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Synthesis of $[B_{12}H_{12}]^{2-}$ based extractants and their application for the treatment of nuclear wastes

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We have the pleasure to dedicate with affection this article to Pr. Henri MONGEOT on the occasion of his retirement, in recognition of his outstanding contributions to boron chemistry

Abstract

Several *closo*-hydroborates bearing phosphite oxide, phosphine oxide or CMPO (carbamoylmethylphosphine oxide) groups, $Cs[(Ph_2P(O))_2N(H)B_{12}H_{11}]$ (**1**), $K[Ph_2P(O)CH_2C(O)N(H)_2B_{12}H_{11}]$ (**2**), $Na[Bz_2N(H)B_{12}H_{10}OCH_2CH_2OCH_2CH_2P(O)(OBu)_2]$ (**5**), $Na[Bz_2N(H)B_{12}H_{10}O(CH_2)_4N(R)C(O)CH_2P(O)(Ph)_2]$ (**9**, $R = Pr^i$; **10**, R = Octyl), $Na[Bz_2N(H)B_{12}H_{10}OCH_2CH_2OCH_2CH_2N(Bu^i)C(O)CH_2P(O)(Ph)_2]^-$ (**11**) were synthesised employing novel neutral bipolar intermediates $[Bz_2N(H)B_{12}H_{10}O(CH_2)_4]$ (**3**) and $[Bz_2N(H)B_{12}H_{10}O(CH_2CH_2)_2O]$ (**4**) as useful synthons. All new compounds were characterised by NMR spectroscopy and mass spectrometry techniques. Their abilities to extract selectively the radionuclides ^{241}Am and ^{152}Eu from nuclear waste solutions were investigated using a liquid–liquid extraction technique. Promising results were obtained with compound **10**, which exhibits enhanced hydrophobicity and solubility in organic extraction solvent.

Keywords: Hydrododecaborate; Oxonium; CMPO; Liquid–liquid extraction; Nuclear waste

1. Introduction

There has been considerable continuous interest in the selective separation of long lived radionuclides from radioactive waste. Presently high activity (HA) liquid waste arising from Purex process which contain β/γ emitters such as: Tc, Se, Cs, etc. or α emitters such as transuranium elements: Np, Am, Cm, are vitrified before long term storage or disposal. It should be of interest to selectively remove long lived from HA waste in order to destroy them by advanced transmutation techniques. Transmutation operations require pure targets; in particular trivalent actinides such as americium or curium have to be separated from other fission products and especially from lanthanides.

One technique which could be adopted for this treatment are hydrometallurgical methods based on the liquid–liquid extraction using molecules capable to selectively bind the target nuclides and transport them to organic phase. In this field, we focused our attention on the selective complexation of trivalent cations from the lanthanide and actinide series, especially ^{152}Eu and ^{241}Am.

Many organic molecules of different constitution have been tested for this application [1–4] (namely crown ethers, functionalised calixarenes, CMPO (carbamoylmethylphosphine oxide), etc.). By comparison to these neutral extractants, hydroborate derivatives present the advantage of forming neutral compounds (ion pairs) with the cationic radionuclides. The resulting ion pairs can be extracted to organic solvents of medium polarity. Even if the cobaltadicarbollide anions (COSAN derivatives) [5] are the most extensively studied compounds, hydrododecaborate derivatives based on $[B_{12}H_{12}]^{2-}$ anion can represent interesting alternative in respect to

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their high stability, lower price and better availability. The parent compound can be functionalised by one or two suitable groups to create resulting monovalent anions containing metal selective groups and hydrophobic enough to transfer the cations into organic phase. The structure of thus obtained anions is different from selective extraction agents based on COSAN moiety, and may, in principle afford another selectivity during the extraction process.

Starting from the *closo*-dodecahydrododecaborate $[B_{12}H_{12}]^{2-}$ anion, synthetic methods for above species were developed with the aim of obtaining hydrophobic anions bearing substituents known for their ability to complex radionuclides of the lanthanide and actinide series. For this specific application, functionalities containing phosphorous oxide groups bonded on organic molecules like calixarenes [4] or even used alone [2] are known to be powerful sequestering agents for these metals. It seemed of particular interest to combine favourable extraction properties of such groups with these of our hydrophobic anions in one molecule. For this reason, we focused our attention on the preparation of hydroborate anions bearing ligand containing $R_2P(O)$ functions, namely phosphine oxide, phosphite oxide and CMPO like groups.

2. Results and discussion

Hydrododecaborate derivatives due to their high stability and weak nucleophilicity possess versatile properties and solution behaviour suitable for broad range of possible applications. These range from the most studied applications for Boron neutron capture therapy (BNCT) [6], to presently studied interesting potential for the preparation of non-linear optical (NLO) materials [7], and also for the synthesis of extractants. For our specific application, classical liquid–liquid extraction technique requires extractants, which combine good solubility in the organic phase, hydrophobicity and selectivity.

