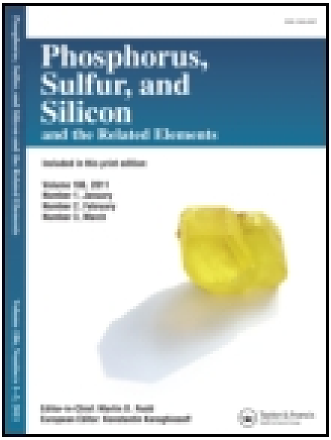

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Polyphosphine Polyoxides as Complexing Agents of Actinides for the Removal from the Nuclear Wastes or from the Human Body

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Polyphosphine Polyoxides as Complexing Agents of Actinides for the Removal from the Nuclear Wastes or from the Human Body

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We synthesized two kinds of polyphosphine polyoxides. The first one has ether bridge, and the second one shows PCP linkage. Complexation properties of these compounds towards minor actinides (Np, Pu and Am) have been evaluated from liquid-liquid extraction and from transport by supported liquid membranes. In decorporation experiment, some of the synthesized phosphonates exhibit *in vivo* good uranyl or neptunium complexation properties.

Keywords: polyphosphine oxides; ether synthesis; Arbuzov reaction; actinides; extraction; decorporation

INTRODUCTION

Nuclear industry produces radioactives wastes divided in three categories, according to their activity. The third group of these wastes are constituted by long life radionuclides like minor actinides (neptunium, plutonium and americium) and fission products (strontium and cesium). In order to confine this group to the smallest possible volume, we have developped, in previous investigations, specific complexing agents for a very efficient separation process using supported liquid membrane (SLM)[1].

The purpose of this work is to extend the families of organophosphorus compounds useful for both extraction of actinides and decontamination of uranyl cation in human organism. Indeed, decorporation therapy is the only effective method of reducing the radiation dose, in case of accidental internal contamination by radionuclides[2].

RESULTS AND DISCUSSION

Synthetic Methods

The formation of P-C-O-C-P bridge is carried out by reaction of sodium alcoolates of hydroxymethylphosphine oxide with various chloromethylphosphines oxides (Figure 1). The chlorine atom in the latter shows low reactivity. It can be only substituted at high temperature, in refluxing toluene[2].

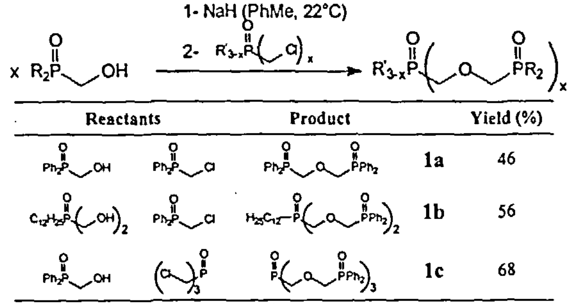

FIGURE 1 Polyphosphine polyoxides with $-CH_2OCH_2-$ bridge.

Compounds with PCCO bridge between phosphorus and oxygen are synthesized by Michael type reactions. The addition of alcoolate to vinylphosphorus compounds leads to ethers with good yields : for example, the reaction of triethanolamine in dioxane with diethyl vinylphosphonate gives the tri-addition compound **2a** with 84 % yield (Figure 2). In a second step, cleavage of ester functions gives quantitatively the triphosphonic acid **2b**. In the same way, diphenylhydroxymethylphosphine oxide gives diphosphine dioxide **3** with moderate yield (46 %).

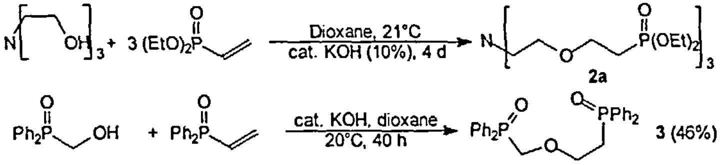

FIGURE 2 Synthesis of PCCO bridge by Michael reaction.

Chloromethylphosphines oxides undergo a Michaelis-Arbuzov reaction when heated at 150°C, for 4 to 10 hours, with trivalent phosphorus esters like phosphites or phosphinites. The reaction affords high yields (80-88 %) in di-, tri- and tetraphosphorylated compounds (Figure 3).

