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FULL PAPER

Aromatic substituted metallacarboranes as extractants of ^{137}Cs and ^{90}Sr from nuclear wastes

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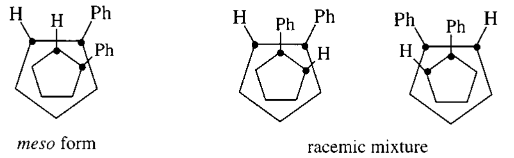
Phenyl- and 1,2-diphenyl-1,2-dicarba-*closo*-dodecaborane have been synthesized and deboronated to yield $[7\text{-}C_6H_5\text{-}7,8\text{-}C_2B_9H_{11}]^-$ and $[7,8\text{-}(C_6H_5)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. Reaction of the monophenyl with KOBu^t and $CoCl_2$ in 1,2-dimethoxyethane (dme) led to $[3,3'\text{-}Co(1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_9H_{10})_2]^-$ **1**$^-$. This has been fully characterized by X-ray analysis. A similar reaction with $[7,8\text{-}(C_6H_5)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ did not yield the expected sandwich compound. On the contrary, reaction of $[7,9\text{-}(C_6H_5)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with KOBu^t and $CoCl_2$ in a mixture of dme and diethylene glycol dimethyl ether led to $[3,3'\text{-}Co\{1,7\text{-}(C_6H_5)_2\text{-}1,7\text{-}C_2B_9H_9\}_2]$ **2**$^-$. The two sandwich complexes were tested for liquid–liquid extraction and transport through supported liquid membranes of ^{137}Cs, ^{90}Sr and ^{152}Eu. Extractions for ^{137}Cs were very good at pH 3 but decreased considerably at pH 1 for H[**1**], while H[**2**] showed good efficiency even at this pH. The extraction of ^{90}Sr was performed with the incorporation of a synergistic linear polyether and was good at pH 3 and 1. For the extraction of ^{152}Eu, compound H[**2**] displayed good efficiency. Transport experiments of Cs using supported liquid membranes were performed with H[**1**] and H[**2**] and *o*-nitrophenyl hexyl ether as the membrane solvent. The permeability of ^{137}Cs for compound H[**2**] was 30.9 cm h^{-1} while for H[**1**] it was 7.95 cm h^{-1}. These permeabilities are much higher than those of usual carriers under comparable conditions.

Introduction

In 1965 the first metallacarboranes, $[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{11})_2]^{n-}$ ($n = 1$ or 2) were reported.[1] Owing to their interesting properties and applications, their chemistry developed very quickly.[2] Current applications of these novel species include: (1) solubility in electron-donating organic solvents, *e.g.* in solvent extraction of radionuclides;[3] (2) isolation, separation and characterization of organic bases, including natural substances;[3] (3) radiometal carriers;[4] and (4) electron acceptor molecules, *e.g.* $[3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{11})_2]$.[5]

Concerning the solvent extraction of radionuclides, nuclear fuel reprocessing operations produce high and medium level liquid wastes (HLLW and MLLW) containing different long-lived radioactive elements as β/γ emitters (Tc, I, Zr, Se, Cs, *etc.*) and α emitters (transuranium actinides: Np, Pu, Am, Cm, *etc.*). In order to simplify the conditioning of such wastes, it would be highly desirable selectively to remove these very long-lived radionuclides. This would decrease the volume of wastes intended for disposal in deep geological repositories, using instead subsurface repositories which are easier to manage.[6] Furthermore, these nuclides, separated from the matrix, could afterwards be turned into short-lived elements or non-radioactive ones through transmutation. One of the generally used chemical separation processes in fuel treatment is liquid–liquid extraction by specific molecules.

Cobaltabis(dicarbollide), $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$, has shown a very high efficiency in the extraction of ^{137}Cs, when nitrobenzene is used as solvent.[3,7] However, the use of this solvent is very inconvenient due to technological and safety reasons. On the other hand, most of the selective sensors for cesium contain nitrobenzene[8] or its derivatives;[9] which shows the importance of introducing aromatic groups in cobaltabis(dicarbollide) derivatives, in order to enhance the extracting capacity of ^{137}Cs.



meso form racemic mixture

Fig. 1 Geometric isomers of complex **1**$^-$ (view from the top of the pentagonal faces).

