Cobalt bis(dicarbollide) ions with covalently bonded CMPO groups as selective extraction agents for lanthanide and actinide cations from highly acidic nuclear waste solutions

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A new series of boron substituted cobalt bis(dicarbollide)(1−) ion (**1**) derivatives of the general formula $[(8\text{-CMPO-}(CH_2\text{-}CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-Co}]^-$ (CMPO = $Ph_2P(O)\text{-}CH_2C(O)NR$, R = C_4H_9 (**3b**), $-C_{12}H_{25}$ (**4b**), $-CH_2\text{-}C_6H_5$ (**5b**)) was prepared by ring cleavage of the 8-dioxane-cobalt bis(dicarbollide) (**2**) bi-polar compound by the respective primary amines and by subsequent reaction of the resulting amino derivatives (**3a**–**5a**) with the nitrophenyl ester of diphenylphosphorylacetic acid. The compounds were synthesized with the aim to develop a new class of more efficient extraction agents for liquid–liquid extraction of polyvalent cations, *i.e.* lanthanides and actinides, from high-level activity nuclear waste. All compounds were characterized by a combination of ^{11}B NMR, ^1H high field NMR, Mass Spectrometry with Electrospray and MALDI TOF ionisation, HPLC and other techniques. The molecular structure of the supramolecular Ln^{3+} complex of the anion **5b** was determined by single crystal X-ray diffraction analysis. Crystallographic results proved that the Ln(III) atom is bonded to three functionalised cobalt bis(dicarbollide) anions in a charge compensated complex. The cation is tightly coordinated by six oxygen atoms of the CMPO terminal groups (two of each ligand) and by three water molecules completing the metal coordination number to 9. Atoms occupying the primary coordination sphere form a tri-capped trigonal prismatic arrangement. Very high liquid–liquid extraction efficiency of all anionic species was observed. Moreover, less polar toluene can be applied as an auxiliary solvent replacing the less environmentally friendly nitro- and chlorinated solvents used in the current dicarbollide liquid–liquid extraction process. The extraction coefficients are sufficiently high for possible technological applications.

Nuclear fuel reprocessing operations produce both high and medium activity liquid waste (HLLW/MLLW). These contain the major long-lived nuclides ^{90}Sr (β, 29 years), ^{137}Cs (γ, 30 years) and α emitters such as the transuranium elements. The problem of handling and storing these wastes has to be solved.[1] One of the possible alternatives for treatment of HLLW might consist of the separation of the long-lived elements and their subsequent destruction by partitioning and transmutation (P&T) technologies, and immobilisation of the radionuclides, which cannot be transmuted, in stable matrices. Considering that the activity of long living elements (Sr^{2+}, Cs^+ and actinides) is removed, the resulting medium activity waste can be disposed of in surface repositories. A lot of effort has been spent during past years in the development of reliable liquid–liquid extraction processes for selective separation of long-lived lanthanides and actinides from HLLW and MLLW.

In the currently most studied methods for extraction of trivalent radionuclides either substituted malonamides (DIAMEX process)[2] or (*N*,*N*-dialkylcarbamoylmethyl)dialkylphosphine oxides (CMPO) (TRUEX process)[3–7] or CMPO substituted calixarenes[8–10] are used. These organic ligands are able to bind tightly the M^{3+} cations in a chelate complex by C=O and P=O donor atoms of the uncharged ligands.[2–7] The typical stoichiometry of the resulting complexes with the simple CMPO-like or malonamide ligands is 1:1 or 1:2 (M^{3+} to ligand ratio). A disadvantage may be seen in the persisting 3+ charge of the resulting particle. As a consequence, the highly polar nitrate anions have to be transferred across the interface together with the target cation for charge compensation. In addition, a characteristic feature of the metal complexes derived from simple bidentate ligands, such as "classical" CMPO and malonamides,[2] is the incorporation of the nitrate ions into the metal primary coordination sphere. Only one example of crystallographically proven complete nitrate ion displacement has been recently reported for the tridentate CMPO-like ligand, bis(phosphinomethyl)pyridine *N*,*P*,*P*′-trioxide (BMNOPOPO).[7]

Singly charged chloro derivatives of cobalt bis(dicarbollide)(1−), *closo*-$[(1,2\text{-}C_2B_9H_{11})_2\text{-}3,3'\text{-Co}]^-$ (**1**) (Fig. 1) were designed more than 25 years ago for the extraction of ^{137}Cs from highly acidic solutions.[11–19] This process enables simultaneous Sr^{2+} extraction when polyethylene glycols are used as synergic

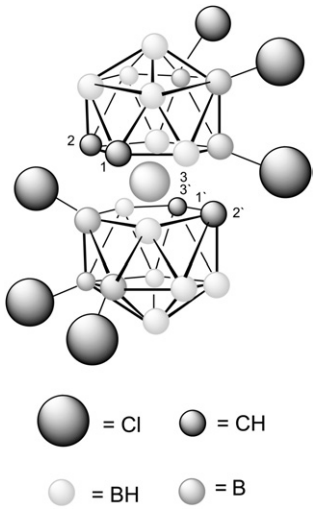


Fig. 1 Schematic drawing of the structure (including cage numbering) of the hexachloro derivative of the anion **1** used in the "classical" cobalt bis(dicarbollide) process.[11–18]

agents. An industrial facility, using a slightly modified process called "UNEX", has been recently launched in Russia.[20,21] The great advantage of this method lies in the high stability of the halogenated anion **1** towards HNO_3 and radiolysis. A disadvantage, on the other hand, is the use of environmentally dangerous solvents such as nitrobenzene or halogenated hydrocarbons. Difficulties still persist in the extraction of trivalent α emitters, despite some synergic mixtures of halogen-protected cobalt bis(dicarbollide) with polydentate ligands which have been designed and tested.[22,23]

As has been shown in recent papers,[24–26] cation transfer to the organic phase can be facilitated if both chelating and strongly hydrophobic cobalt bis(dicarbollide) anionic (1−) charged moieties[11] are linked together in the same molecule by a covalent bond. Such anionic ligands are able to bond metal inside a multi-component molecular assembly and to compensate its charge over a short distance. However, all extraction agents of this type (including oxygen containing substituents at skeletal carbon[25] or boron[24] atoms, or the more promising phosphonic or phosphoric groups[24,26]) exhibited an extensive decrease of their extraction properties with rising HNO_3 concentration.

In this article, we would like to report the appreciable improvement of extraction properties for trivalent metals *via* a method derived from the idea to combine the best properties of the two families of the selective sequestrants, polydentate CMPO and anion **1**. The novel class of compounds of the general formula $[(8\text{-X-}(CH_2\text{-}CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-Co}]^-$ (X = (CMPO) = $Ph_2P(O)CH_2C(O)NR$; R = C_4H_9 (**3b**), $\text{-}C_{12}H_{25}$ (**4b**), $\text{-}CH_2\text{-}C_6H_5$ (**5b**)) has proven to be very effective for transfer of lanthanides and actinides to the organic phase. Very high extraction coefficients, even from strongly acidic solutions with HNO_3 concentrations up to 3 M, or from standard waste solution (1 M HNO_3 + 3 M $NaNO_3$) were achieved.