Hydrododecaborate dianions are known for their good solubility in aqueous phase, therefore the overall charge of the cluster should be first decreased from -2 to -1 creating monoanions being known to be more prone to leave water and enter the organic phase. For this purpose, we have used the ability of $[B_{12}H_{12}]^{2-}$ to react with hydroxylamine-*O*-sulfonic acid yielding the useful intermediate $[NH_3B_{12}H_{11}]^{-}$ [8]. Moreover, the amino hydrogen atoms of that anion can be replaced by suitable groups (alkyl, aryl, ...) when forced reaction conditions are used [9].

Two different routes have been investigated which lead to two diversified groups of extractants (Fig. 1). In the **A** group, hydrododecaborate cluster is bearing only one substituent which should (1) improve the hydrophobicity of the anion and (2) complex selectively cations. In the second series (**B**), the cage is bearing two different groups, one for each expected properties.

2.1. Syntheses of hydrododecaborate derivatives *1* and *2* (*A* type extractants)

As we have found, both chlorodiphenylphosphine and *p*-nitrophenyl(diphenylphosphoryl)-acetate react with $[NH_3B_{12}H_{11}]^{-}$ in the presence of sodium hydride yielding $[(Ph_2P(O))_2N(H)B_{12}H_{11}]^{-}$ (**1**) and $[Ph_2P(O)CH_2C(O)N(H)_2B_{12}H_{11}]^{-}$ (**2**), respectively (Scheme 1).

Both monoanions **1** and **2** were fully characterised by NMR spectroscopy and mass spectrometry. Compound **1** would originate from a two step process. First, $[NH_3B_{12}H_{11}]^{-}$ was reacted under argon atmosphere with a large excess of $ClPPh_2$ to give presumably the corresponding monoanion $[(Ph_2P)_2N(H)B_{12}H_{11}]^{-}$ as an intermediate. This compound was without isolation converted to target compound **1** by oxidation, which readily took place in contact with air. A large excess of chlorophosphine was used to improve the yield of the disubstituted product. Even under these forced conditions, final product contained nearly 15% of monosubstituted derivative $Cs[Ph_2P(O)N(H)_2B_{12}H_{11}]$ according to ^{1}H-NMR spectrum. The separation of these two compounds by chromatography was unsuccessful. On the other hand, the solubility of sample containing both compounds in the above ratio in the organic solvent typically used for liquid–liquid extraction (NPOE, *o*-nitrophenyloctyl ether or NPHE, *o*-nitrophenylhexyl ether) was too low to perform extraction test.

Compound **2** is to our knowledge the first example of $[B_{12}H_{12}]^{2-}$ anion bearing a CMPO like function. As described above for **1**, the reaction gave a mixture of monosubstituted anion **2** and one other species was obtained. From this mixture, compound **2** could be separated by chromatography. The solubility of compound **2** in above organic solvents is much higher than that for **1**. It is also of interest to notice that the substitution reaction, in that case, seems to be slower and 4 days reaction time is necessary. Moreover, **2** exhibits an extraordinary solubility for a monoanion even in aqueous media. Therefore, we can assume that the nitrogen atom bound in the amidic function would have a lower basicity and thus would tend to be less protonized comparing to the classical nitrogen atoms bound to a cage. According to this assumption, **2** would behave rather as a divalent anion in solution. This effect apparently leads to enhanced solubility of this compound in water, and negative results from the extraction tests.

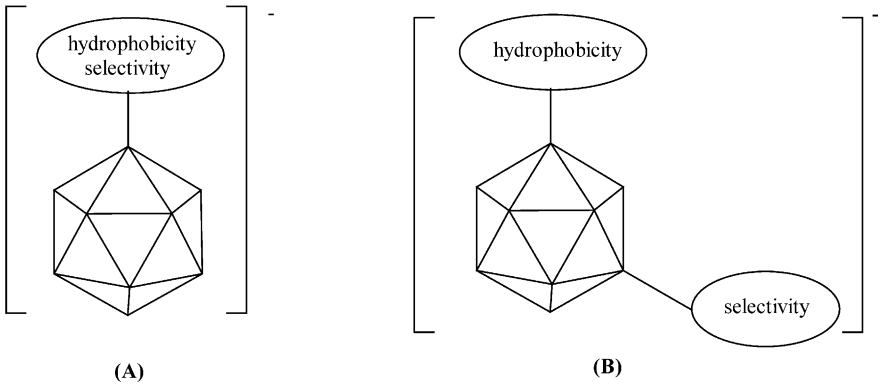
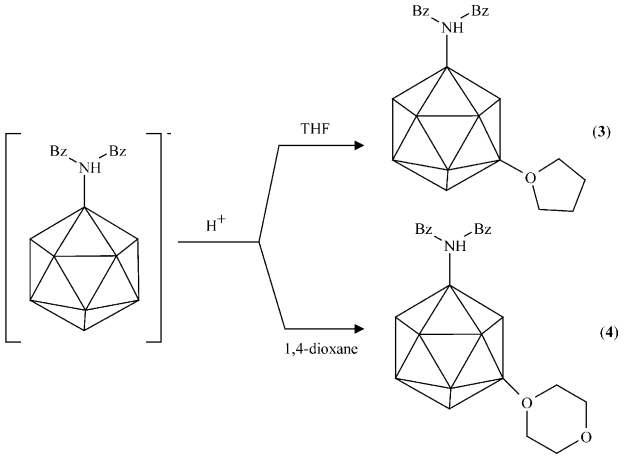


Fig. 1. Two different types of extractants derived from $[B_{12}H_{12}]^{2-}$.

