



## Complexation Studies of Phosphorus Containing Bis and Tris (Benzocrown Ether) Moieties

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### Abstract

The complexation behaviour between salts of  $\text{Li}^+$ - $\text{Rb}^+$  in  $\text{CD}_3\text{CN}$  and tris(benzocrown ether)s **2a,b**  $\text{X}=\text{P}(\text{NMeN}=\text{CH}-\text{B15C5})_3$  ( $\text{X} = \text{O}, \text{S}$ ) and tri[bis(benzocrown ether)]  $[\text{N}=\text{P}(\text{NMeN}=\text{CH}-\text{B15C5})_2]_3$  **3** was investigated by  $^{13}\text{C}$  NMR spectroscopy. Using the program RMNSTAB, the complexation constants for the different possible complexes ( $\text{M}_2\text{L}$ ,  $\text{ML}$  and  $\text{ML}_2$  where L represents one benzo-15-crown-5) were obtained and were compared with those of the corresponding monomer material. A remarkable “biscrown effect” for compounds **2a,b** and **3** was found, especially for potassium and rubidium by the predominant formation of stable  $\text{ML}_2$  complexes. The strong chelate effect make these ligands highly efficient extracting agents for alkali metal picrate salts of  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ , as shown by UV-Vis spectroscopy.

### Introduction

It is well known that the selectivity of crown ethers for a given cation mainly depends on the following points [1]: (i) the relative size of the cavity of the crown ring and the diameter of the cation, (ii) the number of donor atoms in the crown ring and the topological effect, (iii) the relationship between the hardness of the cation and that of the donor atom, (iv) the charge of the cation. When only the size selectivity relationship for cations of the same family, for example alkali metals, is considered,  $\text{ML}$  complexes [i.e., one cation per crown cavity] are formed when the size of the cation is smaller or equal to that of the cavity. Cations are either totally or partially encircled by the ring. In the latter case, the counteranion and/or the solvent complete the coordination sphere. For cations whose sizes exceed that of the crown ether,  $\text{ML}_2$  or intermolecular sandwich complexes [i.e., one cation embedded by two crown cavities] are formed.

These observations are true for molecules containing one ring. However, what phenomena will be observed when more than one crown cavity is linked in such a way that a polymacrocyclic molecule is created and will the formation of intramolecular sandwich complexes be favoured? Several bis(crown ether)s have been prepared for this purpose and most of them show an enhanced ability to complex cations. For example, some bis(12-crown-4) derivatives are highly selective neutral carriers for  $\text{Na}^+$  ions [2]. This selectivity is highly dependent on the length of the chain connecting the two crown ether rings. Similarly the co-operative action

of two crown ether rings has been used to construct bis(15-crown-5) derivatives exhibiting a high  $\text{K}^+$  selectivity. Both systems allowed the formation of  $\text{Na}^+$  or  $\text{K}^+$  selective electrodes which found practical application in the simultaneous determination of these cations in human blood serum and urine [3].

Obviously, the nature of the bridge connecting the crown ether moieties plays an important role. However, up to now, relatively few reports were devoted to the linkers other than mainly polyethylene or polyether units. In the course of our investigations dendrimers bearing bis(benzocrown ether) units [4] and polyphosphazenes containing crown ethers as pendant groups have been reported [5–9]. However detailed complexation studies have never been described.

In this paper we wish to describe our results obtained for poly(benzocrown ether) entities which contain  $\text{Y}=\text{P}(\text{NMeN}=\text{CH}-)_m$  ( $\text{Y} = \text{O}, \text{S}$ ,  $m = 3$ ;  $\text{Y} = \text{N}$ ,  $m = 2$ ) units as linkers between benzo-15-crown-5 cavities. By orientating ( $\text{MM}^+$ ) calculations we found that a pre-arrangement of the linked crown units is possible which should favour intramolecular sandwich complex formation and an enhanced “biscrown effect” may be expected.<sup>1</sup>

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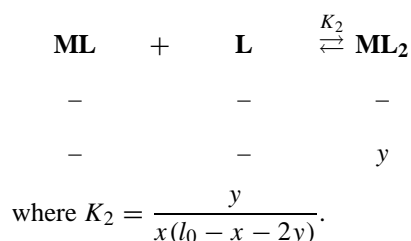
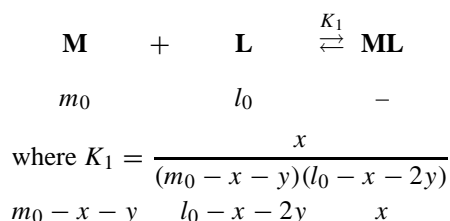
<sup>1</sup> The energetically lowest lying conformations of the molecules investigated in the study show structures in which the benzo groups are aligned in a co-planar fashion thus favouring sandwich formation.

## Experimental section

### NMR

Up to ten equivalents of different salts<sup>2</sup> were successively added (one equivalent at a time) to an acetonitrile solution containing the ligand. <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded after every equivalent added on a Bruker WP 300 NMR spectrometer.

