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ORIGINAL ARTICLE

Mercury(II) and silver(I) receptors based on tetrathiacalix[4]arene hydrazones

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Abstract The extraction ability of phenyl hydrazone derivatives of *cone*- and 1,3-*alternate* tetrathiacalix[4]arenes towards to some alkali, alkaline earth, transition and heavy metal ions has been investigated by picrate extraction method. The synthesized *cone*-tetrathiacalix[4]arene hydrazones show a high efficiency coupled with an excellent selectivity towards for Ag^+ and Hg^{2+} ions. The stoichiometry of complexes and the extraction constants have been determined. The influence of calix[4]arene platform's structure and the electron donor substituents in phenyl fragments on the extraction efficiency has been discussed.

Keywords Receptor · Calix[4]arene · Hydrazone · Hg^{2+} · Ag^+

Introduction

Some toxic heavy metals are widely used in various fields of science and technology. Among them the silver and mercury should be mentioned particularly. Thus, high-tech electronics and microwave technology successfully apply silver for the covering of contacts and conductors in high frequency circuits as well as for coating the inner surfaces of waveguides. This is inevitably resulted in an increase of metal content in the environment. Though the silver does not have a clinically apparent effect on a human, but it is known, that an excess amount of this metal in organism can lead to some diseases, such as coma, pleural edema and hemolysis [1]. Moreover, according to new data, silver can interact with essential nutrients, vitamins E and B12 that can also testify to the potential health hazard of silver [2–5].

Among toxic metals, the mercury and its compounds are considered as the most harmful [4, 6, 7]. Soluble mercury salts which together with food and potable water can penetrate into the human body are especially dangerous due to their ability to accumulate in the organism. The application of the mercury compounds scales step by step down. However, up to date they play still an important role in modern industry and their harmful influence continues to be damaging for people. Therefore, the development of effective methods for the detection, analysis and detoxification of mercury and silver compounds is as before an actual problem of environmental safety.

To detect traces of metal ions, a high selective preconcentration procedure is usually prerequisite. A high content of other metals, such as alkali and alkaline earth ions as well as the comparable amounts of other impurity ions can reduce the accuracy of evaluation of the toxic metals' content in test samples. The extraction in a liquid–liquid system appears to be an advantageous method in

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comparison with another applied for the preconcentration of toxic metals, due to its efficiency, selectivity and economic benefit. The extraction properties of these systems are mainly related to the choice of extractant.

Calix[*n*]arenes are commonly utilized as a convenient platform for the creation of a great variety of receptors due to their 3D structure, and as a rule, they possess more effective binding affinity towards cations, anions and neutral molecules than their acyclic analogues [8–10]. The thermodynamics of calixarene solutions and their metal-ion complexes, involving the interaction with Ag^+ and Hg^{2+} were extensively investigated by Danil de Namor et al. [11–16]. According to the hard-soft acid-base principle, the functionalizing of calix[*n*]arene molecules by groups containing soft donor nitrogen and, especially, sulphur atoms would provide a high binding efficiency towards soft metal ions. Indeed, the calix[4]arenes functionalized by thioethers [17], thiocrown ethers [18, 19], thioamides [13, 20, 21] thiophosphate [14, 22] and ethylthioethoxy [15, 16] groups have revealed a high recovering ability towards Ag^+ and Hg^{2+}. However, only some of them have an acceptable selectivity in a wide range of metal ions. In addition, from the view of the environmentally sound approach the utilizing compounds with N,O-donor groups seems to be more preferable. It is also known that some of calix[*n*]arenes with nitrogen and harder oxygen donor atoms can effectively bind Ag^+ and Hg^{2+} ions [23–26]. The screening of the selective and harmless receptors for Ag^+ and Hg^{2+} in a wide range of metal ions continues to be an actual problem for up to date scientific investigations [14, 27–29].

In recent years, we have reported the synthesis of hydrazide and hydrazone derivatives of calix[4]arenes and their extraction performance against a wide row of metals by liquid–liquid extraction. It was established that some of investigated compounds may be successfully applied for separation of certain transition and heavy metals [27–34]. The key role of preorganization of binding groups on calix[4]arene platform in the complex formation process was unambiguously demonstrated. The influence of the isomeric form of calix[4]arene and the effect of *tert*-butyl groups at the upper rim of the macrocycle on the extraction properties were also shown.

These investigations allowed us to establish that pyridinyl hydrazone derivatives of 1,3-*alternate* terathiacalix[4]arene can separate selectively Cu^{2+}, Ag^+ and Hg^{2+} among other metal ions [30]. On the other hand, the research of binding properties of hydrazone derivatives anchored on the calix[4]resorcine platform has shown that the replacement of pyridinyl groups in hydrazone fragments by the phenyl ones leads to excellent selectivity towards Hg^{2+}. Other metal ions including Cu^{2+} were practically not extracted from water solutions by phenyl hydrazone derivatives of calix[4]resorcines [31]. Moreover, Kumar et al. [27] have recently reported that the *cone* isomer of the calix[4]arene, functionalized 2-[4-(*N*,*N*-dimethylaminophenyl)iminoethoxy] moieties has exhibited a selective fluorescence response towards Hg^{2+}. In whole, the obtained results highlighted the availability of these calix[4]arene derivatives and indicated the further direction for searching more efficient receptors of toxic ions.

Consequently, following our intention to develop the effective receptors of Ag^+ and Hg^{2+}, we present herein the synthesis of new phenyl hydrazone derivatives of tetrathiacalix[4]arene and perform a comparative investigation of their binding properties with the ones obtained for some calix[4]arene derivatives synthesized earlier. The tuning of coordination behavior of the calix[4]arenes has been carried out by varying the isomer forms of calix[4]arene platform and the substituents in phenyl hydrazone fragments. To evaluate the receptor properties of these calix[4]arenes in a wide range of metal ions the solvent extraction method was applied. The extraction efficiency and selectivity as well as stoichiometry of the complexes and extraction constants for Ag^+ and Hg^{2+} ions have been established.

Experimental

Reagents

All chemicals were applied as commercially received without further purification. $CHCl_3$ was distilled over P_2O_5. DMSO-d_6 (99.5 % isotopic purity) for NMR spectroscopy was used from Aldrich. The metal salts for extraction experiments were the following chlorides and nitrates: LiCl, NaCl, KCl, CsCl, $CaCl_2$, $CoCl_2 \cdot 6H_2O$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $AgNO_3$, $CdCl_2 \cdot 2.5H_2O$, $Hg(NO_3)_2 \cdot H_2O$, $Pb(NO_3)_2$, $LaCl_3 \cdot 7H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$ and $LuCl_3 \cdot 6H_2O$.