2.2. Syntheses of hydrododecaborate derivatives **5**, **9**, **10** and **11** (**B** type extractants)

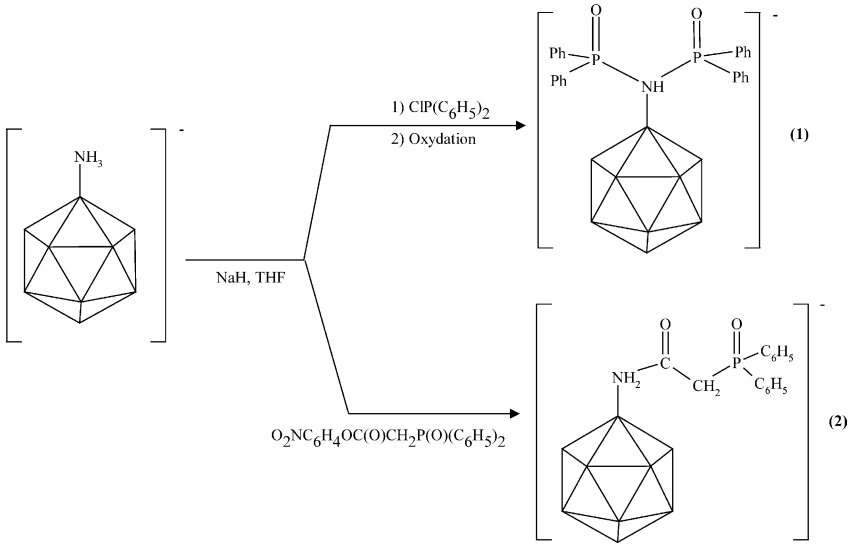
The preparation of disubstituted monoanions was carried out by a similar procedure as described for the oxonium derivatives prepared for BNCT application. Recently, Sivaev et al. [6] have shown that $[B_{12}H_{12}]^{2-}$ yields to $[B_{12}H_{11}O(CH_2)_4]^-$ or $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ by a 'solvent (THF or 1,4-dioxane, respectively) addition' reaction in presence of $Et_2O{\cdot}BF_3$ as acid catalyst. Ring opening reactions under nucleophilic attacks have also been reported [6,10].

As we have found, oxonium derivatives of monosubstituted hydrododecaborate can be obtained following slightly modified procedure to that described above for the parent $[B_{12}H_{12}]^{2-}$ anion. Starting from the free conjugated acid form of the already described hydrophobised dibenzylamino $[Bz_2N(H)B_{12}H_{11}]^-$ anion [9], acid promoted reaction occurred under reflux. These reactions led to the bipolar neutral species **3** and **4** (Scheme 2).



Scheme 2.

It is important to notice that the main difference between these reactions and those described with $[B_{12}H_{12}]^{2-}$ is the nature of the acid catalyst. Since no further purification is needed in this case, the proton of



Scheme 1.

the conjugated acid instead of $Et_2O \cdot BF_3$ can serve with advantage as promoter for this reaction in aprotic solvent. The dioxanate derivative **4** has been obtained with a lower yield similarly to what has been mentioned for $[B_{12}H_{12}]^{2-}$ [6].

The bipolar species **3** and **4** containing oxonium oxygen have been fully characterised by mass spectrometry and NMR spectroscopy. ^{11}B-NMR results suggest that **3** and **4** are mixtures of at least two positional isomers, probably of the minorite amount of 1,2- and main 1,7-isomer. Pattern in the ^{11}B-NMR spectra correspond to this reported already for the analogous disubstituted hydrododecaborate $[1\text{-}Bz_2N(H)B_{12}H_{10}\text{-}7\text{-}C_{10}H_7]^-$ [9]. Nevertheless, the chemical shift of the boron atom bound to the dibenzylamino group is shifted downfield compared to parent $[Bz_2N(H)B_{12}H_{11}]^-$ ion, presumably due to oxygen substitution in a second apical position.

We assume that **3** and **4** are convenient precursors for the preparation of bifunctional hydrododecaborate derivatives for many applications.

Several ring cleavage reactions by a suitable nucleophile, proceeding on α-carbon atom of the THF or 1,4-dioxane have been investigated (Scheme 3), leading to extractants **5**, **9**, **10** and **11** with functional groups bonded via **6**, **7** or **8** atom pendant group.

All these extractants have been fully characterised by mass spectrometry and NMR spectroscopy. In ^{1}H-NMR spectra, the chemical shifts of protons belonging to CMPO like groups correspond with those reported for CMPO substituted calixarene [4].

Compounds **5** and **10** exhibit a very good solubility in organic solvents like NPOE or NPHE. Their abilities to extract selectively ^{241}Am and ^{152}Eu from simulated nuclear waste have been investigated and will be described below. But, unfortunately, compounds **9** and **11** have strong hydrophobic natures but their few solubility in extraction solvent (NPOE and NPHE) do not allow to measure their extraction abilities.