The difference between the chemical shifts of the complexes and those of the ligand  $\Delta\delta$  was determined and plots of  $\Delta\delta$  against the number of equivalents of cation added were obtained. The RMNSTAB [10] program was used to fit the NMR chemical shift data corresponding to one of the following models: (i) ML complex, (ii) ML and ML<sub>2</sub> complexes, (iii) ML and M<sub>2</sub>L complexes, (iv) ML<sub>2</sub> complex, (v) M<sub>2</sub>L complex, where L represents one benzo-15-crown-5 cavity and M, the cation. According to the model chosen before, the program calculates one or two stability constants K. For example, in the case of a mixture of ML and ML<sub>2</sub> complexes, the equilibria are the following:



In this case, two stability constants  $K_1$  (for the ML complex) and  $K_2$  (for the ML<sub>2</sub> complex) will be determined. The RMNSTAB program provides a plot showing percentages of the different species (free ligand and complexes) as a function of the number of equivalents of cation.

### UV/Vis

Binding efficiencies of the crown compounds were evaluated from distribution equilibria of the salt complexes between an aqueous phase and chloroform. The method developed by Pedersen and subsequently used by other investigators [11–14] involves the transfer of a picrate salt from an aqueous metal hydroxide salt solution to the organic phase containing the ligand.

Equal volumes (10 mL) of a chloroform solution of the ligand ( $2.5 \times 10^{-3}$  mol/L per crown ether unit) and of the aqueous picric acid ( $7.0 \times 10^{-5}$  mol/L) containing 0.1 mol/L of metal hydroxide were introduced into a flask, which was

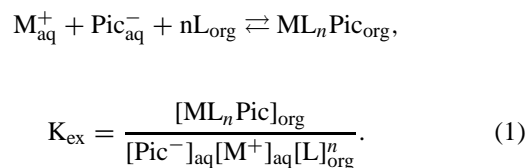
<sup>2</sup> Hexafluorophosphate salts were used in the case of Li<sup>+</sup> and K<sup>+</sup> instead of tetraphenylborate salts for stability and solubility reasons in CD<sub>3</sub>CN.

shaken for two hours at room temperature. The mixture was then allowed to stand for two hours in order to complete the phase separation. The picrate concentration was determined at its maximum of absorption ( $\lambda_{\max} = 357$  nm) on a Varian Cary 1 spectrophotometer. The percentage of picrate extracted was calculated from the difference between the original and final aqueous picrate concentrations. The reported values of the percent of picrate extracted are the average of two independent experiments.

Lithium, sodium, potassium, rubidium and cesium picrates were prepared according to the procedure developed by Pedersen [15]. Before use, the solvents were saturated with each other to prevent volume changes in the phases during extraction. The concentration of  $7.0 \times 10^{-5}$  mol/L for picric acid was chosen because at this concentration using a 1 cm cell, the aqueous phase does not require further dilution if the extraction efficiency is very low.

In the experiments directed to determine extraction equilibrium constants ( $K_{\text{ex}}$ ), chloroform solutions of the ligands of various concentrations ( $7.0 \times 10^{-5}$  to  $2.5 \times 10^{-3}$  mol/L) and aqueous alkali metal picrates ( $7.0 \times 10^{-5}$  mol/L) were brought to equilibrium by the same procedure.

The overall extraction equilibrium between an aqueous solution of alkali metal picrates ( $M^+ \text{Pic}^-$ ) and a chloroform solution of ligand (L) can be defined for a ligand-cation complex ratio as follows:



Subscripts <sub>aq</sub> and <sub>org</sub> refer to the aqueous and organic phases respectively. (Since chloroform is used as the organic solvent, the dissociation of the ion pair  $\text{ML}_n\text{Pic}$  is negligible [16] and the concentration of uncomplexed cation in the chloroform phase is extremely low compared with that of the complex. The concentration of the ligand in the aqueous phase was also found to be quite low.)

The distribution ratio  $D$  of a metal cation between an organic and an aqueous phase is expressed as follows:

$$D = \frac{[\text{ML}_n\text{Pic}]_{\text{org}}}{[\text{M}^+]_{\text{aq}}} \quad (2)$$

From Equations (1) and (2), expression (3) is obtained:

$$K_{\text{ex}} = \frac{D}{[\text{Pic}^-]_{\text{aq}}[\text{L}]_{\text{org}}^n} \quad (3)$$

Reformulation of Equation (3) results in the following Equation (4):

$$\log(D/[\text{Pic}^-]_{\text{aq}}) = n \log[\text{L}]_{\text{org}} + \log K_{\text{ex}} \quad (4)$$

A plot of  $\log(D/[\text{Pic}^-]_{\text{aq}})$  as a function of  $\log[\text{L}]_{\text{org}}$  should give a straight line with a slope of  $n$  indicating the type of complex.  $\log K_{\text{ex}}$  is obtained from the intercept of the straight line with the ordinate axis.