Synthesis

The synthetic routes and the structural formulae of the investigated compounds are shown in Fig. 1. The hydrazones **1** [31], **2a** [35] **5a**, **5b** [36], **5e**, **5f** and **6c** [37] and tetrahydrazide calix[4]arene derivatives **3a** [32], **3b**, **4b** [33] and **4a** [38] were obtained as described earlier.

*4-tert-Butylphenoxyacetylhydrazone of 4-methoxybenzaldehyde (**2b**)*

To a boiling solution of 5 mmol (1.11 g) 4-*tert*-butylphenoxyacetylhydrazide [39] in 10 ml EtOH under stirring were added 5 mmol (0.68 g) of 4-methoxybenzaldehyde. The reaction mixture was refluxed for 2 h. The precipitate was filtered off, washed several times with a mixture of water/EtOH (1:1), and recrystallized from EtOH. Yield: 1.54 g

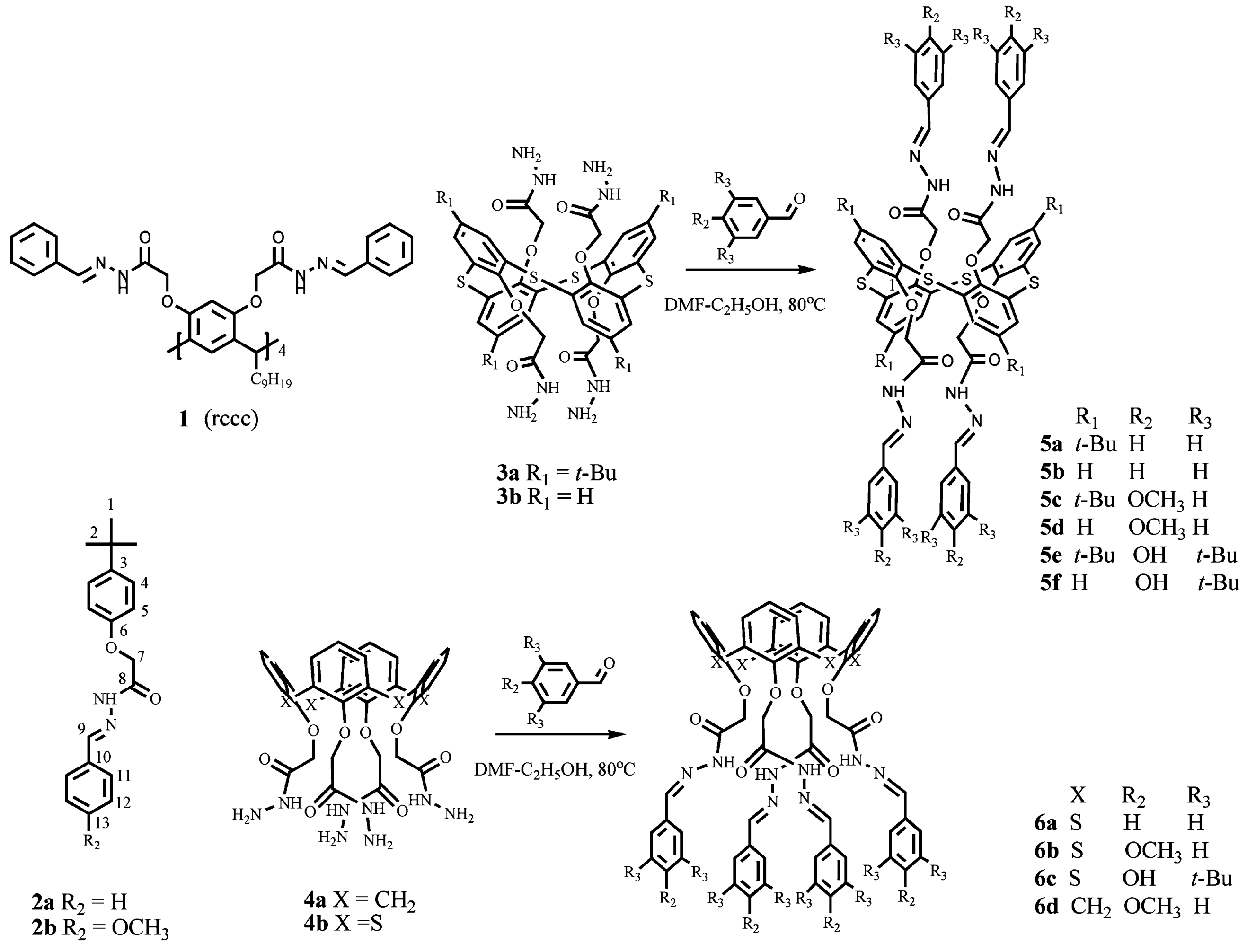


Fig. 1 Synthetic routes and structural formulae of investigated compounds. Numbering system of atoms used in the experimental section

(91 %) as a white powder. mp 150–151 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$) δ: 1.19, 1.20 (s, 9H, C(1)H), 3.75, 3.76 (s, 3H, (O–CH_3)), 4.54, 5.01 (s, 2H, C(7)H); 6.83, 6.84 (br m, 2H, C(12)H), 6.81, 6.83 (br m, 2H, C(5)H); 7.21, 7.24 (br m, 2H, C(4)H); 7.51, 7.62 (br m, 2H, C(11)H); 7.73, 8.05 (br s, 1H, C(9)H); 10.2 (s, 1H, NH). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 31.3 C(1); 34.1 C(2), 53.3 C(O–CH_3); 65.6, 67.3 C(7); 114.3 C(12), 114.5 C(5); 126.2, 126.6 C(4); 128.8, 129.6 C(11), 144.3, C(3), 145.5, 149.9 C(9), 151.1, 155.0 C(6); 161.5, 161.9 C(13); 165.3, 170.6 C(8). IR (ν/cm^{-1}, Nujol): 3438, 3190 (νNH), 1679 (νC=O). Elemental analysis calc. for $C_{20}H_{24}N_2O_3$ (340.42): C, 70.56; H, 7.11; N, 8.23. Found: C, 70.21; H, 7.30; N, 7.98.

