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Calixthioamides as Ionophores for Transition- and Heavy-Metal Cations

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There is an increasing interest in applying *p-tert*-butylcalix[4]arenes as sensing materials in ion-selective electrodes (ISEs). Considerable efforts were made to design calixarenes that are selective for some heavy- or transition-metal ions to be used in ISEs for controlling and monitoring the level of such pollutants in the environment. It has been reported that introduction of softer sulfur atoms instead of oxygen atoms in calix[4]arene substituents promotes their complexing ability towards transition- and heavy-metal ions, which are toxic for human beings and pollute the environment. In this microreview, we present sulfur-containing calix[4]arenes acting as sensing materials for metal cations such as Ag^+, Pb^{2+}, Cu^{2+}, Cd^{2+} but also as efficient extractants for Pd^{2+}, Au^{3+} and Hg^{2+}.

Introduction

Calixarenes are cavity-shaped oligomers obtained from the condensation of *p*-alkylphenols with formaldehyde under alkaline conditions. The most accessible and conformationally most stable are the tetramers, which can exist in four different conformations after substitution: *cone*, *partial cone*, *1,3*- and *1,2-alternate*, as shown in Figure 1.

Since their discovery, calix[4]arenes have received great interest, and much research effort has been made to modify their structure. The modifications concern both the lower part (containing hydroxy groups) and the upper rim (con-

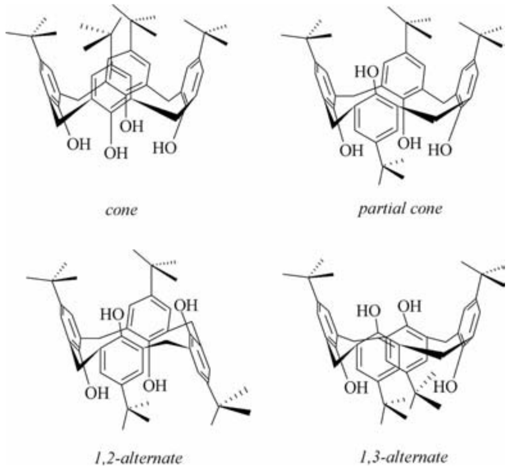

Figure 1. Four different calix[4]arene conformations.

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Prof. Dr. Sc. Maria Bocheńska is a staff member of the Chemical Faculty, of Gdańsk University of Technology (GUT), Poland. Her research interests and activities include supramolecular chemistry and some of its applications. Her group research concerns the design and the synthesis of functional materials with the aim to use them as sensing material in potentiometric sensors, ion-selective membrane electrodes (ISEs) and also in liquid membranes (BLM, SLM or PIM) for selective membrane transport studies. In the academic year 1987–1988, as a post-doc, she was researcher at BYU, Provo, Utah in the laboratory of Prof. J. S. Bradshaw and Prof. R. M. Izatt and in 1989 at ETH, Zurich in the laboratory of the late Prof. W. Simon.

taining alkyl groups). By introducing a large variety of substituents, derivatives of calix[4]arenes with different properties may be obtained.[1]

Lipophilic *p*-*tert*-butylcalix[4]arenes modified at the lower rim have been successfully used as selective molecular receptors having specific binding properties. Recently, the number of publications describing the use of modified *p*-*tert*-butylcalix[4]arenes as sensing material for heavy-metal cations has increased. The potentiometric method with the use of ion-selective electrodes still remains one of the most convenient methods for the determination of metal ions in water due to its ease of application, fast response and low cost.

Special attention is focused on ionophores selective for toxic lead cations. Recently, the application of functionalized calix[4]arenes as ionophores in Pb^{2+}-ion-selective membrane electrodes was investigated. For example, Yaftian and co-workers evaluated tetraphosphorylated calix[4]arene derivatives as active material in such sensors.[2] Calix[4]arene amides were also tested towards Pb selectivity.[3–4] Nevertheless, the selectivity for Pb^{2+}, especially over Na^+, was not satisfying. New, more selective ionophores are still required.