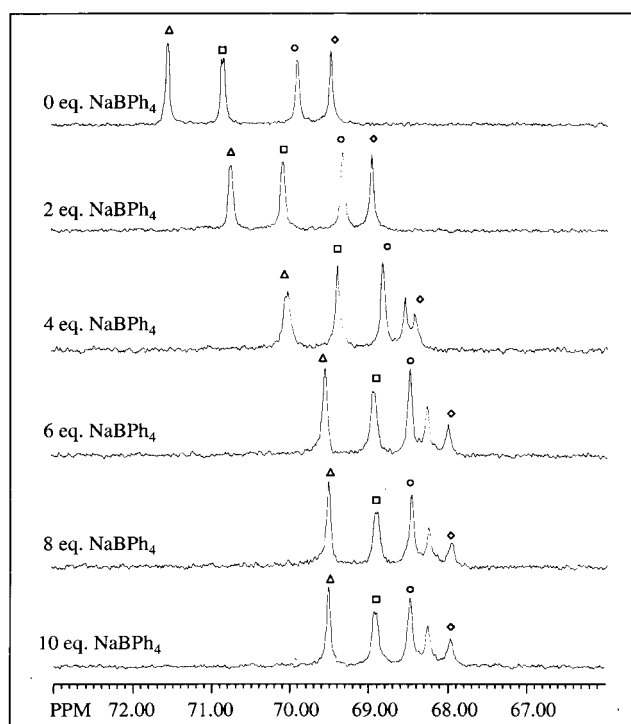
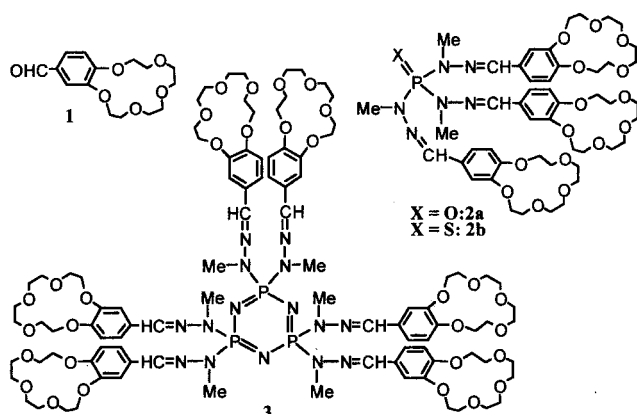


Figure 1. Evolution of the  $^{13}\text{C}$  chemical shifts of the methylene carbon nuclei of the crown ether cavities of compound **3** as a function of  $\text{NaBPh}_4$  equivalents.  $\diamond$  Peak 1;  $\circ$  Peak 2;  $\square$  Peak 3;  $\triangle$  Peak 4.

## Results and discussion

### Distribution equilibria of $ML_n$ complexes

The two kinds of compounds we have investigated are the tris(benzocrown ether)s **2a,b** for which the three benzocrown cavities are linked via a hydrazone bond to an oxo- or thiophosphorus core, and a tri[bis(benzocrown ether)] **3**. In this case the three bis(benzocrown) moieties are linked to a phosphorus atom included in a phosphazene ring (Scheme 1). In a recent paper, we have described the syntheses of these compounds [9], according to the procedure established by Majoral and co-workers [17].

The complexation behaviour of **1**, **2a,b** and **3** was monitored by  $^{13}\text{C}$  NMR spectroscopy. Relevant information was obtained from the variation of the chemical shifts of the

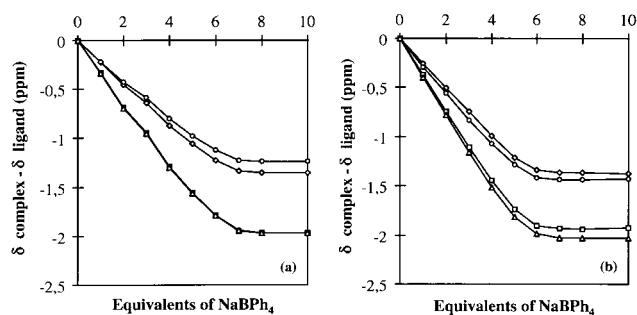


Figure 2. Variation of the  $^{13}\text{C}$  chemical shifts of compound **1** (6 eq.): (a) and compound **3** (1 eq.), (b) as a function of the number of equivalents of  $\text{NaBPh}_4$  in acetonitrile solution.  $\diamond$  Peak 1;  $\circ$  Peak 2;  $\square$  Peak 3;  $\triangle$  Peak 4.

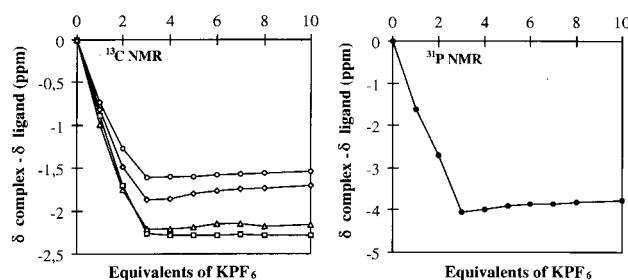


Figure 3. Variation of the  $^{13}\text{C}$  and  $^{31}\text{P}$  chemical shifts of compound **3** as a function of the number of equivalents of  $\text{KPF}_6$  in acetonitrile solution.  $\diamond$  Peak 1;  $\circ$  Peak 2;  $\square$  Peak 3;  $\triangle$  Peak 4 for  $^{13}\text{C}$  chemical shifts.

methylene carbon nuclei in the polyether unit (Figure 1) and also of the arene and imine carbon nuclei. A spectrum was recorded after each addition of the salts of various alkali metals to a crown ether compound.