*General procedure for the preparation of hydrazone derivatives of calix[4]arene **5c**, **5d**, **6a**, **6b** and **6d***

To a suspension of tetrahydrazide **3a**, **3b**, **4a** or **4b** (0.25 mmol) in 6 ml EtOH and 6 ml DMF under stirring 1.5 mmol of the corresponding aldehyde was added. The reaction mixture was heated for 24 h at 80 °C for **5c**, **5d** and at 40 °C for **6a**, **6b** and **6d**. The solvent was removed from the reaction mixture by distillation under vacuum. Hexane was added to the residue and the mixture was heated again. After cooling, the precipitate was filtered off, washed several times with hexane and EtOH, recrystallized from the mixture of EtOH and DMF.

*5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N^2-(4-methoxybenzylidene)hydrazinocarbonyl-methylenoxy]-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate-**5c**)*

Prepared similarly to the general procedure from **3a** (0.25 g) using 4-methoxybenzaldehyde (0.204 g). Yield: 0.33 g (88 %) as a white powder. Mp 231–235 °C. ^{1}H NMR (600.13 MHz, DMSO-d_6, 30 °C) δ: 0.89–1.27 (br m, 36H, C(1)H); 3.75–3.81 (br m, 12H, O–CH_3); 4.40, 5.10 (br s, 8H, C(7)H); 6.92 (br m, 8H, C(12)H); 7.27 (br m, 8H, C(4)H); 7.45, 7.66 (br m, 8H, C(11)H); 7.73, 8.60 (br s, 4H, C(9)H); 10.50, 11.50 (br s, 4H, NH). ^{13}C NMR

(150.9 MHz, DMSO-d_6, 30 °C) δ: 30.6 C(1); 33.6, 34.0 C(2); 55.2 C(O–CH$_3$); 69.6, 70.7 C(7); 113.9 C(12); 126.5 C(5); 128.5 C(11); 129.9 C(4); 142.8 C(3); 142.5, 148.5 C(9); 156.3 C(6); 160.5, 160.7 C(13); 163.7, 168.3 C(8). IR (ν/cm^{-1}, Nujol): 3401, 3215 (νNH), 1694 (νC=O), 1538 (δNH). Elemental analysis Calc. for $C_{80}H_{88}N_8O_{12}S_4$ (1481.86): C, 64.84; H, 5.99; N, 7.56; S, 8.66. Found: C, 64.57; H, 5.75; N, 7.18; S, 9.04. Mass spectrum (MALDI-TOF): *m/z*: 1482 [M+H]$^+$; 1503 [M+Na]$^+$.

*25,26,27,28-Tetrakis[N^2-(4-methoxybenzylidene)hydrazinocarbonylmethylenoxy]-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate-**5d**)*

Prepared similar to the general procedure from **3b** (0.196 g) using 4-methoxybenzaldehyde (0.204 g). Yield: 0.26 g (82 %) as a white powder. Mp 270–271 °C. ^{1}H NMR (600.13 MHz, DMSO-d_6, 30 °C) δ: 3.75, 3.86 (br s, 12H, O–CH$_3$); 4.68, 5.15 (br s, 8H, C(7)H); 6.65, 6.75 (br m, 4H, C(3)H); 6.97, 7.09 (br m, 8H, C(12)H); 7.60, 7.61 (br m, 8H, C(4)H); 7.90, 7.98 (br m, 8H, C(11)H); 7.87, 8.45 (br s, 4H, C(9)H); 9.8, 11.3 (br s, 4H, NH). ^{13}C NMR (150.9 MHz, DMSO-d_6, 30 °C) δ: 55.1, 55.3 (O–CH$_3$); 67.3, 68.2 C(7); 114.2, 114.3 C(12); 123.9, 124.3 C(3); 128.3, 128.7 C(5); 129.2, 129.4 C(11); 135.3, 135.9 C(4); 144.1, 147.4 C(9); 157.6, 158.5 C(10); 160.9, 161.0 (C(13)); 162.0 C(6); 162.6, 168.0 C(8). IR (ν/cm^{-1}, Nujol): 3480, 3199 (νNH), 1719, 1697 (νC=O), 1547 (δNH). Elemental analysis Calc. for $C_{64}H_{56}N_8O_{12}S_4$ (1257.44): C, 61.13; H, 4.49; N, 8.91; S, 10.20. Found: C, 61.45; H, 4.50; N, 9.08; S, 10.22. Mass spectrum (MALDI-TOF): *m/z*: 1279 [M+Na]$^+$; 1295 [M+K]$^+$.

*25,26,27,28-Tetrakis[N^2-(benzylidene)hydrazinocarbonylmethylenoxy]-2,8,14,20-tetrathiacalix[4]arene (cone-**6a**)*

Prepared similarly to the general procedure from **4b** (0.196 g) using benzaldehyde (0.16 g). Yield: 0.25 g (88 %) as a white powder. Mp 180–182 °C. ^{1}H NMR (600.13 MHz, DMSO-d_6, 30 °C) δ: 4.95, 5.25 (br s, 8H, C(7)H); 6.60 (br m, 4H, C(3)H); 7.25 (4H, C(13)H); 7.30 (br m, 8H, C(4)H), 7.38 (br m, 8H, C(12)H); 7.58, 7.64 (br m, 8H, C(11)H); 8.57, 7.91 (br s, 4H, C(9)H); 11.60 (br s, 4H, NH). ^{13}C NMR (150.9 MHz, DMSO-d_6, 30 °C) δ: 73.3 C(7); 124.0 C(3); 125.6 (C(5)); 127.5, 127.8 C(11); 129.1 C(12); 130.7 C(4); 134.5 (C(13)); 144.9, 149.3 C(9); 150.0 C(10); 154.3 C(6); 164.8, 170.6 C(8). IR (ν/cm^{-1}, Nujol): 3467, 3217 (νNH), 1692 (νC=O), 1540 (δNH). Elemental analysis Calc. for $C_{60}H_{48}N_8O_8S_4$ (1137.33): C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 63.19; H, 3.89; N, 9.59; S, 10.94. Mass spectrum (MALDI-TOF): *m/z*: 1137 [M+H]$^+$; 1159 [M+Na]$^+$; 1175 [M+K]$^+$.