This microreview is a brief presentation of the calixthioamides described in the literature, and it summarizes the investigated methods of interaction between ionophores and metal ions. Calixthioamides were mostly applied as sensing materials in ion-selective electrodes and in ion-sensitive chemically modified field-effect transistors (CHEMFETs) but also in extraction studies. The various calixarene thioamides are presented in chronological order.

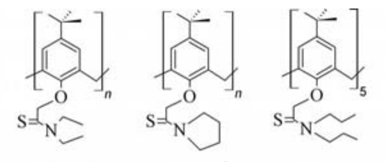
Calixthioamides as Receptors for Heavy-Metal Ions

In 1992, Arnaud et al. published the collected results of liquid–liquid extraction studies carried out according to the Pedersen procedure with *p*-*tert*-butylcalix[4]-, -[5]- and -[6]arenes functionalized with thioamide moieties.[5]

The percentage of cation extracted ($\%E$) from water into dichloromethane was determined from the absorbance (A) of the picrate anion remaining in the aqueous phase after extraction at $\lambda_{max} = 355$ nm and from the absorbance (A_0) of a blank experiment without ligand.

$$\%E = 100(A_0 - A)/A_0$$

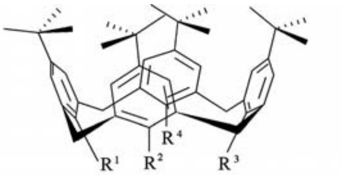
It was shown that thioamides **1**–**5** do not extract alkali, alkaline earth and lanthanide cations. Rather strong affinity for Ag^+ and Pb^{2+} was observed ($\%E \geq 80$ and ≥ 32, respectively). Extraction of Cu^{2+} cations was lower ($\%E \geq 15$) and that of Cd^{2+} in the case of ligands **4** and **5** was not bad ($\%E = 42$ and 38, respectively).[5] The data were compared to those obtained with the corresponding amides,[6] which are good extractants for Na^+ and K^+ cations but also have a high extraction level for Ba^{2+}, Pb^{2+}, Cd^{2+} and Ag^+. In case of the amide corresponding to thioamide **3**, extraction of Mg^{2+} was also not negligible, which led to the conclusion that amides are more efficient extractants but not as selective as their thiocarbonyl analogues. It has been concluded that thioamides having softer sulfur instead of oxygen atoms show preference for heavy-metal cations, and their ability for binding alkali and alkaline earth ions is limited.



1 $n = 4$
2 $n = 6$
3 $n = 4$
4 $n = 5$
5

At about the same time, K. M. O'Connor and coworkers tested tetra(diethyl thioamide) **1** as ionophore for Ag^I in the ion-selective PVC/NPOE (*o*-nitrophenyl octyl ether) membrane electrode and obtained a linear response of 45.67 mV/dec with a detection limit of only about $c = 10^{-4}$ mol/dm^3. However, the authors indicated that Hg^{2+} and Na^+ were the most interfering ions. The worst selectivity coefficient was determined for Ag^+ in the presence of Pb^{2+} ($\log K^{pot}_{Ag/Pb} = -1.7$). After the electrode membrane had been in contact with Pb^{2+} solution for 24 hours, the electrode did not respond to Ag^+ anymore, as a result of poisoning of the membrane by Pb^{2+} ions.[7]

In 1992, Cobben et al. presented the selective recognition of heavy-metal ions by chemically modified ion-sensitive field-effect transistors (CHEMFETs) by using calix[4]arene thiocarbamates **6**–**7** and calix[4]arene thioamides **8**–**13** in the *cone* conformation as the active material in the membrane.[8]