Average resonance signals are observed which indicate rapid dynamic exchanges between complexed and uncomplexed sites on the  $^{13}\text{C}$  NMR time scale at room temperature. When up to six equivalents of sodium salt were added, a significant and characteristic low frequency shift is observed. Further increase of the cation concentration does not influence the spectra. This can be explained by the saturation of the binding capability of the ligand by six  $\text{Na}^+$  equivalents.

The same evolution is seen in Figure 2 in which the experimental curves of the variation of the chemical shifts of the different methylene carbon nuclei of the crown cavity of compound **3** are given as a function of the number of equivalents of sodium salt added in acetonitrile solution (Figure 2a). For comparison, the free 4'-formyl-benzo-15-C-5 **1** was investigated under the same conditions (i.e., 6 equivalents of compound **1** compared to 1 equivalent of **3**, diagram b).

A plateau is reached when six equivalents of sodium salt have been added. When these curves are compared to those of the free crown ether **1**, a similar behaviour is observed. At first glance, this seems to indicate that for both compounds **1** and **3**, saturation of the binding capability is reached when six equivalents of metal salt have been introduced, indicating the formation of 1 : 1 complexes.

In Figure 3 the variations of the  $^{13}\text{C}$  chemical shifts of compound **3** as a function of the number of equivalents of  $\text{KPF}_6$  in acetonitrile solution is represented.

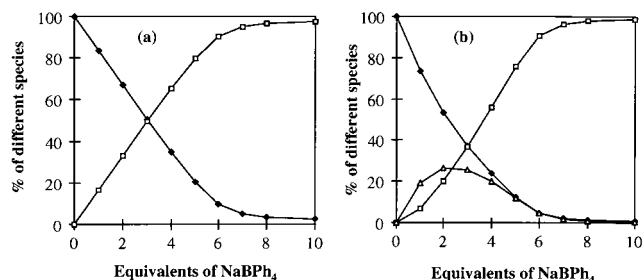


Figure 4. Percentages of different species as a function of the number of equivalents of NaBPh<sub>4</sub> in acetonitrile solution: (a) compound **1** (6 eq.), (b) compound **3** (1 eq.). ♦ free ligand; □ ML complex; △ ML<sub>2</sub> complex.

Table 1. Complexation of NaBPh<sub>4</sub> by **1** and **3**

	<b>1</b>	<b>3</b>
$K_1$ (ML) L/mol	9800	68000
$K_2$ (ML <sub>2</sub> ) L/mol	–	130
$Q$	$7.18 \times 10^{-3}$	$2.94 \times 10^{-3}$

Stability constants are given in L/mol,  $Q$  is the sum of the squared residuals.

In the case of this cation which is larger than the size of the benzocrown cavity, a plateau value is reached when three equivalents of potassium salt have been added to the tri[bis(benzocrown ether)] **3**. The same behaviour was found by following the evolution of the <sup>31</sup>P NMR spectra with K<sup>+</sup> concentration (Figure 3b). Experiments on 6 equivalents of the free crown ether **1** led to curves that are very similar to those shown in Figure 3a. Do these curves mean that there is no active “biscrown effect” for compound **3**?

In order to answer this question, the RMNSTAB program was employed. This program fits  $\Delta\delta$  values for M/L (M = metal concentration, L = benzo-15-C-5 units concentration) ratios derived from NMR spectra under the assumption that all species are in a rapid equilibrium on the NMR time scale. Various equilibria including the species L, ML, M<sub>2</sub>L and ML<sub>2</sub> (see experimental part) can be chosen by the user and usually, only one model leads to a satisfactory fit of calculated and experimental curves. The plots representing the percentages of the different complexes formed in dependence of the metal salt added are shown in Figure 4.

In both cases the ML complex is the predominant species formed with increasing equivalents of Na<sup>+</sup>. However, the tri[bis(crown ether)] ligand shows a seven fold higher complexation constant  $K_1$  [ $K_1(\mathbf{3}) = 68000$ ;  $K_1(\mathbf{1}) = 9800$  (Table 1)]. Furthermore, a small quantity of the sandwich complex ML<sub>2</sub> [ $K_2(\mathbf{3}) = 130$ ] is observed at lower Na<sup>+</sup> concentrations, which is not seen for the free crown ether. For an excess of sodium salt, the complexation behaviour is rather similar. This is not surprising because it is well established that for the B15C5 system in particular, Na<sup>+</sup> complexation occurs preferentially in a 1 : 1 manner. There is relatively little change in the ring and the macromolecule conformation accompanying Na<sup>+</sup> binding [18].