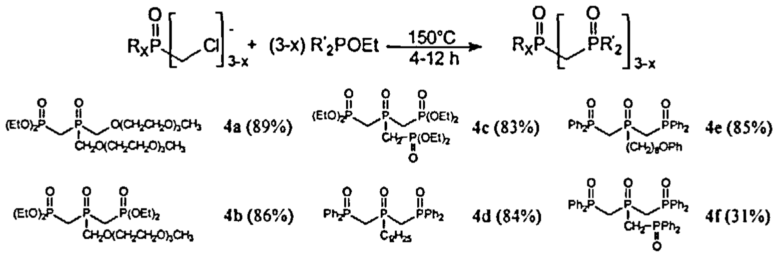

FIGURE 3 Polyphosphorylated compounds with PCP linkage.

Extraction Results

Lipophilic triphosphine trioxides have been tested in liquid-liquid extraction of Pu(IV), Np (V) and Am (III) from 1N HNO_3 aqueous solution. The distribution coefficients D of PCP polyphosphophine polyoxides are better than the reference compound, the carbamoylmethylphosphine oxide 5 (Table I) : particularly, the compound 4e exibits distribution coefficients 12 to 1300 fold higher than 5.

The transport experiments through supported liquid membranes was followed by regular measurement of the radioactivity in the feed solution. As described in the model of mass transfer proposed by Danesi[3], we have then an access to the constant permeabilities $\mathcal{P}$ (Table II).

TABLE I Distribution coefficient D with 10^{-2} M extracting agent in nitrophenylhexylether.

Compound	D_{Np}	D_{Pu}	D_{Am}
4d	2.1	3.0	87
4e	10	773	757
4f	1.5	>100	>100
5	0.85	22	0.57

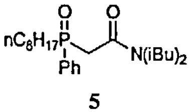

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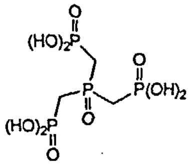
TABLE II Permeability $\mathcal{P}$ ($cm.h^{-1}$) and extracted percentage with 10^{-2} M extracting agent.

Compound	$\mathcal{P}_{Np}$	$\%_{Np}$	$\mathcal{P}_{Pu}$	$\%_{Pu}$	$\mathcal{P}_{Am}$	$\%_{Am}$
4d	-	-	-	-	5,46	100 %
4e	4,24	73 %	10,58	100 %	9,9	100 %
4f	-	-	2,11	51 %	0,36	54 %
5	0,74	50 %	3,44	99 %	0,15	36 %

Triphosphine trioxides with lipophilic moiety (**4d**, **4e**) are able to transport actinides elements, even trivalent actinides (Am III), which are the most solvated and then generally the hardest to extract.

Decorporation Results



6

One of the most active compounds is tris(phosphonomethyl)phosphine oxide **6**. The effectiveness of **6** was tested after intramuscular (im) uranium contamination of OF1 Ico:OF1 mice (Table III). This product enhances the urinary and faeces excretion, even at a concentration of 10 µmol.kg^{-1}. Moreover, it induces noticeable reduction of uranium retention in kidney by around four-fold and deposition in bones, by a factor 1.3. We have also noticed that a concentration of 100 µmol.kg^{-1} does not increase elimination of uranium.

Table III Tissue retention and urinary and faecal excretion of uranium.

		Retention				**Excretion**	
		Injection site	Liver	Kidney	Bone	Urine	Faeces
Control	%t	5.4 %	0.5 %	15 %	30 %	41 %	1.6 %
[L] = 10 µmol.kg^{-1}	%im	7.9 %	0.15 %	3.75 %	23.1 %	56 %	3.6 %
	$\frac{\%im}{\%t}$	**146 %**	**30 %**	**25 %**	**77 %**	**137 %**	**228 %**

CONCLUSION

Polydentate phosphoryl compounds with PCP linkage prove their remarkable ability for extraction of minor actinides and for removal of uranium. This family is more efficient than the carbamoylmethylphosphine oxide **5** in extraction process. In decorporation therapy, these compounds are particularly promising, since compound **6** is one of the first chelating agent which is able to complex *in vivo* neptunium cation.

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