Results and discussion

Synthetic results

The synthesis of C-substituted 1,2-dicarba-*closo*-dodecaboranes (*o*-carboranes) from decaborane $B_{10}H_{14}$ and the appropriate acetylenic species (phenylacetylene and diphenylacetylene) was required to produce the cobaltabis(dicarbollide) derivatives incorporating aromatic rings.[10] Deboronation of $1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$ and $1,2\text{-}(C_6H_5)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with an excess of KOH in EtOH as solvent led to the *nido* species $[7\text{-}C_6H_5\text{-}7,8\text{-}C_2B_9H_{11}]^-$ and $[7,8\text{-}(C_6H_5)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$.[11,12] Reaction of the monophenyl with KOBu^t and $CoCl_2$, in 1,2-dimethoxyethane (dme) as solvent led to the complex $[3,3'\text{-}Co(1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_9H_{10})_2]^-$ **1**$^-$.[12] Two geometric isomers resulted, which we were not able to separate (racemic mixture and *meso* form, Fig. 1) owing to their extremely similar physical properties. However, chemical analyses established their stoichiometric purity although the pattern of the ^{11}B NMR resonances clearly suggests the existence of more than one isomer.

Crystals of $Na[3,3'\text{-}Co(1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_9H_{10})_2]\cdot 0.4C_6H_5\text{-}CH_3$, used for X-ray analysis, were grown from acetone–toluene. The crystal structure contains disordered sodium cations, three crystallographically non-equivalent $[3,3'\text{-}Co(1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_9H_{10})_2]^-$ units and toluene molecules. Unit **A** has crystallographic two-fold symmetry with the metal atom

Table 1 Selected interatomic distances (Å) and angles (°) for Na[**1**]·$0.4C_6H_5CH_3$

	Complex unit		
	A	B	C
Co3–C1	2.115(8)	2.130(8)	2.116(9)
Co3–C2	2.068(8)	2.097(8)	2.081(8)
Co3–B4	2.124(10)	2.115(11)	2.097(12)
Co3–B7	2.110(11)	2.101(10)	2.128(12)
Co3–B8	2.106(12)	2.120(11)	2.102(12)
Co3–C1′		2.133(9)	2.117(9)
Co3–C2′		2.097(9)	2.087(8)
Co3–B4′		2.108(11)	2.083(10)
Co3–B7′		2.109(10)	2.116(10)
Co3–B8′		2.112(11)	2.146(12)
C1–C2	1.601(11)	1.629(11)	1.649(13)
C1–C13	1.511(11)	1.508(12)	1.493(13)
C1′–C2′		1.640(12)	1.620(12)
C1′–C13′		1.544(13)	1.507(12)
B10–Co3–B10*	177.6(4)		
B10–Co3–B10′		176.7(3)	176.8(3)

* Equivalent position: $-x + 1, y, -z + \frac{1}{2}$.

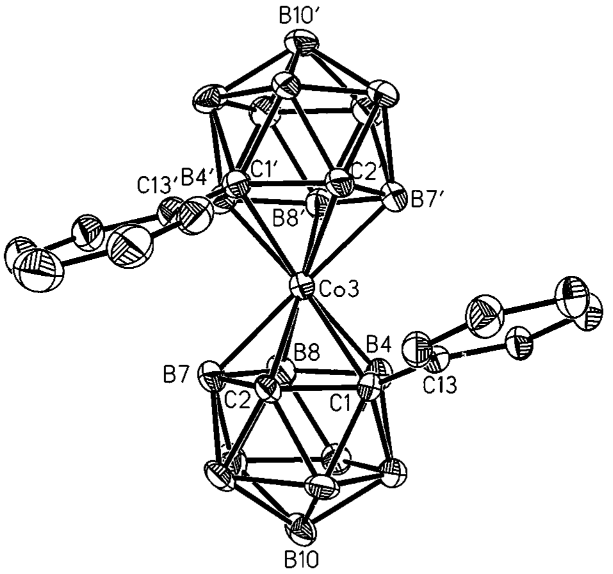


Fig. 2 Perspective view of the complex unit **B** of Na[3,3′-Co(1-C_6H_5-1,2-$C_2B_9H_{10}$)$_2$]·$0.4C_6H_5CH_3$ showing 20% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

