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Heavy metal complexation by *N*-acyl(thio)urea-functionalized cavitands: synthesis, extraction and potentiometric studies

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Abstract—The synthesis and binding properties of resorcinarene-based cavitands functionalized with *N*-acylthiourea moieties towards different cations are described. Extraction studies with metal (Pb^{2+}, Cu^{2+}, Ag^+, Hg^{2+}, Cd^{2+}, Eu^{3+}, Fe^{3+}, K^+, Na^+, and Ca^{2+}) picrates and the incorporation in ion selective electrodes (ISEs), show that there is more than a 40% increase of the Ag^+ extraction for *N*-acylthiourea ionophores (**2**, **3**, and **8**) in comparison with *N*-benzoyl-*N*′-benzylthiourea (**9**). Ionophore **8**, which has a C_3 chain between the platform and the ionophore, extracts two times more Cu^{2+} than the more rigid one (**2**). Stoichiometry studies showed for ligand **2** a ligand/metal ratio of 1:1, while for model compound **9** a ratio of 1:2 was found. Potentiometric studies of electrodes revealed that cavitands **2**, **3**, and **8** induce a significantly different selectivity pattern compared to the cation-exchanger used, as well as model compound **9**. Especially, a considerable enhancement of the selectivity towards Ag^+ and Pb^{2+} over K^+, Ca^{2+}, and Na^{2+} ions was observed.

1. Introduction

N-Acylthioureas represent an important class of ionophores which are already known for a long time as metal chelating agents.[1] They are very useful for the removal of heavy metal cations from waste water[2] and as selective extractants for separation[3] and concentration of precious metal cations such as Pd^{2+} and Pt^{2+}.[4] Several groups have reported their strong binding with Cu^{2+}.[5,6] *N*-acylthioureas have also been used as ionophores in ion selective electrodes for the detection of Pb^{2+}, Hg^{2+}, and Cd^{2+}.[7]

Complexation of transition and heavy metal cations is favored by the presence of soft donor atoms such as nitrogen, sulfur or phosphorus, but also ligands containing the harder oxygen atoms can bind these cations. *N*-acylthioureas have sulfur, nitrogen and oxygen as donor atoms, allowing them to act as monodentate sulfur donors, bidentate oxygen and sulfur, or oxygen and nitrogen donors. They can also coordinate through the keto- or enol–thione form, depending of the ligands, the metal ions, and counter anions present.[8]

For the coordination of a metal ion more than one *N*-acylthiourea ligand is necessary. In the literature many examples are known of preorganization of ligating sites on a molecular platform, giving rise to improved complexation properties.[9] Appropriately functionalized calix[4]arenes[10,11] are being used for the complexation of alkali and alkaline earth metal ions and to a lesser extent heavy and transition metal ions.[12]

In this paper we describe our results of the use of the more rigid resorcinarene-based cavitand platform[13] for the attachment of *N*-acyl(thio)urea ligating sites. The complexation, extraction, and sensing behavior of the resulting ionophores (Chart 1) will be discussed.

2. Results and discussion

2.1. Synthesis

Reaction of tetrakis(aminomethyl)cavitand[14] (**1**) with ethoxycarbonyl isothiocyanate in chloroform gave *N*-acylthiourea derivative **3** in 69% yield (Scheme 1). In the ^{1}H

Keywords: Heavy metals; Complexation; Cavitands; Ion selective electrodes.

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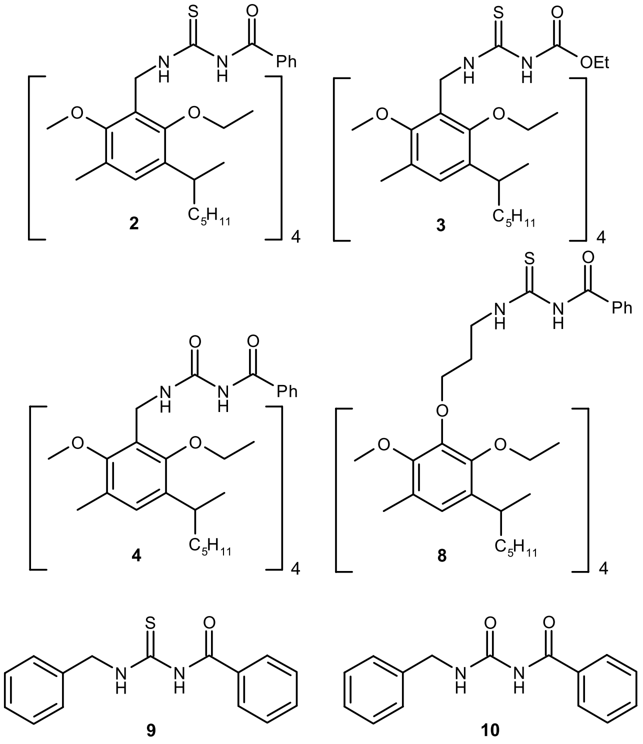
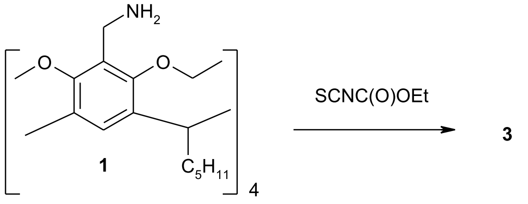


Chart 1. *N*-Acyl(thio)urea derivatives.



