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## Supramolecular Chemistry

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### Ion-selective electrodes based on *p*-*tert*-butyl-homooxalixarene di(ethyl)amides

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## Ion-selective electrodes based on *p*-tert-butyl-homooxalixarene di(ethyl)amides

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The diethyl amides of *p*-tert-butyl-dihomooxalix[4]arene (**1**), *p*-tert-butyl-hexahomotrioxalix[3]arene (**2**) and *p*-tert-butyl-calix[4]arene (**3**) were used as active materials in ion-selective membrane electrodes to check the detection of different kinds of cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and tetramethylammonium cation). The electrode characteristics and selectivity coefficients were determined and compared. Optimisation of the PVC membrane composition was achieved using three different plasticisers (bis(2-ethylhexyl) adipate, *o*-nitrophenyl octyl ether and bis(2-butylpentyl) adipate). Amide **3** shows selectivity for Na<sup>+</sup>, whereas compounds **1** and **2** exhibit the highest selectivity for Pb<sup>2+</sup> among all the studied cations. The X-ray crystal structure of dihomooxalix[4]arene tetra(diethyl)amide (**1**) was determined, revealing it to be in the cone conformation.

**Keywords:** calix[4]arene; homooxalixarenes; amide derivatives; ion-selective electrodes; Pb(II) ionophores; X-ray crystallographic structure

### Introduction

Over the past three decades, research in calixarene chemistry has been carried out with considerable amount of details (1, 2). The successes in calixarene research are mainly due to their relatively easy functionalisation on both upper and lower rims to give a large variety of derivatives.

In the field of host–guest chemistry, chemical sensors (3, 4) are without doubt one of the most developed applications of the calixarene molecules. In particular, the use of neutral ionophores containing carbonyl groups at the lower rim for preparing ion-selective electrodes (ISEs) has been largely investigated, since the initial work of Diamond and McKerverey (5). Among these ionophores, functionalised calixarenes with ester groups have been the most tested, but studies with ketone and amide groups have also been performed. Owing to the biological importance of ions such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, those studies have been mainly focused on these kinds of cations, although ISEs for cations other than the alkali and alkaline earth, such as transition and heavy metal cations, have also been assessed. The harmful impact that toxic metal ions such as cadmium, mercury and lead can have on environmental quality and consequently on human health can explain the increasing interest in finding effective sensors for these metal ions. For example, the monitoring

of lead in drinking water is important to ensure that its concentration remains below the acceptable level. This cation forms complexes with hard oxygen donor atoms as well as with nitrogen and sulphur that are considered to be softer bases. Thus, a variety of compounds have been tested so far as active materials for Pb-ISEs.

Following our previous studies on ISEs based on calix[4]arene amide derivatives (6, 7), we have now extended them to homooxalixarenes (8), namely dihomooxalix[4]arene and hexahomotrioxalix[3]arene amide derivatives (9, 10). These are calixarene analogues in which one or all of the CH<sub>2</sub> bridges have been replaced by CH<sub>2</sub>OCH<sub>2</sub> groups. They are more flexible molecules than calix[4]arenes, but can still possess a cone conformation, the most appropriate for complexation, being potential hosts for the larger cations, mainly the dihomooxalix[4]arene derivatives.

In this paper, the performances of *p*-tert-butyl-dihomooxalix[4]arene tetra(diethyl)amide (**1**) and *p*-tert-butyl-hexahomotrioxalix[3]arene tri(diethyl)amide (**2**) are tested as ion-selective membrane electrodes towards a large variety of cations, including alkali, alkaline earth, transition and heavy metals, and using three different plasticisers (bis(2-ethylhexyl) adipate, DEHA; *o*-nitrophenyl octyl ether, *o*-NPOE and bis(2-butylpentyl) adipate,