Experimental

General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[27] although some operations, such as column chromatography, were carried out in air. The starting zwitterionic compound *closo*-$[(8\text{-}(C_4H_8O_2)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-Co}]^0$ (**2**) was prepared according to the literature procedure[28] from the commercially available anion **1** (Katchem Ltd., Prague, Czech Rep.). *p*-Nitrophenyl(diphenylphosphoryl) acetate was prepared according to the published procedure[8] using Sigma-Aldrich chemicals. Toluene (Lachema, Brno, Czech Rep.) was dried over Na metal, THF was dried over Na metal and methylphenylketylsodium, CH_2Cl_2 was dried over P_2O_5, and the solvents were freshly distilled before use. High-surface-area sodium hydride made at IIC was used with a BET surface area of about 1 $m^2\ g^{-1}$. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out on silica gel (Aldrich 200–400 mesh). The purity of the individual chromatographic fractions was monitored by analytical TLC on Silufol (silica gel on aluminium foil; yellow-orange spots, eventually detected by iodine vapours, followed by 2% aqueous AgNO3 spray) and HPLC. Melting points were determined in a Koeffler melting point apparatus in sealed capillaries.

Physical measurements

Proton (^1H) and boron (^{11}B) NMR spectroscopy were performed at 11.75 T on a Varian Unity-500 instrument. The samples were measured in deuterioacetone. The procedure for [^{11}B–^{11}B]-COSY[29,30] and ^1H–{^{11}B(selective)}[31] NMR experiments were essentially as described in other papers from our laboratories.[32] NMR chemical shifts are given in ppm to high-frequency (low field) of Ξ = 160.380 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.05 ppm.) and Ξ = 499.878 MHz ($SiMe_4$) for ^1H (quoted ±0.01 ppm.), Ξ being defined as in the literature.[29,30] Residual solvent ^1H resonances were used as internal secondary standards, ^{31}P were measured at 80.979 MHz and referenced to 85% H_3PO_4 as the external standard. Coupling constants $^1J(^{11}B\text{–}^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution 2 Hz and are given in Hz.

The NMR data are presented in the text below in the following format: ^{11}B NMR: ^{11}B chemical shifts $\delta(^{11}B)$ (ppm), $J(^{11}B\text{–}^1H)$ in parentheses, selectively decoupled $\delta(^1H)$-$\{^{11}B_{selective}\}$ in square brackets, assignment by relative intensities, [^{11}B–^{11}B]-COSY, and ^1H–{^{11}B(selective)} experiments (for ^1H); ^1H NMR: chemical shifts $\delta(^1H)$ (ppm); ^{31}P NMR: ^{31}P {1H} chemical shifts $\delta(^1H)$ (ppm).

IR spectra were measured in Nujol mull using a PYE UNICAM PU 9512 spectrometer. Mass spectrometry measurements were performed on a Bruker Biflex MALDI-TOF mass spectrometer and also on a Bruker Esquire-LC Ion Trap instrument using electrospray ionisation. Negative ions were detected. Samples dissolved in acetonitrile (concentrations 1 mg ml^{-1}) were introduced into the ion source by infusion of 3 μl min^{-1}, drying temperature was 300 °C, drying gas flow 5 l min^{-1}, nebulizing gas pressure 10 psi.

Analytical HPLC

Chromatographic procedure: the ion-pair RP chromatographic method for separation of hydrophobic borate anions with DAD detection was used[33] based on results described earlier in the literature[34] by authors from this laboratory. Similar conditions were used as for previous series of similar compounds.

X-Ray crystallography

A single crystal of the lanthanum complex of **5b** was mounted on a glass capillary and measured in a cold gas stream on a Nonius KappaCCD diffractometer. Crystal structure determination of **5b**, structure solution: the structure was solved by the direct method (SIR92) and refined by a full matrix least squares procedure based on F^2 (SHELXL97 and SHELXLH).[35] The absorption was neglected. Hydrogen atoms were placed into idealised positions and refined as riding

on their pivot atom with temperature factor restricted to 1.2 [U_{eq}(pivot atom)]. The crystal suffered from disorder of one borane cage, as indicated by large temperature factors, however its other positions could not be distinguished because of the low quality of the crystal. Also the position of atoms of solvating dichloromethane is only partially occupied. In the void area of the unit cell, several separated residual peaks can be found with rather high electron density (1.6 e Å^{-3}). They did not afford suitable distances for hydrogen bonds to support the idea that they belong to partially occupied positions of water molecules. Since several other solvents were present during crystallization, it was preferred to leave these residuals unresolved. However, the molecular structure of the complex itself was determined unambiguously.

Crystal data for 5b. $C_{93.5}H_{151}B_{54}ClCo_3LaN_3O_{15}P_3$, M = 2584.97, triclinic, a = 15.0120(2), b = 16.2310(3), c = 31.7030(5) Å, α = 88.9600(8), β = 86.8770(9), γ = 84.1900(9)°, T = 150(2) K, Z = 2, space group $P\bar{1}$ (no. 2), U = 7673.0(2) Å^3, μ(Mo-K$_\alpha$) = 0.688 mm^{-1}, 99 772 reflections measured, 24 235 unique (R_{int} = 0.065) which were used in all calculations, final $R(F^2)$ = 0.083 (for $I > 2\sigma(I)$); $wR(F^2)$ = 0.256 (all data).

CCDC reference number 190859. See http://www.rsc.org/suppdata/nj/b2/b202374c/ for crystallographic files in CIF or other electronic format.

Extraction tests

Extraction experiments at NRI were performed in glass test tubes with polyethylene stoppers at laboratory temperature (23 ± 1 °C). The phase volume ratio was 1:1 (2 ml of each phase). The samples were shaken for 1 hour (10 minute intervals were sufficient for attaining extraction equilibrium) on a horizontal shaker. After shaking, the test tubes were centrifuged and 1 ml samples of each phase were taken for radioactivity measurement. All used reagents were of A.R. quality, as were the solvents. The distribution of Eu was investigated using carrier-free ^{152,154}Eu (radiochemical purity). The radioactivity of samples was measured using a single-channel γ analyser with a NaI (Tl) well detector. In CEA Cadarache, the procedure was the same, the samples were spiked with ^{152}Eu and ^{241}Am, the radioactivity of aqueous and organic phases was determined by γ spectrometry (Eurysis Mesures). The measurement duration was adapted to obtain reproducibility between ±5%. Distribution coefficients of lanthanides were obtained from ICP/MS analysis of aqueous phases before and after extraction.

General synthetic procedure for synthesis of the 8-(RNHCH$_2$CH$_2$OCH$_2$CH$_2$O) derivatives (3a–5a) by [(8-(C$_4$H$_8$O$_2$)-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)-3,3′-Co]^0 (2) ring cleavage

To the stirred toluene solution (200 ml) of the primary amine (6 mmol) a toluene solution of the dioxanate **2** was dropwise added (5 mmol) during 1 h, and the content of the flask was then stirred for an additional *ca.* 3 h at 60 °C. The reaction course was monitored by TLC, and the heating was stopped when the spot of the starting zwitterionic species **2** disappeared on TLC (R_F = 0.47, CH_2Cl_2). After cooling down, ethanol (10 ml) was added followed by water (20 ml). The solvents were evaporated almost to dryness, diluted hydrochloric acid (1 M, 30 ml) was added and the products were extracted into benzene (three times by 25 ml). A small volume of water (10 ml) was added to the combined benzene extracts and the solvents were evaporated. The residue was dissolved in a chloroform–acetonitrile solvent mixture (3:1) and the products were purified by flash chromatography on a silica gel column using the same mobile phase for elution. After evaporation of the respective fractions to dryness orange powders resulted. Their purity was controlled by HPLC. For the yields, TLC R_F values, HPLC k', NMR shifts and other properties see data collected below.