Scheme 1.

NMR spectrum the benzylic methylene hydrogens shifted upfield from δ 3.61 to δ 4.75 due to the introduction of a thiocarbonyl group.

In order to study the influence of a longer spacer between the platform and the ligating site, tetrahydroxycavitand[15] (**5**) was reacted with 3-bromopropylphthalimide in the presence of NaH as a base in DMF to give tetrakis[(phthalimido)-propoxy]cavitand (**6**) in 65% yield. Subsequent removal of the phthalimido groups with hydrazine hydrate and reaction of the resulting tetrakis(aminopropoxy)cavitand (**7**) with benzoyl isothiocyanate gave cavitand **8** in 50% yield (Scheme 2). In the ^{1}H NMR spectrum the methylene group adjacent to the nitrogen shifts from δ 3.25 in **7** to δ 3.93 in **8**.

In all the cases the introduction of the ligating sites clearly followed from the mass spectra and satisfactory elemental analyses. The other ionophores used, viz. **2**,[16] **4**,[16] **9**,[17] and **10**[18] were prepared by literature procedures.

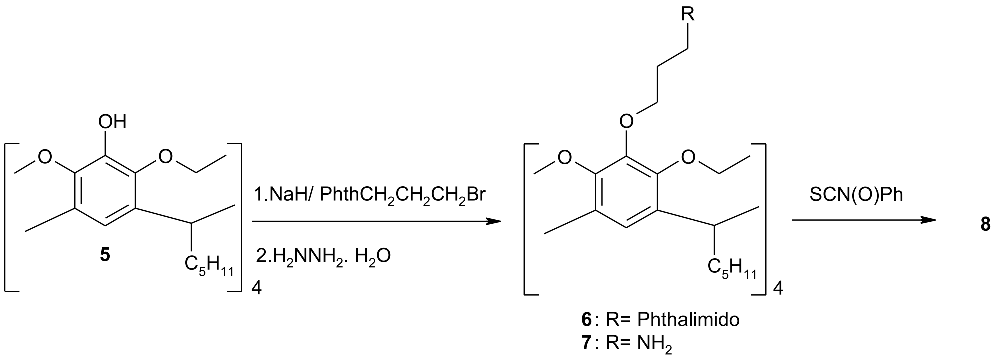
2.2. Liquid–liquid extraction

With the different *N*-acyl(thio)urea containing ionophores, **2**, **3**, **4**, **8**, **9**, and **10** extraction experiments were performed with various heavy metal ions according to the standard picrate extraction method.[14,19] The results, expressed as a percentage of extracted cation (%*E*), are summarized graphically in Figure 1.

All tetrafunctionalized compounds exhibit high extraction values for Ag^+, especially the *N*-acylthiourea derivatives **2**, **3**, and **8**. The extraction levels are higher than those observed for other sulphur-containing calix[4]arene-based ionophores.[20] Moreover, ionophores **2**, **3**, and **8** display high Ag^+/Pb^{2+} selectivities: $S_{Ag+/Pb2+}=26.3$, 42.4, and 52.6, respectively, in comparison with values of 11.4 and 8.1 reported for *p-tert*-butyldihomooxacalix[4]arene and a *p-tert*-butylcalix[4]arene with phenylketones as ligating sites, respectively.[21]

Surprisingly, both tetrakis[(benzoylthioureido)methyl]-cavitand **2** and the corresponding model compound **9** have more or less the same extraction profile. However, tetrakis-[(benzoylthioureido)propoxy]cavitand **8**, only having a longer spacer than **2**, is able to extract twice the amount of Cu^{2+} than **2** (29%) and model compound **9** (22%). It is striking that **8** extracts two times more Hg^{2+} than Cd^{2+}, since these cations have a similar ionic radius.[22] Apparently, the slightly improved extraction properties come from the higher flexibility of the ligating sites, rather than the preorganization.

In the case of compound **4** preorganization clearly plays a role in the complexation of the alkali and alkaline earth metal ions as follows from comparison of the data of **4** and model compound **10**. Model compound **10** shows almost no extraction of K^+ (3%) and Ca^{2+} (4%), and only 15% of Na^+ was extracted, whereas **4** is able to extract K^+ (37%),



Scheme 2.

