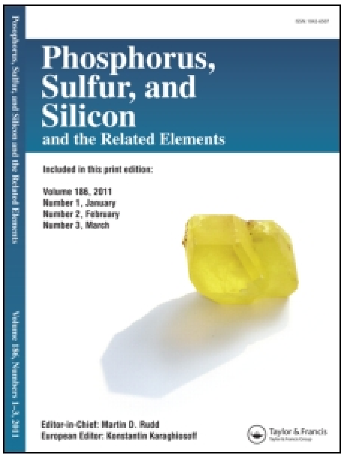

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Complexation Behavior of Phosphate and Phosphazene Derivatives Containing Three or Six Benzo-15-crown-5 Cavities

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COMPLEXATION BEHAVIOR OF PHOSPHATE AND PHOSPHAZENE DERIVATIVES CONTAINING THREE OR SIX BENZO-15-CROWN-5 CAVITIES

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Tris(benzocrown ether)s ***2a,b*** *$X{=}P(NMeN{=}CH\text{-}B15C5)_3$ (X=O, S) and tri[bis(benzocrown ether)] $[N{=}P(NMeN{=}CH\text{-}B15C5)_2]_3$* ***3*** *strongly chelate with alkali metal salts and their efficiency and selectivity in binding these salts are compared with those of the monomeric crown* ***1****. Data obtained from salt distribution equilibrium in water-chloroform show these ligands to be excellent extracting agents, especially for K^+ and Rb^+. Furthermore, compound* ***3*** *is able to transport K^+ selectively.*

Keywords: Biscrown effect; phosphazene derivatives; selective transport

INTRODUCTION

For many years crown ethers have been known to solve alkali salts into organic solvents. Their selectivity for a given cation depends on several factors[1] (topology, thermodynamics, acidity, etc.), but the most important one is the *size-fit* between the two antagonists. When only this point is considered, for alkali metal salts and for "free" crown ethers, ML complexes [i.e., one cation per crown cavity] are formed when the size of the cation (M) is smaller or equal to the size of the cavity (L). The cations are either totally or partially encircled by the ring. In the latter case, the counter anion and/or the solvent complete the coordination sphere. For larger cations, the most stable complexes are obtained when the coordination sphere of the cation is satisfied by another crown cavity to give ML_2 (sandwich) complexes. An enhanced stability and

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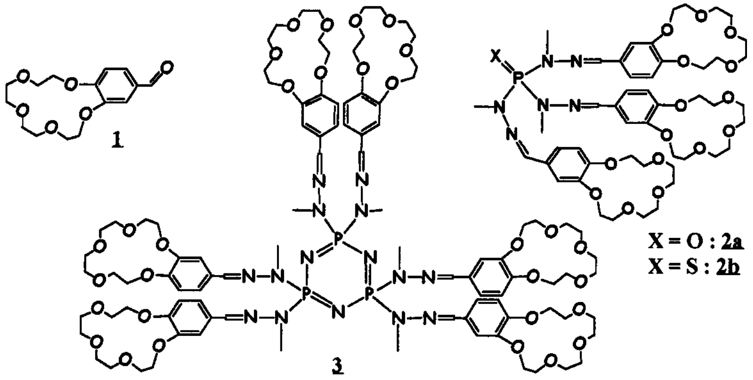
selectivity has been demonstrated when intramolecular ML_2 complexes can be formed.[2] This requires the linkage of two crown ethers. In that case, the selectivity becomes highly dependent on the structure of the bridge connecting the cavities.

RESULTS AND DISCUSSION

The aim of this study was to investigate the efficiency towards the extraction of alkali metal salts ($M^+ = Li^+ - Cs^+$) of benzo-15-crown-5 moieties when tethered by a phosphodihydrazone unit. The two different phosphate derivatives **2a**,**b** and the cyclophosphazene **3** shown in Scheme 1 were easy to synthesize and were obtained in quantitative yields.[3] They are stable against hydrolysis and insoluble in water.



SCHEME 1 Polymacrocyclic compounds **2a**,**b** and **3** and the precursor **1**.