3a. Terminal group: ($C_4H_9NH_2$-), yield 97%; M.p. 215–217 °C; MS m/z: 486.3 (483.3, 100%); TLC R_F ($CHCl_3$:CH_3CN 3:1): 0.45; HPLC k'(58% aqueous CH_3CN, 3 mmol hexylamine acetate): 11.1. ^{11}B NMR: 24.6 s (B8), 6.67 (B8′)(142)[3.082], 0.52 (B10′)(139)[2.921], −2.54 (B10)(142)[2.686], −5.04 (B4′, 7′)(153)[2.690], −6.60 (B9, 12, 9′, 12′)(139)[2.093, 1882], −9.26 (B4, 7)(142)[2.902], −17.23 (B5′, 11′)(146)[1.594], −20.20 (B5, 11)(153)[1.552], −22.46 (B6′)(173)[1.662], −28.70 (B6)(139)[1.454]. ^{1}H NMR: 8.05 br s (2H, NH), 4.085 s (2H, 2 $CH_{carb.}$), 3.985 s (2H, 2 $CH_{carb.}$), 3.932 m (2H, CH_2-O), 3.744 m (2H, CH_2-O), 3,640 m (2H, CH_2-O), 3.52 m (2H, O-CH_2-CH_2-N), 3.358 m (2H, CH_2-N), 1.888 m (2H, CH_2-CH_2-N), 1.474 m (2H, CH_2-CH_3), 0.969 t (3H, CH_3).

4a. Terminal group: ($C_{12}H_{25}NH_2$-), yield 89%; M.p. 68–70 °C; MS m/z: 598.4 (595.4, 100%); TLC R_F ($CHCl_3$:CH_3CN 3:1): 0.57; HPLC k'(70% aqueous CH_3CN, 3 mmol hexylamine acetate): 14.0. ^{11}B NMR: 24.60 s (B8), 6.65 (B8′)(135)[3.097], 0.53 (B10′)(139)[2.931], −2.54 (B10)(142)[2.695], −5.06 (B4′, 7′)(153)[2.693], −6.62 (B9, 12, 9′, 12′)(139)[2.101, 1.886], −9.29 (B4, 7)(142)[2.907], −17.23 (B5′, 11′)(146)[1.594], −20.23 (B5, 11)(154)[1.535], −22.41 (B6′)(144)[1.672], −28.65 (B6)(139)[1.454]. ^{1}H NMR: 8.05 br s (2H, NH), 4.073 s (2H, $CH_{carb.}$), 3,973 s (2H, $CH_{carb.}$), 3.918 m (2H, CH_2-O), 3.739 m (2H, CH_2-O), 3.651 m (2H, CH_2-O), 3.526 m (2H, O-CH_2-CH_2-N), 3.33 m (2H, CH_2-N), 1.937 m (2H, CH_2-CH_2-N), 1.473 m (2H, CH_2), 1.363 m (2H, CH_2), 1.29 m (14H, CH_2), 0.882 t (3H, CH_3).

5a. Terminal group: ($C_6H_5CH_2NH_2$-), yield 93%; M.p. 236–238 °C; MS m/z: 520.3 (518.3, 100%); TLC R_F ($CHCl_3$:CH_3CN 3:1): 0.46; HPLC k'(58% aqueous CH_3CN, 3 mmol hexylamine acetate): 12.0. ^{11}B NMR: 24.38 s (B8), 6.31 (B8′)(142)[2.92], 0.42 (B10′)(139)[2.925], −2.59 (B10)(139)[2.697], −4.97 (B4′, 7′)(139)[2.736], −6.72 (B9, 12, 9′,12′)(135)[2.128, 1.820], −9.12 (B4, 7)(139)[2.910], −17.27 (B5′, 11′)(142)[1.623], −20.25 (B5, 11)(157)[1.573], −22.41 (B6′)(144)[1.666], −28.70 (B6)(150)[1.465]. ^{1}H NMR: 8.428 br s (2H, NH_2), 8.009 m (1H, Ar), 7.634 m (2H, Ar), 7.475 m (2H, Ar), 4.63 m (2H, Ph-CH_2-N), 3.953 s (2H, $CH_{carb.}$), 3.933 s (2H, $CH_{carb.}$), 3.740 m (4H, CH_2-O), 3.638 m (2H, O-CH_2-CH_2-N), 3.485 m (2H, O-CH_2).

General synthetic procedure for CMPO substituted compounds 3b–5b

The respective zwitterionic derivatives **3a**–**5a** were dried under vacuum at 60 °C for 12 h. Then 4 mmol of each derivative was dissolved in THF (25 ml), NaH (9 mmol) was added, and the resulting slurry was stirred at room temperature for 2 h. Then the nitrophenyl ester of diphenylphosphoryl acetic acid (6 mmol) in THF was dropwise added during 30 min, the contents of the reaction flask were heated up to 60 °C and kept at this temperature until the spot of starting species persisted on TLC. After cooling down, ethanol (10 ml) was carefully added followed by water (20 ml). Solvents were vacuum evaporated almost to dryness and the residue was dissolved in toluene (50 ml) and washed twice with cold (0 °C) 10% aqueous $NaHCO_3$ (30 ml) followed with water (five times 30 ml). After addition of water (10 ml) toluene was evaporated to dryness. The residue was dissolved in a chloroform–acetonitrile solvent mixture (3:1) and the products were purified by flash chromatography on a silica gel column using the same mobile phase for elution. After evaporation of the respective

Table 1 Selected bond lengths [Å] and angles [°] for **5b**

La(1)–O(2A)	2.470(5)	La(1)–O(1C)	2.513(5)
La(1)–O(2C)	2.496(5)	La(1)–O(1A)	2.515(6)
La(1)–O(2B)	2.508(5)	La(1)–O(1B)	2.538(5)
La(1)–O(3W)	2.562(5)	La(1)–O(1W)	2.595(5)
La(1)–O(2W)	2.577(5)		
O(2A)–La(1)–O(2C)	78.07(18)	O(1C)–La(1)–O(3W)	67.19(17)
O(2A)–La(1)–O(2B)	84.98(17)	O(1A)–La(1)–O(3W)	69.44(17)
O(2C)–La(1)–O(2B)	79.52(17)	O(1B)–La(1)–O(3W)	133.97(18)
O(2A)–La(1)–O(1C)	66.88(17)	O(2A)–La(1)–O(2W)	132.72(18)
O(2C)–La(1)–O(1C)	68.30(16)	O(2C)–La(1)–O(2W)	143.61(18)
O(2B)–La(1)–O(1C)	140.50(17)	O(2B)–La(1)–O(2W)	84.19(17)
O(2A)–La(1)–O(1A)	68.20(17)	O(1C)–La(1)–O(2W)	135.26(18)
O(2C)–La(1)–O(1A)	135.12(17)	O(1A)–La(1)–O(2W)	64.92(17)
O(2B)–La(1)–O(1A)	69.11(17)	O(1B)–La(1)–O(2W)	70.98(18)
O(1C)–La(1)–O(1A)	119.85(17)	O(3W)–La(1)–O(2W)	75.65(18)
O(2A)–La(1)–O(1B)	143.16(18)	O(2A)–La(1)–O(1W)	137.76(17)
O(2C)–La(1)–O(1B)	72.77(17)	O(2C)–La(1)–O(1W)	89.70(17)
O(2B)–La(1)–O(1B)	68.14(16)	O(2B)–La(1)–O(1W)	132.73(17)
O(1C)–La(1)–O(1B)	119.83(17)	O(1C)–La(1)–O(1W)	71.01(17)
O(1A)–La(1)–O(1B)	120.20(17)	O(1A)–La(1)–O(1W)	135.18(17)
O(2A)–La(1)–O(3W)	82.83(19)	O(1B)–La(1)–O(1W)	64.71(16)
O(2C)–La(1)–O(3W)	135.43(17)	O(3W)–La(1)–O(1W)	78.11(17)
O(2B)–La(1)–O(3W)	138.42(17)	O(2W)–La(1)–O(1W)	77.88(17)

