

# C-substituted bis(dicarbollide) metal compounds as sensors and extractants of radionuclides from nuclear wastes

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## Abstract

[3,3'-M(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> (M = Co<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>3+</sup>) compounds have been implemented in PVC membranes to study their performance as Cs<sup>+</sup> sensors in ion selective electrodes. They show a near-Nernstian response close to 51 mV (decade)<sup>-1</sup>. The three display a similar behaviour, and the [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> anion was chosen as the parent chemical on which C-substitution, both alkyl or aromatic, were done. The species [3,3'-Co(1-CH<sub>3</sub>-2-(CH<sub>2</sub>)<sub>n</sub>OR-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>-</sup> ([4]<sup>-</sup>; n = 3, R = -CH<sub>2</sub>CH<sub>3</sub>; [5]<sup>-</sup>; n = 3, R = -(CH<sub>2</sub>)<sub>2</sub>OCH<sub>3</sub>; [6]<sup>-</sup>; n = 3, R = -(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>; [7]<sup>-</sup>; n = 6, R = -(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), and [3,3'-Co(1-C<sub>6</sub>H<sub>5</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> ([8]<sup>-</sup>) and [3,3'-Co(1,7-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-1,7-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>-</sup> ([9]<sup>-</sup>) were tested for <sup>137</sup>Cs, <sup>90</sup>Sr and <sup>152</sup>Eu in extraction. Permeability tests on supported liquid membranes with H[6], H[7] and H[9] have shown that these compounds present the highest values reported so far for this sort of radionuclide transport experiments. The structure of the carrier N((CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>)<sub>4</sub>[9] is reported. Crystals were monoclinic, space group P2<sub>1</sub>/c (no.14), a = 18.255(4) Å, b = 15.871(9) Å, c = 18.684(14) Å, β = 105.64(3)°, V = 5213(5) Å<sup>3</sup> and Z = 4. The carbons apart structure may be one of the reasons of the excellent performance of this compound in Cs<sup>+</sup> transport in SLM with nitrophenylhexyl ether as a solvent. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Nuclear wastes; Metal sensors; Metal extractants; Dicarbollides; Boron cages

## 1. Introduction

Nuclear waste reprocessing operations produce both high level and medium level activity liquid wastes (HLW/MLW). The major nuclides in these radioactive wastes are those with long half-lives, mainly β/γ emitters or α emitters such as transuranium elements. This is why great efforts have been devoted throughout the world to propose harmless storage of these wastes. The burial of vitrified reprocessed HLWs (containing fission products and α emitters) has been considered as the safest method for their permanent disposal, whereas MLWs are treated by evaporation in order to concentrate their radioactivity into the smallest possible volume. This treatment nevertheless leads to large volumes

of concentrates composed of active and inactive salts (mainly: NaNO<sub>3</sub>, 4 mol l<sup>-1</sup> and HNO<sub>3</sub>, 1 mol l<sup>-1</sup> as the matrix). The greater part of these concentrates has to be disposed off in geological formations after embedding due to their activity in long-lived radionuclides (actinides, strontium, cesium, etc.). Therefore it would be desirable to remove these long-lived radionuclides from the contaminated liquid wastes before embedding. These would allow a large part of these wastes to be directed to a subsurface repository, and a very small part containing most of the long-lived radionuclides to be disposed off, after conditioning, in geological formation [1].

The field of metallocarborane chemistry was initiated by Hawthorne in 1965 [2]. Since that time, metallocarboranes from all areas of the periodic table have been prepared using the dicarbollide ligand C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> [2,3]. These derivatives have become of increasing interest

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with regard to their solubility [4], isolation, separation and characterisation of organic bases, radiometal carriers [5], electron acceptor molecules [6], among other areas. One of these organometallic complexes,  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  ( $[1]^-$ ), has attracted the most attention because of its robustness, its stability in the presence of strong acid ( $\text{HNO}_3$ ), at relatively high temperatures and under a very high radiation [7]. This stability allows it to be considered for nuclear waste remediation. Its hexachloro protected analogue,  $[1\text{-Cl}_6]^-$ , is remarkable as an extractant. The large size to charge ratio and the hydrophobic nature of  $[1]^-$  and  $[1\text{-Cl}_6]^-$  allows extraction of cesium and strontium ions from an aqueous phase to an organic phase, leaving other alkaline and higher-valent metals behind [4,7,8]. The ions  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  are used for thermoelectric generators and sterilization of medical equipment, among other areas, making the possibility of recycling them very attractive [9].