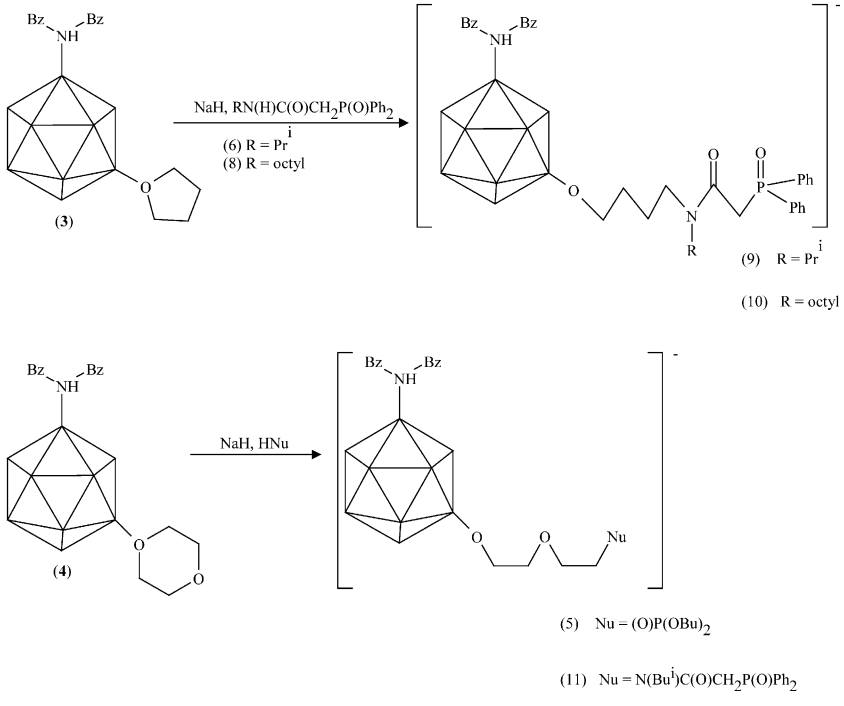
2.3. Extraction of ^{241}Am(III) and ^{152}Eu(III)

As it has been mentioned above, only compounds **5** and **10** have been tested. The results obtained have been reported in Tables 1 and 2. The values of the distribution coefficients of ^{241}Am and ^{152}Eu have been measured for different acidity of the aqueous phase.

Tables 1 and 2 show that both extractants **5** and **10** present a remarkable efficiency in low acidity medium (0.01 M HNO_3). Moreover, promising results have been obtained with **10**, which exhibits a strong efficiency for acidity up to 0.1 M HNO_3. In any case, the results

Table 1
Distribution coefficients for ^{152}Eu and ^{241}Am measured with **5** (organic phase, 10^{-2} M **5** in NPHE; aqueous phase HNO_3).

Acidity (M)	D (^{152}Eu)	D (^{241}Am)
0.01	> 100	> 100
0.1	1.45	3.5
1	0.06	0.09



Scheme 3.

Table 2
Distribution coefficients for ^{152}Eu and ^{241}Am measured with **10** (organic phase, 10^{-2} M **10** in NPHE; aqueous phase HNO_3)

Acidity (M)	D (^{152}Eu)	D (^{241}Am)
0.01	> 100	> 100
0.1	> 100	> 100
1	2.1	3.5
3	0.85	1.2

obtained with ^{241}Am are slightly upper than those obtained with ^{152}Eu.

On one hand, the values obtained for low acidity medium are larger than those measured in similar conditions by using rather CMPO derivatives [2] or calixarenes [4] or cavitands [3] based extractants. On the other hand, the latter are much more efficient than both compounds **5** and **10** for high acidity medium. Therefore, these hydroborate based compounds represent interesting supplementary extractants for high efficiency extraction in a wide range of acidity medium.

Despite a possible degradation of the cluster at high acidity medium, the dependence of the distribution coefficients on the acidity of the aqueous phase can be related to the overall extraction equilibrium constant (K_{Ex}) as it is proposed in Fig. 2.

Measurements reported in Tables 1 and 2 clearly confirm these assumptions and a rapid decrease of the distribution coefficients is observed when acidity increases.

3. Experimental

3.1. Starting materials and instruments

All sensitive compounds were handled under atmosphere of pure Ar using vacuum-line, Schlenk techniques and an efficient dry box with solvents purified by standard methods [11]. $(Et_3HN)_2B_{12}H_{12}$ was provided by KATCHEM Ltd., Prague. ^{11}B-, ^{31}P- and ^{1}H-NMR spectra were recorded on a Bruker AM300 spectrometer in CD_3CN or $(CD_3)_2CO$ at 96.29 MHz with $Et_2O{\cdot}BF_3$ as external reference (positive values downfield), at 146.2 MHz with 85% H_3PO_4 as external reference and

$$M^{X+}_{(aq)} + x\ H^+,L^-_{(org)} \rightleftharpoons ML_{x\,(org)} + x\ H^+_{(aq)}$$

$$K_{ex} = \frac{[ML_x] * [H^+]^x}{[M^{X+}] * [H^+,L^-]^x} \quad \text{or} \quad D_M = \frac{[ML_x]}{[M^{X+}]}$$

$$\text{thus} \quad D_M = K_{ex} * \frac{[H^+,L^-]^x}{[H^+]^x}$$

Fig. 2. Relation between the distribution coefficient (D_M) and the acidity of the aqueous phase (K_{ex}: extraction equilibrium constant).