*25,26,27,28-Tetrakis[(N^2-(4-methoxybenzylidene)hydrazinocarbonylmethylenoxy]-2,8,14,20-tetrathiacalix[4]arene (cone-**6b**)*

Prepared similar to the general procedure from **4b** (0.196 g) using 4-methoxybenzaldehyde (0.204 g) Yield: 0.28 g (89 %) as a white powder. Mp 174–176 °C. ^{1}H NMR (600.13 MHz, DMSO-d_6, 30 °C) δ: 3.76 (br s, 12H, O–CH$_3$); 5.05, 5.27 (br s, 8H, C(7)H); 6.60 (br m, 4H, C(3)H); 6.90 (br m, 8H, C(12)H); 7.1 (br m, 8H, C(4)H); 7.50 (br m, 8H, C(11)H), 7.87, 8.45 (br s, 4H, C(9)H); 11.6 (br s, 4H, NH). ^{13}C NMR (150.9 MHz, DMSO-d_6, 30 °C) δ: 55.2 (O–CH$_3$); 72.7 C(7); 114.0 (C(12)); 125.6 C(5); 126.2 C(3); 128.5 (C(11)); 130.0 (C(4)); 144.1, 148.5 C(9); 148.7 C(10); 154.3 (C(6)); 160.7 (C(13)); 163.8, 168.9 C(8). IR (ν/cm^{-1}, Nujol): 3464, 3214 (νNH), 1681 (νC=O), 1541 (δNH). Elemental analysis Calc. for $C_{64}H_{56}N_8O_{12}S_4$ (1257.44): C, 61.13; H, 4.49; N, 8.91; S, 10.20. Found: C, 61.12; H, 4.12; N, 8.54; S, 10.42. Mass spectrum (MALDI-TOF): *m/z*: 1257 [M+H]$^+$, 1279 [M+Na]$^+$, 1295 [M+K]$^+$.

*25,26,27,28-Tetrakis[N^2-(4-methoxybenzylidene)hydrazinocarbonylmethylenoxy]-calix[4]arene (cone-**6d**)*

Prepared similar to the general procedure from **4a** (0.18 g) using 4-methoxybenzaldehyde (0.204 g). Yield: 0.18 g (60 %) as a white powder. Mp 272–276 °C. ^{1}H NMR (600.13 MHz, DMSO-d_6, 30 °C) δ: 3.65, 3.74 (br s, 12H, O–CH$_3$); 3.32, 4.70 (8H, –CH$_2$–bridge); 4.68, 4.92 (br s, 8H, C(7)H); 6.62, 6.88 (br m, 4H, C(3)H); 6.57, 6.93 (br m, 8H, C(12)H); 6.60, 7.35 (br m, 8H, C(4)H); 7.26, 7.53 (br m, 8H, C(11)H), 7.93, 8.14 (br s, 4H, C(9)H); 11.60, 11.70 (br s, 4H, NH). ^{13}C NMR (150.9 MHz, DMSO-d_6, 30 °C) δ: 29.1, 30.2 (–CH$_2$–bridge); 55.1, 55.2 (O–CH$_3$); 72.6, 74.3 C(7); 113.8, 114.4 C(12); 122.8, 125.5 C(3); 126.4, 126.4 C(10); 128.5, 128.8 (C(11)); 128.5, 129.2 (C(4)); 134.4, 135.8 C(5); 144.3, 148.5 C(9); 153.7, 155.6 (C(6)); 160.5, 160.6 C(13); 165.5, 170.3 C(8). IR (ν/cm^{-1}, Nujol): 3464, 3210 (νNH), 1702, 1668 (νC=O). Elemental analysis Calc. for $C_{68}H_{64}N_8O_{12}$ (1185.28): C, 68.91; H, 5.44; N, 9.45. Found: C, 68.79; H, 5.07; N, 9.14. Mass spectrum (MALDI-TOF): *m/z*: 1185 [M+H]$^+$, 1207 [M+Na]$^+$.

Apparatus

Microanalyses of C, H and N were carried out with a CHN-3 analyzer. Melting points of compounds were measured with a Boetius hotstage apparatus. IR absorption spectrum of Nujol emulsion of compound **5**–**6** were recorded on a Vector-22 Bruker FT-IR spectrophotometer with a resolution of 4 cm^{-1}. NMR experiments were performed on a

Bruker AVANCE-600 spectrometer at 303 K equipped with a 5 mm diameter broadband probe head working at 600.13 MHz in ^{1}H and 150.864 MHz in ^{13}C experiments. Chemical shifts in ^{1}H and ^{13}C spectra were reported relative to the solvent as internal standard (DMSO $\delta(^{1}H) = 2.50$ ppm, $\delta(^{13}C) = 39.5$ ppm). Assignment was accomplished by means of 2D ^{1}H–^{13}C HSQC and 2D ^{1}H–^{13}C HMBC methods. The pulse programs for all NMR experiments were taken from the Bruker software library. A mass spectrum (MALDI) was detected on a Bruker Ultraflex III MALDI-TOF/TOF mass spectrometer.

Extraction procedure and measurements

The $CHCl_3$ was saturated with H_2O before use to prevent volume changes during the extraction. Aqueous metal picrate solutions (5 ml) buffered at pH 6.0 and the solutions of extractant (5 ml, 2.5×10^{-5} to 1×10^{-3} M) in $CHCl_3$ were magnetically stirred in a flask. The extraction equilibrium was reached after vigorous stirring for 1.5 h at 25 °C. Then two phases were allowed to settle for 1 h and afterwards separated by centrifugation. The absorbances A_1 of aqueous phase after extraction and A_0 of aqueous phase before extraction were measured at $\lambda_{max} = 355$ nm (the wavelength of maximum absorption of the picrate ion). All data were obtained from three independent experiments. The aqueous metal picrate solutions ([metal salt] = 1×10^{-2} M; [picric acid] = 2.5×10^{-4} M) were prepared by stepwise addition of a 2.5×10^{-4} M aqueous picric acid solution to the calculated amounts of metal salts. The obtained solutions were stirred at pH 6.0 with acetic-acetate buffer for 1 h. For alkali ions tris(hydroxymethyl)aminomethane-HCl (0.05 M) was used as a buffer. Blank experiments showed that no metal-picrate extraction occurred under the same conditions in the absence of calixarenes. The picrate transfer in the presence of calixarene and buffer (pH = 6) but in the absence of transition metal cations was not observed also ($E < 2$ %).

The percent of extraction was calculated as ratio $E\,\% = 100 \times (A_0 - A_1)/A_0 = \alpha \times 100\,\%$. E % uncertainties are generally ≤ 2 %. The log K_{ex} and n values for the extraction process (see below Eqs. 1, 2) were determined from the plot of log Q versus $\log[L]_{org}$ where $Q = \alpha/z(1-\alpha)^{z}$ as described elsewhere [31, 32].

