

## NEW EXTRACTANTS FOR PARTITIONING OF FISSION PRODUCTS

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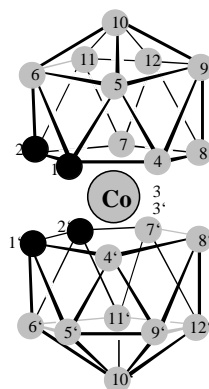
### Abstract

New progress made in the field of dicarbollide [*closo-commo*-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>-3Co)]<sup>-</sup> (COSANs) based extractants for partitioning of fission product from spent nuclear fuel, especially Sr<sup>2+</sup> and actinides, made during past years in the Czech Republic, are described in the paper. The synthetic methods for two classes of new extraction agents containing in the molecule either hydrophobic arylene bridge substituents or metal selective groups with donor atoms able to co-ordinate polyvalent cations have been developed. The structures of the recently prepared extraction reagents are presented, along with ideas on which syntheses were based and the basic relations between structures and extraction properties of the compounds.

## 1. Introduction

Extraction process for removal of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  from radioactive waste, based on cobaltadiborane anion [*closo-commo*-(1,2- $\text{C}_2\text{B}_9\text{H}_{11}$ ) $_2$ -3Co] $^-$  (COSANs) (see Figure 1) derivatives as extractants, was designed by IIC ASCR and NURI Re in 1972 and further developed during subsequent decade [1-4]. The parent COSAN was later chlorinated in order to protect positions B(8) and B(8') of the cage toward oxidation. The hexachloroderivative, [(8,9,12- $\text{Cl}_3$ - $\text{C}_2\text{B}_9\text{H}_8$ ) $_2$ -3-Co] $^-$  COSAN was found appreciably more stable towards  $\text{HNO}_3$ , radiation, and even more hydrophobic than the parent compound. Drawback of chlorinated COSANs based process lies, however in the use of polar and environmentally dangerous solvents i.e. nitrobenzene, or halogenated hydrocarbons. Presently, there is a co-operative research on this technology between USA and Russia, but details in the open literature are scarce [5]. In Russia, a plant based on a modified process based on Russian-Czech Patent [6] was launched in autumn 1996.

Figure 1. Schematic structure of the parent [*closo-commo*-(1,2- $\text{C}_2\text{B}_9\text{H}_{11}$ ) $_2$ -3Co] $^-$  (COSAN) anion (for clarity, terminal hydrogen atoms are omitted)



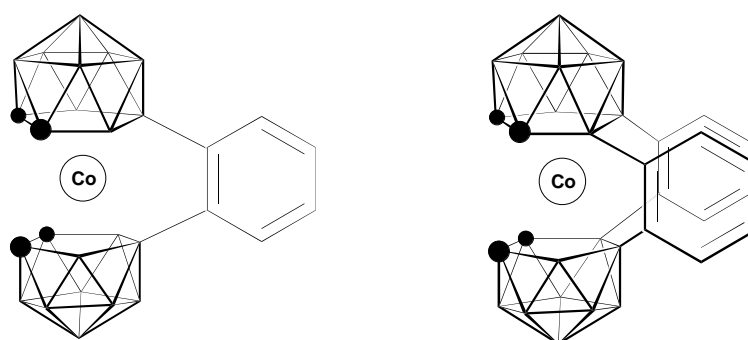
The targets of the recent and current investigations proceeding under framework of two INCO-Copernicus EEC Projects [7] have been directed to find more powerful extractants effective also for actinides and to minimise environmental risks, i.e. they should be able to meet with the EEC ecological requirements. New extractants of *closo*-borate type have been tailored with the aim to find selective reagents for individual fission products and to improve solubility of boron type extractants in solvents ecologically more acceptable than nitrobenzene, originally used in the above-mentioned dicarbollide process. Two groups of extractants were prepared starting both from sandwich skeleton of COSAN incorporating hydrophobic and selective substituents into extractant molecule.