occupying the symmetry axis. Units **B** and **C** are at common positions and show pseudo-twofold symmetry. Despite the crystallographic dissimilarity, the three complex units are geometrically very similar: (i) in each unit the mutual orientation of the two dicarbollide ligands is practically identical, the conformation of the co-ordinated pentagonal C_2B_3 faces being staggered so that the non-substituted cluster carbon of one face is oriented between the cluster carbons of the other face; (ii) in each unit the dihedral angles between the pentagonal C_2B_3 faces [6.1(9)–8.2(6)°] as well as the B(10)–Co(3)–B(10′) jackknife angles [176.7(3)–177.6(4)°] are equal within experimental errors. A view of the complex unit **B** is shown in Fig. 2, and selected interatomic distances and angles are reported in Table 1.

Several attempts at complexation of [7,8-(C_6H_5)$_2$-7,8-$C_2B_9H_{10}$]$^-$ to cobalt were made in our group, but it was a non-straightforward reaction which did not allow the isolation of the product, even under forcing reaction conditions, *e.g.* increasing the temperature of the refluxing or the reaction time. The reason may be due to the steric crowding caused by the aromatic rings. As it was known that [7,8-(C_6H_5)$_2$-7,8-$C_2B_9H_{10}$]$^-$ isomerizes at high temperature to give [7,9-(C_6H_5)$_2$-7,8-$C_2B_9H_{10}$]$^-$,[13] this compound was used to form the corresponding cobaltabis(dicarbollide) derivative under similar conditions as those for [7-C_6H_5-7,8-$C_2B_9H_{11}$]$^-$. However, higher temperatures were needed for the reaction to proceed, and a mixture of dme and diethylene glycol dimethyl ether (dime) (5:1 v/v) was used as solvent. Precipitation with [N{$(CH_2)_3CH_3$}$_4$]Br led to the pure compound [N{$(CH_2)_3CH_3$}$_4$][3,3′-Co{1,7-(C_6H_5)$_2$-1,7-$C_2B_9H_9$}$_2$], [N{$(CH_2)_3CH_3$}$_4$][**2**], in 55% yield.

As has been stated, the use of nitrobenzene as solvent increases considerably the efficiency in the extraction of caesium.[3,7] Likewise, most extraction essays are carried out in solvents incorporating a nitrophenyl group (*e.g.* nitrophenyl hexyl ether and nitrophenyl octyl ether), as will be described. This apparently necessary presence of the nitrophenyl group in caesium extraction or detection motivated us to synthesize the *closo* compound 1-*p*-$C_6H_4NO_2$-1,2-$C_2B_{10}H_{11}$[14] with the purpose of preparing the cobaltabis(dicarbollide) derivative. After successful partial degradation, no convenient route to the corresponding cobaltabis(dicarbollide) derivatives was found and the complex could not be isolated. Incorporation of the moiety $C_6H_4NO_2$ on boron atoms was then proposed as an alternative and reaction of [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ with $AlCl_3$ and nitrobenzene was attempted. It was expected that the nitrophenyl group could be introduced at the 8,8′ positions. Analysis of the NMR data led us to hypothesize the formation of the zwitterion [3,3′-Co(8-C_6H_5ONO-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] as well as several chlorinated products. The absence of a negative charge in this zwitterion made it useless for extraction purposes.

Extraction and transport through supported liquid membranes

The cobaltabis(dicarbollide) derivatives presented in this paper have been first tested in liquid–liquid extraction of ^{137}Cs, ^{90}Sr and ^{152}Eu. Table 2 presents the distribution coefficients of ^{137}Cs (D_{Cs}), of ^{90}Sr (D_{Sr}) and of ^{152}Eu (D_{Eu}), defined as the equilibrium ratio of the radionuclide between the organic and the aqueous phases.