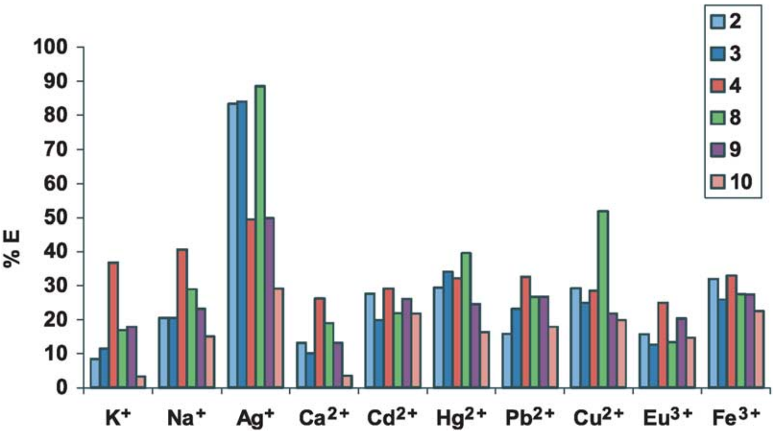


Figure 1. Extraction results of *N*-acyl(thio)urea derivatives. Conditions: $[L]_{o,i}=10^{-3}$ M; $[M^{n+}]_{w,i}=10^{-3}$ M; $[LiPic]_w=10^{-4}$ M; $[HNO_3]_w=10^{-3}$ M; pH 3.

Na^+ (41%) and Ca^{2+} (26%) in substantially higher percentages. However, in general, **4** extracts the different cations more or less to the same extent.

The stoichiometry coefficient p was determined using Eq. 1 taking into account that only one complex is present and that the metal is unassociated in the aqueous phase.

$$\log D = \log K_{ex} + n\log[Pic^-]_{aq} + p\log[L]_{org} \quad (1)$$

The representation of log D versus log [L] should be linear with a slope of p, where p indicates the number of ligand molecules involved per cation in the extracted species. Plots of log D versus log [L] for the extraction of Cu^{2+} by compound **2** and model compound **9** are given in Figure 2. For the complexation of **2** with Cu^{2+} the plots are linear with slopes close to one, in agreement with the formation of 1:1 complexes. In the case of model compound **9** the slope is close to 2 indicating the formation of 1:2 complexes, which is in agreement with the reported complexation behavior.[23] The same stoichiometries were obtained for Pb^{2+}.

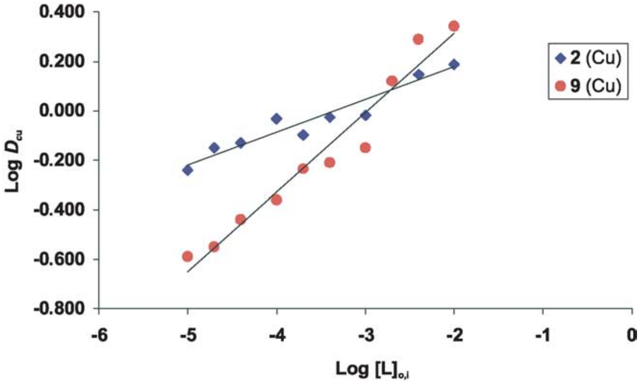


Figure 2. Plots of log $D_{Cu^{2+}}$ versus log $[L]_{o,i}$ of **2** and **9**. Conditions: $[Cu^{2+}]_{w,i}=10^{-4}$ M; $[LiPic]_w=10^{-3}$ M; $[HNO_3]=10^{-3}$ M; pH 3.

2.3. Potentiometric studies

The *N*-acylthiourea derivatives **2**, **3**, **8**, and **9** were examined as ionophores in *o*-NPOE/PVC membranes containing also 30% mol of lipophilic anionic additives. To obtain unbiased $K^{pot}_{I,J}$ values, the calibration plots for various cations were collected starting from the most discriminating ones.[24] The preliminary selectivity order for each ionophore was established after the preliminary screening of the electrode selectivities. The electrodes exhibited a Nernstian or near-Nernstian response in pure solutions of the moderate and highly discriminating cations, at least within the range 10^{-3}– 10^{-1} M. When a flattening (or a reversing) of the calibration curves was observed, the selectivity coefficients were obtained from the Nernstian part of the response curve at lower activities.

The logarithmic values of the selectivity coefficients calculated for Pb^{2+} as the primary cation ($\log K^{pot}_{Pb,J}$) are presented in Figure 3. Comparison of the results obtained for membranes containing *N*-acylthiourea derivatives and those for membranes containing only ion-exchanger (KTFPB) revealed that ionophores **2**, **3**, **8**, and **9** induce selectivities significantly different from the so-called Hofmeister series. This indicates that the compounds studied are capable of selective interactions with cations within the polymeric membrane phase. The incorporation of *N*-acylthiourea cavitands **2**, **3** or **8** into a polymeric membrane containing KTFPB led to dramatic changes in the electrode selectivity for Pb^{2+} over Na^+, K^+, and Ca^{2+} ions. A less pronounced improvement of the selectivity over Na^+ and Ca^{2+} could be seen in the case of model compound **9**.