at 300 MHz, respectively. The following abbreviations are used: s, singlet; d, doublet; m, multiplet; u, unresolved signal. Mass spectrometry measurements were performed in the Mass Spectrometry Laboratory, Central Analytical Service of the CNRS, Solaize (France). A hybrid mass spectrometer ZAB-2-SEQ (Micros) was used for the analyses by SIMS technique. Other measurements were performed using the electrospray (ES) method on a VG-platform micromass spectrometer. Samples were introduced in the spectrometer as MeCN or C_3H_6O solutions.

3.2. Synthesis of $Cs[(Ph_2P(O))_2N(H)B_{12}H_{11}]$ (**1**)

$(Et_3HN)_2B_{12}H_{12}$ was converted to $(Me_3HN)_2B_{12}H_{12}$ by passing on a C20 H Duolite resin charged with protons following by addition of Me_3N. $(Me_3HN)_2B_{12}H_{12}$ was converted by reaction with aq. hydroxylamine-*O*-sulfonic acid into the monoamino derivative $(Me_3HN)[B_{12}H_{11}NH_3]$ as described in the literature [8].

Solid $(Me_3HN)[B_{12}H_{11}NH_3]$ (1.278 g, 5.87 mmol) was dried overnight at 70 °C under vacuum. Freshly distilled THF (100 ml) and NaH (0.704 g, 29.33 mmol) were introduced into the reaction flask under anhydrous conditions. The mixture was stirred for 3 h at room temperature (r.t.) and then refluxed for 30 min. A solution of chlorodiphenylphosphine (12.943 g, 58.70 mmol, 11 ml) in 20 ml THF was slowly added dropwise (30 min). The mixture was allowed to cool down to r.t. and then THF was distilled in vacuo. After dissolution in a water–MeCN mixture, the product was passed on a C20 H Duolite resin charged with protons and converted into Cs salt by addition of CsOH yielding 1.68 g of solid in which the disubstituted compound **1** is the major product according to NMR results.

The product was analysed by ^{11}B-, ^{1}H-NMR spectroscopy, FTIR and mass spectrometry. Mass spectrometry clearly showed the presence of $[(Ph_2P(O))_2{-}NH{-}B_{12}H_{11}]^-$ and $[Ph_2P(O){-}NH_2{-}B_{12}H_{11}]^-$.

FTIR (cm^{-1}): 3220 (NH), 2490 (BH), 1165 (PO); ^{11}B-NMR (δ, ppm, CH_3CN): −6.5 (s, B), −15.6 (d, 5B), −16.5 (d, 5B), −19.7 (d, B); ^{1}H-NMR (δ, ppm, CD_3CN): 7.49–7.87 (m,18.5H, CH), 4.97 (s, 1.15H, NH), 1.1–1.7 (u, 11H, BH); MS (*m*/*z*): 358 $[Ph_2P(O){-}NH_2{-}B_{12}H_{11}]^-$, 558 $[\mathbf{1}]^-$.

3.3. Synthesis of $K[Ph_2P(O)CH_2C(O)N(H)_2B_{12}H_{11}]$ (**2**)

p-Nitrophenyl(diphenylphosphoryl)acetate, $Ph_2P(O)$-$CH_2C(O)OC_6H_4NO_2$, was prepared by the reaction of diphenylphosphorylacetic acid with *p*-nitrophenol and thionyl chloride in dry $CHCl_3$ as described in the literature [4].

In a typical experiment, 1.0 g of $(Me_3HN)[B_{12}H_{11}NH_3]$ (4.60 mmol) was dried overnight as described above and then dissolved in 100 ml of freshly distilled THF. Sodium hydride (0.4 g, 16.7 mmol) was added slowly to the solution until no gas evolution was observed. *p*-Nitrophenyl(diphenylphosphoryl)acetate (1.77 g, 4.65 mmol) were introduced into reaction flask under Ar atmosphere. The mixture was stirred 4 days at r.t. and then cooled down to −10 °C. Then 50 ml of a MeOH–water (1/1) solution was added slowly. The solution was concentrated under vacuum and the anionic products were precipitated as tetramethylammonium salts by the addition of an excess of tetramethylammonium chloride. NMR analyses showed that the residue contained a mixture of $[Ph_2P(O)CH_2C(O)N(H)_2B_{12}H_{11}]$ (**2**) and another product which was not fully characterised. Compound **2** was purified by chromatography performed with a glass column filled with silicagel (70–230 mesh, Aldrich) with CH_2Cl_2–MeCN (3/1) as eluent. The separation was monitored by TLC on DEAE cellulose [12] with 2 M aq. solution of NH_4NO_3 as eluent. The spots were detected by spraying with a solution of $PdCl_2$ (0.5% in 5% HCl). Pure compound **2** was finally obtained 1.23 g, (yield: 61%).