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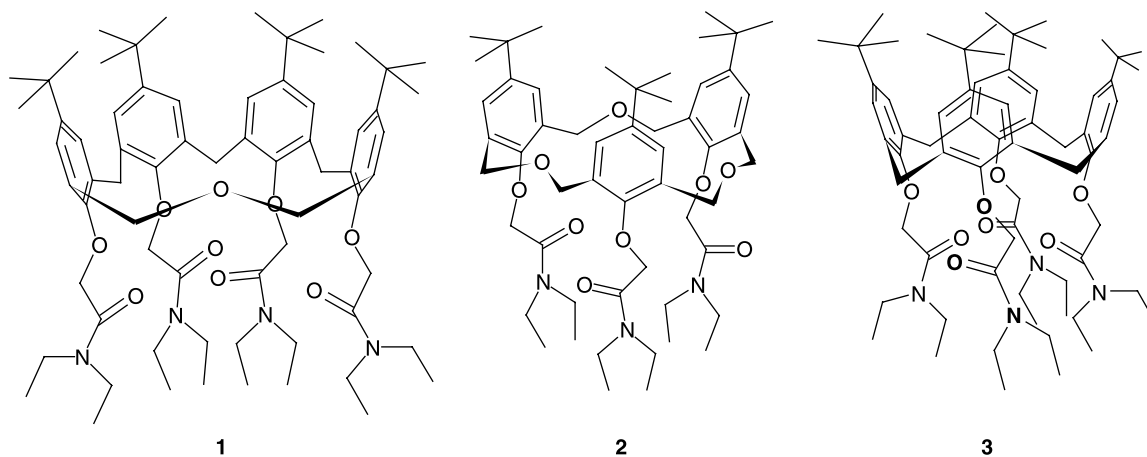


Figure 1. Structural formula of the calixarenes studied.

BBPA) in the membranes. The *p*-*tert*-butylcalix[4]arene tetra(diethyl)amide (**3**) is also studied in this work, and the results of the three derivatives (Figure 1) are compared and discussed in terms of size and conformational effects. The X-ray crystal structure of dihomooxacalix[4]arene tetraamide **1** is determined.

## Results and discussion

### X-ray structure determination

The X-ray single crystal structural analysis revealed that dihomooxacalix[4]arene (diethyl)amide **1** adopts a pinched cone conformation with the *tert*-butyl groups pitched away from the cavity (Figure 2). The conformation of compound **1** was analysed by calculation of the dihedral angles between the phenyl rings A, B, C and D (11). Rings A and C are almost parallel to each other (dihedral angle is only 5.15(18)°), whereas the rings B and D are almost perpendicular (75.75(9)°). Notably, the angle is much less

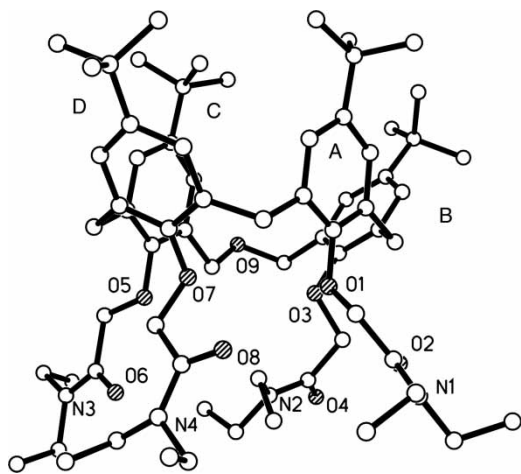


Figure 2. Crystal structure of dihomooxacalix[4]arene tetra(diethyl)amide **1**.

than the commonly observed value of 90° for regular calix[4]arenes. The presence of the oxygen bridge (O9) is the most probable cause of this deformation. Hydrogen bonds or interactions with the solvent molecules are not observed.

Attempts to obtain crystals of the complexes metal-ligand, especially with lead, were unsuccessful.

