Cobaltabis(dicarbollide) derivatives as extractants for europium from nuclear wastes

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Carbon substituted derivatives of $[3,3'\text{-Co}(1\text{-Me-}2\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ incorporating lipophilic chains [R = $(CH_2)_3O(CH_2)_2OMe$ 1, $(CH_2)_3OCH_2CHMe_2$ 2, $(CH_2)_6O(CH_2)_3Me$ 3, $(CH_2)_3Me$ 4], are synthesized for the first time and tested for extraction of ^{152}Eu; compound 3 showed the best performance, and it proved to have higher efficiency in transport at low acidity than the well known calixarene derivatives.

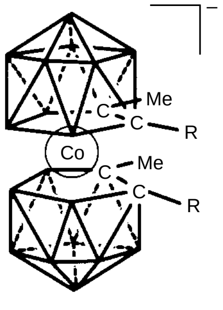
Up to now, a large variety of metallacarboranes have been prepared using the $[7,8\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$ (dicarbollide) ligand.[1,2] Of them, $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ [cobaltabis(dicarbollide)] has attracted the most attention, as it is very robust, withstanding strong acid, moderate base, high temperatures and intense radiation.[3] The stability of this ion makes it interesting in nuclear waste remediation.[3,4]

Cobaltabis(dicarbollide) is capable of removing caesium ions (and with much less efficiency strontium and trivalent lanthanides and actinides) with high selectivity from acidic fission product solution.[3,4]

The problem of removing caesium and strontium from nuclear wastes has been widely treated previously.[3–7] However, the extraction of trivalent actinides has still to be investigated. Since the properties of lanthanides and trivalent actinides are very similar, and handling of lanthanides is easier, the transplutonium elements were simulated by the γ emitter ^{152}Eu. We report here on some C-substituted derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, which in addition to maintaining the extracting properties of ^{137}Cs and ^{90}Sr, have proven to be very efficient in the extraction of ^{152}Eu.

Following a synthetic procedure developed previously in our group,[8] the reaction of $[7\text{-Me-}8\text{-R-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ [R = $(CH_2)_3O(CH_2)_2OMe$, $(CH_2)_3OCH_2CHMe_2$, $(CH_2)_6O(CH_2)_3Me$, or $(CH_2)_3Me$],[9] with $KOBu^t$ and $CoCl_2$ in dimethoxyethane at reflux for 30 h leads, after precipitation with aqueous CsCl, to a set of new products which are purified by TLC [ethyl acetate–acetonitrile (10 : 2)]; R_f (**1**) = 0.38, R_f (**2**) = 0.62, R_f (**3**) = 0.65, R_f (**4**) = 0.65 (Fig. 1).

A mixture of two geometric isomers were produced in this synthesis, which we were not able to separate (racemic mixture and *meso* form), owing to their extremely similar physical properties, however, chemical analyses establish their stoichiometric formulae. The shape of the NMR resonances clearly suggests the existence of more than one isomer.§



1 R = $(CH_2)_3O(CH_2)_2OMe$
2 R = $(CH_2)_3OCH_2CHMe_2$
3 R = $(CH_2)_6O(CH_2)_3Me$
4 R = $(CH_2)_3Me$

Fig. 1 Cobaltabis(dicarbollide) derivatives

Table 1 lists the distribution coefficient of europium, D_{Eu}, defined as the equilibrium ratio of europium between the organic and the aqueous phases. These were determined as previously described,[12] with the feed phase being an aqueous HNO_3 solution containing the radionuclides and the organic receiving phase being nitrophenyl hexyl ether.

At pH 3, compound **4** shows a very low D_{Eu}. The values of D_{Eu} are much better for compounds **2** and **3** which have only one oxygen atom in the alkylic chain. When a second oxygen atom is incorporated, as for compound **1**, D_{Eu} decreases. The results of the tests also show that the larger the exocluster chain the better the performance of the extracting agent. Compound **3** gives the best extraction coefficient. Attempts to synthesize cobaltabis(dicarbollide) derivatives with longer exocluster chains led to products which were difficult to isolate.

The distribution coefficient of the cation strongly decreases as acidity increases in the feeding solution.[4b] Despite this decrease of extracting ability in acidic medium, compounds **2** and **3** display good efficiency for the extraction of ^{152}Eu at pH 3.