FTIR (cm^{-1}): 3235 (NH), 3059–2853 (CH), 2488 (BH), 1542 (CO), 1162 (PO); ^{31}P-NMR (δ, ppm, C_3H_6O): 33.7; ^{11}B-NMR (δ, ppm, C_3H_6O): −5.18 (s, 1B), −15.16 (d, 5B, B(7–11)), −16.12 (d, 5B, B(2–6)), −18.60 (d, 1B); ^{1}H-NMR (δ, ppm, $(CD_3)_2CO$, D_2O): 7.44–7.80 (m, 10H, aromatic CH), 5.7 (s, ca. 1H, NH), 4.1 (d, 2H, P(O)CH_2C(O)), 1.16–1.46 (u, 11H, BH); MS (*m*/*z*): 306 [**2**-C_6H_5–O]$^-$.

3.4. Synthesis of $[Bz_2N(H)B_{12}H_{10}O(CH_2)_4]$ (**3**)

The hydrophobic monoanion $[Bz_2N(H)B_{12}H_{11}]^-$ was prepared and purified following the method previously described by our group [9].

In a typical experiment, $Me_4N[Bz_2N(H)B_{12}H_{11}]$ was first converted into its conjugate acid by overlaying a suspension of the tetramethylammonium salt in 150 ml of HCl (4 M) by Et_2O (50 ml). The organic layer was separated and the aq. phase was washed with 3 × 30 ml of Et_2O. The combined organic phases were carefully evaporated in vacuo at r.t. yielding a glassy yellow solid $H[Bz_2N(H)B_{12}H_{11}]$.

All the following experiments were performed under Ar atmosphere. $H[Bz_2N(H)B_{12}H_{11}]$ (1.5 g, 4.43 mmol) was dissolved into 50 ml of freshly distilled THF. The solution was refluxed for 2 h yielding the title bipolar neutral compound and anionic impurities. Then 30 ml of THF were evaporated under vacuum and the product was purified by chromatography performed with a glass column filled with silicagel (70–230 mesh, Aldrich) with CH_2Cl_2–MeCN (3/1) as eluent. The separation was monitored by TLC on DEAE cellulose [12] with 2 M aq. solution of NH_4NO_3 as eluent (R_F 0.15, product; R_F 0.6, 0.8, impurities). This separation yielded $[Bz_2N(H)B_{12}H_{10}O(CH_2)_4]$ (0.98 g, 54%) as white crystals.

FTIR (cm^{-1}): 3231 (NH), 3042–2874 (CH), 2503 (BH); ^{11}B-NMR (δ, ppm, C_3H_6O): 5.6 (s, 1B, BO), −2.2 (s, 1B, BN), −17.8–−18.3 (m, 9B), −20.6 (d, 1B); ^{1}H-NMR (δ, ppm, $(CD_3)_2CO$): 6.9–7.3 (m, 10H, benzyl CH), 5.0 (m, 3H, benzyl CH_2+NH), 4.4 (m, 4H, THF CH_2), 4.1 (d, 2H, benzyl CH_2), 2.1 (m, 4H, THF CH_2), 1.2–1.7 (u, 10H, BH); MS (ES, *m*/*z*): 409.4 [M].

3.5. Synthesis of $[Bz_2N(H)B_{12}H_{10}O(CH_2CH_2)_2O]$ (**4**)

This bipolar neutral derivative was obtained by following the same procedure as described above and with using 1,4-dioxane instead of THF. It is important to note that the yield (41%) is lower in that case. This compound was analysed by ^{11}B- and ^{1}H-NMR spectroscopy and mass spectrometry. No significant difference has been noticed between the ^{11}B-NMR spectrum of these two bipolar neutral species.

^{11}B-NMR (δ, ppm, C_3H_6O): 5.6 (s, 1B, BO), −2.2 (s, 1B, BN), −17.8–−18.3 (m, 9B), −20.6 (d, 1B); ^{1}H-NMR (δ, ppm, $CDCl_3$): 6.9–7.3 (m, 10H, benzyl CH), 4.9 (m, 3H, benzyl CH_2+NH), 4.0 (d, 2H, benzyl CH_2), 3.7 (m, 8H, dioxane CH_2), 1.2–1.7 (u, 10H, BH); MS (ES, *m*/*z*): 425.4 [M].

3.6. Synthesis of $[Bz_2N(H)B_{12}H_{10}OCH_2CH_2OCH_2CH_2P(O)(OBu)_2]Na$ (**5**)

Commercial dibutyl phosphite, $(BuO)_2P(O)H$ (0.187 g, 0.96 mmol), was converted into its Na salt by reaction with NaH (24 mg, 1.0 mmol) in dry THF (50 ml). This solution was added slowly at r.t. to a solution of **4** (0.39 g, 0.92 mmol) in dry THF. The mixture was stirred at r.t. overnight. Thirty millilitres of a solution MeOH–water (1/1) was added slowly. The solution was concentrated under vacuum and precipitated as tetramethylammonium salt by adding a large excess of NMe_4Cl. Then after dissolution in a water–MeCN mixture, the product was passed on a C20 H^+ Duolite resin charged with protons and converted into Na salt by addition of NaOH (yield: 0.50 g, 85%).