## 2. Results and discussion

During past years, attention has been paid on the increase of the hydrophobicity of the molecules introducing arylene rings (phenyl (1), tolyl (2), ethylbenzyl (3), xylyl (4), biphenyl (5), tetraline (6), etc.) bonded in positions 8,8' of the COSAN molecule as a bridge substituents (see Figure 2, for example). Extraction experiments proved that several promising extractants were successfully prepared. The novel class of 4,8', 8,4'- $\text{R}_2$ -Bis-arylene bridged COSANs (R = Ph (7), R = tolyl (8), R = ethylphenyl (9)), and especially the basic member of the series bisphenylene-COSAN (7), exhibit extreme complexation properties for caesium cation, overcoming significantly extraction ability of dicarbollide itself and displaying enhanced solubility in aromatic solvents. Indeed, bis-bridged class

of COSAN derivatives allowed for use of aromatic solvents (toluene, xylene, etc.) in extraction, provided that some aromatic sulfo compounds were added to the organic phase as so-called “solubilizers” [7]. X-ray studies of the  $\text{Cs}^+$  complex of the anion (7) revealed, that that the angle  $72^\circ$  between planes of phenylene substituents of this species is very favourable in order  $\text{Cs}^+$  cation can be strongly captured [8]. Distribution ratio of  $\text{Cs}^+$  using above anions has been found so high, that imposes a consecutive problem of its back-extraction. This could be only accomplished using nitric acid of high concentration. On the other hand, in comparison with chlorinated COSANs, these compounds seem less stable towards oxidation effect of nitric acid. According to the preliminary extraction studies it seems that addition of urea to the extraction system would probably suppress this effect.

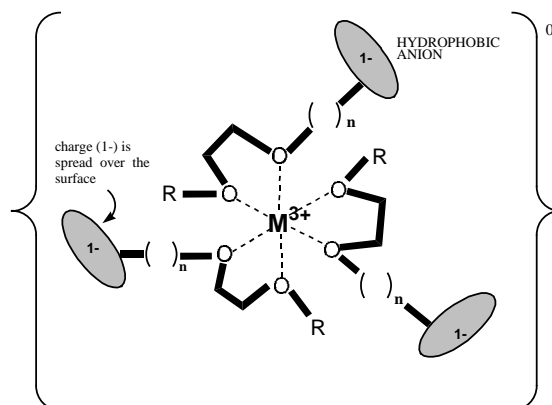
Figure 2. Schematic structures of the 8,8' phenylene – COSAN (1) and 4,8', 8,4' – bis-phenylene bridged COSAN (7)



The present study is devoted to COSAN and hydroborate based extractants containing selective groups, including phenoxy groups, linear polyethyleneglycol chains, crown ethers and phosphorus containing moieties, which should allow for selective transfer of strontium and especially  $\text{M}^{3+}$  and  $\text{M}^{4+}$  lanthanides and actinides into low polar organic phase without use of any additive.

The target syntheses are based on the idea originated from our previous experience in the synthesis and testing of a large number of borate extractants. According to our knowledge, the polyvalent cations  $\text{M}^{3+}$  and  $\text{M}^{4+}$  can be effectively extracted only provided that the anionic COSAN-based extractant amalgamates in one molecule both, hydrophobic anionic part, and a ligating selective moiety containing electron donor atoms, i.e. oxygen, phosphorus, sulphur, etc. able of tight coordination to the cation. Such functionalised anionic particles are able to build up, in solution, a multi-component “supercomplex” with the cation. Formation of the complex in the extraction system proceeds spontaneously *via* a self-assembly mechanism. Inner shell of these complexes contains encapsulated metal particle bonded to polar donor atoms, outer shell of the “supercomplexes” is composed by hydrophobic hydroborate core. The charge of the cation is then fully compensated by the inherent negative charge of several particles of the extractant, and the hydrophobic electroneutral supercomplex is pulled into organic phase. With the increasing number of hydrophobic anion particles involved in the complex, the tendency for the transport to the organic phase would increase. The validity of this principle (i.e. 3:1 complex formation for  $\text{M}^{3+}$  and its transfer to organic phase, schematically depicted on Figure 3), was confirmed by extraction results, and a recent electrochemical study [9].