The distribution coefficients of the metals decrease with pH in the feed solution due to the equilibrium of the cation M^{n+}, which is governed in acidic media for a basic cobaltabis(dicarbollide) by eqn. (1).[7] Protons in the organic phase are provided

$$nH^+(org) + M^{n+}(aq) \rightleftharpoons nH^+(aq) + M^{n+}(org) \quad (1)$$

by the cobaltabis(dicarbollide) and by the nitric acid in the aqueous phase, with an extraction constant K_{ex} [eqn. (2)].

$$K_{ex^{n+}} = \frac{[H^+(aq)]^n\,[M^{n+}(org)]}{[H^+(org)]^n\,[M^{n+}(aq)]} \quad (2)$$

In a first approach, for the extraction of trace level radioactive cations producing a small change in the nitric acid concentration, distribution coefficients can be linked to the extraction constant by the relationship (3) where $[H^+CoB_2^-]$

$$D_{M^{n+}} = \frac{M^{n+}(org)}{M^{n+}(aq)} = K_{ex}\,\frac{[H^+CoB_2^-]}{[HNO_3]} \quad (3)$$

corresponds to the concentration of the protonated cobaltabis(dicarbollide) species, H[**1**] or H[**2**]. The higher the nitric acid concentration the lower will be the distribution coefficient.

For the extraction of ^{137}Cs, both tested compounds show a very high extraction efficiency at pH 3 ($D > 1000$), regardless of the nature of the exo-cluster group. This efficiency is expected to be lower on increasing the acidity of the medium. This is the behavior displayed by H[**1**], for which D decreases from >1000 to 4, just by varying the pH value from 3 to 1. However, H[**2**] shows a good efficiency even at pH 1.

In the extraction of ^{90}Sr the compounds show a very high extraction efficiency, even at pH 1, upon the incorporation of

Table 2 Distribution coefficients (D_M) in aqueous HNO_3–nitrophenyl hexyl ether of the different radionuclides extracted by the protonated form of cobaltabis(dicarbollide) derivatives

	D_{Cs}		D_{Sr}		D_{Eu}		
Compound	pH 3	pH 1	pH 3	pH 1	pH 1*	pH 3	pH 1
H[**1**]	>1000	4	8	$<10^{-3}$	>1000	55	0.02
H[**2**]	>1000	27	22	0.08	>1000	>1000	$<10^{-3}$

* Essays carried out with addition of a linear polyether (polyethylene glycol) to the organic phase (0.003 M).

a synergistic linear polyether added to the organic phase. For the extraction of ^{152}Eu, distribution coefficients at pH 3 are excellent for compound H[**2**]. Previous results with $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ derivatives incorporating long lipophilic chains have shown excellent extractive properties.[15] The results obtained in the extraction of cesium by these compounds led us to perform some transport experiments by using supported liquid membranes (SLM) with *o*-nitrophenyl hexyl ether as the membrane solvent. Preliminary results carried out with compounds H[**1**] and H[**2**] showed that the best transport performance was with the latter.

The transport of radionuclides from aqueous HNO_3 solutions was monitored by measurement of the decrease of radioactivity in the feed solution by γ spectrometry analysis. This allowed determination of the constant permeabilities P/cm h^{-1} of ^{137}Cs permeating through the SLM for 24 h by plotting the logarithm of the ratio $C:C^0$ *vs.* time, as described in the model of mass transfer proposed by Danesi,[16] eqn. (3), where C is

$$\ln\left(\frac{C}{C^0}\right) = -\varepsilon\frac{S}{V}Pt \qquad (3)$$

concentration of the cation in the feed solution at time t (mol l^{-1}) C^0 the initial concentration of the cation in the feed solution (mol l^{-1}), ε the volume porosity of the SLM (%), S the membrane surface area (cm^2), V the volume of the feed and stripping solutions (cm^3) and t the time (h). Under these conditions, at pH 3, both compounds display very interesting results; the permeability for compound H[**2**] is 30.9 cm h^{-1}, showing an extraction of 92.9% of caesium in 1 h. Compound H[**1**] displays a slower transport with a permeability of 7.95 cm h^{-1}, *e.g.* an extraction of 52% in 1 h. As a comparison, permeabilities ranging from 1 to 4 cm h^{-1} have been measured for several ‘carriers’ such as calix[4]arene, crowns-6, carbamoylmethylphosphine oxides or disphosphine dioxides under comparable conditions. Better permeabilities were achieved with calixarenes incorporating carbamoylmethylphosphine oxide moieties (4–7 cm h^{-1}). Although these results are very promising, fine modifications on these compounds are still needed to improve their extraction capacity at lower pH.[17]

In fact, a linear behavior is only observed in the first part of the experiment, until $t = 1$ h. This effect may be explained by the fact that counter transport of metal ions by cobaltabis(dicarbollide) anions is driven by the transfer of protons from the stripping phase into the feed phase. The complexation equilibrium is (4) where CoB_2^- corresponds to the cobaltabis(dicarbollide) anion, *i.e.* **1**$^-$ or **2**$^-$.