On the other hand, there are presently a large number of ion-selective electrodes (ISEs) available for the selection of  $\text{Na}^+$  and  $\text{K}^+$  [10], only a few have proved to be selective towards  $\text{Cs}^+$  [11]. Some attempts have been made to produce  $\text{Cs}^+$ -sensors in the past, either by using liquid membrane electrodes [12], or plasticized PVC-membrane electrodes [13], as used in this paper. However, those liquid membranes that produce near-Nernstian responses (near  $57 \text{ mV} (\text{decade})^{-1}$ ) [12c] rely on the presence of nitrobenzene in the membrane, and when attempts were made to produce  $\text{Cs}^+$ -sensors without it, the responses suffered, reducing the Nernstian response to  $24.5 \text{ mV} (\text{decade})^{-1}$  [12d] for the liquid membrane electrode, and to  $40\text{--}43 \text{ mV} (\text{decade})^{-1}$  [13a] for the PVC-membrane electrodes.

The  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$   $[1]^-$  anion, has been used as a highly selective  $^{137}\text{Cs}$  sequestering agent in extraction processes, in the presence of  $\text{Na}^+$ , with nitrobenzene [4] as the receiving phase. However, nitrobenzene is an ecologically unacceptable solvent, so that other receiving phases are required for environmental applications. In order to determine the influence of nitrobenzene in the selectivity process, with the aim of producing Cs selective ISEs, which can be related to the transport membranes, a study with bis(dicarbollide) complexes of  $\text{Co}^{3+}$  ( $\text{Cs}[1]$ ),  $\text{Fe}^{3+}$  ( $\text{Cs}[2]$ ) and  $\text{Ni}^{3+}$  ( $\text{Cs}[3]$ ) as sensors for cesium ISE's was performed. The study was also intended to discern which of the three anions was more selective towards  $\text{Cs}^+$ , in order to choose one for the subsequent studies. The results obtained, however, indicated that the three anions were comparable in their behaviour in ISEs. Since the  $\text{Co}^{3+}$  complex provides easier synthetic routes, higher yield and higher stability, it was chosen for the studies on the extraction of radionuclides. Organic compounds incorporating oxygen in the molecule have been also tested for this type of processes [11b,14]. Accordingly we

prepared several ether C-substituted cobaltacarboranes [15,16] in order to improve the efficiency shown by  $[1]^-$  and  $[1\text{-Cl}_6]^-$ . To allow the substitution of nitrobenzene by more convenient solvent systems, the synthesis of aromatic C-substituted cobaltacarboranes was proposed also [17].

This paper reports the implementation of  $\text{Cs}[1]$ ,  $\text{Cs}[2]$ , and  $\text{Cs}[3]$  in PVC membranes to be studied as ISE for  $\text{Cs}^+$ . Their selectivity towards other ions is studied and discussed. The crystal structure of  $[\text{N}((\text{CH}_2)_3\text{CH}_3)_4][3,3'\text{-Co}(1,7\text{-(C}_6\text{H}_5)_2\text{-}1,7\text{-C}_2\text{B}_9\text{H}_9)_2]^-$  is described. Finally, a general discussion on the radionuclide extraction performance of the C-substituted cobaltabis(dicarbollide) compounds is provided [18].

## 2. Discussion

### 2.1. Cesium(I) sensors based on bis(dicarbollide) complexes

The ISEs constructed for the study of cesium sensors were of the all solid-state PVC membrane electrode type and were prepared and assembled as described previously [19]. However, variations were made in the composition [20] to optimize the selectivity and sensitivity of the ligand involved.