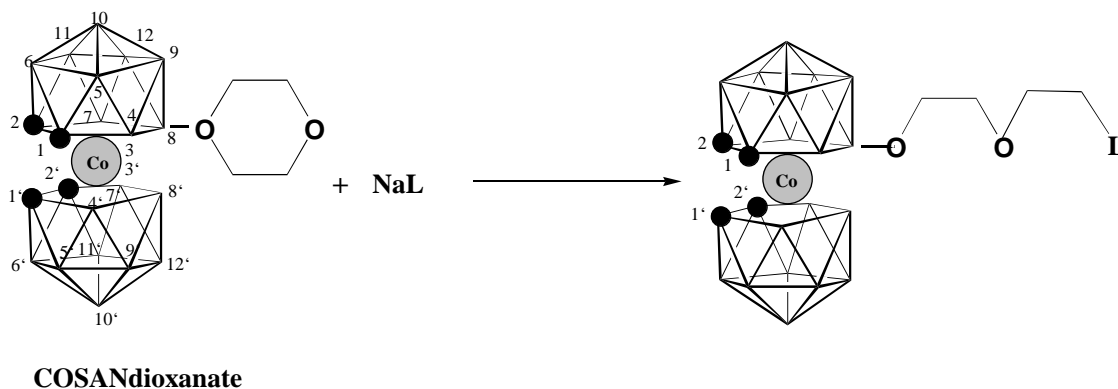
Figure 3. Schematic drawing of the complex particle formation



A significant advantage of COSAN lies also in remarkable flexibility of its possible substitution modifications by groups behaving as mono- to poly-donors.

Synthetic strategies to most of such compound have been based on 8-dioxane-COSAN (**10**) [10] derivative ring opening procedure by a suitable organic base, deprotonized *in situ* using NaH (see Figure 4). This method seems synthetically the most feasible, efficient, and high-yield way for synthesis of series of COSAN based anionic species with solvent extraction properties (SER). The series of organic terminal groups successfully attached on COSAN *via* compound **10** dioxane ring opening include: 1.t-Octylphenoxide (**11**), 3-CF<sub>3</sub>-phenoxide (Trifluorocresol) (**12**), 2-Benzylphenoxide (**13**), 2-phenylphenoxide (**13**), 2-MeO-phenoxide (Guaiacol) (**14**), [(BUO)<sub>2</sub>P = O] (**15**) and [(PhO)<sub>2</sub>P = O] (**16**) (last two as an end-group with powerful sequestering properties). Recently, also diphenylphosphine oxide moiety has been chosen for its well-known properties to act, even alone, as efficient sequestering agents for lanthanides and actinides. The species containing the Ph<sub>2</sub>P(O) (**17**) moiety as terminal group bonded on the diethyleneglycol chain was prepared *via* reaction of NaPPh<sub>2</sub> with COSDIOX and subsequent air oxidation of the zwitterionic intermediate by air. All SER of this type are capable to transfer the target ions (M<sup>3+</sup>) from aqueous solution into aromatic hydrocarbons without any other additives.