In the case of potassium (Figure 5), when the free crown ether is taken up to three equivalents of potassium salt, al-

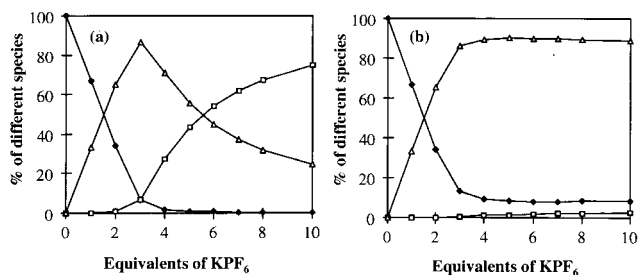


Figure 5. Percentages of different species as a function of the number of equivalents of KPF<sub>6</sub> in acetonitrile solution: (a) compound **1** (6 eq.), (b) compound **3** (1 eq.). ♦ free ligand; □ ML complex; △ ML<sub>2</sub> complex.

Table 2. Complexation of KPF<sub>6</sub> by **1** and **3**

	<b>1</b>	<b>3</b>
$K_1$ (ML) L/mol	97000	100
$K_2$ (ML <sub>2</sub> ) L/mol	17000	74000
$Q$	$1.04 \times 10^{-3}$	$4.63 \times 10^{-3}$

Stability constants are given in L/mol,  $Q$  is the sum of the squared residuals.

most all crown cavities are involved in the formation of a ML<sub>2</sub> complex.

However, when further K<sup>+</sup> cations are added, this complex is destabilised in favour of the ML complex. In contrast to the tri[bis(crown ether)] **3** the sandwich complex remains stable in the presence of an excess of K<sup>+</sup>. These observations show that a [ $K_3(\mathbf{3})$ ]<sup>3+</sup> sandwich complex is much more stable than a 1 : 1 [ $K_6(\mathbf{3})$ ]<sup>6+</sup> complex (Table 2). The formation of this intramolecular sandwich complex occurs obviously with a significant change of the conformation of the ligand as compared with the [ $Na_6(\mathbf{3})$ ]<sup>6+</sup> complex: the [ $K_3(\mathbf{3})$ ]<sup>3+</sup> sandwich complex exhibits a strong variation of the <sup>31</sup>P NMR chemical shifts ( $\Delta\delta = 4$  ppm at 3 equivalents of K<sup>+</sup> ions added, see Figure 3) while for the [ $Na_6(\mathbf{3})$ ]<sup>6+</sup> complex this variation amounts to only 0.6 ppm when 6 equivalents of Na<sup>+</sup> ions were added.

In Figure 6, the equilibrium distribution of the L, ML, M<sub>2</sub>L and ML<sub>2</sub> species in acetonitrile solutions containing an excess (10 equivalents) of different alkali metals MX (M = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>; X = PF<sub>6</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>) is graphically depicted.

For sodium, as already discussed (Figure 4), almost 100% of complexes formed are ML complexes for both compounds **3** and **1**. In the case of potassium, intramolecular

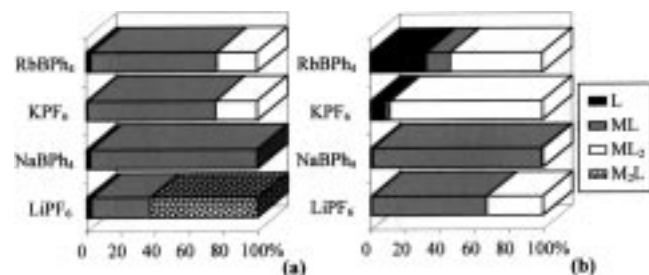


Figure 6. Percentages of complexes formed for acetonitrile solutions containing ten equivalents of alkali metals salts: (a) compound **1** (6 eq.), (b) compound **3** (1 eq.).

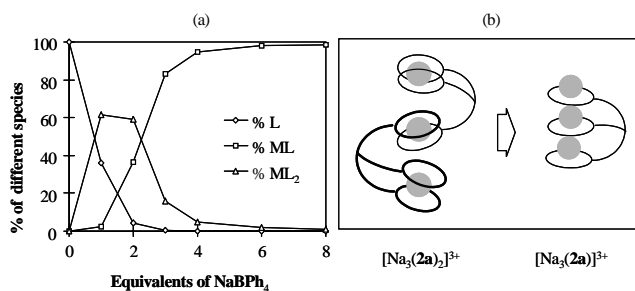


Figure 7. (a) Percentages of different species as a function of the number of equivalents of NaBPh<sub>4</sub> in acetonitrile solution (compound **2a**), (b) Evolution from ML<sub>2</sub> to ML complexes for compounds **2a,b**.  $\diamond$  free ligand;  $\square$  ML complex;  $\triangle$  ML<sub>2</sub> complex.

sandwich complex formation to give ML<sub>2</sub> units is predominant when phosphazene **3** is used as ligand under these conditions. The free crown ether **1** shows the expected behaviour (i.e., mainly formation of the ML complex in the case of metal ion excess). As for M<sup>+</sup> = K<sup>+</sup>, the observation of ML complexes as the main product is also made when Rb<sup>+</sup> ions are reacted with crown ether **1**. In contrast, **3** gives again mainly sandwich complexes with Rb<sup>+</sup>. However a relatively large amount of the crown cavities (25%) remains uncomplexed. Moreover, in this case, the <sup>31</sup>P NMR spectra exhibit two signals when up to three equivalents of rubidium salt were added indicating a slower exchange on the NMR time scale between the complexed and the uncomplexed sites than for Na<sup>+</sup> and K<sup>+</sup>. These results allow us to assume that the distance between the two crown cavities involved in the sandwich complex could be a limitation for the complexation of larger cations. With lithium ions, M<sub>2</sub>L complexes (i.e., two cations per crown cavity) are observed with the free benzocrown unit as complexing agent. The formation of this complex is assumed to be due to the small size and hence the high charge density of the cation. Remarkably M<sub>2</sub>L complex formation is not observed with the tri[bis(crown ether)] **3** for which a ML complex is predominant. Note however, that about 30% of LiL<sub>2</sub> sandwich complexes are present.