fractions to dryness orange powders resulted. Purity of the fractions was controlled by analytical HPLC. Alternatively, instead of using LC, the compounds can be purified by dissolution in the minimum amount of hot aqueous 50% ethanol and precipitated by addition of excess of $CaCl_2$ in water. After cooling down the orange powders are filtered, washed with water and dried. Larger samples of the respective calcium salts (2–15 g) were tested at NRI Řež. For the yields based on the respective amino derivatives **3a**–**5a**, TLC R_F values, HPLC k', NMR chemical and other properties see data collected below.

3b. Terminal group: ($Ph_2P(O)CH_2(CO)NC_4H_9$-), yield 95%; M.p. 126–128 °C; MS m/z: 729.1 (727.1, 100%); TLC R_F ($CHCl_3$:CH_3CN 3:1): 0.41; HPLC k'(58% aqueous CH_3CN, 3 mmol hexylamine acetate): 6.98. ^{11}B NMR: 23.56 s (B8), 4.95 (B8′)(127)[2.97], 0.34 (B10′)(146)[2.78], −2.59 (B10)(142)[2.745], −4.44 (B4′, 7′)(157)[2.695], −7.17 d, −8.01d (B4, 7, 9, 12, 9′, 12′)(150, overlap)[2.40, 1.896, 2.951], −17.35 (B5′, 11′)(158)[1.632], −20.25 (B5, 11)(154)[1.535], −22.22 (B6′)(144)[1.572], −28.41 (B6)(139)[1.421]. ^{1}H NMR: 7.872 m (4H, Ar), 7.548 m (2H, Ar), 7.659 m (4H, Ar), 4.32 d (2H, CH_2-P), 4.19 s (4H, $CH_{carb.}$), 3.609 m (4H, CH_2-O), 3,582 m (2H, CH_2-O), 3,413 m (2H, O-CH_2-CH_2-N), 3.48 m (2H, CH_2-N), 2.859 s (H_2O), 1.354 m (2H, CH_2-CH_2-N), 0.99 m (2H, CH_2), 0.84 m (16H, CH_2), 0.667 t (3H, CH_3).^{31}P NMR: 35.09. IR spectra (ν/cm^{-1}): 510 s, 731 s, 843 w, 967 m, 1178 s, 1452 s, 1476 s, 1575 s, 1601 s, 1708 m, 2526 s (B–H), 2920 vs, 3400 m.

4b. Terminal group: ($Ph_2P(O)CH_2(CO)NC_{12}H_{25}$-), yield 91%; M.p. 76–78 °C; MS m/z: 841.6; TLC R_F ($CHCl_3$:CH_3CN 3:1): 0.46, HPLC k'(70% aqueous CH_3CN, 3 mmol hexylamine acetate): 6.01. ^{11}B NMR: 23.37 s (B8), 6.05 (B8′)(127)[2.97], 0.84 (B10′)(146)[2.78], −2.42 (B10)(142)[2.745], −4.58 (B4′, 7′)(157)[2.695], −6.60, −7.41 d (B9, 12, 9′, 12′)(150, overlap)[2.40, 1.896], −8.54 (B4, 7)(177)[2.951], −17.08 (B5′, 11′)(158)[1.632], −20.18 (B5, 11)(154)[1.535], −22.05 (B6′)(144)[1.572], −28.26 (B6)(139)[1.421]. ^{1}H NMR: 7.963 d (4H, Ar), 7.757 d (2H, Ar), 7.659 m (4H, Ar), 4.540 d (2H, CH_2-P), 4.114 s (4H, $CH_{carb.}$), 3.741 m (4H, CH_2-O), 3,61 m (2H, CH_2-O), 3,592m (2H, O-CH_2-CH_2-N), 3.394 m (2H, CH_2-N), 1.660 m (2H, CH_2-CH_2-N), 1.520 m (2H, CH_2), 1.284 m (16H, CH_2), 0.885 t (3H, CH_3). ^{31}P NMR: 44.37. IR spectra (ν/cm^{-1}): 510 m, 718 m, 741 m, 975 m, 1118 s, 1175 m, 1452 s, 1476 s, 1588 m, 1608 m, 1708 w, 2525 s (B–H), 2920 vs, 3400 w.

5b. Terminal group: ($Ph_2P(O)CH_2(CO)NCH_2C_6H_5$-), yield 82%; M.p. 253–255 °C; MS m/z: 763.0 (761.0, 100%); TLC R_F ($CHCl_3$:CH_3CN 3:1): 0.39, HPLC k'(58% aqueous CH_3CN, 3 mmol hexylamine acetate): 7.10. ^{11}B NMR: 23.37 s (B8), 4.68 (B8′)(142)[3.367], 0.36 (B10′)(146)[2.921], −2.57 (B10)(146)[2.753], −4.46 (B4′, 7′)(150)[2.714], −7.22, −8.62 (B4, 7, 9, 12, 9′, 12′)(142)(138)[2.184, 1.922, 2.90], −17.30 (B5′, 11′)(154)[1.584], −20.30 (B5, 11)(157)[1.584], −22.17 (B6′)(153)[1.632], −28.60 (B6)(140)[1.478]. ^{1}H NMR: 7.909 m (4H, Ar), 7.858 m (1H, Ar), 7.617 m (2H, Ar), 7.548 m (4H, Ar), 7.224 m (4H, Ar), 4.706 br.s (2H, N-CH_2-Ph), 4.23 s (2H, $CH_{carb.}$), 4.168 s (2H, $CH_{carb.}$), 4.031 d (2H, CH_2-P(O)), 3.604 m (2H, CH_2-O), 3,61 m (2H, CH_2-O), 3.385 m (2H, O-CH_2-CH_2-N), 3.415 m (2H, CH_2-N), 2.443 s (2H, H_2O). ^{31}P NMR: 30.37. IR spectra (ν/cm^{-1}): 520 m, 720 s, 732 s, 843 w, 1102 m, 1116 m, 1180 m, 1210 m, 1452 m, 1476 s, 1597 s, 2527 s (B–H), 2920 vs, 3400 w.

The lanthanum complex of **5b** was precipitated upon dissolution of the above sodium salt in aqueous 60% ethanol and addition of the equimolar quantity of $La(NO_3)_3$ dissolved in 0.5 M HNO_3. The precipitate was filtered, rinsed three times with water and dried. Then 20 mg of the salt was dissolved in a test tube in a small quantity of aqueous acetone (70%) and overlayered with benzene. Small yellow-orange crystals were obtained upon standing for several days, solvent was decanted and crystals were used for X-ray crystallography.