To evaluate the stoichiometry of the complex formation with Ag^{+} and Hg^{2+} the Job plots method was also applied. Series of isomolar solutions containing various mole amounts of picric acid and ligand (their total concentration 2.5×10^{-4} M) and constant amount of metal ions (1×10^{-2} M) were prepared. The obtained solutions were stirred at acetic-acetate buffer with pH 6.0 for 1 h, separated and spectrophotometrically measured at $\lambda_{max} = 355$ nm. The maximum at the plot dependence of picric acid content in organic layer versus its initial mole fraction in water indicates the ratio of the stoichiometry coefficients of picric acid and ligand in the complex. Taking the eq. 1 (see bellow) as well as the metall cation's charge into account, the complex's stoichiometry was determined.

Results and discussion

Synthesis of receptors

The hydrazone derivatives of calix[4]arene: octahydrazone **1**, monohydrazones **2a**, **2b** as well as tetrahydrazones in different isomer forms: **5a–f** (1,3-*alternate*) and **6a–6d** (*cone*) were obtained by condensation of corresponding hydrazides with aldehydes (Fig. 1). The synthesis of some of these hydrazones was described earlier in our previous works [31, 35–37] (See details in "Experimental" part). The condensation of *cone* isomers of tetrahydrazide tetrathiacalix[4]arene, having *tert*-butyl groups at the upper rim, usually results in bisacetylhydrazone derivatives with N,N'-diacetylhydrazine intramolecular bridge [37, 40, 41]. Therefore, in this work we have synthesized the *cone* isomers of thia- and calix[4]arene hydrazones **6a–d** which do not have *tert*-butyl groups at the upper rim of the macrocyclic platform.

The presence of several hydrazone fragments and polar groups in the molecules **5** and **6** leads to a large number of conformers, as well as to the numerous hydrogen bonding and steric interactions. Therefore, the IR spectra of these compounds contain broadened absorption bands, and many various signals are observed in their ^{1}H NMR spectra. The assignment of these signals in experimental was performed similarly to our previous works [34, 41, 42].

Effect of pH on liquid–liquid phase transfer of picric acid by hydrazone derivatives

The presence of a lone electron pair on the nitrogen atoms in hydrazone molecules provides their basic properties. As a result the HPic transfer from the aqueous to organic phase at pH 2–4 for the investigated compounds **5–6** becomes dramatically high ($E > 10$–70 %) (Fig. 2). Therefore, to receive the correct data for extraction yields as well as to simplify the calculations of the complex stoichiometry and extraction constants for the synthesized hydrazones, we have performed the liquid–liquid extraction experiments at pH = 6.0 with the use of buffer. Under such conditions the hydrolysis of metal ions and the transfer of picric acid from aqueous to organic phase ($E < 2$ % see Fig. 2) appeared to be negligible.

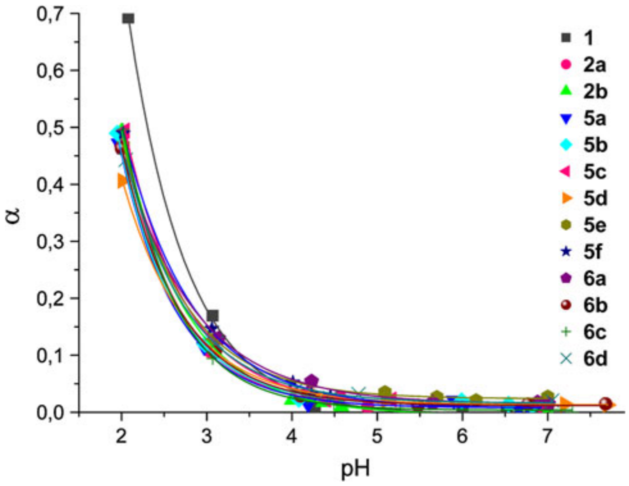


Fig. 2 Effect of pH on a degree of transfer of HPic in the systems containing extractants **1**, **2a**, **2b**, **5a–f** and **6a–d**. [HPic] = 2.5 × 10^{-4} M; $[L_1] = 1.25 \times 10^{-4}$ M; $[L_{\mathbf{2a,b}}] = 1 \times 10^{-3}$ M, $[L_{\mathbf{5a–f,\ 6a–d}}] = 2.5 \times 10^{-4}$ M

Metal extraction

The extraction process at pH 6 for hydrazones **2a**, **2b**, **5a–f** and **6a–d** can be described by Eq. 1:

$$M^{z+}_{aq} + z\mathrm{Pic}^-_{aq} + nL_{org} \leftrightarrows [M^{z+}L_n\mathrm{Pic}^-_z]_{org} \qquad (1)$$

where M^{z+}, Pic^-, L, $[M^{z+}L_n\mathrm{Pic}^-_z]$ denote the metal ion, picrate anion, ligand, ion-pair metal complex and the subscripts aq and org mean that the species exist in the aqueous or organic phase. The equilibrium concentration of picrate anion in the aqueous phase was determined spectrophotometrically. The extraction constant (K_{ex}) was evaluated from Eq. 2:

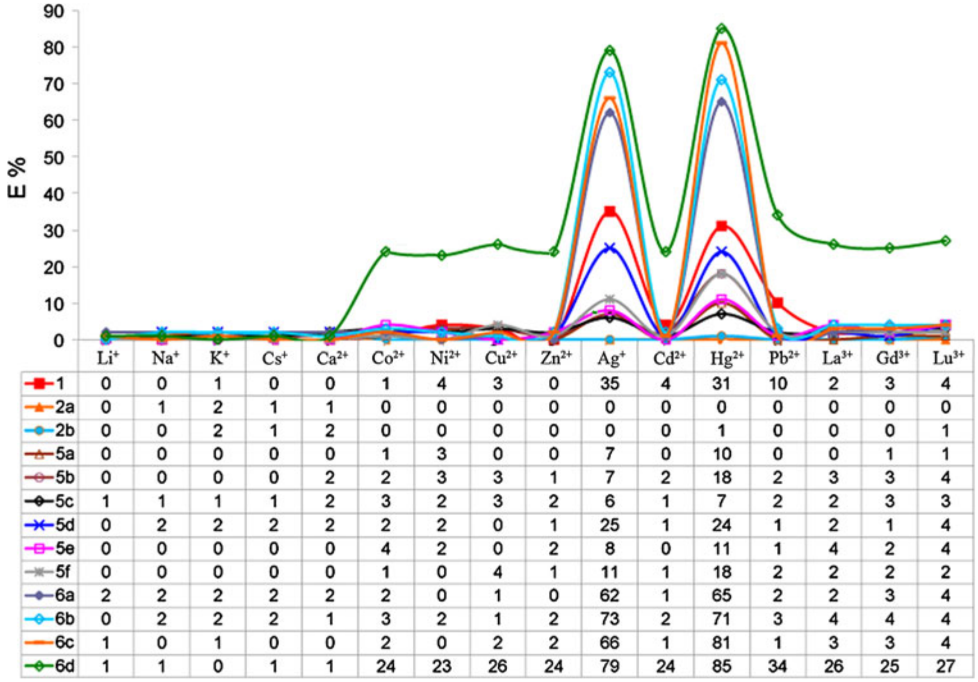
$$K_{ex} = [M^{z+}L_n\mathrm{Pic}^-_z]_{org} / [M^{z+}]_{aq}[\mathrm{Pic}^-]^z_{aq}[L]^n_{org} \qquad (2)$$

The extraction data obtained for the synthesized hydrazones are summarized in Fig. 3, 4 and Table 1.