Due to the fact that compounds **2**, **3**, **8**, and **9** possess a soft ligating C═S group it was expected that they might exhibit complexation properties toward soft metal cations. Indeed, electrodes with membranes based on *N*-acylthiourea ionophores showed an enhanced selectivity towards Ag^+ compared to membranes with cation-exchanger. Moreover, the selectivity varied depending on the architecture of the *N*-acylthiourea derivative. The largest value of $\log K^{pot}_{Pb,Ag}$ was determined for ionophore **3**. It was also found that the electrodes with membranes containing ionophores (except for compound **3**) provided an increased selectivity towards Cu^{2+} compared to membranes without ionophore. At this point it should be stressed that the value of $\log K^{pot}_{Pb,Cu}$ for the electrodes based on **8** is only roughly estimated, because during the very first calibration in copper nitrate solutions the electrodes responded to Cu^{2+} ion in a super-Nernstian fashion. Moreover, after 24 h contact of the membrane with 10^{-2} M copper nitrate solution, the electrode lost its initial selectivity and the response to Cu^{2+}.

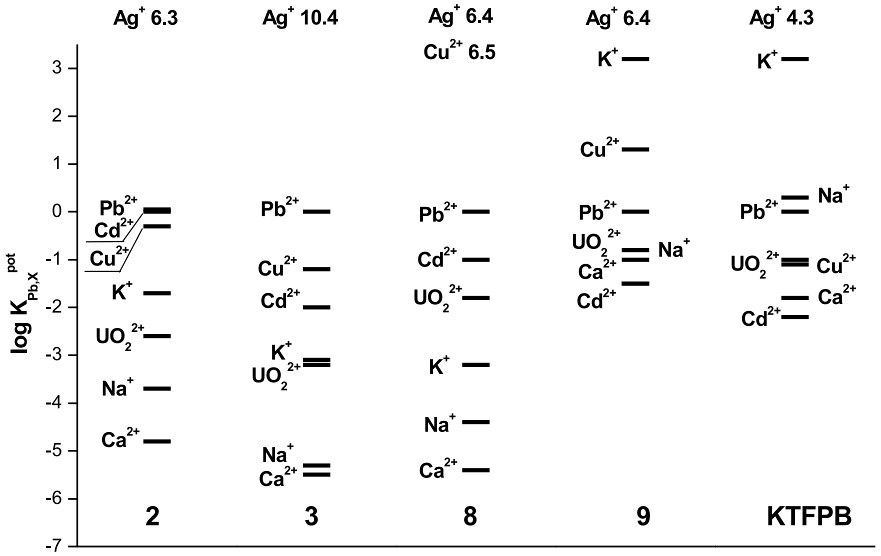


Figure 3. Selectivity coefficients for electrodes prepared with PVC/*o*-NPOE (1:2) membranes containing compounds **2**, **3**, **8**, **9**, and lipophilic sites (KTFPB) as well as membranes with ion-exchanger only.

Table 1. Formal complex formation constants, log β_{IL_n},[a] obtained with ionophores **2**, **3**, **8**, and **9** in PVC/*o*-NPOE (1:2) membranes, using the segmented sandwich method

Cation	log β_{IL_n}, Membrane			
	2[b]/KTFPB	**3**[b]/KTFPB	**8**[b]/KTFPB	**9**[c]/KTFPB
Pb^{2+}	8.9	11.6	11.4	8.8
Cd^{2+}	10.3	11.8	9.8	7.4
Cu^{2+}	8.1	12.4	(18.7)[d]	11.3
Ag^{+}	7.2	10.1	8.0	6.4
Na^{+}	4.9	4.9	4.4	5.3
UO_2^{2+}	5.4	10.3	8.9	8.4

[a] Standard deviations ≤0.3 (from at least three replicate measurements).
[b] The stoichiometry of the ion–ionophore complexes was assumed to be 1:1.
[c] The stoichiometry of the ion–ionophore complexes was assumed to be 1:2.
[d] Standard deviation ≤1.3 (from at least three replicate measurements).

Anionic response was observed in solutions more concentrated than 10^{-3} M. This could indicate very strong and irreversible complexation of Cu^{2+} by **8** or unidentified interactions between Cu^{2+} and the *N*-acylthiourea ligating sites leading, for example, to changes in Cu^{2+} oxidation state or changes in ionophore structure (the membranes become slightly greenish). Interestingly, this type of behavior has not been noted for other *N*-acylthiourea ionophores studied in this work. However, a similar phenomenon was observed before for azothiacrown ethers.[25]

It is well established that selectivity coefficients for neutral carrier-based membranes are typically related to the differences in the free energies of solvation of the ions in the sample and membrane phase, the stability constants of the ion–ionophore complexes in the membrane, and the concentrations of the ionophore and ionic sites in the membrane.[26] However, the main factor that is primarily responsible for the selectivity of polymeric membrane electrodes is the selectivity of ion–ionophore interactions that can be expressed by relative stability constants of complexes formed by an ionophore with primary and interfering ions within the membrane phase.