Figure 4. Schematic drawing of the general route leading to the synthesis of anionic species 11-21



On the other hand, all the above anions (**11-17**) have proved to be effective  $\text{Eu}^{3+}$  extractants only under neutral or slightly acidic conditions. No one of the investigated SER of this type seemed promising for technological application in strongly acidic medium. The unfavourable dependence on pH could be explained in terms of protonation of a strongly basic oxygen  $\text{B}_{(8)}\text{-O-R}$  leading to a  $[\text{SER}^{\ominus} \cdot \text{H}^{(+)}]$  “zwitterion”, no longer capable to sequester the target ion and especially to compensate its (+) charge. To test this idea, the low efficient dibutyl ester **15** was converted *via* alkaline hydrolysis to the PHOSDIOX with the monobutyl ester of phosphonic acid (**18**) as the terminal group and after complete hydrolysis to PHOSDIOX Acid (**19**) with  $-\text{P}(\text{O})(\text{OH})_2$  group on the spacer chain. Indeed, these compounds were found reasonably more effective and amazingly specific for  $\text{Eu}^{3+}$ . However, a decrease of  $D_{\text{Eu}^{3+}}$  values with increase of  $\text{HNO}_3$  concentration could still be seen (see Tables 1 and 2).

From the study made on a series of model, purely organic phosphonic acid derivatives followed: the oxygen in the spacer arm between COSAN and phosphorus containing moiety plays no role in sequestration of the  $\text{Eu}^{3+}$ -ion. Probably the acidity of the end group and its donating properties are decisive for cation binding.

Table 1. Extraction of some fission products by PHOSDIOX extractant **18**

$C_{\text{HNO}_3}$	$D_{\text{Cs}}$	$D_{\text{Sr}}$	$D_{\text{Eu}}$
0.01	50.5	10.9	9.98
0.03	–	–	36.5
0.05	–	–	191
0.08	–	–	847
0.11	6.18	0.22	1519
0.31	–	–	160
1.01	0.368	0.004	1.94
2.01	0.113	–	0.252
3.01	0.047	–	0.111

0.05 M PHOSDIOX in toluene (obtained solution), up to 0.05 M  $\text{HNO}_3$ , some reagent losses to the aqueous phase.

Table 2. Europium extraction by PHOSDIOX acid **19**

$C_{\text{HNO}_3}$	0.01	0.05	0.11	0.51	1.01	1.51	2.01	3.01
$D_{\text{Eu}}$	111	2 376	4 959	63.1	3.99	1.32	0.45	0.08

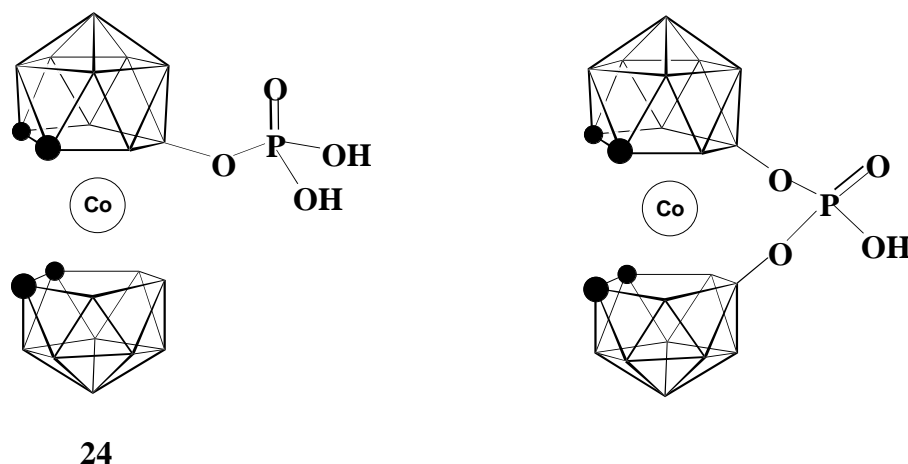
0.05 M PHOSDIOX acid in toluene, in all cases reagent losses to the aqueous phase.

Two compounds of the above type with  $(\text{CH}_2\text{-15-crown-5})$  (**20**) and  $(\text{CH}_2\text{-21-crown-7})$  (**21**) terminal groups bonded *via* diethyleneglycol chain were prepared and tested. Especially the last compound exhibits good selectivity and enhanced extraction properties for  $\text{Sr}^{2+}$ .