The extracting ability of compounds **2a**,**b** and **3** was evaluated by measuring the distribution equilibrium of alkali metal picrate salts between an aqueous and a chloroformic phase by UV/Vis spectroscopy and was compared to **1** (Figure 1). Clearly, the extracting ability of compound **1** towards all alkali cations is weak (<25%) even at high ligand concentrations, while all polymacrocyclic phosphorus compounds **2a**,**b** and **3** show excellent extraction properties. Especially for K^+ and Rb^+, which are efficiently extracted (>80%) into the organic phase, and remarkably even under stoechiometric conditions. Furthermore, the selectivity for the different cations ($Na^+ > K^+ > Rb^+ > Cs^+$ for **1**) is inverted when the polymacrocyclic phosphorus compounds are employed. Indeed, while compound **1** extracts Na^+ better, the tethered ligands show an obvious inclination for larger cations. **2a**,**b** and **3** show further

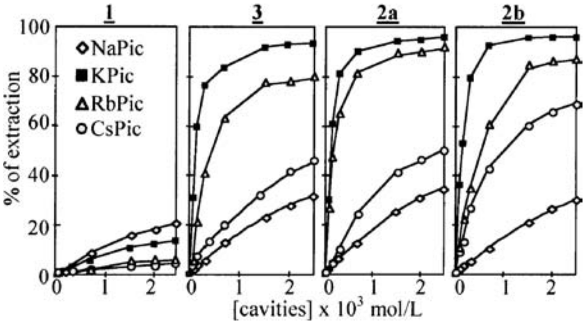


FIGURE 1 Variation of extraction percentages of alkali metal picrates as a function of crown cavities concentration. $[M^+] = 7.0 \times 10^{-5}$ mol/L; [crown ether cavities] $= (0.0 - 2.5 \times 10^{-3}$ mol/L).

interesting details concerning the extractions' selectivities. Indeed, Cs^+ is more efficiently extracted by the thiophosphate ligand **2b** than by **2a**, indicating that even minor changes in the ligand backbone have a considerable effect.

The composition of organic solutions containing these ligands in dependence of the L:M ratios has been previously investigated[4] by fitting the observed chemical shift differences in ^{13}C NMR spectra to possible complexation equilibrium models by means of the RMNSTAB program. When **2a**,**b** or **3** are reacted with Li^+ and Na^+, the formation of ML complexes prevails, which is also the case for the monocyclic compound **1**. ML_2 complexes become the major species when the larger alkali ions are bounded by **2a**,**b** and **3**. Especially, K^+ and Rb^+ form highly stable ML_2 complexes, while ML complexes $[K(\mathbf{1})]^+$ and $[Rb(\mathbf{1})]^+$ prevail with **1** under the same conditions. Considering the results obtained by ^{13}C NMR investigation, the strong chelate effect observed for **2a**,**b** and **3** can only be attributed to the formation of stable intramolecular sandwich complexes.

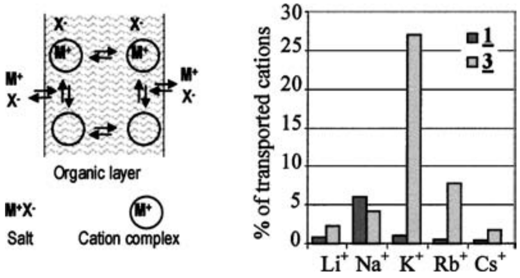


FIGURE 2 Cation transport experiments on compounds **1** and **3**. $[M^+] = 7.0 \times 10^{-5}$ mol/L (2 ml); $[L] = 10^{-4}$ mol/L (25 ml).

However, are they still able to transport cations from an aqueous phase to another one via an organic media (membrane) containing the ligand? To answer that question we have performed some transport experiments with compound **3**, and the results obtained by UV/Vis spectroscopy were compared with those obtained for monomer **1** (Figure 2).

As is clearly shown in Figure 2, compound **3** is able to carry potassium salts selectively.

CONCLUSION

This study demonstrates clearly that the particular organization imposed by the phosphodihydrazone spacer provides a “quasi rigid pincer” which can tightly surround large cations and selectively transport potassium ions. The next step, which consists of grafting our “pincer” on a solid support to perform chromatographic experiments, is under investigation.

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