Results and discussion

Synthesis and properties of the CMPO substituted cobalt bis(dicarbollides) 3b–5b

Preliminary synthetic attempts were based on the direct use of the recently reported reliable method, *i.e.* dioxane-ring cleavage of the bi-polar species **2**,[28] producing B(8) substituted

Table 2 Distribution coefficients of different lanthanides for organic $(Ph)_2$CMPO (0.25 M)and OcPhCMPO (0.25 M) in NPHE (nitrophenyl hexyl ether) as a function of acidity

	$(Ph)_2$CMPO (0.25 M)						OcPhCMPO (0.25 M)					
$[HNO_3]$/M:	0.01	0.1	1	2	3	4	0.01	0.1	1	2	3	4
La	0.18	0.37	21	33	27	15.6	1.3	12	63	48	51	38
Ce	0.17	0.40	23	37	31	19	0.9	9.1	14	11	13	12
Nd	0.14	0.46	17.6	27	24	16	2.2	22	> 100	> 100	100	75
Eu	0.12	0.15	10.2	16.7	17.1	14	1.6	15	> 100	> 100	90	75
Dy	0.09	0.03	3.1	6.8	10	11.4	0.5	3	40	37	49	24
Ho	$< 10^{-2}$	$< 10^{-2}$	1.5	4.0	6.9	10	0.4	1.6	24	23	32	16
Yb	0.07	< 0.1	0.34	1.45	4. 5	7.6	0.3	0.3	7.2	7.3	13	9.1
Lu	$< 10^{-2}$	$< 10^{-2}$	0.18	0.92	2.65	4.75	0.3	0.2	5.3	5.2	9.5	6.6

Table 3 Distribution coefficients of Eu^{3+} obtained for OcPhCMPO (10^{-2} M) and a mixture containing OcPhCMPO (10^{-2} M) and brominated cobalt bis(dicarbollide) (10^{-2} M) in NPHE as a function of acidity

$[HNO_3]$/ M	OcPhCMPO (10^{-2} M)	OcPhCMPO (10^{-2} M) + Br_6-cobalt bis(dicarbollide) (10^{-2} M)
0.01	$< 10^{-3}$	> 100
0.1	0.011	100
1	0.19	55
2	0.18	15
3	0.10	7

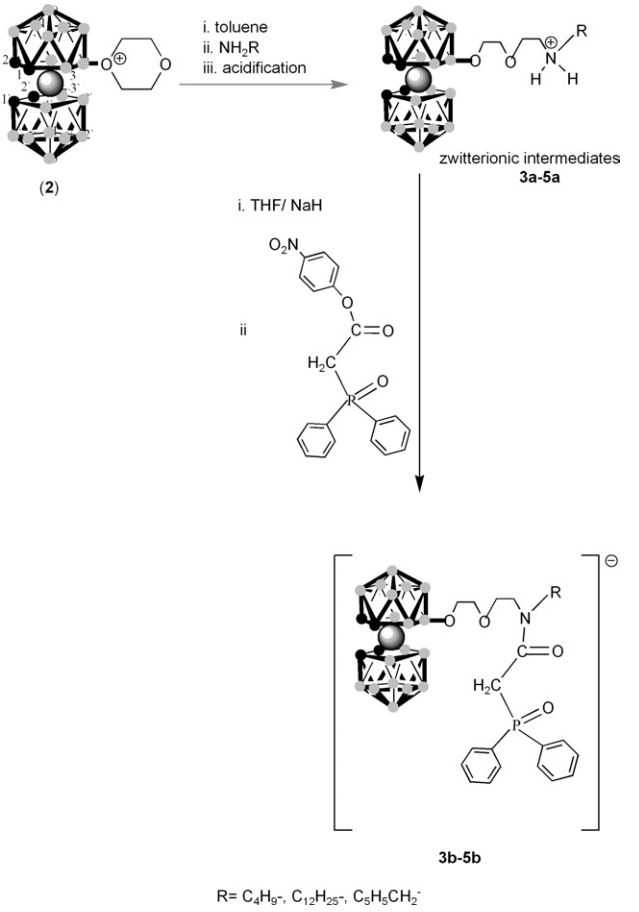
compounds in high yields. As has been already described, the dioxane ring of this compound, containing an oxonium oxygen atom, can be easily opened by almost any nucleophile X^- (phenolate, dialkyl- or diaryl-phosphite)[24] producing the respective functionalised anionic species. On the other hand, in this particular case, the direct reaction of *N*-alkylcarbamoyldiphenylphosphine oxides deprotonated *in situ* by NaH in THF as solvent failed. The reaction led to mixtures of at least two or three anionic species. The observed difficulties apparently arose from the simultaneous presence of several reactive sites in the CMPO molecule (*i.e.* RNH group, the acidic CH_2 group or HO–C moiety (due to possible tautomerism)). As a consequence, several bonding modes of the selective groups resulted. The pure anionic species were successively isolated from complex reaction mixtures using chromatography. Despite high extraction coefficients observed for most of such samples, this procedure had to be abandoned due to its poor reproducibility and low yields.

Finally, a more effective, two step synthetic procedure was developed (see Scheme 1). In the first step, the species **2** was treated with the primary amine in dilution. This reaction led to diethylene glycol spacer bonded bi-polar species with secondary amino derivatives **3a**–**5a**. These compounds, deprotonated by NaH, were subsequently reacted with the reactive *p*-nitrophenyl ester of diphenylphosphoryl acetic acid.[8] The products, bonded exclusively *via* the amidic nitrogen atom, were obtained in high yields and purity (see Experimental). The three resulting species **3b** to **5b** differ in the alkyl or aryl substituent at the nitrogen atom of the CMPO group.

The solubility of the Na^+ salts of all species **3b**–**5b** in some low polar solvents (benzene, toluene) was substantially enhanced in respect to the cobalt bis(dicarbollide) parent species **1** and its chlorinated derivatives.[11] This is very important for the possible application of the compounds as selective extractants. Boron atom substitution provides the direct blocking of the most reactive skeletal site B(8). Also some steric protection of the second (B(8′)–H) position can be expected. This may account for the observed reasonable stability of compounds **3b**–**5b** in strongly acidic and basic solutions (for details see extraction part below).

NMR and X-ray diffraction results

^{11}B NMR spectra of all zwitterionic species **3a**–**5a** and anions **3b**–**5b** are almost identical and closely resemble those of the previously published series of similar compounds with phenolic and phosphonic substituents.[24a] Only in the spectrum of anion **5b**, some signals are slightly shifted. Also the B–H signals could be assigned based on the $^1H\{^{11}B_{selective}\}$ NMR spectra of all compounds in the series, despite the complexity of the spectra. The spectral patterns and intensities in ^1H NMR spectra correspond to the presence of one particular selective group per cage. For peak assignment see Experimental. Compounds **3b**–**5b** exhibit one peak in the $^{31}P\{^1H\}$ spectra at 35.08 (**3b**), 49.06 (**4b**) and 30.12 (**5b**) ppm, respectively.



Scheme 1 Two-step reaction path leading to successful N-bonding of the CMPO moiety to the B(8) position of the cobalt bis(dicarbollide)s.

The mass spectra of all compounds were obtained using two different ionisation techniques: MALDI TOF and electrospray ionisation techniques (see Experimental). The mass spectrometric results are in clear agreement with the composition of all compounds **3a**–**5a** and **3b**–**5b** under study.