### Potentiometric studies: ISE

The ionophoric properties of di(ethyl)amides **1**, **2** and **3** were studied by using them in ISE. All these compounds had been synthesised according to the literature and obtained in a cone conformation (12–14). Owing to the high lipophilicity of the macrocyclic ligands possessing four (**1** and **3**) or three (**2**) *tert*-butyl groups, all the electrodes prepared were stable and long lasting. The potentiometric responses of these ISEs towards a variety of ions, including alkali ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ ), alkaline earth ( $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ), transition ( $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) and heavy metals ( $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ), were measured. Among these cations with varying sizes, charges and nature, the strongest response was induced by the presence of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Pb}^{2+}$ . This behaviour was expected, as the homooxa ligands are strong binders for those cations (9, 10) and the high selectivity of calix[4]arene amides, like derivative **3**, for  $\text{Na}^+$  is also known (6, 15).

The electrode membrane was optimised using three different plasticisers: DEHA, BBPA and NPOE. DEHA has a structure similar to BBPA, which in many cases is a good plasticiser for  $\text{Na}^+$ -selective membrane electrodes (enhancing the  $\text{Na}^+$ -response), whereas the  $\text{Pb}^{2+}$  cation usually prefers a more polar plasticiser such as NPOE. The membrane compositions and the characteristics of the electrodes are presented in Table 1 and illustrated in Figures 3 and 4.

In the case of homooxa di(ethyl)amides **1** and **2**, the data (Table 1) reveal that the use of DEHA as plasticisers

Table 1. Characteristics of the electrodes.

Ionophore	Plasticiser	Detected ion	Slope (mV/decade)	Linear range ( $-\log C$ )
<b>1</b>	DEHA	Na <sup>+</sup>	50.3	5–1
		K <sup>+</sup>	49.7	4.5–1
		Pb <sup>2+</sup>	28.8	5.5–2
<b>2</b>	DEHA	Na <sup>+</sup>	52.3	4.5–1
		K <sup>+</sup>	46.5	4–1
		Pb <sup>2+</sup>	30.5	6–2
<b>1</b>	NPOE	Na <sup>+</sup>	34	5.5–2
		K <sup>+</sup>	39.4	5–2
		Pb <sup>2+</sup>	37.4	6–4
<b>2</b>	NPOE	Na <sup>+</sup>	46.2	4.5–1
		K <sup>+</sup>	26.7	4–1
		Pb <sup>2+</sup>	31.4	5.5–2
<b>1</b>	BBPA	Na <sup>+</sup>	50.3	5–2
		K <sup>+</sup>	43.4	5–2
		Pb <sup>2+</sup>	39.6	5–3
<b>2</b>	BBPA	Na <sup>+</sup>	51.2	4–1
		K <sup>+</sup>	47.2	3–1
		Pb <sup>2+</sup>	51.3	6–1
<b>3</b>	BBPA	Na <sup>+</sup>	62.5	5–2
		K <sup>+</sup>	39.2	3–1
		Pb <sup>2+</sup>	35.4	4–1

gives the best results relative to both mono and divalent cations, as the slopes of the electrode responses are close to the Nernstian values (59.15 and 29.58 mV/decade, respectively). Comparison between the three calixarene-based electrodes shows that homooxacalixarenes **1** and **2** exhibit the best behaviour for Pb<sup>2+</sup>, while calix[4]arene amide **3** shows a preference for Na<sup>+</sup> cations.

Potentiometric selectivities for the electrodes based on ionophores **1**, **2** and **3** in all membranes were determined by a separate solution method (SSM) (16). The selectivity coefficients expressed as  $\log K_{M,X}^{\text{pot}}$  are presented in diagram form in Figure 5. The selectivity coefficients for compound **1** are the best in PVC/NPOE membrane ( $\log K_{\text{Pb,Na}}^{\text{pot}} = -2.5$ ). However, low upper detection limit (narrow linear range) and anionic response of this