It could be clear observed that monohydrazones **2a**, **2b** do not extract metal ions from aqua solutions ($E < 3$ %). The preorganization of hydrazone groups on calix[4]arene platform promotes considerably their affinity towards Ag^+ and Hg^{2+}. Really, the 1,3-*alternate* thiacalix[4]arenes become already capable to bind effectively these ions. The extraction efficiency goes up after removing *tert*-butyl groups from upper rim of 1,3-*alternate* tetrathiacalix[4]arene isomers ($E_{\mathbf{5d}}$ (Ag^+) ~ 25 %, $E_{\mathbf{5d}}$ (Hg^{2+}) ~ 24 %). In spite of decreasing of lipophilicity of the molecules, the weakening of steric difficulties facilitates the process of metal recovery by these compounds.

The possibility of a cooperative coordination of four binding hydrazone groups in *cone* isomers of tetrathiacalix[4]arene results in dramatic increase of the extraction efficiency for Ag^+ ($E_{\mathbf{6a}}/E_{\mathbf{5b}} \approx 8.7$, $E_{\mathbf{6b}}/E_{\mathbf{5d}} \approx 2.9$, $E_{\mathbf{6c}}/E_{\mathbf{5f}} \approx 6$) and Hg^{2+} ($E_{\mathbf{6a}}/E_{\mathbf{5b}} \approx 3.6$, $E_{\mathbf{6b}}/E_{\mathbf{5d}} \approx 2.6$, $E_{\mathbf{6c}}/E_{\mathbf{5f}} \approx 4.5$) (Fig. 3). In the case of applying other metal ions the extraction yields, including the possible transfer of picric acid, do not exceed an experimental error ($E < 4$ %). This fact testifies about remarkable binding selectivity of *cone* tetrathiacalix[4]arenes **6a–6c** towards Ag^+ and Hg^{2+} appearing in a wide range of metal ions.

Fig. 3 Extraction percentages (E %) of metal picrates from water into $CHCl_3$ at 25° C by hydrazones **1**, **2a**, **2b**, **5a–f** and **6a–d**. [HPic] = 2.5 × 10^{-4} M, $[M^{z+}] = 1 \times 10^{-2}$ M, $[L_1] = 1.25 \times 10^{-4}$ M, $[L_{\mathbf{2a,b}}] = 1 \times 10^{-3}$ M, $[L_{\mathbf{5a–e,6a–d}}] = 2.5 \times 10^{-4}$ M; pH = 6.0



	Li^+	Na^+	K^+	Cs^+	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Hg^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}	Lu^{3+}
1	0	0	1	0	0	1	4	3	0	35	4	31	10	2	3	4
2a	0	1	2	1	1	0	0	0	0	0	0	0	0	0	0	0
2b	0	0	2	1	2	0	0	0	0	0	0	1	0	0	0	1
5a	0	0	0	0	0	1	3	0	0	7	0	10	0	0	1	1
5b	0	0	0	0	2	2	3	3	1	7	2	18	2	3	3	4
5c	1	1	1	1	2	3	2	3	2	6	1	7	2	2	3	3
5d	0	2	2	2	2	2	2	0	1	25	1	24	1	2	1	4
5e	0	0	0	0	0	4	2	0	2	8	0	11	1	4	2	4
5f	0	0	0	0	0	1	0	4	1	11	1	18	2	2	2	2
6a	2	2	2	2	2	2	0	1	0	62	1	65	2	2	3	4
6b	0	2	2	2	1	3	2	1	2	73	2	71	3	4	4	4
6c	1	0	1	0	0	2	0	2	2	66	1	81	1	3	3	4
6d	1	1	0	1	1	24	23	26	24	79	24	85	34	26	25	27

The introduction of 4-methoxy- or 4-hydroxy- groups into benzylidene fragments of hydrazones in 1,3-*alternate* (**5c–e**) and *cone* (**6b–c**) isomers also promotes a considerable increase of Ag^+ and Hg^{2+} ions recovery by these compounds (for example, 1,3-*alternate*: $E_{\mathbf{5b}}$ ($R_2 = H$) = 7 % → $E_{\mathbf{5d}}$ ($R_2 = OCH_3$) = 25 % for Ag^+; *cone*: $E_{\mathbf{6a}}$ ($R_2 = H$, $R_3 = H$) = 65 % → $E_{\mathbf{6c}}$ ($R_2 = OH$, $R_3 = t{-}Bu$) = 81 % for Hg^{2+}). The methoxy and, especially, the hydroxyl groups posses a positive mesomeric effect and act as electron donors [43]. Such groups enhance the imine nitrogen basicity in the hydrazone fragments that leads to a more effective binding of the mentioned above compounds with Ag^+ and Hg^{2+} ions.

We have also aimed to compare the efficiency and selectivity of the metal recovery by hydrazone derivatives based on tetrathia-, calix[4]arene and calix[4]resorcine platforms. Calix[4]arene **6d** as well as its thia- analogue **6b** was found do not bind alkali ions. Calix[4]arene **6d** has comparable extraction efficiency towards Ag^+ and Hg^{2+} with its tetrathia- analogue **6b**. Thus, this fact indicates that the bridge sulfur atoms of the tetrathiacalix[4]arene macrocycle **6d** do not participate in the binding of transition metal ions. Obviously, the coordination is realized due to the terminal hydrazone groups.