The complex formation constants were determined by means of the segmented sandwich method.[27] The values of the complex formation constants for ionophores **2**, **3**, **8**, and **9** and chosen cations are collected in Table 1.[†] It was found that cavitand **3** with [–NH–C(S)–NHC(O)OEt] groups forms slightly stronger complexes than the one with [–NH–C(S)–NHC(O)Ph] moieties (**2**) with most of the examined cations. This can be explained by the fact that ethoxycarbonyl moieties interact stronger than phenylcarbonyl groups with hard and soft Lewis acids.[28] In addition, the ethoxy substituents are smaller and more flexible than the –C(O)Ph moieties.[29]

The complex formation constants, log β_{ML}, for **8** with Pb^{2+} and especially Cu^{2+} are significantly larger than those for **2** (Table 1). This indicates that the presence of a longer spacer (–C_3H_6– in **8** vs –CH_2– in **2**) might create a better architecture of the cavity for complexation of these cations. However, the value of log β_{CuL} is given in brackets and

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[†] It should be noted that no direct correlation can be made between the extraction data (Fig. 1) and the formation constants (Table 1), since in the first case the partitioning coefficient of the cations involved has to be taken into account.

should be treated as an approximation. This is due to the fact that the reproducibility of the potential measurements was much worse than in other cases ($\Delta\log \beta_{\mathrm{CuL}} \leq \pm 1.3$) and, as mentioned above, electrodes with membranes doped with **8** did not exhibit a linear response to the logarithm of the Cu^{2+} activity in sample solutions.

For ionophores **2** and **9**, additional membranes with a different amount of the ionophore (5–100 mmol/kg) and constant content of anionic additives (1 mmol/kg) were prepared in order to check the stoichiometry of the complexes formed with chosen cations (Cu^{2+} and Pb^{2+}).

The results obtained for Cu^{2+} are illustrated in Figure 4. The linear relationships between the EMF and logarithmic values of free ionophore concentration suggest that one sort of complexes is predominant in the membrane.[30] The slope of the regression line close to 30 mV indicates a 1:1 **2**-Cu^{2+}complexation, while in the case of **9**-Cu^{2+} a complexation with 1:2 stoichiometry can be expected (the slope is close to 60 mV). The same behavior was found in the case of Pb^{2+}.

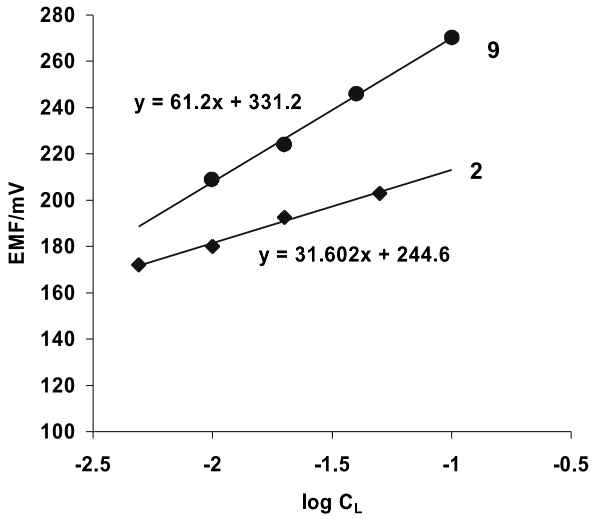

Figure 4. Dependence of the sandwich membrane electrodes' potential values on the content of ionophore: **2** and **9**.

Comparison of the relative values of the stability constants, $\log \beta_{\mathrm{ML}}$, and the hydrophobicity of the cations with the respective selectivity coefficients, $\log K^{\mathrm{pot}}_{\mathrm{Pb,M}}$, reveals that the stronger Cu^{2+} interference (higher values of $\log K^{\mathrm{pot}}_{\mathrm{Pb,M}}$) for membranes with ionophores **8** and **9** as well as the Ag^{+} interference in the case of the membrane containing **3** are related to a higher affinity of these ionophores to Cu^{2+} or Ag^{+} than to Pb^{2+} compared to cavitand **2** (see $\log \beta_{\mathrm{ML}}$ for Cu^{2+} or Ag^{+} vs Pb^{2+}).

3. Conclusion

We have demonstrated that *N*-acylthiourea tetrafunctionalized cavitands are reasonable to good ionophores for the extraction and detection of soft metal ions with a preference for Ag^{+}. The attachment of four *N*-acylthiourea moieties to a molecular platform clearly improves the complexation behavior. In the case of ionophores **2**, **3**, and **8** a 40% increase of the Ag^{+} extraction was observed, compared with the corresponding model compound **9**. The importance of flexibility of the ligating sites clearly follows from the different complexation behavior of ionophores **2** and **8**, only differing in length of the spacer between the platform and the ligating site. The latter ionophore shows a very good affinity for Cu^{2+}. In all cases there is a good correlation between the liquid–liquid extraction and ISE data.