Each different composition was incorporated into an electrode body and the resulting sensor was calibrated with  $\text{CsCl}$ . The sensor which produced the nearest-to-Nernstian response was taken as having the most suitable membrane composition for the ligand. (This was found to be: dioctylphthalate, (the plasticizer): 61 wt.%; poly(vinyl chloride), (the medium): 30 wt.% and  $[1]^-$ ,  $[2]^-$  or  $[3]^-$ , (the ligand): 9 wt.%). That composition was then used for all calibrations thereafter.

The sensors were tested over a period of 4 weeks for their sensitivity to interfering ions. The selectivity coefficients ( $K_{\text{Cs}^+/\text{M}}^{\text{pot}}$ ) can be seen in Table 1.

Table 1  
Selectivity coefficients,  $K_{\text{Cs}^+/\text{M}}^{\text{pot}}$  of sensors  $[1]^-$ ,  $[2]^-$  and  $[3]^-$

Interference Ion (M)	$[1]^-$	$[2]^-$	$[3]^-$
$\text{Na}^+$	$3.9 \times 10^{-2}$	$1.7 \times 10^{-2}$	
$\text{Co}^{2+}$	$3.5 \times 10^{-4}$	$1.5 \times 10^{-4}$	
$\text{Ca}^{2+}$	$2.3 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.4 \times 10^{-2}$
$\text{Pb}^{2+}$	$3.2 \times 10^{-1}$	$8.8 \times 10^{-3}$	
$\text{K}^+$	$2.3 \times 10^{-1}$	$2.3 \times 10^{-1}$	$2.7 \times 10^{-1}$
$\text{Ni}^{2+}$	$1.8 \times 10^{-4}$	$1.7 \times 10^{-4}$	$3.7 \times 10^{-4}$
$\text{Rb}^+$	$2.4 \times 10^{-1}$	$2.4 \times 10^{-1}$	
$\text{Mg}^{2+}$		$3.7 \times 10^{-4}$	
$\text{Zn}^{2+}$	$2.7 \times 10^{-4}$	$2.6 \times 10^{-4}$	
$\text{Cu}^{2+}$		$6.4 \times 10^{-4}$	

<sup>a</sup> Obtained by the fixed interference method, using background concentrations of  $10^{-1} \text{ M}$  for all interfering ions.

Table 2  
Cesium response characteristics of sensors [1]<sup>-</sup>, [2]<sup>-</sup> and [3]<sup>-</sup>

Sensor	[1] <sup>-</sup>	[2] <sup>-</sup>	[3] <sup>-</sup>
Detection limit	$2.3 \times 10^{-5}$	$1.0 \times 10^{-5}$	$1.2 \times 10^{-5}$
Slope (mV decade <sup>-1</sup> )	52	51	50
Time response (s)	<10	<10	<1
Lifetime (weeks)	>4	>4	<3

The calibration curves of the sensors exhibit near-Nernstian responses for all three complexes, [1]<sup>-</sup>; [2]<sup>-</sup> and [3]<sup>-</sup>, with slopes of 52, 51, 50 mV (decade)<sup>-1</sup>, respectively, within an activity range from 10<sup>-1</sup> to 10<sup>-4</sup> M. They display reasonable selectivity over the interfering ions Na<sup>+</sup>, Co<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup>, and have a lower detection limit in the 10<sup>-5</sup> M range. All three sensors were found to respond to Rb<sup>+</sup> and K<sup>+</sup>, which have proved to be interferences in the selection of cesium. Only sensor [1]<sup>-</sup> was found to respond to Pb<sup>2+</sup>. The sensors were found to respond in the following order [2]<sup>-</sup> > [1]<sup>-</sup> > [3]<sup>-</sup>, with the metals causing the least interference to ligand [2]<sup>-</sup>.