6 $R^1 - R^4 = OCH_2CH_2SC(S)N(C_2H_5)_2$
7 $R^1 = R^3 = OCH_2CH_2SC(S)N(C_2H_5)_2$, $R^2 = R^4 = OnPr$
8 $R^1 = R^3 = OCH_2C(S)N(CH_3)_2$, $R^2 = R^4 = OH$
9 $R^1 = R^2 = OCH_2C(S)N(CH_3)_2$, $R^3 = R^4 = OH$
10 $R^1 - R^4 = OCH_2CH_2OCH_2C(S)N(CH_3)_2$
11 $R^1 = R^3 = OCH_2CH_2OCH_2C(S)N(CH_3)_2$, $R^2 = R^4 = OnPr$
12 $R^1 = R^3 = OCH_2C(S)N(CH_3)_2$, $R^2 = R^4 = OnPr$
13 $R^1 - R^4 = OCH_2C(S)N(CH_3)_2$

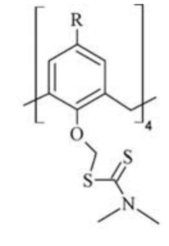
Ionophore **6**, having four thiocarbamoyl groups, incorporated into a PVC/DOP (dioctyl phthalate) CHEMFET membrane, gave Nernstian response to Cu^{2+} ions with a slope of 31 mV/dec in the presence of Ca^{2+} (the selectivity coefficient was $\log K^{pot}_{Cu/Ca} = -1.7$), Cd^{2+} ($\log K^{pot}_{Cu/Cd} = -2.0$) and Pb^{2+} ($\log K^{pot}_{Cu/Pb} = -1.6$) ions. Potassium cations acted in this case as the most interfering ion, probably because of the higher partition coefficient for K^+ compared to that for Cu^{2+} ions for the membrane plasticized with dioctyl phthalate (PVC/DOP). The same compound, **6**, incorporated in the PVC/NPOE membrane showed better selectivity towards K^+.[8] Nevertheless, the electrode with this plasticizer did not respond reproducibly to Cu^{2+} ions.

Ionophore **7**, possessing only two thiocarbamoyl groups, in the PVC/DOP membrane, does not respond reproducibly to Cu^{2+} ions. By replacing the plasticizer by NPOE and by increasing the amount of the ionophore in the membrane, better results were obtained. Nevertheless, despite the selective response towards Cu^{2+} ions, a slope of 54–59 mV/dec was obtained. This was explained as the formation of monovalent ion-pair species (CuA^+) in the solution as well as in the membrane.[8]

Nernstian response to Cd^{2+} ions was observed for two disubstituted ionophores **8** (substituted in aromatic rings A and C) and **9** (substituted in rings A and B). Ionophore **8** was more selective than **9** in the presence of Ca^{2+} cations. Further investigations with compounds **10** and **11** possessing extended cavities proved that these ionophores provide better selectivity for Cd^{2+} ions relative to K^+ and Ca^{2+} ions in comparison to the ionophores **8** and **9**. Generally, compound **10**, which was tetrasubstituted, showed better selectivity than **11**, the disubstituted analogue. No selectivity was found in case of ionophore **10** in the presence of Pb^{2+} and Cu^{2+} ions. Two electrodes with ionophores **12** and **13** in the PVC/NPOE membrane showed selectivity for Pb^{2+}. The selectivity coefficients, given as $\log K$ for ionophore **13** and in parentheses for **12**, were: $\log K^{\text{pot}}_{\text{Pb/K}} = -5.2$ (–2.8), $\log K^{\text{pot}}_{\text{Pb/Ca}} = -4.3$ (–4.2), $\log K^{\text{pot}}_{\text{Pb/Cd}} = -4.2$ (–1.7), $\log K^{\text{pot}}_{\text{Pb/Cu}} = -3.4$ (–2.7). It was confirmed that the electrode with ionophore **13**, having four thioamide groups, was more selective and gave better Nernstian response than the electrode with ionophore **12**.[8]