4. Experimental

4.1. General

NMR experiments were performed using a Varian Unity 300 WB NMR spectrometer operating at 300 and 100 MHz for the ^{1}H and ^{13}C nuclei, respectively. All spectra were recorded in $CDCl_3$. Residual solvent protons were used as internal standard and chemical shifts are given in ppm relative to tetramethylsilane (TMS). Fast atom bombardment (FAB) mass spectra were measured on a Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. All solvents were purified by standard procedures. All other chemicals were analytically pure and were used without further purification. All reactions were carried out under an inert argon atmosphere. Melting points (uncorrected) of all compounds were obtained on a Reichert melting point apparatus.

4.1.1. Tetrakis[(ethoxycarbonylthioureido)methyl]cavitand 3. A solution of tetrakis(aminomethyl)cavitand **1** (150 mg, 0.16 mmol) and ethoxycarbonyl isothiocyanate (252 mg, 0.96 mmol) in acetonitrile (10 mL) was stirred overnight at room temperature. The white precipitate was filtered off and dried in vacuo to afford **3** (160 mg, 69%), mp 143–146 °C; FAB-MS: *m/z* 1457.0 ($[M+H]^{+}$, calcd 1457.0); ^{1}H NMR ($CDCl_3$) δ 9.86 (s, 4H, CH_2NHCO), 7.93 (s, 4H, CSNHCO), 7.05 (s, 4H, ArH), 6.01 (d, 4H, $J=7.3$ Hz, OCH_2O), 4.75–4.80 (m, 12H, ArCHAr, $ArCH_2NH$), 4.41 (d, 4H, $J=7.3$ Hz, OCH_2O), 4.21 (q, 8H, $J=7.3$ Hz, OCH_2), 2.18–2.23 (m, 8H, CH_2), 1.27–1.45 (m, 36H, CH_2+CH_3), 0.94 (t, 12H, $J=6.2$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 176.8, 151.8, 150.5, 136.3, 120.0, 118.4, 98.4, 61.0, 38.4, 30.1, 28.2, 20.7, 12.3, 12.2. Anal. calcd for $C_{72}H_{96}N_8O_{16}S_4$: C, 59.32; H, 6.64; N, 7.69; S, 8.80. Found: C, 59.16; H, 6.51; N, 7.75; S, 8.75.

4.1.2. Tetrakis(phthalimidopropoxy)cavitand 6. A suspension of tetrol **5** (500 mg, 0.57 mmol) and NaH (219 mg, 9.12 mmol) in dry DMF (50 mL) was heated for 30 min at 65 °C. Subsequently, bromopropylphthalimide (3 g, 11.4 mmol) was added and heating was continued for 3 days at 90 °C. After removal of the solvent, the residue was dissolved in EtOAc (25 mL), whereupon 1 N HCl was added till pH 7. The solution was washed with water (3× 25 mL) and brine (1×25 mL) and dried over $MgSO_4$. Evaporation of the solvent gave a brown oil, which was further purified by flash chromatography (SiO_2, EtOAc/hexanes, 1:2) to afford pure **6** (373 mg, 65%) as a white solid, mp 150–153 °C; FAB-MS: *m/z* 1629.7 ($[M+H]^{+}$, calcd 1629.3); ^{1}H NMR ($CDCl_3$) δ 7.82–7.86 and 7.69–7.73 (2m, 4+4H, ArH), 6.79 (s, 4H, ArH), 5.90 (d, 4H, $J=7.0$ Hz, OCH_2O), 4.70 (t, 4H, $J=8.0$ Hz, ArCHAr), 4.43

(d, 4H, $J=7.0$ Hz, OCH_2O), 4.02 (t, 8H, $J=5.8$ Hz, OCH_2), 3.91 (t, 8H, $J=5.4$ Hz, CH_2N), 2.14–2.19 and 2.04–2.13 (2m, 8+8H, CH_2+CH_2), 1.27–1.42 (m, 24H, CH_2), 0.91 (t, 12H, $J=6.9$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.7, 147.7, 143.8, 138.3, 133.3, 131.7, 122.6, 113.5, 99.0, 70.5, 36.5, 34.9, 31.6, 29.4, 28.9, 27.1, 22.1, 13.6. Anal. calcd for $C_{96}H_{100}N_4O_{20}$: C, 70.75; H, 6.18; N, 3.44. Found: C, 70.78; H, 6.40; N, 3.17.