$$Cs^+(aq) + H^+CoB_2^-(org) \rightleftharpoons Cs^+CoB_2^-(org) + H^+(aq) \qquad (4)$$

Thus, in order to get maximum efficiency, the pH of the feed phase must be sufficiently high completely to deprotonate the carrier in the interface. Similarly, the pH of the receiving phase must be low enough to force a complete reversal of the complexation–deprotonation balance, to encourage maximum stripping. As indicated in Table 2, the distribution coefficients D_{Cs} decrease considerably with the pH. This means that, for a certain amount of transported caesium from the feed to the stripping phase, the same quantity of protons has been counter-transported from the stripping to the feed phase, and consequently the pH of the feed phase has decreased. This leads to a lower extraction of caesium after a certain time, *i.e.* the transport becomes slower. This is why the Danesi model is not valid after a certain time. In fact, this model is based on the hypothesis that reextraction takes place immediately and completely, which is not true in this case if the pH decreases, inducing an asymptotic line.

In conclusion, cobaltabis(dicarbollide) derivatives are monoanionic compounds suitable for the extraction of radionuclides. This, along with their low charge density and resistance to radiation, makes them suitable for the removal of cationic radionuclides from nuclear wastes. The introduction of aromatic rings to the cluster permits one to modulate the extraction properties of the compound. The presence of two phenyl groups per cluster led to the best performance at pH 3 for the extraction of caesium. Transport experiments confirmed the interest in implementing cobaltabis(dicarbollide) derivatives on SLM to separate caesium from nuclear wastes.

Experimental

Commercial $B_{10}H_{14}$ was purified by sublimation at 0.01 mmHg (*ca.* 1.33 Pa). 1-Phenyl- and 1,2-diphenyl-1,2-dicarba-*closo*-dodecaborane were synthesized according to the literature.[10] The compound $[3,3'\text{-}Co(1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_9H_{10})_2]^-$ **1**$^-$ was prepared according to a previous paper.[12] 1,2-Dimethoxyethane and diethylene glycol dimethyl ether were dried with sodium–benzophenone. All organic and inorganic salts were analytical reagent grade and used as received. The solvents were reagent grade. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed in our analytical laboratory on a Perkin-Elmer 240B microanalyzer. Infrared spectra of KBr pellets were obtained on a Nicolet 710-FT spectrophotometer, NMR spectra on a Bruker ARX-300 spectrometer equipped with the appropriate decoupling accessories.

Preparations

$[N\{(CH_2)_3CH_3\}_4][3,3'\text{-}Co\{1,7\text{-}(C_6H_5)_2\text{-}1,7\text{-}C_2B_9H_9\}]$, $[N\{(CH_2)_3CH_3\}_4]$[2]. In a two-necked flask, $[N(CH_3)_4][7,9\text{-}(C_6H_5)_2\text{-}7,9\text{-}C_2B_9H_{10}]$[13] (0.360 g, 1.00 mmol) was dissolved in anhydrous 1,2-dimethoxyethane (25 cm^3) and anhydrous diethylene glycol dimethyl ether (5 cm^3) under dinitrogen and stirring. Then, potassium *tert*-butoxide (1.36 g, 10.5 mmol) and anhydrous $CoCl_2$ (1.48 g, 10.5 mmol) were added. The reaction mixture was refluxed for 72 h. After cooling, the solvent was evaporated in vacuum and the residue extracted with 1 M HCl(aq)–diethyl ether. After drying the ether layer with $MgSO_4$, the solvent was evaporated. The residue was dissolved in a mixture of ethanol (2 cm^3) and water (10 cm^3) and treated with an excess of $[N\{(CH_2)_3CH_3\}_4]Br$ in water. The dark red precipitate was filtered off, washed with water and *n*-hexane and dried in vacuum to afford $[N\{(CH_2)_3CH_3\}_4]$[**2**] (yield 0.183 g, 55%). FTIR (KBr): ν/cm^{-1} = 3079, 3051, 3030, 3016 [ν(C–H)$_{aryl}$], 2966, 2938, 2875 [ν(C–H)$_{alkyl}$], 2566 [ν(B–H)], 1483, 1448, 1384 [δ(C–H)$_{alkyl}$]. ^1H NMR (300 MHz, CD_3COCD_3, 25 °C, $SiMe_4$): δ 7.60–6.75 (m, 20 H, CH$_{aryl}$), 3.50–3.44 (m, 8 H, NCH$_2$),