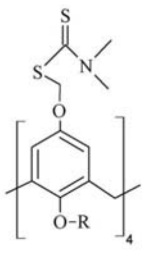
The same ionophores (**12** and **13**) were later applied in Pb-selective electrodes by Malinowska et al.[9] The electrode membranes plasticized with NPOE gave almost theoretical Nernstian response for Pb^{2+} when the internal electrolyte solution was $PbCl_2$ (5×10^{-3} mol/dm^3). The same conclusion was formulated: tetrasubstituted thioamide **13** is more selective for Pb^{2+} ions than the disubstituted thioamide **12**, over a great variety of cations studied, such as Li^+, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} ($\log K^{\text{pot}}_{\text{Pb/M}} < -3$). The same ligand, **13**, in membrane plasticized by BBPA [bis(butylpentyl)adipate] was also studied, but in this case Na^+ cations interfered strongly. The influence of Hg^{2+} cations on those membranes was also tested, and it was found that, in case of ionophore **12**, the mercury ions not only strongly interfered, but Hg had a poisoning effect on the membrane with ionophore **12**, whereas in case of the **13**, the electrode almost retained the response toward Pb^{2+} cations.[9]

Yordanov et al. studied extractability of some cations by using compound **14**.[10–14] A year later, compound **15**, similar to **14** but without *tert*-butyl groups, was synthesized.[12–13] Extraction of Hg^{2+}, Hg_2^{2+}, $MeHg^+$, Ag^+, Pd^{2+}, Au^{3+}, Pt^{2+}, Ni^{2+}, Pb^{2+} and Cd^{2+} cations was performed from aqueous metal salt solutions (1 mM in 0.1 M HNO_3) to a $CHCl_3$ solution of the corresponding calix[4]arene. Both ligands extracted Pd^{2+} and Au^{3+} ions quantitatively, whereas for the rest of the cations, the percentage of extraction was much lower but satisfying. The lowest extraction was shown for species like Hg_2^{2+}, $MeHg^+$ by compound **15**. No extraction of Pb^{2+}, Cd^{2+}, Ni^{2+} or Pt^{2+} was observed for ligand **14**. Although, Pd^{2+} and Pt^{2+} have similar ionic radius, they were extracted differently.[11] Moreover, soft sulfur atoms should bind more strongly to the softer platinum cation. The authors explained this fact by the different lability of the two complexes. The crystal structures of the free ligands **14** and **15** were determined, and the X-ray diffraction data were discussed.[6–13]



14 R = *t*Bu
15 R = H

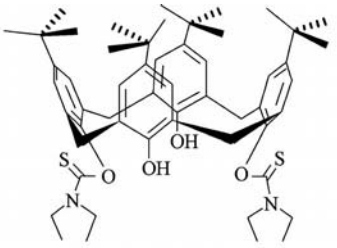
In 1997, Yordanov et al. investigated the extraction of some metal ions by compounds **16** and **17**, in which the same sulfur-containing moieties as those in compound **14** were attached to the upper rim of the calix[4]arene. Two derivatives were synthesized: one with free OH groups (compound **16**) and one with OMe (compound **17**) at the lower rim. The extraction procedure was applied to Ag^+, Hg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+} and Au^{3+} ions.[15] For compound **16**, the extraction of the named cations led to the formation of gelatinous precipitates; therefore, the extraction percentage could not be determined. Derivative **17** showed very good selectivity for Au^{3+} (%E = 99) over Ag^+ (%E = 14) and for Pd^{2+} (%E = 100) and Hg^{2+} (%E = 73) over Ni^{2+} (%E < 1). The extraction selectivity was found to be similar to that of the derivatives substituted at the lower rim.[12]



16 R = H
17 R = CH_3

In 1998 Yordanov and Roundhill studied the binding properties of gold, palladium, mercury and silver salts with compound **15** by electronic absorption spectroscopy[16] in order to better understand the possible sites of metal coordination at the centre of the ligand complexes. The additional bands, which are redshifted in the presence of Pd^{2+}, Au^{3+}, Hg^{2+} and Ag^+ ions, were due to the charge-transfer bands, indicating that the ligand is complexed to the metal ion by a metal–sulfur interaction.