The bis(dicarbollide) complexes have proved to be a useful material in the selection of cesium (I), producing responses comparable to those reported previously [12,13] and without the use of nitrobenzene. However the relatively low  $K_{Cs/M}^{pot}$  observed, clearly proves that nitrobenzene plays a crucial role in the selectivity process, a factor that is also found when extraction is performed. The general characteristics of the sensors can be seen in Table 2. As can be seen from Tables 1 and 2, the general performance of [1]<sup>-</sup>, [2]<sup>-</sup> and [3]<sup>-</sup> was very much comparable. As this was not so from the synthetic point of view and their stability, C-substituted derivatives of [1]<sup>-</sup> were synthesized to perform the extraction tests in the aim of avoiding as much as possible the use of nitrobenzene in the essays.

## 2.2. Extractants derived from [1]<sup>-</sup>

The results obtained above led us to synthesize a new family of [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> derivatives incorporating ether groups, [3,3'-Co(1-CH<sub>3</sub>-2-(CH<sub>2</sub>)<sub>n</sub>OR-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>-</sup>, which are presented graphically in Fig. 1 ([4]<sup>-</sup>: n = 3, R = -CH<sub>2</sub>CH<sub>3</sub>; [5]<sup>-</sup>: n = 3, R =

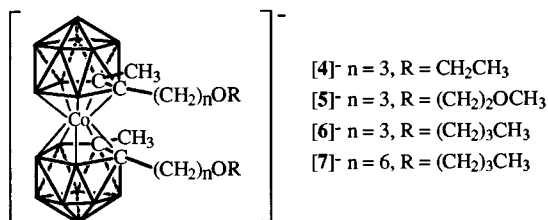


Fig. 1. Polyether C-substituted compounds.

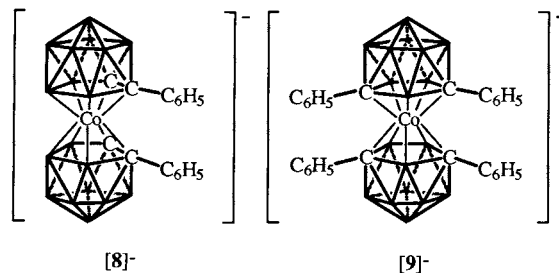


Fig. 2. Aromatic C-substituted compounds.

-(CH<sub>2</sub>)<sub>2</sub>OCH<sub>3</sub>; [6]<sup>-</sup>: n = 3, R = -(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>; [7]<sup>-</sup>: n = 6, R = -(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) [15,16].

The very high efficiency in the extraction of <sup>137</sup>Cs found for [1]<sup>-</sup>, when nitrobenzene was used as solvent [4,8] led us to introduce aromatic groups in the exocuster chain of [1]<sup>-</sup>. Thus, the molecules [3,3'-Co(1-C<sub>6</sub>H<sub>5</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> ([8]<sup>-</sup>) and [3,3'-Co(1,7-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-1,7-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>-</sup> ([9]<sup>-</sup>) were synthesized (Fig. 2) [17].

Complex anion [9]<sup>-</sup> was obtained from [7,9-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> with K<sup>t</sup>BuO and CoCl<sub>2</sub>. Crystals of [N((CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>)<sub>4</sub>][9], grown from dichloromethane: n-hexane (1:1), enabled elucidation of the molecular structure of the compound. A drawing of the complex anion is illustrated in Fig. 3, crystal data are given in Table 3, and selected interatomic distances and angles are listed in Table 4. The conformation of the coordinated C<sub>2</sub>B<sub>3</sub> faces is staggered. The cluster carbons C7 and C7' as well as the phenyl groups connected to C7 and C7' are close to each other. This orientation of the phenyl groups causes steric crowding between these phenyl rings. To reduce the steric crowding, the rings are bent away from each other thus also increasing the C7...C7' distance and slightly twisting the C<sub>2</sub>B<sub>3</sub> faces. Accordingly, in the co-ordinated C<sub>2</sub>B<sub>3</sub> faces the atoms