The excellent results obtained for compound **3** prompted us to use it in transport tests at pH 3 using a reported method.[12] The transport of ^{152}Eu from aqueous HNO_3 solutions was followed by regular measurement of the decrease of radioactivity in the feed solution by γ spectrometry analysis. This allowed determination of the permeability constants P (cm h^{-1}) of ^{152}Eu permeation through the supported liquid membrane (SLM) for 3.5 h, as is described in the model of mass transfer proposed by Danesi[10]

$$\ln(C/C^0) = -\varepsilon \frac{S}{V} Pt$$

where C^0 and C are the concentrations of the cation in the feed solution at time t = 0 and t (mol dm^{-3}); ε is volumic porosity of the SLM (%); S is membrane surface area (cm^2); V is volume of feed and stripping solutions (cm^3); and t is time (h).

Transport experiments were carried out with addition of a linear polyether, nonylphenylnonaethylene glycol (Slovafol 909) to the organic phase (0.003 M) and using aqueous 1 M methylene diphosphonic acid (MDPA) as complexing agent in the stripping phase, to improve the transport of Eu.

Table 1 Distribution coefficients of ^{152}Eu (D_{Eu}) in aqueous HNO_3–nitrophenyl hexyl ether

	D_{Eu}		
Compound	pH = 3	pH = 2	pH = 1
1	16	9	0.06
2	> 1000[a]	> 1000[a]	0.05
3	> 1000	—	0.15
4	3.5	0.09	0.05

[a] A precipitate appears, which leads to a lack of precision in the determination of the distribution coefficient *D*.

It is found that transport is very rapid at pH 3. Under these conditions, compound **3** shows a permeability P of 8.9 cm h^{-1}, *i.e.* an extraction of 31.2% after 1 h or 91.3% after 3.5 h. Calixarene derivatives, which are known as excellent extractants for this type of radionuclides, show a value of 7.0 cm h^{-1} for ^{239}Pu (feeding phase: aqueous 1 M HNO_3),[11] *i.e.* lower than the value obtained with compound **3**. Furthermore, with other carriers such as diphosphine dioxides under similar conditions, transport is much slower: a permeability of 1.4 cm h^{-1} for ^{237}Np and 3.4 cm h^{-1} for ^{239}Pu were reported (feeding phase: aqueous 1 M HNO_3).[12]

This report shows that the efficient ^{137}Cs extractants, $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$, can be adequately tuned by appropriate cluster C-substitution to enhance ^{152}Eu and hopefully transplutonides. By this monoxygen C-substitution, the ^{152}Eu affinity of the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ derivatives has been extraordinarily enhanced with respect to the non-substituted parent compound, and its affinity towards ^{137}Cs and ^{90}Sr has not been decreased. For instance, **3** displays $D_{Cs} > 1000$ and $D_{Sr} = 8$ at pH 3, with $P = 15.8$ and 22.3 cm h^{-1}, respectively. Owing to the existence of more specific ^{137}Cs extracting agents such as calixarene or $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$, it should be possible to separate the elements. However, many questions arise in terms of the coordinating mode of these ligands towards ^{152}Eu that require further work, such as the position of the oxygen in the organic chain, or why the membrane transport is accelerated when polyethyleneglycols are incorporated in it.

This work was supported by EU project CIPA-CT93-0133. J. B. also thanks the Generalitat de Catalunya for a Predoctoral Grant (FIAP/96-98.469).

Footnotes and References

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§ Compound **1**: ^{11}B NMR: δ {−13.97 [d, ^1J(BH) 192.6 Hz], −10.01 (m), −8.58 [d, ^1J(BH) 160.5 Hz], −4.78 [d, ^1J(BH) 128.4 Hz], −3.54 [d, ^1J(BH) 128.4 Hz], −1.22 [d, ^1J(BH) 128.4 Hz], 16B}, 7.31 [d, ^1J(BH) 96.3 Hz, 2B]. ^{11}B NMR data for the other compounds are analogous to that of **1**.

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Received in Basel, Switzerland, 6th August 1997; Revised Manuscript received 22nd October 1997; 7/07835H