Tetrahydrazone **6a** binds Ag^+ and Hg^{2+} ions approximately two times more effectively than the octahydrazone of calix[4]resorcine **1** (for comparison: $E_{\mathbf{6a}}(Ag^+) = 62$ %, $E_{\mathbf{6a}}(Hg^{2+}) = 65$ %; $E_{\mathbf{1}}(Ag^+) = 35$ %, $E_{\mathbf{1}}(Hg^{2+}) = 31$ %). An increase of a number of binding groups under going from thiacalix[4]arene to calix[4]resorcine does not lead to an expected enhancement of the extraction efficiency. This phenomenon is obviously explained by unfavourable disposition of endo-oriented acetylhydrazone groups in calix[4]resorcine, which is less effective for the cooperative binding than in the case of closely located exo-oriented groups in tetrathiacalix[4]arene.

As it was previously indicated, the calix[4]arenes functionalized by thio-groups can reveal a high recovering ability towards Ag^+ and Hg^{2+}. Indeed, a quantitative extraction of Ag^+ (E = 99 %) was observed for the p-*tert*-butyltetrathiacalix[4]arene substituted at the narrow rim by diethylthiophosphate ester groups (−PS(OEt) [21]. However, the other metal ions have been also notably extracted by this compound (for example, $E(Cu^{2+}) = 11$ % and $E(Pb^{2+}) = 13$ %). The selectivity of metal recovery (S) by this compound in the row of metals was calculated as the ratio of percentages of the cations extracted: $S = E(Ag^+)/E(Pb^{2+}) = 7.6$. Review [44] summarizes the data obtained for the liquid–liquid extraction of toxic ions (Cd^{2+}, Hg^{2+} and Pb^{2+}) by 57 calixarenes. Among these compounds the 5,11,17,23-*tert*-butyl-25,26,27,28-(2-N,N-dimethyldithiocarbamoylethoxy)calix[4]arene has exhibited the highest selectivity towards Hg^{2+} (S = 20) and Ag^+ (S = 18) relatively Cd^{2+} and Pb^{2+} ions [45]. Unfortunately, the comparison with other well extracted d-ions has not been carried out. In our case, such selectivity towards Ag^+ (S = 16 (**6a**), 18 (**6b**), 17 (**6c**)) and Hg^{2+} (S = 16 (**6a**), 18 (**6b**), 20 (**6c**)) was successfully achieved by the synthesized tetrahydrazones **6a–c** in a wide range of metal ions. The selectivity data have been calculated based on the fact that the extraction degree for other metal ions did not exceed 4 % (Table 1). In the case of low yields of extraction the experimental error and the transfer of picric acid can contribute into determination of selectivity values and underestimate them. Therefore, the applicaton in future of more sensitive and accurate analitical methods may help to obtain more perfect and remarkable results for the selectivity.

The stoichiometry of extracted complexes with Ag^+ and Hg^{2+} and the extraction constants have been determined from log Q vs log $[L]_{org}$ plots (see Experimental Section) for the most effective receptors **6a–c**. All graphs of extraction dependences for *cone* isomers **6a–c** with Ag^+ and Hg^{2+} have an equal slope (n ≈ 1 and 2 respectively) regardless of excess or insufficiency of the ligand (Fig. 4). This indicates the 1:1 for Ag^+ and 1:2 for Hg^{2+} (M^{z+}/L) stoichiometry of the extracted complexes in a wide range of concentration. These results are in accordance with data obtained for the complex stoichiometry determined by the Job plots. The transfer of Pic^- anion achieved the maxima at 0.5 mol fraction in all cases (Fig. 5). This fact clearly confirms that Ag^+ and doubly charged Hg^{2+} metal ions form complexes 1:1 and 1:2 (M^{z+}/L), respectively.

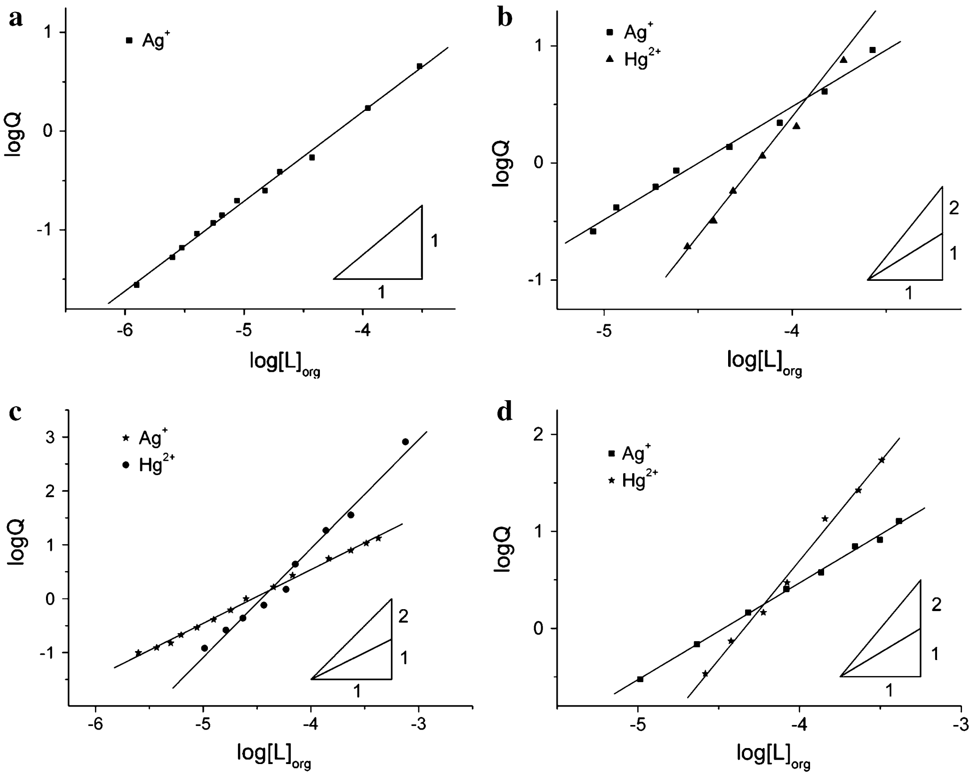
In our previous investigations we have shown that tetrahydrazide **4b** (*cone*) could be utilized for the group separation of d-ions from alkali- and f- metals [33]. Tetrahydrazide **4b** forms one order more stable complexes with Ag^+ ($K_{ex\ \mathbf{4b}} = 10^{7.5}$), than tetrahydrazones **6a–c** ($K_{ex\ \mathbf{6a–c}} = 10^{6.3–6.5}$) (Table 1). In the case of Hg^{2+}, approximately two orders higher extraction constants than