The molecular structure of the Ln^{3+} complex of anion **5b** (see Fig. 2) proved that the Ln^{3+} cation is nine coordinated and is surrounded with three ligating anions **5b**. The selective CMPO parts of three anionic ligands **5b** participate in the coordination, each by one (P=O) and (C=O) donating group, forming thus three six membered chelate rings. The coordination number to nine is completed by coordination of three molecules of water in a tri-capped trigonal prismatic arrangement. Oxygen atoms from the diethylene glycol spacer are not involved in the primary coordination sphere of the cation, but interact with three molecules of water by hydrogen bond formation. The distances of Ln^{3+} to coordinated oxygen atoms form three distinct groups (La–O=P) 2.470(5)–2.508(5); (La–O=C) 2.513(5)–2.538(5) and La–O–water 2.562(5)–2.595(5) Å. For more detailed information see the selected inter-atomic distances and angles reported in Table 1. The metal cation is encapsulated inside the polar cavity formed by (P=O), (C=O) NR_2 moieties and ethylene glycol O atoms. The latter two moieties, however, do not participate in the metal binding. The outer sphere of the complex is composed of phenyl rings closer to the metal and the surface of cobalt bis(dicarbollide) cages. The complex stoichiometry 1:3 agrees with the full compensation of the cationic charge and seems exceptional in the series of the simple bi-dentate CMPO ligands. (On the other hand, at high nitric acid concentration the metal to ligand ratio is probably close to the typical value of 1:2; for details see the extraction part.) The geometric parameters of the cobalt bis(dicarbollide) cluster fall within the usual range.

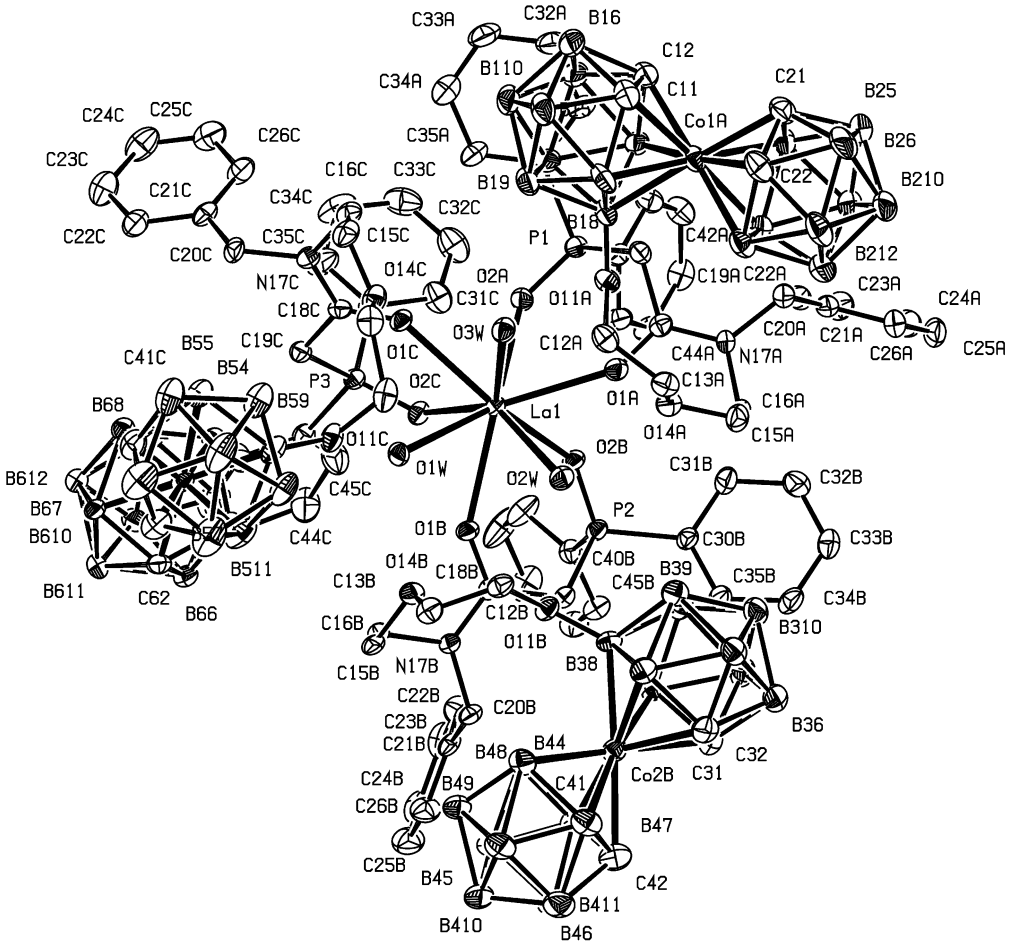


Fig. 2 Molecular structure of **5b** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms, solvating 0.5 CH_2Cl_2 and C_6H_6 molecules were omitted for clarity.

Extraction results

The cobalt bis(dicarbollide)s behave similarly as cation exchangers. In contact with an aqueous phase their extraction efficiency decreases with increasing proton concentration and valence of the cation:

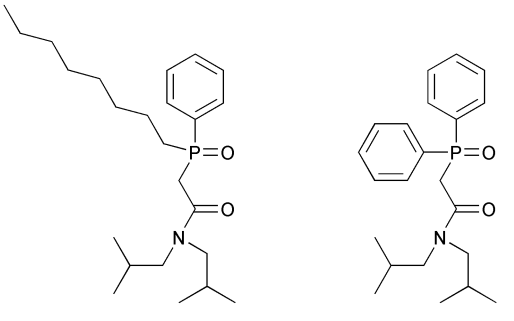
$$M^{n+}{}_{aq} + nH^+CoB_2{}^-{}_{org} \Leftrightarrow nH^+{}_{aq} + M^{n+}{}_{org},\ n\,CoB_2{}^-{}_{org}$$

$$D_{M^{n+}} = K_{eq}\frac{[H^+CoB_2{}^-]^n}{[H^+]^n}$$

In order to circumvent this acidity effect on the cobalt bis(dicarbollide) systems, addition of the synergic agents like phosphine oxides or CMPO compounds is necessary for M^{3+} extraction. This might result in a suitable extraction system for hard cations such as lanthanides and, eventually, actinides. Alternatively, extractant combining CMPO and cobalt bis(dicarbollide) in one large molecule has to be considered. A comparative study of the extraction properties of organic CMPO molecules and their simple synergic mixtures with cobalt bis(dicarbollide)s with the anionic ligands **3b**–**5b**, where the CMPO moiety is attached to the boron cage by a covalent bond, is presented below.

The TRUEX process[3–7] uses (*N*,*N*-diisobutylcarbamoylmethyl)octylphenylphosphine oxide (OcPhCMPO, see Fig. 3a). More recently, also (*N*,*N*-diisobutylcarbamoylmethyl)diphenylphosphine oxide ($(Ph)_2$CMPO, see Fig. 3b) was extensively studied by Russian teams.[36] The presence of one phenyl ring on the phosphorus atom plays an important role in the selectivity of organic CMPO extractants for particular lanthanide ions (see Table 2). On the other hand, the character of the amidic nitrogen substituent seems not be decisive in this point.