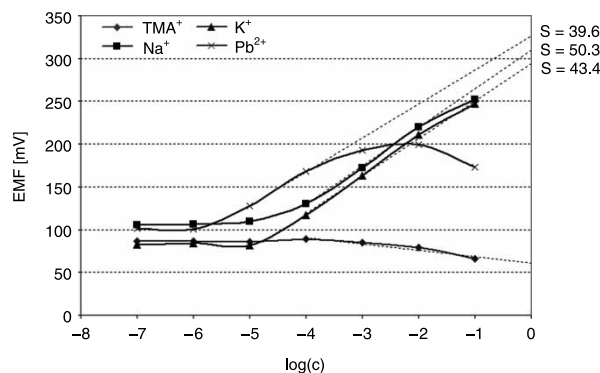


Figure 3. Electrode characteristics containing ligand **1** in a PVC/BBPA membrane.

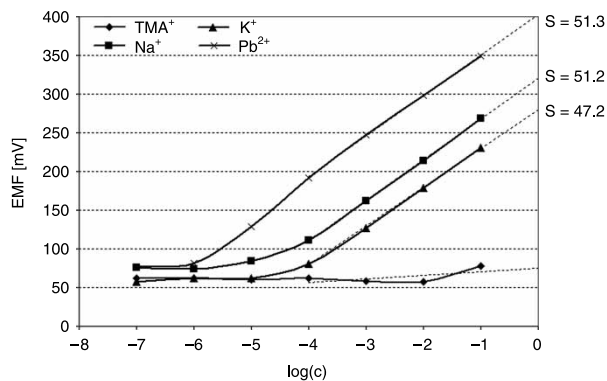


Figure 4. Electrode characteristics containing ligand **2** in a PVC/BBPA membrane.

electrode (Table 1) suggest strong interaction of ligand **1** and Pb(II) cation. The case of compound **2** is different. The selectivity coefficients for Pb/Na in less polar plasticiser are better ( $\log K_{\text{Pb,Na}}^{\text{pot}} = -1.5$ ) than in PVC/NPOE membrane ( $\log K_{\text{Pb,Na}}^{\text{pot}} = -0.3$ ). The analogous amide **3**, based on classical calix[4]arene, is definitely sodium selective with selectivity coefficient  $\log K_{\text{Pb,Na}}^{\text{pot}} = -3.3$ .

Potentiometric selectivity coefficients reflect the ion–ligand complex formation constants directly in the membrane. The selectivity coefficients obtained for the electrodes with PVC/BBPA membranes were used to determine those constants, using the simple method proposed by Pretsch (17). The values obtained are shown in Table 2.

The equilibrium constants are related to the estimated concentration of the species in the organic membrane phase and to the activities of the ions in the aqueous phase, so they are not proper thermodynamic parameters. Values in Table 2 show that the interactions of dihomooxacalix[4]arene amide **1** and calix[4]arene amide **3** in PVC/BBPA membrane with Na<sup>+</sup> are of similar strength, whereas those with hexahomotrioxacalix[3]arene amide **2** are weaker. This is probably due to its higher conformational flexibility. The replacement of the methylene bridges with dimethyleneoxa bridges in triamide **2** increases its flexibility. The  $\Delta G^\ddagger$  barriers for conformational inversion in CDCl<sub>3</sub> are <9, 12.9 and 15.7 kcal/mol for the corresponding parent calixarenes of **2**, **1** and **3**, respectively (18). Moreover, **2** possesses only three amide groups and consequently only six coordination sites are available to surround the cations, compared with the eight sites of the tetraamides. In the case of K<sup>+</sup> interactions, amide **1** exhibits the highest constant value, reflecting its larger cavity size, more suitable to accommodate a larger cation. These constants determined in the membrane for ligands **1** and **3**, although lower, follow the same selectivity trend observed in the 1:1 stability constants previously determined in methanol (9). In the case of Pb<sup>2+</sup>, triamide **2** shows the highest constant value