A similar study was also performed for tris(crown ether)s **2a,b**. The graph representing the percentages of the different complexes formed as a function of the metal salt added is shown in Figure 7a for compound **2a**.

As already seen, for one equivalent of sodium salt added to three equivalents of crown cavities, about 60% of ML<sub>2</sub> complexes are formed. By further addition of cation, this sandwich complex degrades in favour of ML complexes.

In Figure 7b a model is proposed which can explain these observations. At concentrations below a 2:3 metal:cavity ratio, a [Na<sub>3</sub>(**2a**)<sub>2</sub>]<sup>3+</sup> complex is formed which contains exclusively intra- and intermolecular ML<sub>2</sub> units. Increasing the Na<sup>+</sup> concentration above a 2:3 ratio leads to a rapid decrease of the ML<sub>2</sub> concentration. Exactly the same behaviour as **2a** could be observed for **2b**. We have no indication of the formation of ML<sub>3</sub> complexes in which all three crown cavities surround one metal centre. Note that the percentage of NaL<sub>2</sub> complexes is significantly higher when **2a,b** are used as ligands than with **3**.

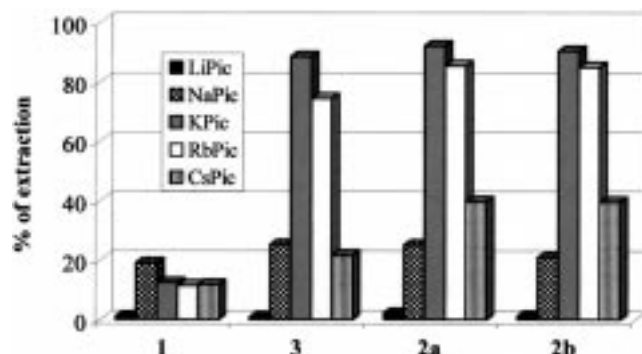


Figure 8. Extraction percentages of different alkali-metal picrates under standard conditions. [crown cavities] =  $2.5 \times 10^{-3}$  mol/L; [M<sup>+</sup>] =  $7.0 \times 10^{-5}$  mol/L.

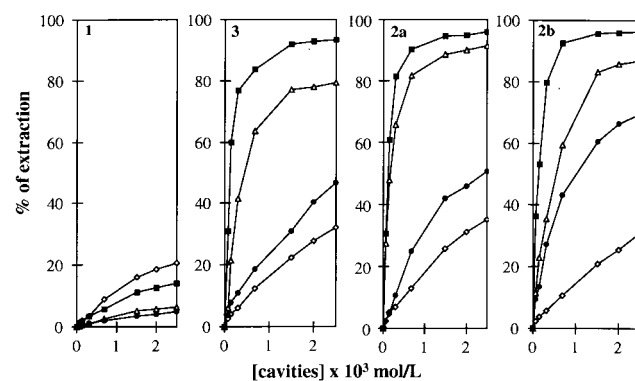


Figure 9. Variation of extraction percentages of alkali metal picrates as a function of crown ether cavities concentration. [M<sup>+</sup>] =  $7.0 \times 10^{-5}$  mol/L.  $\diamond$  NaPic;  $\blacksquare$  KPic;  $\triangle$  RbPic;  $\bullet$  CsPic.

#### Extraction studies using UV/Vis spectroscopy

A comparison of the extracting ability of compounds **1**, **2a,b** and **3** was performed by measuring the distribution equilibrium of alkali metal picrate complexes between an aqueous and a chloroform phase by UV/Vis spectroscopy (Figure 8).

It is obvious that none of the ligands extract lithium, which remains solvated in the aqueous phase. Sodium is similarly extracted for all compounds. This result is expected because in all cases we have ML complexes in which the co-operativity of the benzocrown ethers is not involved. On the other hand, potassium and rubidium are extracted efficiently by more than 80% when compared to **1**. No doubt that this property is due to the stability of the intramolecular sandwich complexes, evoked by the proximity of the crown cavities. Rubidium and cesium are relatively better extracted by the tris(benzocrown ether)s **2a,b** than by the hexamacrocyclic phosphazene **3**. This may be due to an enhanced flexibility of two of the three crown cavities providing more room to host larger metal ions.