4.1.3. Tetrakis(aminopropoxy)cavitand 7.

A solution of **6** (608 mg, 0.38 mmol) and hydrazine hydrate (247 mg, 7.7 mmol) in a 9:1 mixture of EtOH (27 mL) and THF (3 mL) was refluxed overnight. After addition of concentrated HCl (0.5 mL) refluxing was continued for another hour. Upon cooling of the reaction mixture 2 M NaOH was added till pH 10 to give a precipitate. The precipitate was filtered off and was washed with H_2O (5 mL). The residue was dissolved in CH_2Cl_2 (15 mL) and the resulting solution was dried over $MgSO_4$. Evaporation of the solvent gave **7** (248 mg, 58%), mp 188–190 °C; FAB-MS: *m/z* 1109.7 ($[M+H]^+$, calcd 1109.7); ^1H NMR ($CDCl_3$) δ 7.71–7.73 (m, 8H, NH_2), 6.69 (s, 4H, ArH), 6.18 (d, 4H, $J=7.8$ Hz, OCH_2O), 4.64 (t, 4H, $J=8.0$ Hz, ArCHAr), 4.47 (d, 4H, $J=8.0$ Hz, OCH_2O), 4.07 (t, 8H, $J=5.1$ Hz, OCH_2), 3.25–3.33 (m, 8H, CH_2N), 2.02–2.21 (m, 8+8H, CH_2+CH_2), 1.27–1.42 (m, 24H, CH_2), 0.84 (t, 12H, $J=7.3$ Hz, CH_3). Anal. calcd for $C_{64}H_{92}N_4O_{12}\cdot 3CH_2Cl_2$: C, 57.47; H, 7.34; N, 4.00. Found: C, 57.14; H, 7.10; N, 4.12.

4.1.4. Tetrakis[(benzoylthioureido)propoxy]cavitand 8.

A solution of **7** (200 mg, 0.18 mmol) and benzoyl isothiocyanate (227.5 mg, 1.44 mmol) in chloroform (10 mL) was stirred at room temperature for 3 days. The solution was washed with H_2O (2×20 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by flash chromatography (SiO_2, CH_2Cl_2/hexanes 3:2) to give **8** (159 mg, 50%) as a yellowish solid, mp 90–92 °C; FAB-MS: *m/z* 1761.5 ($[M+H]^+$, calcd 1761.7); ^1H NMR ($CDCl_3$) δ 9.02 (s, 4H, NH), 7.80 (d, 8H, $J=8.1$ Hz, ArH), 7.30–7.64 (m, 12H, ArH), 6.83 (s, 4H, ArH), 5.93 (d, 4H, $J=7.2$ Hz, OCH_2O), 4.74 (t, 4H, $J=8.4$ Hz, ArCHAr), 4.50 (d, 4H, $J=6.9$ Hz, OCH_2O), 4.04 (t, 8H, $J=5.1$ Hz, OCH_2), 3.93 (q, 8H, $J=5.4$ Hz, CH_2N), 2.15–2.20 (m, 8H, CH_2), 2.08 (q, 8H, $J=5.4$ Hz, CH_2), 1.27–1.42 (m, 24H, CH_2), 0.91 (t, 12H, $J=6.9$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 179.9, 166.8, 148.3, 144.2, 138.9, 133.4, 132.0, 129.1, 127.0, 114.3, 99.8, 71.1, 43.4, 37.0, 32.1, 29.9, 28.8, 27.7, 22.7, 14.1. Anal. calcd for $C_{96}H_{112}N_8O_{16}S_4$: C, 65.43; H, 6.41; N, 6.36; S, 7.28. Found: C, 64.60; H, 6.15; N, 6.75; S, 7.05.

4.2. Picrate extractions

4.2.1. Solutions.

The 10^{-4} M salt stock solutions were prepared by dissolving the required amounts of the appropriate metal nitrate $M^{n+}(X^-)_n$ and LiPic in 10^{-3} M HNO_3 adjusting the total volume of the solution to 100 mL using volumetric glassware. The pH of the solutions was close to pH 3, and adjusted to pH 3 by adding small amounts of LiOH. The metal picrate solutions were prepared in situ in the stock solutions. The 10^{-3} M stock solutions of the ligands were prepared by dissolving the appropriate amount of ligands in 20 mL of CH_2Cl_2.

4.2.2. Procedure.

Equal volumes (1.0 mL) of the organic and the aqueous solutions were transferred into a stoppered glass vial and stirred at ambient temperatures (about 23 °C) for 17 h. The solutions were disengaged by centrifugation (1600 rpm for 10 min). The concentration of picrate ion in the aqueous and organic phase was determined spectrophotometrically ($\lambda_{max}=355$ nm). Each measurement was repeated three times. Blank experiments showed that no picrate extraction occurred in the absence of ionophore. The percentage of the cation extracted into the organic phase ($\%E=E\times 100\%$), defined as the ratio of the activity in the organic phase (A_o) and the total activity in both the organic and the aqueous phase (A_w), is expressed by the following equation:

$$\%E=(A_o/(A_o+A_w))100\% \tag{2}$$

4.3. Potentiometric measurements

4.3.1. Reagents.

The membrane components potassium tetrakis[3,4-bis(trifluoromethyl)phenyl]borate (KTFPB), 2-nitrophenyl octyl ether (*o*-NPOE), high molecular weight poly(vinyl chloride) (PVC), and tetrahydrofuran (THF, distilled prior to use) and all salts were purchased from Fluka (Ronkonkoma, NY). Aqueous solutions were obtained by dissolving the appropriate salts in Nanopure purified water.