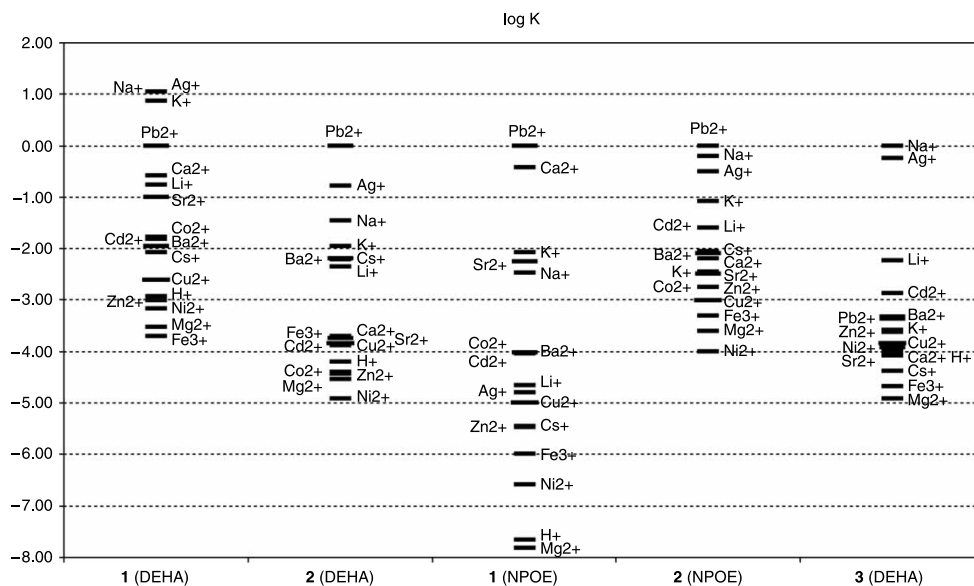


Figure 5. Potentiometric selectivity coefficients of ligands **1**, **2** versus  $\text{Pb}^{2+}$  in PVC/DEHA and PVC/NPOE membrane  $\log K_{\text{Pb,M}}^{\text{pot}}$  and of ligand **3** versus  $\text{Na}^+$  in PVC/DEHA ( $\log K_{\text{Na,M}}^{\text{pot}}$ ) for comparison.

closely followed by tetraamide **1**, whereas for **3** that value is approximately 2.5 log units lower. It seems that more importantly than the number of donating sites, it should be the conformational rearrangement that the pendant arms of the ligands can suffer upon complexation, to better accommodate that cation. However, it is worthwhile pointing out that the coordination number of  $\text{Pb}^{2+}$  is 6 (19). Thus, three phenolic oxygen atoms and three carbonyl oxygen atoms should suffice for inclusion of that cation.

The fact that plasticisers of a different nature, i.e. ether (NPOE) and ester (DEHA and BBPA), induce different  $\text{Pb}^{2+}$ -selectivity in homooxalixarene amides **1** and **2** seems to suggest that different coordination types occur in the two membranes. The selectivity  $\text{Pb}^{2+}/\text{Na}^+$  of ligand **1** is better in NPOE than in DEHA, which has also been observed for other calix[4]arenes. This suggests that in ligand **1** the  $\text{Pb}^{2+}$  cation is complexed by the same type of oxygen atoms as in calix[4]arene **3**, i.e. phenoxy and carbonyl oxygen atoms. By contrast, the selectivity  $\text{Pb}^{2+}/\text{Na}^+$  by ligand **2** in NPOE is worse than that in DEHA, which might suggest that  $\text{Pb}^{2+}$  cation is

complexed in a different part of the compound. Nevertheless, results previously obtained either by NMR or by molecular mechanics/*ab initio* techniques for ligand **2** (10) and also with an analogous derivative (20) indicate that the oxygen atoms of the  $\text{ArCH}_2\text{OCH}_2\text{Ar}$  bridges do not participate in metal binding.