Subsequently the extracting ability of each ligand **1**, **2a,b** and **3** for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> ions as a function of the concentration of crown ether cavity was investigated (Figure 9). In each experiment an aqueous solution containing  $7.0 \times 10^{-5}$  mol/L of metal picrate was extracted with an equal volume of a chloroform solution containing different concentrations ( $0.0$ – $2.5 \times 10^{-3}$  mol/L) of ligand (i.e., the L/M ratio was varied from 0 to about 30).

Table 3. Variation of the slope  $n$  determined from  $\log(D/[Pic^-]_{aq}) = n \log [L]_{org} + \log K_{ex}$ 

	<b>1</b>		<b>3</b>		<b>2a</b>		<b>2b</b>	
	$n$	$\log K_{ex}$	$n$	$\log K_{ex}$	$n$	$\log K_{ex}$	$n$	$\log K_{ex}$
Na <sup>+</sup>	0.9	6.2	0.9	6.4	0.9	6.2	0.8	6.0
K <sup>+</sup>	0.9	5.8	1.5	10.7	1.9	12.2	1.7	11.6
Rb <sup>+</sup>	0.9	5.5	1.7	10.2	1.7	10.4	1.5	10.1
Cs <sup>+</sup>	0.7	4.7	0.8	6.2	1.1	8.0	1.2	7.5

$D$  = distribution ratio of  $M^+$  over the organic and aqueous phase.  $K_{ex}$  is the extraction constant. The slope  $n$  was determined from curves obtained for a wide range of L : M ratios (0–30).

The extracting ability as expressed by the percentage of metal ions extracted into the organic phase of the free benzocrown ether **1** remains weak (< 25%) for all alkali cations even at high ligand to alkali metal concentrations. On the contrary, all polymacrocyclic phosphorus compounds **2a,b** and **3** show better extraction properties. Especially the larger cations potassium and rubidium are efficiently extracted into the organic phase under almost stoichiometric conditions (i.e., in the range of L : M ratios of 2 : 1 to 1 : 1). When about a tenfold excess of crown ether cavity is used more than 90% of K<sup>+</sup> ions have been extracted by **2a,b**. These cations are only poorly extracted by the free crown ether **1**. The new ligands **2a**, **2b** and **3** show further interesting details concerning the extraction selectivities. Cesium ions are more efficiently extracted by the thiophosphate ligand **2b** than by **2a** indicating that even minor changes in the ligand backbone have a considerable effect.

In order to verify the results concerning the distribution of L and  $ML_n$  complexes obtained by NMR techniques, we have used the equation  $\log(D/[Pic^-]_{aq}) = n \log[L]_{org} + \log K_{ex}$  (4) to determine  $n$ . The distribution,  $D$ , of metal ions over the organic and aqueous phase and the picrate concentration  $[Pic^-]_{aq}$  was derived from the UV/Vis spectra of each mixture and the crown cavity concentration  $[L]_{org}$  was taken as being equal to the uncomplexed concentration of **1**, **2a,b**, and **3** neglecting traces which may be soluble in the aqueous phase. The results are compiled in Table 3.

The monocyclic crown ether **1** shows slopes close to one for all cations  $M^+ = Na^+ - Cs^+$  as expected from the NMR investigations indicating that ML complexes prevail. However, at poor extraction percentages ( $Cs^+ < 5\%$ ) values of the slopes ( $n$ ) are less precise. The polymacrocyclic extracting agents **2a,b** and **3** give  $n$  values  $\geq 1.5$  for K<sup>+</sup> and Rb<sup>+</sup> complexes clearly indicating the formation of sandwich  $ML_2$  complexes. However, for Na<sup>+</sup> and Cs<sup>+</sup>,  $n$  values  $\leq 1.2$  are also observed with these ligands. In the case of sodium, this result is in accordance with the predominant formation of ML complexes as was evidenced by evaluation of the NMR spectra. The low  $n$  values determined in extraction experiments with cesium do not necessarily mean that only ML complexes are formed. It is more likely that few  $ML_2$  sandwich complexes also exist in equilibrium with rather large amounts of non-complexed benzocrown ether cavities as in the case of rubidium (see Figure 6). The extraction constants  $K_{ex}$  parallel roughly the extraction percentages shown in Figure 9. The polymacrocyclic ligands **2a,b**, and

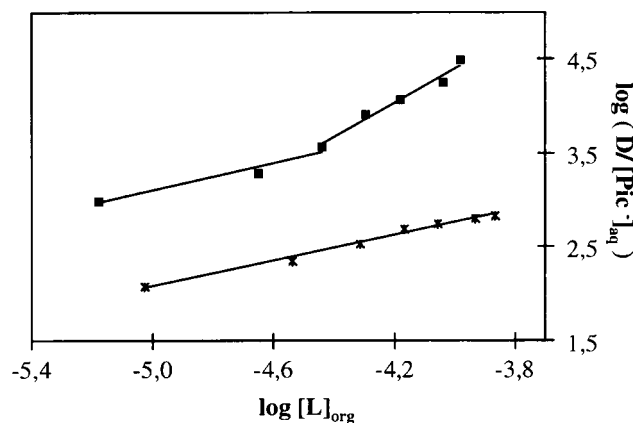


Figure 10. Variation of  $\log [L]_{org}$  as a function of  $\log (D/[Pic^-]_{aq})$  for KPic. Compounds **1** (\*) and **3** (■);  $[M^+] = 7.0 \times 10^{-5}$  mol/L.