^{11}B-NMR (δ, ppm, C_3H_6O): 4.6 (s, 1B, BO), −3.1 (s, 1B, BN), −17.8–−18.6 (m, 9B), −23.7 (d, 1B); ^{31}P-NMR (δ, ppm, $CDCl_3$): 31.7; ^{1}H-NMR (δ, ppm, $CDCl_3$): 6.9–7.4 (m, 10H, benzyl CH), 5.0 (m, 3H, benzyl CH_2+NH), 4.1 (d, 6H, benzyl CH_2+OC$H_2$$CH_2CH_2CH_3$), 3.7–3.9 (m, 8H, dioxane CH_2), 1.67 (m, 4H, $OCH_2CH_2CH_2CH_3$), 1.43 (m, 4H, $OCH_2CH_2CH_2CH_3$), 0.95 (t, 6H, $OCH_2CH_2CH_2CH_3$), 1.2–1.7 (u, 10H, BH); MS (FAB$^-$, *m*/*z*): 617.4 [**5**]$^-$.

3.7. Synthesis of $(R)HNC(O)CH_2P(O)(Ph)_2$ (**6**, $R = Pr^i$; **7**, $R = Bu^i$)

In a typical experiment, *p*-nitrophenyl(diphenylphosphoryl)acetate [4] was dissolved in a large excess of isopropylamine or isobutylamine, respectively. The solution was stirred at r.t. overnight. Then excess of alkylamine was eliminated under vacuum and the product was recrystallised from hot MeOH (yield: 92% (**6**) and 89% (**7**)). These amides have been characterised by FTIR and ^{1}H-NMR spectroscopy.

^{1}H-NMR (δ, ppm, $CDCl_3$): **6**: 7.83–7.51 (m, 10H, ArH), 3.58 (d, 2H, P(O)CH_2C(O)), 3.0 (d, 6H, CH_3), 1.0 (m, 1H, CH); **7**: 7.81–7.50 (m, 10H, ArH), 3.62 (d, 2H, P(O)CH_2C(O)), 3.32 (m, 2H, NCH_2CH$(CH_3)_2$), 1.95 (m, 1H, NCH$_2$C$H(CH_3)_2$), 1.10 (m, 6H, NCH$_2$CH(C$H_3)_2$); FTIR (cm^{-1}) **6** and **7**: ca. 3290 (NH), ca. 3060–2850 (CH), ca. 1540 (CO), ca. 1160 (PO).

3.8. Synthesis of $(CH_3(CH_2)_7)HNC(O)CH_2P(O)(Ph)_2$ (**8**)

Octylamine (0.68 g, 5.27 mmol) was dissolved in 100 ml of EtOH free dry THF. *p*-Nitrophenyl(diphenylphosphoryl)acetate (2.34 g, 6.14 mmol) was added slowly in the reaction flask. The mixture was stirred at 45 °C during 72 h. Then the solution was cooled down to r.t. and 80 ml of water was added slowly. The organic phase containing the product was extracted and the aq. phase was washed with 3×20 ml of $CHCl_3$. The combined organic phases were dried with anhydrous Na_2SO_4 and subsequently evaporated to dryness yielding crude product **8**, which was purified by recrystallisation from hot MeOH (30 ml) (yield: 2.10 g, 92%). The FTIR spectrum of **8** exhibits no significant difference compared to those of **6** and **7**, except of course for the bands relative to the alkyl groups.

^{1}H-NMR (δ, ppm, CD_2Cl_2): 7.85–7.51 (m, 10H, Ar*H*), 3.58 (d, 2H, P(O)CH_2C(O)), 3.29 (m, 2H, octyl CH_2), 1.36 (m, 12H, octyl CH_2), 0.93 (t, 3H, octyl CH_3).

3.9. Synthesis of $K[Bz_2N(H)B_{12}H_{10}O(CH_2)_4N$-$(R)C(O)CH_2P(O)(Ph)_2]$ (**9**, $R = Pr^i$, **10**, $R =$ octyl)

Both title compounds were prepared following the same procedure. In a typical experiment, 1.58 mmol of well dried **6** (respectively **8**) were dissolved in 50 ml of freshly distillated THF. Sodium hydride (2.2 mmol, 0.053 g) was added slowly to the solution under stirring. Gaz evolution was observed. The mixture was stirred 1 h at r.t. Then a solution of 0.40 g of **3** (0.97 mmol) in dry THF (50 ml) was added dropwise to the reaction flask. The solution was stirred 5 h at r.t., and then refluxed 5 h. After cooling, the excess of NaH was removed by the addition of 30 ml of EtOH and 30 ml of water. The solution was concentrated and the product was extracted with $CHCl_3$ (3×100 ml) by washing the aq. solution. The organic solution was evaporated to dryness under vacuum giving pure **9** (resp. **10**) (yield: ca. 0.49 mmol, ca. 51%).