4.3.2. Membrane preparation.

The polymeric membranes used for the determination of stability constants contained ionophore (20 mmol/kg) and KTFPB (2 mmol/kg) in PVC/*o*-NPOE (1:2 by weight) polymeric matrix (total 140 mg), unless otherwise indicated in the text. The membrane components were dissolved in freshly distilled THF (1.4 mL). The solution was placed in a glass ring (22 mm i.d.) mounted over a glass plate and then covered with another glass plate to slow down the solvent evaporation. After 24 h, the resulting membrane (of the approximate thickness 130–140 μm) was peeled from the glass plate and discs of 7 mm diameter were cut out.

The procedure for the preparation of polymeric membranes evaluated for the potentiometric ion response was similar to that described above. The total amount of membrane components was 200 mg and the membranes consisted of 1 wt% of ionophore, 30 mol% of KTFPB and PVC/*o*-NPOE (1:2 by weight).

4.3.3. Potentiometric response to cations and selectivity measurements.

Membrane discs were mounted in conventional ISE electrode bodies (Type IS 561; Philips, Eindhoven, The Netherlands) for electromotive force (EMF) measurements. All measurements were performed at ambient temperature (22±1 °C) using a galvanic cell of the following type: $Ag/AgCl_{(s)}$/3 M KCl/1 M CH_3COOLi/sample/ion-selective membrane/0.001 M NaCl solution/$AgCl_{(s)}/Ag$. The EMF values were measured using a custom made 16-channel electrode monitor. Details of this equipment have been described previously.[31]

The performance of the electrodes was examined by measuring the EMF for aqueous solutions of examined cations over the concentration range of 10^{-7}–10^{-1} M.

Potentiometric selectivity coefficients were determined by the separate solution method (SSM) according to the procedure described in literature.[32] Selectivity coefficient $K_{I,J}^{\text{pot}}$ values were obtained from adequate, unbiased E^0 measurements for each cation, based on the equation:

$$K_{I,J}^{\text{pot}} = \exp\left\{\frac{z_I F}{RT}(E_J^0 - E_I^0)\right\} \tag{3}$$

where R, T, and F are the gas constant, absolute temperature, and the Faraday constant, respectively. The charge of primary ion, I, is indicated as z_I and potentials obtained by an extrapolation of the linear part of calibration curve to $\log a = 0$ for primary and interfering ions are put as E_{I}^0 and E_{J}^0, respectively.

Activity coefficients were calculated according to the Debye–Hückel approximation.[33]

4.3.4. Potentiometric determination of stability constants. The measurement setup was the same as described above. Experiments were carried out according to the procedure described in Ref. 27a,b. Two sets of membranes were prepared: membranes with and without ionophore. A series of 7 mm i.d. membrane discs were cut from the parent membranes, and these disks were conditioned over 2–3 days in appropriate salt solutions (10^{-1} M NaCl, 10^{-2} M $CuCl_2$, 10^{-2} M $CdCl_2$, 5×10^{-3} M $PbCl_2$, 10^{-3} M $AgNO_3$.

To determine the stability constants for a given ionophore and a given cation, two measurements, for a membrane without ionophores and then for a sandwich membrane, were carried out. The sandwich membrane was made, after drying of individual membranes, by attaching of the membrane with ionophore to the membrane without ionophore. The segmented membrane was then mounted into a Philips electrode body (membrane with ionophore faced the sample solution) and immediately immersed into an appropriate salt solution (identical as for conditioning of the membrane). The potential was recorded as the mean of the last minute of a 10 min measurement period in the test solution. The potential of the electrodes with sandwich membranes remained free of diffusion-induced drifts for 20–50 min, depending on the ionophore incorporated within the membrane and the ion measured. The membrane potential values ΔEMF were calculated by subtracting the cell potential for a membrane without ionophore from that of the sandwich membrane. The formation constant, β_{IL_n}, was calculated from Eq. 4:[27a,b]

$$\beta_{\text{IL}_n} = \left(L_{\text{T}} - \frac{n}{z_I}R_{\text{T}}^{-}\right)^{-n} \exp\left(\frac{z_I F}{RT}\Delta\text{EMF}\right) \tag{4}$$

where n is the complex stoichiometry, L_{T} and R_{T} are the concentrations of ionophore and ionic site additives in the membrane, respectively.

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