Table 3 Crystallographic data for Na[**1**]$\cdot$0.4$C_6H_5CH_3$

	Na[**1**]$\cdot$0.4$C_6H_5CH_3$
Chemical formula	$C_{16}H_{30}B_{18}CoNa\cdot 0.4C_7H_8$
Crystal system	Monoclinic
M	535.75
Space group	*C*2/*c* (No. 15)
a/Å	39.479(3)
b/Å	21.677(5)
c/Å	24.156(3)
β/°	125.600(6)
U/Å^3	16 809(5)
Z	20
T/°C	21
λ/Å	0.710 69
D_c/g cm^{-3}	1.059
μ/cm^{-1}	5.33
$R1^a$ [$I > 2\sigma(I)$]	0.0927
$wR2^b$ [$I > 2\sigma(I)$]	0.2566

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o$. $^b wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{\frac{1}{2}}$

1.89–1.79 (m, 8 H, NCH_2CH_2), 1.51–1.39 [m, 8 H, $N(CH_2)_2CH_2$], 0.99 [t, ^3J(HH) = 7.5 Hz, 12 H, CH_3) and 3.8–1.3 (br, 18 H, BH). ^{11}B NMR (96 MHz, CD_3COCD_3, 25 °C, $BF_3\cdot Et_2O$): δ 0.8 [d, ^1J(BH) = 130 Hz, 4B], −3.8 (2B), −5.1 (2B), −6.1 (2B), −8.5 (2B), −10.2 (2B), −12.7 (2B) and −13.6 (2B). $^{13}C\{^1H\}$-NMR (75 MHz, CD_3COCD_3, 25 °C, $SiMe_4$): δ 148.2, 144.3, 129.5, 129.4, 128.7, 127.9, 127.6, 126.4, 125.7, 125.2, 124.7 (C_{aryl}), 80.4, 76.1, 72.5, 61.6 ($C_{cluster}$), 58.5 (NCH_2), 23.5 (NCH_2CH_2), 19.5 [$N(CH_2)_2CH_2$] and 12.9 (CH_3) (Found: C, 60.66; H, 8.55; N, 1.69. Calc. for $C_{32}H_{47}B_{18}CoN\cdot 2C_6H_{14}$: C, 60.63; H, 8.67; N, 1.61%).

[3,3′-Co(8-C_6H_5ONO-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]. In a two-necked flask, Cs[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] (0.250 g, 0.548 mmol) and $AlCl_3$ (0.190 g, 1.425 mmol) were dissolved in anhydrous nitrobenzene (25 cm^3) under dinitrogen and stirring. The mixture was heated to 80 °C for 4 h. On cooling, the precipitate was filtered off and washed with nitrobenzene. The solid was discarded as the IR spectrum showed no B–H band between 2500 and 2600 cm^{-1}. Nitrobenzene was evaporated in vacuum and the residue washed with 5% HCl. After column chromatography (*n*-hexane–CH_2Cl_2 1:1), [3,3′-Co(8-C_6H_5-ONO-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] was isolated (yield 0.020 g, 9%). ^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C, $SiMe_4$): δ 8.71 [d, ^3J(HH) = 9, 2 H, CH_{aryl}], 8.29 [t, ^3J(HH) = 9, 1 H, CH_{aryl}], 7.98 [t, ^3J(HH) = 9 Hz, 2 H, CH_{aryl}], 4.42 (br, 1 H, $C_{cluster}H$), 4.10 (br, 1 H, $C_{cluster}H$) and 3.5–1.5 (br, 17 H, BH). ^{11}B NMR (96 MHz, CD_3COCD_3, 25 °C, $BF_3\cdot Et_2O$): δ 19.9 [s, 1B, B(8)], 7.3 [d, ^1J(BH) = 138, 1B], 4.8 [d, ^1J(BH) = 78, 1B], −2.5 [d, ^1J(BH) = 173, 1B], −4.3 [d, ^1J(BH) = 147, 4B], −7.3 [d, ^1J(BH) = 146, 4B], −15.1 [d, ^1J(BH) = 161, 2B], −17.7 [d, ^1J(BH) = 167, 2B], −20.8 [d, ^1J(BH) = 210, 1B] and −24.2 [d, ^1J(BH) = 171 Hz, 1B]. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3COCD_3, 25 °C, $SiMe_4$): δ 140.6, 130.3, 125.5, 124.1 (C_{aryl}), 66.2, 53.0 and 47.8 ($C_{cluster}$).