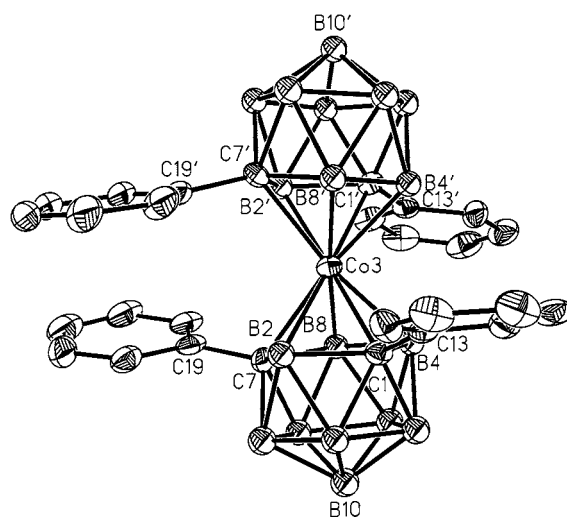


Fig. 3. A view of complex anion [9]<sup>-</sup> showing 20% displacement ellipsoids.

Table 3  
Crystallographic data for [N((CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>)<sub>4</sub>][9]

Compound	[N((CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ) <sub>4</sub> ][9]
Chemical formula	C <sub>44</sub> H <sub>74</sub> B <sub>18</sub> CoN
<i>F<sub>w</sub></i>	870.55
<i>a</i> (Å)	18.255(4)
<i>b</i> (Å)	15.871(9)
<i>c</i> (Å)	18.684(14)
$\beta$ (°)	105.64(3)
<i>V</i> (Å <sup>3</sup> )	5213(5)
<i>Z</i>	4
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no.14)
<i>T</i> (°C)	21
$\lambda$ (Å)	0.71069
$\rho$ (g cm <sup>-3</sup> )	1.109
$\mu$ (cm <sup>-1</sup> )	3.61
<i>R</i> 1 <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0656
<i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1256

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR2 = \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2}^{1/2}$$

deviate from the relevant least-squares planes even by 0.070(5) Å. Despite the movement of the close phenyl groups, the shortest contact distance between carbon atoms of the rings is 3.113(12) Å, which is ca. 0.6 Å shorter than the sum of corresponding van der Waals radii [21]. Tetrabutylammonium cations in the structure provide the charge balance.

### 2.3. Extraction experiments and transport through SLM

The bis(dicarbollide) derivatives [4]<sup>-</sup>, [5]<sup>-</sup>, [6]<sup>-</sup>, [7]<sup>-</sup>, [8]<sup>-</sup> and [9]<sup>-</sup> have been tested in the liquid–liquid extraction of <sup>137</sup>Cs, <sup>90</sup>Sr and <sup>152</sup>Eu from the aqueous HNO<sub>3</sub> phase to the organic nitrophenyl hexyl ether. Table 5 presents the distribution coefficient (*D*) of the different radionuclides for each complex [15–17].

Table 4  
Selected interatomic distances (Å) and angles (°) for [N((CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>)<sub>4</sub>][9]

Co3–C1	2.159(8)
Co3–B2	2.109(9)
Co3–B4	2.111(9)
Co3–B8	2.130(9)
Co3–C7	2.216(8)
Co3–C1'	2.184(7)
Co3–B2'	2.105(8)
Co3–B4'	2.113(9)
Co3–C7'	2.205(8)
Co3–B8'	2.140(9)
C1–C13	1.521(11)
C7–C19	1.516(11)
C1'–C13'	1.502(10)
C7'–C19'	1.524(10)
B10–Co3–B10'	174.7(2)

Table 5  
Distribution coefficients (*D*) of the different radionuclides in aqueous HNO<sub>3</sub>–nitrophenyl hexyl ether