9: ^{11}B-NMR (δ, ppm, C_3H_6O): 5.8 (s, 1B, BO), −4.2 (s, 1B, BN), −16.1–−18.6 (m, 9B), −20.0 (d, 1B); ^{1}H-NMR (δ, ppm, $CDCl_3$): 7.85–7.21 (m, 20H, Ar*H*), 5.02 (d, 2H, benzyl CH_2), 4.05 (d, 2H, benzyl CH_2), 3.24 (d, 2H, OCH_2CH$_2$CH$_2$CH$_2$N), 3.10 (m, 1H, Pr^i C*H*), 2.81 (m, 2H, OCH$_2$CH$_2$CH$_2$CH_2N), 1.43 (m, 4H, OCH$_2$CH_2CH_2CH$_2$N), 1.07 (m, 6H, Pr^i CH_3), 1.15–1.79 (u, 10H, BH); MS (FAB$^-$, *m*/*z*): 708 [**9**]$^-$.

10: ^{11}B-NMR (δ, ppm, C_3H_6O): 5.8 (s, 1B, BO), −4.0 (s, 1B, BN), −16.2–−18.9 (m, 9B), −20.9 (d, 1B); ^{1}H-NMR (δ, ppm, $CDCl_3$): 7.85–7.21 (m, 20H, Ar*H*), 4.98 (d, 2H, benzyl CH_2), 4.10 (d, 2H, benzyl CH_2), 3.40 (m, 2H, octyl CH_2), 3.24 (d, 2H, OCH_2CH$_2$CH$_2$CH$_2$N), 3.08 (m, 2H, octyl CH_2), 2.81 (m, 2H, OCH$_2$CH$_2$CH$_2$CH_2N), 1.43 (m, 4H, OCH$_2$CH_2CH_2CH$_2$N), 1.29 (m, 12H, octyl CH_2), 1.79–1.15 (u, 10H, BH), 0.91 (t, 3H, octyl CH_3); MS (FAB$^-$, *m*/*z*): 780 [**10**]$^-$.

3.10. Synthesis of $Na[Bz_2N(H)B_{12}H_{10}(OCH_2CH_2)_2$-$N(Bu^i)C(O)CH_2P(O)(Ph)_2]$ (**11**)

Compound **11** was prepared following the same procedure described above, using **4** instead of **3** and **7** instead of **6** (or **8**). The yield obtained (53%) is similar to those obtained for **9** and **10**.

^{11}B-NMR (δ, ppm, C_3H_6O): 5.3 (s, 1B, BO), −3.9 (s, 1B, BN), −16.9–−19.2 (m, 9B), −21.3 (d, 1B); ^{1}H-NMR (δ, ppm, $CDCl_3$): 7.85–7.21 (m, 20H, Ar*H*), 4.98 (d, 2H, benzyl CH_2), 4.10 (d, 2H, benzyl CH_2), 3.9–3.7 (m, 6H, dioxane CH_2), 3.30 (m, 2H, NCH_2CH$(CH_3)_2$), 2.81 (m, 2H, OCH$_2$CH_2N), 1.95 (m, 1H, NCH$_2$C$H(CH_3)_2$), 1.79–1.15 (u, 10H, BH), 1.10 (m, 6H, NCH$_2$CH(C$H_3)_2$); MS (FAB$^-$, *m*/*z*): 739 [**11**]$^-$.

3.11. Liquid–liquid extraction of actinides and lanthanides

The tests were performed on simulated waste solutions which consist in 4 mol l^{-1} HNO_3 spiked with ^{152}Eu and ^{241}Am. The activity was 1500 kBq l^{-1} which corresponds to the following concentration [Eu] = 1.5×10^{-9}, [Am] = 5.2×10^{-8}. A 10^{-3} mol l^{-1} solution of the extractant in NPHE or NPOE was used as the organic phase. Equal volumes (1 ml) of both phases were shaken in sealed tubes for 1 h. The concentration of actinides in each phase was determined by liquid scintillation using a Tri Carb liquid scintillation analyser (Packard, a Canberra Company) [13]. Therefore, 0.100 ml of each phase was added to 19.9 ml of a scintillating liquid (insta gel) before the measurements. The distribution coefficients of the cations are defined by *D* where

$\Sigma[M_{org}]$ and $\Sigma[M_{aq}]$ denote the total concentration of metal species in the organic and in the aq. phase, respectively.

$$D = \frac{\sum [M_{org}]}{\sum [M_{aq}]}$$

4. Conclusion

Two types of functionalised cluster derivatives were prepared starting from *closo*-dodecahydrododecaborate anion. It seems that the simultaneous control of both most important factors i.e. solubility and hydrophobicity is difficult to reach by introducing only one substituent into the molecule like in the **A** type anions. Promising results have been obtained for the **B** type anions, and especially for compound **10**. In any case, the crucial step is to obtain cluster anions soluble in the organic extraction solvent. As it has been established in Fig. 2, a good solubility of the extractant, which permit to increase its concentration in solution, should compensate the effect of the acidity. Since a wide range of chemical modifications can be applied to such derivatives, on the basis of the results obtained with compound **10**, further attention will be focused on modifying the nature of the substituents with the aim of increasing selectivity, solubility and therefore efficiency of our extractants.

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