Chlorination derivatives of Cs[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] were isolated after elution with more polar solvent mixtures (thf, CH_3CN). The IR and NMR spectra of these products compare well with those previously reported.[18]

Crystallography

Single crystal data for Na[3,3′-Co(1-C_6H_5-1,2-$C_2B_9H_{10}$)$_2$]$\cdot$0.4$C_6H_5CH_3$ were obtained at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo-Kα radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centred reflections. Data obtained were corrected for Lorentz-polarization effects, and for dispersion. Corrections for empirical absorption (ψ scan) were also applied. As the reflection power at high reflection angles was very poor, limited data were collected. A total of 11 127 reflections giving 10 940 unique reflections (R_{int} = 0.0426) were collected by ω–2θ scan mode (2θ_{max} = 45°).

The structure was solved by direct methods by using the SHELXS 86 program[19] and least-squares refinements and all subsequent calculations were performed using the SHELXL 97 program system.[20] The asymmetric unit of the structure consists of one half of the [3,3′-Co(1-C_6H_5-1,2-$C_2B_9H_{10}$)$_2$]$^-$ complex unit (labelled **A**) having two-fold symmetry, two other units (labelled **B** and **C**) at common positions, one toluene solvent molecule and 2.5 disordered sodium cations. Refinement of all atoms, except the sodium cations, revealed seven residual electron maxima of 1.0–1.8 e Å^{-3} in large cavities between the complex anions and we assumed that the maxima represent partially occupied sodium cations. Site occupation parameters of the sodium positions, resulting from refinement of the sodium cations with equivalent isotropic displacement parameters, were fixed in the final refinement. Non-hydrogen atoms of the toluene solvent were refined with isotropic, the remaining non-hydrogen atoms with anisotropic, displacement parameters. Hydrogen atoms were included in the calculations at the fixed distances from their host atoms and treated as riding atoms using the SHELXL 97 default parameters.

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Determination of distribution coefficients

The distribution coefficients *D*, were determined at room temperature (25 °C) by mixing the same volume of each phase at 100 revolutions min^{-1} in a polypropylene test-tube, and then measuring the radioactivity in each phase by γ spectrometry. To perform the extraction experiments, the extractant was washed previously with an aqueous 1 M HNO_3 solution, leading to the formation of the protonated species (H[**1**] and H[**2**]). Then, 5 cm^3 of the organic phase, *i.e.*, a 0.01 M solution of the studied extractant in *o*-nitrophenyl hexyl ether, and aqueous feed solution (5 cm^3; HNO_3 containing traces of ^{137}Cs, ^{90}Sr and ^{152}Eu) were mixed. To determine D_M in the stripping experiments, 4 cm^3 of the last organic phase were mixed with aqueous stripping solution (4 cm^3) containing a lanthanide complexing agent [oxalic acid (0.5 M) or sodium citrate (0.25 M)]. Duplicate runs of each experiment were routinely performed.

Supported liquid membranes

A thin flat sheet SLM device described by Stolwijk *et al.*[21] was used. The volume of both aqueous solutions was 50 cm^3. The membrane was a ®Celgard 2500 (of 25 μm thickness and 45% volume porosity) polypropylene microporous support soaked with a 0.01 M solution of the test compound in *o*-nitrophenyl hexyl ether. The surface area of the membrane was about 15–16 cm^2, depending on the device; the mass of the organic phase was about 25 μg. This mass was determined by measuring the activity of the membrane after soaking it in an organic phase containing nuclides.

Permeability determination

The transport of ^{137}Cs from synthetic aqueous solutions of HNO_3 (pH 3) was monitored by measurement of the decrease in radioactivity in the feed solution and of the increase in the strip solution [sodium citrate (0.25 M)] by γ spectrometry analysis. This allowed determination of the constant permeabilities *P*/cm h^{-1} of caesium permeation through the SLM for 24 h, by plotting the logarithm of the ratio $C:C^0$ *vs.* time.

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