Compound	<i>D</i> <sub>Cs</sub>		<i>D</i> <sub>Sr</sub>		<i>D</i> <sub>Eu</sub>	
	pH 3	pH 1	pH 3	pH 1	pH 3	pH 1
H[4]	>100	3	13	<0.01	90	0.01
H[5]	>100	–	2	–	28	–
H[6]	>100	>100	55	0.3	40	4.8
H[7]	>100	10	8	0.08	>100	0.15
H[8]	>100	4	8	<10 <sup>-3</sup>	55	0.02
H[9]	>100	27	22	0.08	>100	<10 <sup>-3</sup>

For the extraction of <sup>137</sup>Cs, the polyether substituted compounds show a very high extraction efficiency at pH 3 (*D* > 100) regardless of the nature of the exocuster chain. This efficiency is expected to be lower if the acidity of the medium is increased. This behaviour is displayed by [4]<sup>-</sup>, whose *D* value decreases from >100 to 3, just by varying the pH value from 3 to 1. However, [6]<sup>-</sup>, which is very similar to [4]<sup>-</sup>, but with the longest alkyl chain next to the oxygen atom, maintains an excellent efficiency for the extraction of <sup>137</sup>Cs even at pH 1. Anion [6]<sup>-</sup> shows again the best performance for the extraction of <sup>90</sup>Sr but the *D* value decreases strongly with decreasing pH. For the extraction of <sup>152</sup>Eu, it seems that the larger the exocuster chain the better the performance of the extracting agent. Therefore, [7]<sup>-</sup> shows the best performance in the extraction of <sup>152</sup>Eu. The lower efficiency in the extraction of <sup>90</sup>Sr and <sup>152</sup>Eu shown by compound [6]<sup>-</sup> and the excellent results obtained in the extraction of <sup>137</sup>Cs, should permit a selective extraction of Cs<sup>+</sup> from a mixture containing all the radionuclides in solution. This result led us to perform some transport experiments by using supported liquid membranes (SLM) with NPHE (nitrophenylhexyl ether) as the membrane solvent. Preliminary results carried out with compounds H[4], H[5], H[6] and H[7] showed that the best transport performance was for compound H[6]. Also the aromatic compound H[9] showed a good efficiency in the extraction of Cs<sup>+</sup> even at pH 1 [17]. These two, H[6] and H[9], were used to study the Cs<sup>+</sup> transport by SLM. Compound [7]<sup>-</sup>, displaying the best efficiency in the extraction of <sup>152</sup>Eu, was used for its transport studies.

At pH 3, transport of <sup>137</sup>Cs was very efficient with compound [6]<sup>-</sup>, and a permeability of 30.6 cm h<sup>-1</sup> was obtained. An extraction of 93% of Cs<sup>+</sup> in 1 h was achieved. Under the same conditions, the aromatic substituted compound H[9] displays very interesting results. Its permeability is 30.9 cm h<sup>-1</sup>, showing an extraction of 93.2% of Cs<sup>+</sup> in 1 h.

In the case of the transport of europium, transport with compound H[7] is very rapid at pH 3, showing a permeability of  $8.9 \text{ cm h}^{-1}$ , i.e. an extraction of 31.2% after 1 h or 91.3 after 3.5 h.

For comparison, permeabilities ranging from 1 to  $4 \text{ cm h}^{-1}$  have been measured for several 'carriers' such as calix[4]arenes crown 6, CMPO (carbamoyl-methylphosphine oxides) or diphosphine dioxides under comparable conditions. Improved permeabilities were achieved with calixarenes incorporating CMPO moieties ( $4\text{--}7 \text{ cm h}^{-1}$ ) [22]. Thus, generally speaking, the cobalta(dicarbollide) carriers are considerably faster transport agents than others well-recognized as doing this job, such as those indicated above.