In 1997, Arnaud et al. presented the first X-ray crystal structure of the lead complex of *p-tert*-butylcalix[4]arene diethylthioamide **1**. The structure showed the *cone* conformation of the thioamide, in which Pb^{2+} is bound to four ethereal oxygen and four thiocarbonyl sulfur atoms.[17] In the same year, Drew et al. revealed the X-ray structure of diethylthioamide **18** substituted only at the A and C positions. The calix[4]arene had a pinched *cone* conformation.[18]



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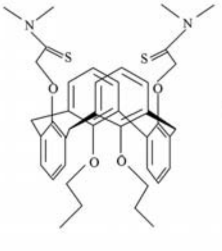
Lugtenberg et al. (1997) revealed novel calix[4]arene thioamides in the *1,3-alternate* conformation and studied their selectivities for Pb^{2+} and Cd^{2+} ions in chemically modified field-effect transistors.[19] CHEMFETs with ionophore **19** (in *1,3-alternate* conformation) in PVC/NPOE membranes gave Nernstian response with a slope of 30 mV/dec for Pb^{2+} and was selective in the presence of interfering cations such as Cd^{2+}, Ca^{2+}, Cu^{2+}, K^+.[19] The results were compared with the data obtained by Cobben et al. with the corresponding *cone*-conformer (**12**) of ionophore **19**.[8] It was clearly pointed out that the *1,3-alternate* conformer is more selective towards Pb^{2+} ions in the presence of other cations than the *cone* conformer. It was explained that, in the *1,3-alternate* conformation, there is no interaction with hard oxygen atoms of the two propoxy moieties, and cation–π interactions favour complexation with the more polarizable Pb^{2+} ions. Nernstian response towards Cd^{2+} in the presence of $Ca^{2+}$and K^+ ions was observed for ionophore **20** in CHEMFETs with PVC membranes plasticized by DOP. In addition, the authors reported that those CHEMFETs are also selective for Cd^{2+} in the presence of Cu^{2+} ions, which was not observed for CHEMFETs with the *cone* conformer of ionophore **10**, having four $CH_2CH_2OCH_2C(S)N(CH_3)_2$ groups attached to the phenol oxygen atoms.[8] It is worth pointing out that ionophore **20** is the first calix[4]arene that shows selectivity for Cd^{2+} in the presence of Pb^{2+}; however, the selectivity is only $\log K^{\text{pot}}_{\text{Cd/Pb}} = -0.7$.[19]



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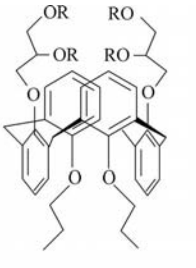

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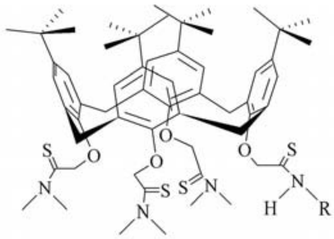
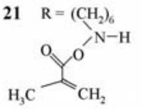
R = $CH_2C(S)N(Me)_2$

In 1998, Lugtenberg et al. performed experiments for different Pb^{2+}-selective CHEMFETs containing covalently attached or free calix[4]arene thioamide derivatives (compounds **21** or **22**, respectively) in the presence of covalently attached borate or free borate in polysiloxane membranes.[20]



21 R = $(CH_2)_6$



22 R = $n\text{C}_6\text{H}_{13}$

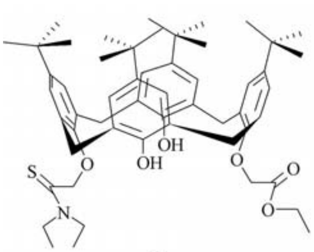
It was proved that CHEMFETs with covalently attached borate and with **21** or **22** as active material do not show linear response for Pb^{2+} cations, resulting in low selectivity with such sensors.[20] In addition, the authors presented the effect of exposure to a continuous water stream on the durability of the CHEMFETs. It was concluded that CHEMFETs with covalently attached calixarene **21** and free borate still exhibited good selectivity and linear response for Pb^{2+} cations even after 19 weeks of exposure to a water stream. In contrast, CHEMFETs containing free ionophore **22** and free borate lost their selectivity and linearity under the same conditions. By applying a covalently attached ionophore, the authors addressed the problem of durability of CHEMFETs.[20]