Table 1 The extraction constants and stoichiometry of complexes of hydrazones **1** and **6a–c** with Ag^+ and Hg^+

Cation	Metal:ligand stoichiometry	log K_{ex}			
		1	**6a**	**6b**	**6c**
Ag^+	1:1	5.8 ± 0.1	6.3 ± 0.2	6.5 ± 0.1	6.4 ± 0.1
Hg^{2+}	1:1	9.2 ± 0.2[a]	–	–	
	1:2	–	14.1 ± 0.2	14.6 ± 0.2	14.5 ± 0.4

[a] Data from Ref. [31]

Fig. 4 Log Q versus log $[L]_{org}$ for Ag^+ and Hg^{2+} extracted by **1** (a), **6a** (b), **6b** (c) and **6c** (d), **4b**,**c** (b) in $CHCl_3$. $[HPic] = 2.5 \times 10^{-4}$ M, $[M^{z+}] = 1 \times 10^{-2}$ M, pH = 6.0



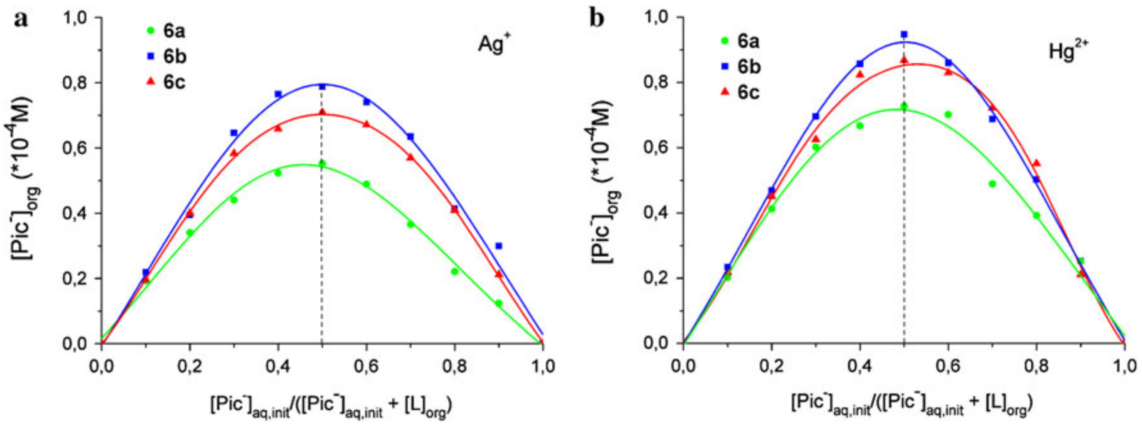


Fig. 5 Job plots for Pic⁻ extracted by tetrahydrazones **6a–c** in the presence of Ag^+(a) and Hg^{2+} (b). $[HPic]_{aq} + [L]_{org} = 2.5 \times 10^{-4}$ M, $[M^{z+}] = 1 \times 10^{-2}$ M, pH = 6.0

for Ag^+ have been obtained for tetrahydrazone derivatives of thiacalix[4]arenes ($K_{ex\ 4b} = 10^{12.6}$ and $K_{ex\ 6a\text{–}c} = 10^{14.1\text{–}14.6}$). The 1,3-*alternate* tetrahydrazide **3b** has also revealed a high selectivity in the series of d-ions. The maxima of extraction were observed for Ni^+, Ag^+ and Cd^{2+}, but the other d-metal ions have been also extracted enough effectively (E_{3b} = 13–40 % for Co^{2+}, Cu^{2+}, Zn^{2+}).

To determine the selectivity of metal recovery by using K_{ex} it is commonly required to estimate these values for the different metal ions forming complexes of equal stoichiometry. However, in the case of low extraction yields to define these values is rather difficult. Therefore, the extraction constants for calix[4]arenes **6a–c** with the weak extracted metal ions have been evaluated for the maximal value $E \approx 4$ % (Table 1)) assuming the 1:1 ($K_{ex}(Me^+) = 10^{4.2}$) or 1:2 ($K_{ex}(Me^{2+}) = 10^{11.4}$) complex stoichiometry. In these cases the extraction selectivity for Ag^+ and Hg^{2+} by tetrahydrazones **6a–c** achieves more than two and three orders of magnitude ($K_{ex}(Ag^+)/K_{ex}(Me^+) = 10^{6.3\text{–}6.5}/10^{4.2} = 10^{2.1\text{–}2.3}$, $K_{ex}(Hg^{2+})/K_{ex}(Me^{2+}) = 10^{14.1\text{–}14.6}/10^{11.4} = 10^{2.7\text{–}3.2}$), respectively.

Whereas the tetrahydrazides **3b** and **4b** as well as some of thio-derivatives of calix[4]arenes demonstrate high extraction efficiency towards d-metals, the tetrahydrazones **6a–c** reveal high selectivity of Ag^{+} and Hg^{2+} ion recovery among the wide row of metal ions.

Conclusion

We have synthesized novel phenyl hydrazone derivatives of tetrathiacalix[4]arene in 1,3-*alternate* and *cone* isomer forms. The liquid–liquid extraction experiments with s- (Li^{+}, Na^{+}, K^{+}, Cs^{+} and Ca^{2+}), p- (Pb^{2+}), d (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}) and f- (La^{3+}, Gd^{3+} and Lu^{3+}) metal ions have shown that the new and early synthesized *cone* calix[4]arene isomers are excellent receptors for the recovery of Ag^{+} and Hg^{2+} ions from aqueous environment. The extraction selectivity for Ag^{+} and Hg^{2+} ions relative to other metal ions ($Ag^{+}/Me^{n+} \geq 16$–18 and $Hg^{2+}/Me^{n+} \geq 16$–20) achieves two and three orders of magnitude K_{ex}, respectively.

It was experimentally demonstrated that in order to obtain effective receptors for Ag^{+} and Hg^{2+} the applying of tetrathiacalix[4]arene macrocyclic platform is more preferable than the use of calix[4]arene or calix[4]resorcine one. A high binding efficiency towards these metal ions is obviously provided by the preorganization of acetylhydrazone groups on the *cone* platform of tetrathiacalix[4]arene without participation of bridge sulfur atoms. The introduction of electron-donor substituents in phenyl fragments of hydrazone groups improves the affinity of these compounds towards Ag^{+} and Hg^{2+} ions.

These results could be as a stimulus for further investigations in this field in order to obtain new data for the extraction selectivity, allowing the development of sensitive methods for the detection and preconcentration of trace amounts of Ag^{+} and Hg^{2+}.

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