### 3. Conclusions

Bis(dicarbollide) complexes of  $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{3+}$  have proved to be useful materials in the detection of  $\text{Cs}^+$  avoiding the presence of nitrobenzene although its absence may explain the still low selectivity coefficients with regard to interfering metal ions. The three complexes display a comparable behaviour although  $\text{Fe}^{3+}$  seems to offer the best performance. Notwithstanding so, the  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  derivatives were chosen for extraction purposes because of the small differences among them and because it was the more stable and produced the best yields. It was expected that the modification of the nature of the compounds through C-substitution of the cluster should allow modulation of the extracting properties of the compound. It has been found that the introduction of a two-oxygen chelating chain does not represent an enhancement of the extractive properties. Monooxygen chains provide a better performance, so modification of the length of the monooxygen alkyl chain led to have the best performance at pH 3 for the extraction of  $^{90}\text{Sr}$  with H[6] and for the extraction of  $^{152}\text{Eu}$  with H[7]. At pH 1, compound H[6] displays the best performance for  $^{137}\text{Cs}$ .

The transport experiments confirmed the interest of implementing cobaltabis(dicarbollide) derivatives such as H[6] and H[9] on SLM to separate  $^{137}\text{Cs}$  from nuclear wastes and have proven to have the larger permeabilities found up to now as compared to other well accepted  $\text{Cs}^+$  carriers.

Many questions remain unanswered such as the coordinating mode of these ligands towards the radionuclides that require further work, the position of the oxygen in the organic chain, or why the membrane transport is accelerated when polyethyleneglycols are incorporated in it while more than one oxygen in the chain lowers the extraction capacity. The structure of the phenyl substituted compound  $[\text{N}((\text{CH}_2)_3\text{CH}_3)_4][9]$  has been elucidated in this work. It is one of the few examples of carbons apart cobaltabis(dicarbollides)

studied in extraction processes and has shown to have the best performance for the extraction of  $\text{Cs}^+$  at pH 3.

## 4. Experimental

### 4.1. Sensors for ISEs

ISEs were prepared according to the procedure described in the literature [23].

An Orion double-junction reference electrode was used for all calibrations. It consists of an inner filling solution, saturated with  $\text{AgCl}$ , and an outer filling solution, 10%  $\text{KNO}_3$ . The calibrations were monitored by using a potentiometer (Sirtek CDP-90) linked to a computer (IBM), which was capable of monitoring up to seven sensors simultaneously. Chemicals of analytical reagent grade were used without further purification to prepare solutions of the principal metal ion,  $\text{Cs}^+$ , and all interfering ions. Deionized water was used at all times. The dicarbollide complexes were synthesized as described previously by Hawthorne et al. [24].

### 4.2. X-ray structure determination of $[\text{NBu}_4][3,3'\text{-Co}(1,7\text{-}(\text{C}_6\text{H}_5)_2\text{-}1,7\text{-C}_2\text{B}_9\text{H}_9)_2]$ ( $[\text{NBu}_4][9]$ )

Several attempts to obtain single crystals of better quality were made but without success. Single-crystal data collection was performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized  $\text{Mo-K}_\alpha$  radiation. The unit cell parameters were determined by least-squares refinement of 20 carefully centred reflections. Data obtained were corrected for Lorentz and polarization effects, and for dispersion. Corrections for empirical absorption ( $\psi$  scan) were also applied. As reflection power at high reflection angles was very poor, limited data were collected. A total of 5312 reflections giving 5061 unique reflections ( $R_{\text{int}} = 0.0761$ ) were collected by  $\omega/2\theta$  scan mode ( $2\theta_{\text{max}} = 45^\circ$ ).

The structure was solved by direct methods by using the SHELXS86 program [25] and least-squares refinements and all subsequent calculations were performed using the SHELX-97 program system [26].

Boron atoms were refined with isotropic but rest of the 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 SHELX97 default parameters.

## 5. Supplementary material

Tables including crystal data and structure refinement, interatomic distances and angles, positional and

thermal parameters, anisotropic displacements parameters for non-hydrogen atoms and least-squares planes for  $[N((CH_2)_3CH_3)_4][9]$  (18 pages) have been deposited with the Cambridge Crystallographic Data Centre (CCDC-116928). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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