In 1999, Ceresa and Pretsch determined the stability constant of the Pb^{2+} complex with compound **13** in a PVC/DOS (dioctyl sebacate) membrane. The value of $\log\beta_{\mathbf{13}\text{–Pb}} = 15.9$ indicated that a rather strong complexation of stoichiometry 1:1 occurred with Pb^{2+} cations. The stability constants of complexes with other cations were also relatively high: $\log\beta = 12.1$ (**13**-Cu^{2+}) and $\log\beta = 10.0$ (**13**-Cd^{2+}). This ionophore was highly selective for Pb^{2+} in the presence of other cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Cd^{2+}. Potentiometric selectivity coefficients were lower than –4.0.[21]

In the same year, T. Sokalski et al. described the influence of the composition of the internal electrolyte solution on the response of Pb^{II}-selective membrane electrodes.[22] The commercially available ionophore **13** was used, and the results were compared with those obtained by Malinowska in 1994.[9] The internal filling solution contained: EDTA (10^{-2} mol/dm^3), $PbCl_2$ (10^{-3} mol/dm^3) and NaCl (10^{-2} mol/dm^3 or 2 mol/dm^3). It was concluded that the inner electrolyte should contain a higher concentration of the interfering ion and a lower concentration of the primary ion. Very low detection limits were thus obtained, below 10^{-10} mol/dm^3.[22]

In 2001, Arena et al. modified the *1,3-alternate* dithioamide calix[4]arene frame reported by Lugtenberg et al. (compound **18**) by introducing two allyl groups on the two opposite aromatic rings in order to link the later obtained derivative to silica gel. Selective complexation of Pb^{2+} and Hg^{2+} ions was investigated by UV/Vis titration in CH_3CN and by ^1H NMR spectroscopy. The UV/Vis spectroscopic investigations showed that, upon titration of Cd^{2+} or Na^+ salt solutions, no change of the ligand spectrum was observed, whereas upon addition of Pb^{2+} or Hg^{2+} salt solution, significant changes in shape and shifts of peaks were noted. The stoichiometries of the metal/ligand complex species determined by SPECFIT and HYPERQUAD programs indicated 1:1 (metal/ligand) but also a small amount of 1:2 for Pb and Hg complexes. NMR spectroscopic investigations also confirmed the formation of complexes.[23]

In 2001 G. P. Nicholson, P. D. Beer et al. patented the method of preparation of some novel calixarenes and their use for the sequestration of metal ions.[24] Among them are **23**, having one ester and one thioamide group, and **24**, which is the analogous monoacid and monothioamide. Lawesson's reagent as a thionating agent was used in those synthetic procedures. Both sulfur-containing calix[4]arenes presented here were able to extract Cd^{2+} ions from solution at pH 9.4.



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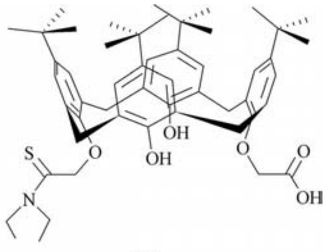

