the extraction efficiency and the selectivity can be further increased if one or two benzo or cyclohexyl moieties are attached to the crown ether. Other possible applications of the above species, for metal complexation applications and in electrochemistry for ion selective electrode materials, for example, can be anticipated.

Acknowledgements

The authors gratefully acknowledge Dr. Clara Viñas (ICMAB, CSIC, Barcelona) for remeasurement of and confirmation of the MS spectra of compounds **3**, **4** and **6** by the MALDI-TOF technique, Scientific Instruments, Ltd. (Brno, Czech Republic) and Bruker Saxonia Analytik, GmbH, (Esquire application Team, Leipzig, Germany) for electrospray MS demo measurements of compound **5** and Dr. J. Fusek (Institute of Inorganic Chemistry, AS CR) for all NMR measurements.

The authors are grateful for support from EEC Project IC15-CT98-0221, Grant Agency of Czech Republic (Grants Nos. 104/99/1096 and 203/99/M037, the latter for purchase of the KappaCCD) and also for partial support from the Ministry of Education of the Czech Republic (Projects LN 00A028 and LB98233, the latter for NMR network).

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