Organic CMPO extractants and their synergic mixtures. Using $(Ph)_2$CMPO and OcPhCMPO, high distribution coefficients have been achieved for the lightest lanthanides and neodymium or europium, respectively, but only if these extraction agents were used in high concentrations (0.25 M) (see Table 2). A decrease of the distribution coefficients was observed for the heaviest lanthanides. Cerium showed a different behaviour, because (due to ageing) some of the Ce(III) was oxidized to Ce(IV). At low concentration (10^{-2} M) in NPHE, CMPO



a) OcPhCMPO *b) Ph_2CMPO*

Fig. 3 Schematic drawings of the structures of organic diphenyl-CMPO and octylphenyl-CMPO designed for use in extraction of lanthanides and actinides.[3–5,36,37]

Table 4 The dependence on the nitric acid concentration of Eu extraction by **3b** and **4b** in different solvents[a]

	3b		**4b**		
$[HNO_3]$/M	Nitro-benzene	Dichloro-ethane	Toluene	Cumene[b]	Dichloro-ethane
0.2	—	1810	1392	1158	3976
0.5	330	1730	1323	695	2339
0.8	—	1250	1290	435	1967
1.0	259	604	974	263	1433
1.5	—	288	953	233	663
2.0	73.3	115	474	16.9	260
2.5	—	60.5	234	6.86	114
3.0	21.2	34.2	120	2.80	54.4
4.0	6.95	9.33	35.0	0.98	15.2
5.0	2.45	2.95	12.1	0.47	4.42
8.0	0.165	—	—	—	—

[a] 0.01 M extractant in the given solvent. [b] Extractant not fully dissolved.

displayed low extraction efficiency. The synergic addition of bromine protected cobalt bis(dicarbollide) of the same concentration strongly enhanced the extraction (Table 3).

Chemically bonded compounds 3b–5b. Three novel CMPO-like compounds **3b–5b** are in general very efficient extractants of trivalent lanthanides and actinides, even from strongly acidic media, since for the 4 M nitric acid concentration 95% of the nuclides were extracted (see Tables 4 and 5). The same is valid for standard waste solution (SWS; 1 M $HNO_3 + 4$ M $NaNO_3$). This fact can be exemplified by comparison of the D_{Eu} distribution ratios of **3b** for extraction from 4 M HNO_3 (6.95) with that from SWS (99.6). These data clearly evidence the higher robustness of the extractant towards high concentrations of sodium cations, with respect to that of protons. Other fission products, with the exception of lanthanides and actinides, were practically not extracted under the conditions of effective Eu extraction. The dependence of Sr extraction on extractant concentration exhibits a slope of 1.20 which would indicate the formation of $[Sr(\mathbf{3b})]^{+}$ species in the organic phase (with D_{Sr} less than 10^{-1} for 0.1 M extractant).

Very high distribution ratios indicate the possibility of use of these extractants for technological separations of lanthanides and actinides from the acidic HLLW, especially those containing large amounts of sodium.

The behaviour of **3b** and **4b** is very similar. The substitution of the alkyl chain by a benzyl ring in **5b** leads to a slight decrease of the distribution coefficients. On the other hand, for all three compounds, the selectivity for americium *versus* europium is not significant.

The influence of acidity on Eu extraction by **3b** and **4b** into different solvents is shown in Tables 4–6. It can be seen that, even in the case of extreme stability of the tested extractants

Table 5 Distribution coefficients of europium and americium for **3b–5b** (10^{-2} M) in NPHE as a function of acidity

		$[HNO_3]$/M						
Extractant in NPHE		10^{-3}	10^{-2}	10^{-1}	1	2	3	4
3b	D_{Eu}	>100	>100	>100	>100	>100	73	18
	D_{Am}	>100	>100	>100	>100	96	68	16
4b	D_{Eu}	>100	>100	>100	>100	>100	66	23
	D_{Am}	>100	>100	>100	>100	>100	61	21
5b	D_{Eu}	>100	>100	>100	>100	58	53	18
	D_{Am}	>100	>100	>100	>100	55	42	16

Table 6 The dependence of Eu extraction on extractant **3b** concentration (in nitrobenzene) at different HNO_3 concentrations

	$[HNO_3]$/M			
[Extractant]/M	0.5	1.0	2.0	3.0
0.0001	0.0315	0.0063	—	—
0.0003	0.463	0.0615	—	—
0.0005	2.05	0.200	—	—
0.0008	2.49	0.787	—	—
0.001	13.2	1.84	0.164	0.0691
0.003	183	23.9	2.68	0.731
0.005	238	114	11.6	3.64
0.008	—	211	40.9	11.6
0.010	—	263	73.8	19.4

in nitric acid, back-extraction using high acid concentrations would not be practically possible.

From Fig. 4 it can be clearly seen that the extraction coefficients for **3b** sharply rise with concentration of the extractant in the organic phase. The compound is very efficient in extracting europium from nitric acid up to considerably high concentrations. The given dependences of D_{Eu} on **3b** concentration represent straight lines with consecutive slopes 2.14, 2.43, 2.66 and 2.29 (with correlation factors near $R^2 = 0.99$) for nitric acid concentrations 0.5 M, 1.0 M, 2.0 M and 3.0 M, respectively. This indicates rather a formation of extracted moiety $[Eu{\cdot}\mathbf{3b}_2]^{+}$ in the organic phase than the complex with the expected stoichiometry 1:3. The presumed extraction mechanism can be written as:

$$Eu^{3+}{}_{aq} + 3[\mathbf{3b}]^{-}{}_{org} = [Eu(\mathbf{3b})_2]^{+}{}_{org} + [\mathbf{3b}]^{-}{}_{org}$$

The extraction of Eu^{3+} macroquantities by **4b** in toluene and 1,2-dichloroethane is illustrated by the results in Table 7. From the inspection of the values of distribution ratios it follows that there is an important change and a steep decrease in distribution ratios in the range of theoretical saturation of the organic phase. For an excess of Eu^{3+} ions present in the system, the composition of the extracted species changes, in respect of a lower number of associated extractant moieties from $[Eu(\mathbf{4b})_3]$ to $[Eu(\mathbf{4b})_2]^{+}$, as mentioned above. Nevertheless, it can be seen that even the high concentrations of nitric acid (up to 3 M) do not prevent the full saturation of the organic phase.

The very high distribution ratios for Eu imposed the question: could any back-extraction be accomplished? The use of high concentrations of nitric acid (8–10 M) has had to be

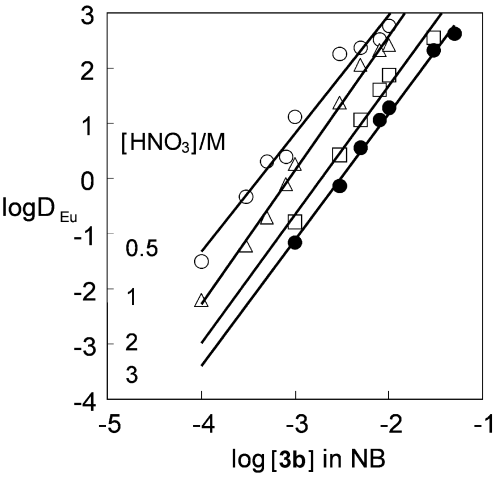


Fig. 4 Extraction of microamounts of Eu^{3+} by **3b** into nitrobenzene at various aqueous acidities.