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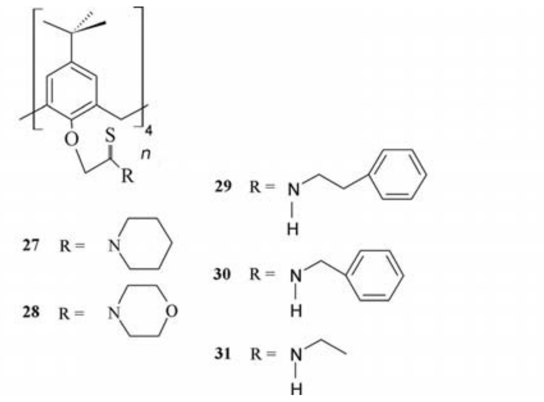
In 2002, No, Kim, et al. presented two tetrahomodioxacalix[4]arene tetrathioamides in *1,2-alternate* conformation (compounds **25** and **26**). Metal picrate extraction experiments with compounds **25** and **26** were investigated, and strong affinity towards the Ag^+ ion was indicated.[25] Mass spectral analysis showed that a complex of type M_2L was formed with Ag^+ cations.

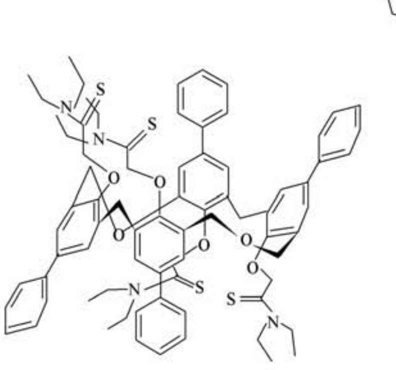
Recently, we synthesized and applied ligands **27**–**31** together with the analogous compound **1** as ionophores in ion-selective membrane electrodes and checked their Pb^{2+}-selectivity.[26–27]



Tertiary thioamides **1**, **27** and **28** formed stable, long lasting electrodes, whereas the lifetime of the electrodes based on secondary thioamides **29**–**31** was much shorter (2–3 weeks).

The best ionophore properties were shown by ligand **27**, for which the selectivity coefficients were remarkable ($\log K^{\text{pot}}_{\text{Pb/M}} \leq -4$), except for Cu^{2+} ($\log K^{\text{pot}}_{\text{Pb/Cu}} = -0.83$ and $\log K^{\text{pot}}_{\text{Pb/Cu}} = -0.54$ in PVC/BBPA and PVC/NPOE membranes, respectively).[27] However, in case of Cu^{2+}, the electrode slope was S = 57.6mV/dec, which is typical for monovalent ions. It had already been reported that anions in the sample may be associated in the membrane, the cation–ionophore complex leading to an increased slope.[8] Ionophores **1**, **27** and **28** were tested in membranes with two different plasticizers: NPOE and BBPA. The selectivity coefficients are generally better or slightly better in PVC/NPOE membranes; however, the selectivity over cadmium is worse in PVC/NPOE than that in PVC/BBPA membranes. This might suggest a stronger affinity of cadmium to NPOE plasticizer than other cations.

The complex formation constants in the membrane were also determined.[26,27] The ionophores formed stable com-



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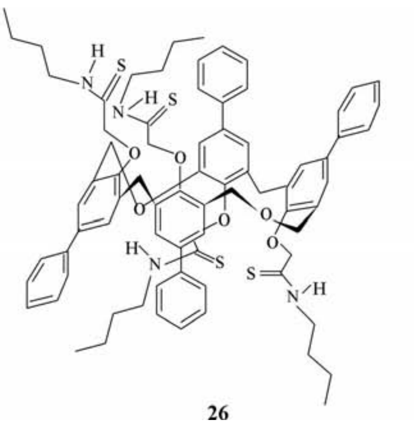

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plexes of 1:1 stoichiometry with the tested cations such as Pb^{2+}, Cu^{2+}, Cd^{2+}, Na^+, Cs^+ and K^+. As expected, the highest stability constants were obtained with Pb^{2+} cations for thioamides **27**–**31**. Ionophore **27** formed the strongest complex with Pb^{2+}, regardless of the plasticizer used, NPOE or BBPA, and the values of the stability constants are much higher than those for ionophore **13** of similar structure, which is known as a commercially available Pb^{2+}-selective ionophore.[27] In case of ligand **27**, the stability constants for the Pb^{2+}, Cu^{2+} and Cd^{2+} complexes were also determined in acetonitrile solution by UV absorption spectroscopy and for Ag^+ complexes by potentiometry with use of an Ag^+/Ag electrode. The values of stability constants of the metal complexes determined with both methods (within the membrane and in acetonitrile solution) tend to decrease in the same order: $Pb^{2+} > Cu^{2+} > Cd^{2+}$.[27]