**3** show  $K_{ex}$  values for K<sup>+</sup> and Rb<sup>+</sup> ions which are some orders of magnitude higher than the ones found for **1**. The tris(benzocrown ether) phosphate derivatives **2a,b** have the highest extraction constants for cesium ions, while those of **1** and **3** are similar and about 1.5 orders of magnitude lower. However, these  $K_{ex}$  values, according to Equation (4), only give reliable results when the stoichiometry of the  $ML_n$  complex is the same and/or does not vary over the investigated range of  $[L]_{org}$ .

Since the ligands investigated in this study are very efficient extracting agents, significant changes in the UV/Vis absorptions can be used to track changes of slope  $n$  (and hence of the  $ML_n$  composition) at low L concentrations. In Figure 10 a plot of  $\log (D/[Pic^-]_{aq})$  versus  $\log [L]_{org}$  is represented for various L : M ratios, which were increased from 0.1 (points to the left) to about 2 (points to the right).

When K<sup>+</sup> ions are extracted with the hexamacrocyclic phosphazene **3**, an inflection point is clearly seen when the L : M ratio exceeds 0.71. Below this value, the slope  $n$  to the left in Figure 10 is close to 1 while above this ratio, i.e., when the cavity concentration becomes larger than the metal ion concentration, the slope is closer to 2. With **1**, the slope remains close to one for all M : L ratios.

From these experiments we could independently verify the conclusions, i.e., the preferred formation of intramolecular sandwich  $ML_2$  complexes for larger cations, from analysis of the NMR chemical shift differences by the RMN-STAB program. We are therefore confident that the results obtained by this method, which gives a considerably easier

and more detailed insight into the distribution of L, M<sub>2</sub>L, ML and ML<sub>2</sub> complexes, is at least in tendency correct.

## Conclusion

The aim of this study was to investigate the ability of poly-macrocyclic phosphorus compounds to extract alkali metal cations M<sup>+</sup> = Li<sup>+</sup>–Cs<sup>+</sup>. The two different phosphate derivatives X=P(NMe-N=CH-B15C5)<sub>3</sub> (**2a**: X = O, **2b**: X = S) and the cyclophosphazene [N=P(NMe-N=CH-B15C5)<sub>2</sub>]<sub>3</sub> **3** in which benzo-15-crown-5 (B15C5) moieties are linked by a methylhydrazone linker to a phosphorus centre are easy to synthesise and air and water stable. The composition of organic solutions containing these new ligands as a function of the L:M ratios was investigated by fitting the observed chemical shift differences in <sup>13</sup>C NMR spectra to possible distribution equilibrium models by means of the RMNSTAB program. When **2a,b** or **3** are reacted with Li<sup>+</sup> and Na<sup>+</sup>, the formation of 1:1 ML complexes prevails as is also the case for the monocyclic compound **1**.

However, small amounts of ML<sub>2</sub> sandwich complexes also seem to be present. At higher metal ion concentrations (M:L ≈ 3) all crown ether cavities are occupied by a metal ion. Sandwich complexes ML<sub>2</sub> become the predominant species when the larger alkali ions K<sup>+</sup> and Rb<sup>+</sup> are complexed by **2a,b** and **3**. K<sup>+</sup> especially forms highly stable ML<sub>2</sub> complexes. Interestingly, even at higher metal ion concentration, the formation of ML<sub>2</sub> complexes is favoured while some crown ether cavities still remain uncomplexed. ML complexes seem to be present only in minor amounts in contrast to experiments with **1** where 1:1 complexes [K(**1**)]<sup>+</sup> and [Rb(**1**)]<sup>+</sup> prevail under the same conditions.

The strong chelate effect evoked by **2a,b** and **3**, make these ligands highly efficient extracting agents for K<sup>+</sup> and Rb<sup>+</sup> as shown by UV-Vis spectroscopy. Remarkably, even at very low ligand concentrations these new ligands proved to be very efficient. Already at about stoichiometric ML<sub>2</sub> ratios, 90% of potassium ions were extracted into the organic phase. This allowed us to verify our results obtained from NMR spectroscopy independently by another spectroscopic method. Furthermore, the selectivity for the different cations (Na<sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup> > Cs<sup>+</sup> > Li<sup>+</sup> for **1**) is inverted when the polymacrocyclic phosphorus compounds are employed. Indeed, while monocyclic formyl-B15C5 **1** extracts Na<sup>+</sup> ions better, the polymacrocyclic compounds show a higher selectivity for the larger cations K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>.

Other polymacrocyclic compounds in which the crown ether moieties were tethered together by organic bridges

also proved to be quite efficient in the extraction of larger alkali cations [19]. However, to our knowledge none of them reached the efficiencies of the compounds studied here under the same conditions. Obviously, the tetrahedral Y=P(NMeN=CH-)<sub>m</sub> core (Y= O, S, m = 3; Y = N, m = 2) evokes a favourable pre-organisation of the B15C5 units to facilitate intramolecular complex sandwich formation.

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