More recently, new synthetic methods for direct attachment of phosphorus containing substituents on COSAN cage have been successfully developed starting from COSAN-OH (**22**) and COSAN- $(\text{OH})_2$  (**23**). The ancient synthetic procedures [11] leading to hydroxyderivatives of COSAN were revised and substantially improved. The species **22** and **23** were used as useful synthons for bonding a large variety of metal selective phosphorus containing groups on the cage. Non bridged 8- $(\text{HO})_2\text{PO-O-}$  COSAN acid

(**24**), 8-PhPO(OH)-O-COSAN (**25**), and bridged 8,8- $\mu$ -HO(O)P(O)<sub>2</sub>COSAN (**26**) and 8,8- $\mu$ -Ph(O)P(O)<sub>2</sub>COSAN (**27**) anions containing phosphorus moiety were prepared in amounts sufficient for testing. Further attention has been paid to improve their extraction properties and the solubility in less polar solvents. Compound containing the bridging diethylphosphoramidate (**28**) moiety was synthesised and characterised.

Figure 5. Examples of anionic compounds with non bridged **23** and bridged **25** B-O-P bonded phosphorus containing selective group



From the standpoint of Eu<sup>3+</sup> extraction neither non-bridged phosphoric acid derivatives **24**, **25** nor their bridged analogue **27** were exceptionally effective reagents. Best extraction results have been observed with the species **26** with the -8,8'-O<sub>2</sub>>P(O)(OH) bridge substituent, which has been found efficient in europium extraction (see data in Tables 3 and 4). This compound exhibit maximum on nitric acid concentration dependence of Eu<sup>3+</sup> extraction, the maximum distribution ratio being over 10<sup>3</sup> at 0.2M HNO<sub>3</sub> then falling down but still sufficiently high at 1 M concentration.

Table 3. The Eu extraction by different bridge-type extractants **26-28**

C <sub>HNO<sub>3</sub></sub>	D <sub>Eu</sub>						
	0.1	0.3	0.5	1.0	2.0	3.0	5.0
<b>26</b>	158	61.6	16.0	4.79	0.910	0.462	0.247
<b>27</b>	32.2	–	–	0.124	–	–	–
<b>28</b>	45.7	29.9	–	4.82	1.55	–	–

0.01 M extractant in xylene.

Table 4. Acid dependence on europium extraction by phosphoric acid bridged COSAN **26**

C <sub>HNO<sub>3</sub></sub>	0.01	0.03	0.05	0.1	0.3	1.0	3.0
D <sub>Eu</sub>	157	157	363	158	61.1	4.79	0.46

0.01 M compound 26 in xylene.

All compounds presented above were adequately characterised by HPLC, FAB M.S., high field multinuclear NMR and some of them by X-ray diffraction. The structures of all extraction reagents were presented at the meeting, along with comprehensive extraction tests results.

General drawback of nearly all mentioned – otherwise successful – extractants still seems to be their not sufficiently high solubility in low polar solvents. It is believed that further substitution of their molecules can increase their hydrophobicity and solubility in solvents of interest. The development of new possible extractants still continues within the framework of the EEC Project. Therefore more efficient extractants could be found, which technology should be developed in the future. According to the last results, a solution could be reached, COSAN extractants developed very recently on the similar basis provided  $D_{Eu^{3+}}$  extraction coefficient in the order of hundreds from standard waste solution (1M  $HNO_3$  + 4M  $NaNO_3$ ) using 0.01 M extractant and either toluene or xylene as the solvent.

Up to date, the samples of extractants were prepared in several gram quantities. If the process based on their use is accepted for technological use, Katchem Prague, Ltd. is supposed to be their main producer, and the technology of large scale production scale should be developed and optimised in co-operation with IIC.

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The partial support from EEC Project IC-CT-155-221, the Grant Agency of the Czech Republic (Grant 104-99-1096) and the grant of Czech Ministry of Education OK 429(2000) was highly appreciated.

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