Ligand **27**, possessing the strongest affinity to Pb^{2+}, was successfully used to determine lead in real samples.[27] Ligand **27** was already studied in 2009 by K. Toth et al., who published the results on the adsorptive stripping voltammetric determination of Pb^{2+} with calixthioamide **27** as ionophore.[28] This method is based on the accumulation of lead ions from the solution phase onto the surface of a chemically modified bismuth film electrode by complexation with the ionophore at open circuit. The cyclic voltammetry curves showed reduction and oxidation peaks corresponding to the electrochemical reaction of lead, which proved the Pb^{2+}–ligand complexation.[28]

The application of calixthioamide-based chemically modified carbon paste electrodes in voltammetric stripping analysis was introduced by Arrigan, Svehla, et al. to be used for accumulation of Pb^{2+}, Cu^{2+} and Hg^{2+} ions.[29] We also studied the extractive properties of calix[4]thioamides **27**–**31**, and the data were compared with those obtained with already known compound **1**, which was resynthesized in our work as well.[30]

As expected, all of the ligands studied were inefficient extractants for alkali, alkaline earth and lanthanide cations. We noted that they all extract Ag^+ almost quantitatively ($\%E \geq 80$), whereas the extraction levels of Pb^{2+} and Cu^{2+} depend strongly on the type of thioamide function attached to the calix[4]arene. Compounds **27** and **28**, possessing tertiary thioamide moieties, extracted Pb^{2+} and Cu^{2+} in fair amounts ($\%E$ = 66.4 and 51 for Pb^{2+} and 29.4 and 14.5 for Cu^{2+}, respectively), and this is comparable with the values obtained for the compound **1** ($\%E$ = 56 and 19, respectively).[27,30] In contrast, compounds **29**–**31**, bearing secondary thioamide functions, did not extract those cations, probably due to intra- and intermolecular hydrogen bonding.[30] We also presented the X-ray crystal structures of free ligands **27**,[27] **28**, **29** and **31**, proving their pinched *cone* conformation and the structure of the 1:1 complex Pb^{2+}-**29** (Figure 2).[30]

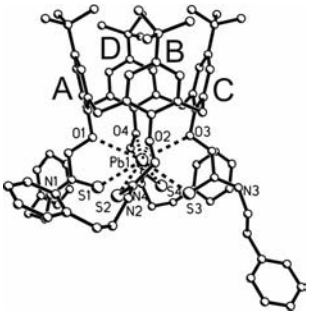

Figure 2. Molecular structure of the Pb^{2+}-**29** complex (side view).

The conformation of the complex is more regular than that of free ligand **29**. As expected, all thiocarbonyl sulfur atoms are directed towards the lead cation, which is bound to four ethereal oxygen atoms and four thiocarbonyl sulfur atoms. It was evident that the conformation of free ligand **29** was readjusted for coordination of the cation.

Conclusions

Calixarenes functionalized with various thioamide moieties function as receptors for heavy-metal cations. In particular, sulfur-containing calixarenes with SC=S pendant groups in the molecule are good extractants for metals such as Au^{3+}, Pd^{2+} and Hg^{2+}, while calixthioamides with C=S moieties are the promising ionophores for selective complexation of transition- and heavy-metal cations like Pb^{2+}, Ag^+, Cd^{2+} and Cu^{2+}. It is worth to stress that very few publications deal with the determination of stability constants of the complexes, which is extremely important in studies of binding properties of new ligands. Collected examples of calixarene derivatives bearing the thioamide or thiocarbonyl function proved that those compounds are of particular value and they require special attention. They can be used not only in controlling the level of toxic heavy metals, but also in their removal.

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