## Conclusions

The performance of the ISEs based on homooxalixarene amides **1** and **2** and on calix[4]arene amide **3** indicated a high affinity of the homooxa ligands for the heavy metal cation  $\text{Pb}^{2+}$ , whereas calix[4]arene **3** showed selectivity for  $\text{Na}^+$ . From the comparison between the three plasticisers (DEHA, *o*-NPOE and BBPA) used in the PVC-membrane, it is clear that their role is not negligible.

The X-ray diffraction studies revealed a cone conformation for dihomooxalix[4]arene tetra(diethyl)-amide **1**, confirming that all the three amides exist in the same conformer in the electrode membranes.

## Experimental

### Crystallography

Compound **1** (15 mg) was dissolved in the minimal amount of methylene chloride and treated with 1 ml of methanol. After several days, transparent crystals, suitable for crystallography, were obtained.

The structure of **1** was determined by single crystal X-ray diffraction. The data were collected at 120 K on a

Table 2. Complex formation constants ( $\log \beta$ )<sup>a</sup>.

Ionophore	$\text{Na}^+$	$\text{K}^+$	$\text{Pb}^{2+}$
<b>1</b>	$5.51 \pm 0.08$	$5.08 \pm 0.03$	$7.93 \pm 0.05$
<b>2</b>	$4.83 \pm 0.08$	$3.80 \pm 0.05$	$8.22 \pm 0.05$
<b>3</b>	$5.52 \pm 0.04$	$2.85 \pm 0.04$	$5.58 \pm 0.02$

<sup>a</sup>SD shown is from at least three replicate measurements.

Table 3. Crystal data and structure refinement details for **1**.

Identification code	<b>1</b>
Empirical formula	C <sub>69</sub> H <sub>102</sub> N <sub>4</sub> O <sub>9</sub>
Molecular weight	1131.55
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 10.9809(10) Å, $\alpha$ = 97.039(9)° <i>b</i> = 13.7265(19) Å, $\beta$ = 94.628(7)° <i>c</i> = 22.678(2) Å, $\gamma$ = 100.731(10)°
Volume	3314.3(6) Å <sup>3</sup>
<i>Z</i>	2
Density (calculated)	1.134 mg/m <sup>3</sup>
Absorption coefficient	0.074 mm <sup>-1</sup>
<i>F</i> (000)	1232
Crystal size	0.41 × 0.13 × 0.12 mm <sup>3</sup>
Theta range for data collection	2.36–25.50°
Index ranges	–13 ≤ <i>h</i> ≤ 13, –16 ≤ <i>k</i> ≤ 12, –26 ≤ <i>l</i> ≤ 27
Reflections collected	24,116
Independent reflections	12,324 [ <i>R</i> (int) = 0.0540]
Completeness to $\theta = 25.50^\circ$	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.97425
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	12,324/0/770
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.018
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0743, <i>wR</i> 2 = 0.2015
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1187, <i>wR</i> 2 = 0.2283
Largest diff. peak and hole	0.759 and –0.313 e/Å <sup>3</sup>

KM4CCD diffractometer equipped with a Sapphire2 CCD detector. Enhanced X-ray Mo K $\alpha$  radiation source with a graphite monochromator was used. The preliminary calculations were done using CrysAlis software package (11). The structure was solved by direct methods and all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least squares procedure based on *F*<sup>2</sup>. All hydrogen atoms were refined using isotropic model with *U*<sub>iso</sub> values fixed to be 1.5 times *U*<sub>eq</sub> of C atoms for CH<sub>3</sub> or 1.2 times *U*<sub>eq</sub> for CH<sub>2</sub> and CH groups. Refinement was carried out using SHELXL-97 program package (21). Ethyl group bound to N4 (labelled C63 and C64) was refined as disordered over two positions with the probabilities of 0.521(12)/0.479(12).

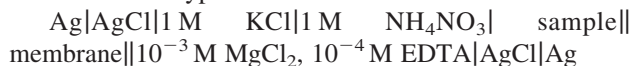
Crystal data and structure refinement details for compound **1** are presented in Table 3.