Table 7 Extraction of Eu macroquantities with **4b** (0.01 M from 3 M HNO_3) into toluene and dichloroethane

	D_{Eu}		c^{Eu}_{org}	
[Eu]/M	Toluene	Dichloroethane	Toluene	Dichloroethane
0	126	54.0	—	—
1×10^{-4}	106	53.8	9.91×10^{-5}	9.82×10^{-5}
3×10^{-4}	100	43.7	2.97×10^{-4}	2.93×10^{-4}
5×10^{-4}	99.2	32.6	4.95×10^{-4}	4.85×10^{-4}
8×10^{-4}	95.1	28.6	7.92×10^{-4}	7.73×10^{-4}
1×10^{-3}	82.7	24.5	9.88×10^{-4}	9.61×10^{-4}
3×10^{-3}	18.8	8.45	2.85×10^{-3}	2.68×10^{-3}
5×10^{-3}	2.06	1.47	3.37×10^{-3}	2.98×10^{-3}
8×10^{-3}	0.811	0.788	3.58×10^{-3}	3.52×10^{-3}
1×10^{-2}	0.608	0.533	3.78×10^{-3}	3.48×10^{-3}

Table 9 Tests of chemical stability of **3b** (0.01 M in nitrobenzene); D_{Eu} values obtained upon contact with nitric acid and sodium hydroxide

Time/days	3 M HNO_3	8 M HNO_3	1 M NaOH
0	20.5	20.5	20.5
1	19.2	21.9	21.2
4	18.1	3.43	19.8
7	18.7	1.70	18.9
14	18.3	0.959	19.5
28	18.2	0.834	19.3
42	12.7	0.523	19.6
49	11.0	0.500	19.0
56	10.3	0.483	18.5
63	8.80	0.418	16.6
71	7.68	0.380	15.2

excluded, due to a notable destruction of extractant in such an oxidizing medium. Thus other possible options were tested. The results of back-extraction studies are given in two parts of Table 8. The first part of this table shows that none of the most used complexing agents was fully successful in back-extracting Eu from the organic phase, including DTPA (diethylenetriamine pentaacetic acid) used alone. This indicates the very high complexing ability of the extractant. The last rows of this table indicate that practical back-extraction is possible using mixtures of inorganic salts and DTPA, the mixtures with ammonium phosphate and oxalate being the most effective. The later back-extracting mixture brings also advantages for incinerability during the final immobilization by a vitrification process. In the case of this back-extraction agent, the organic phase was not affected by the extraction cycle and the extraction ability was fully recovered after the back-extraction step. In some instances, even higher distribution factors were obtained in the second than in the first extraction step. This may be probably explained by the assumption that, due to the strong chelating effect of these ligands, the calcium cation present in some synthetic samples was not completely removed even after acid washings with strong HNO_3.

The main factor governing the extractant use is its solubility in suitable solvents. Good solubility of **3b**–**5b** was observed in benzene, toluene and more polar solvents like nitrobenzene, 1,2-dichloroethane and NPOE (nitrophenyl octyl ether). Though 0.01 M solutions can be prepared in toluene, significantly lower solubility in other aromatic solvents, like xylene and cumene, was surprisingly observed.

An important criterion of extractants applicability is their chemical stability. The results of tests of **3b** stability in solutions of nitric acid and sodium hydroxide are presented in Table 9. The organic solutions were in continuous contact with the respective solution (one hour of shaking each day), a portion of the organic phase was washed by 3 M nitric acid and the extractant stability was verified by Eu extraction from 3 M nitric acid. The results indicate that the extractant is fairly stable in 3 M HNO_3 (28 days) and in 1 M NaOH (71 days). For 8 M HNO_3, however, the extractant decomposition starts approximately between 1 and 4 days. On the other hand, it should be noted that the tested 3 M nitric acid concentration lies above the concentration range present in most HLLW (usually approx. 1 M HNO_3).

Table 8 Eu back-extraction from the organic phase by 0.01 M ligand **3b** in toluene

Composition of the aqueous phase	D_{Eu}[a]
0.5 M Na_4EDTA	879
0.1 M tert. NH_4 citrate	6.90
0.1 M prim. Na citrate	350
0.1 M tert. Na citrate	44.8
0.1 M citric acid	2565
0.1 M oxalic acid	1802
5% Na_5DTPA	2.03
0.1 M tert. ammonium phosphate	12.2
0.1 M tert. ammonium phosphate + 5% Na_5DTPA	0.027
0.1 M prim. ammonium oxalate	0.824
0.1 M prim. ammonium oxalate + 5% Na_5DTPA	0.030
0.1 M urea nitrate	86.7
0.1 M urea nitrate + 5% Na_5DTPA	0.108

[a] D_{Eu} before the extraction step = 532.

Conclusions of extraction tests. The novel anionic CMPO-like extractants for M^{3+} elements proved to have extremely high extraction efficiency even from solutions of high acidity, about four orders of magnitude better than conventional CMPO compounds, and even better than their synergic mixtures with cobalt bis(dicarbollide)s. Eu can be effectively back-extracted from the organic phase using mixtures of inorganic salts with the complexing agent DTPA. The chemical stability of tested extractants is, with the exception of highly concentrated nitric acid solutions (8 M), reasonably good both for acidic and basic media. The extractants exhibit very favourable separation factors for sodium (D_{Eu}/D_{Na}) so that Eu can be effectively separated from waste solutions with high sodium content. On the other hand, the selectivity Eu/Am is low, therefore a possible use of such compounds may consist of the removal of the whole M^{3+} class of cations from highly acidic waste before the pertinent second step, *i.e.* the separation of the respective nuclides by another process, *e.g.* "SANEX",[2] which in turn cannot be applied at high HNO_3 concentrations.

The above mentioned positive results imply the possibility that this class of compounds may be applicable in a technological process.

As can be seen from the extraction results, the nitrogen atom substitution can play a role in tailoring the extraction properties. The presence of large alkyl groups on nitrogen brings improvement in extraction properties, probably due to increased solubility. In addition, further improvement of the extraction properties can be anticipated from the interplay with the substituents on the phosphorus atom. The diphenylphosphine oxide end of the CMPO moiety remains still not optimised. Phosphorus substitution is known from the literature[3–5] to bring the main selectivity properties of the "classical" organic CMPO derivatives (see also data in Table 2). Therefore, further improvements can be expected from a more detailed study of the N and P substitution. Probably, the overall stability in the acidic range might appreciably increase[11] on protection of the most reactive B(8′) cage position by a suitable substituent.

Conclusions

The covalent N-bonding of the CMPO moiety to the cobalt bis(dicarbollide) sub-cluster has been achieved *via* a reliable and reproducible two-step procedure, starting from compound **2**. Preparative procedures provided good yields and purity and can be scaled up without problems; therefore the compounds **3b**–**5b** can be available even in large scale. The X-ray crystallography results obtained on the lanthanum complex of anion **5b** indicate the tight cation bonding inside the inner polar cavity enveloped with an outer hydrophobic sphere. The metal to ligand 1:3 supramolecular complex is fully charge compensated.

The extraction results argue for the markedly positive effect of covalent bonding of the selective sequestering CMPO group on the cobalt bis(dicarbollide) cage. New compounds proved significantly better Eu extraction efficiency than organic CMPO alone or synergic mixtures of hexabrominated bis(dicarbollide) anion and CMPO. Comparing the extraction coefficients, compounds **3b**–**5b** seem to resemble the recently reported polydentate extractants based on calixarenes substituted with CMPO groups.[8,37]

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