### Potentiometric studies

#### Membrane preparation and EMF measurements

The membranes were prepared by dissolving about 4 mg of each ionophore, 60 mg of PVC, 120 mg of plasticiser (BBPA, DEHA and *o*-NPOE) and 0.4 mg of KTpCIPB salt with a lipophilic anion, about 184 mg in total, in

1.5 ml of dried and distilled THF. Each solution was poured into a glass ring (24 mm in diameter). After slow evaporation of the solvent overnight, several membranes of 7-mm diameter were cut from each mother membrane and were incorporated into Ag/AgCl electrode bodies of IS 561 type (Moeller S.A., Zurich). A double-junction reference electrode (Radelkis OP0820P) and 1 M NH<sub>4</sub>NO<sub>3</sub> solution in the bridge cell were used. The EMFs were measured at 20°C using a Lawson Lab 16 EMF, multi-channel voltmeter. The electrodes were conditioned in 10<sup>-4</sup> M HNO<sub>3</sub>. The measurements were carried out in separate solutions of known cation concentrations starting from 10<sup>-8</sup> to 10<sup>-1</sup> M. pH 4 was adjusted and stabilised by addition of HNO<sub>3</sub>. The measurements were carried using the cells of the type:



#### Determination of selectivity coefficients

The potentiometric response of the electrodes for a series of cations was studied using chlorides or nitrates. The selectivity coefficients (log *K*<sub>M,X</sub><sup>pot</sup>) were determined by the SSM and were calculated (Equation (1)) using the EMF values extrapolated from the characteristics of the

Table 4. Composition of the PVC/BBPA membranes.

	$L_T$ (mmol/kg)	$R_T$ KTpCIPB (mmol/kg)	BBPA (mg)	PVC (mg)
Blank	0	5.52	121.0	61.0
<b>1</b>	24.21	5.40	120.5	61.5
<b>2</b>	23.85	5.43	120.0	60.0
<b>3</b>	23.13	5.33	120.0	62.5

electrodes studied for the cation 1 M concentration (16):

$$\log K_{M,X}^{\text{pot}} = \frac{(E_X - E_M)z_M F}{2.303RT} + \left(1 - \frac{z_M}{z_X}\right) \log a_X. \quad (1)$$

In Equation (1), M and X correspond to the primary and the interfering cations, respectively, and  $z_M$  and  $z_X$  correspond to their charges.

#### Determination of complex formation constants in the electrode membrane

The values of the complex formation constants ( $\log \beta$ ) for ionophores **1**, **2** and **3** in PVC/BBPA membranes were estimated by the method described by Pretsch and Ceresa (17). The composition of these membranes is given in Table 4. Tetramethylammonium cation ( $\text{TMA}^+$ ) was used as a reference ion. The calculation is based on the assumption that the ionophores form stable 1:1 complexes with metal ions such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Pb}^{2+}$ . The values of the complex formation constants were calculated from the following equation:

$$\beta = \frac{K_{M,\text{TMA}}^{\text{pot}}(\text{IE})}{K_{M,\text{TMA}}^{\text{pot}}(L)[L_T - R_T]}, \quad (2)$$

where  $L_T$  is the total concentration of the ionophore within the membrane,  $R_T$  the total concentration of the lipophilic anionic site (KTpCIPB) in the membrane,  $K_{M,\text{TMA}}^{\text{pot}}(\text{IE})$  the selectivity coefficient for the membrane without ionophore,  $K_{M,\text{TMA}}^{\text{pot}}(L)$  the selectivity coefficient for the membrane with ionophore ( $L$ ) and  $M = \text{Na}^+$ ,  $\text{K}^+$  and  $\text{Pb}^{2+}$ .

#### Supplementary material available

Crystallographic data for the structure **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 702250.

#### Acknowledgements

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