

Pyridinyl hydrazone derivatives of thiacalix[4]arene as selective extractants of transition metal ions

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Abstract The recognition ability of pyridinyl hydrazone derivatives of *cone*- and *1,3-alternate* tetrathiacalix[4]arenes towards transition and alkali metals has been investigated by picrate extraction method. The stoichiometry of complexes and the extraction constants have been determined. It has been found that hydrazones do not extract alkali metal ions but show an excellent affinity towards transition and heavy metal cations. The removal of *tert*-butyl groups from calix[4]arene platform in the case of *cone* and *1,3-alternate* isomers leads to an increase of d-ion extraction selectivity or efficiency.

Keywords Thiacalix[4]arene · Hydrazone · Transition metal ions · Liquid–liquid extraction · Selectivity

Introduction

With the rapid and growing industrialization we have faced with the environmental pollution problem caused particularly by the excessive disposal of heavy metals and other pollutants [1, 2]. The removal of trace amounts of transition

metals from industrial and technical products is also an urgent task. Thus, the presence of these metals in oil refining products reduces their oxidative stability [3]. The various high sensitive analytical techniques are now developed to control the trace amounts of transition metal ions, especially those which possess cumulative and toxic properties. However, a high content of alkali and alkaline-earth ions in industrial samples and particularly in saline natural water leads to the difficulties in instrumental detection of transition metals [4, 5]. In this connection, the prior preconcentration and separation of transition metals from alkali and alkaline-earth ones seems to be very important. To solve this problem the compounds having receptor properties can be successfully used. The presence of preorganized binding sites in these molecules is a necessary requirement for the realization of such receptor functions [6]. Calix[*n*]arenes are compounds with three-dimensional spatially organized structure, which can be utilized as a suitable platform for the design of artificial receptors [7–9]. The functionalizing of calix[*n*]arene molecules by donor groups containing oxygen and nitrogen atoms provides their ability to coordinate hard and soft transition metal ions. Hydrazone derivatives of calix[4]arenes are turned out to be effective extractants of transition metal ions in the presence of alkali and alkaline-earth metal ions [10–12]. In this context hydrazone derivatives of calix[4]arene acetylhydrazides should be also very promising for liquid extraction of transition metal ions.

In this paper we have studied the extraction affinity of tetrathiacalix[4]arenes functionalized by pyridinyl hydrazone moieties towards alkali, alkaline-earth and transition metal ions and explored the influence of the structure of calix[4]arene platform on their binding properties. These properties have been investigated by liquid–liquid extraction method using the aqueous solutions of metal picrates.

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The extraction efficiency and selectivity, the stoichiometry of the complexes and extraction constants for transition metals have been established.

Experimental

Reagents

All chemicals were used as commercially received without further purification. CHCl_3 was distilled over P_2O_5 . $\text{DMSO-}d_6$ (99.5% isotopic purity) from Aldrich was used for NMR spectroscopy. The metal salts for extraction experiments were the following chlorides and nitrates: LiCl , NaCl , KCl , CsCl , CaCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NiCl_2 , CuCl_2 , ZnCl_2 , AgNO_3 , $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$.

Synthesis

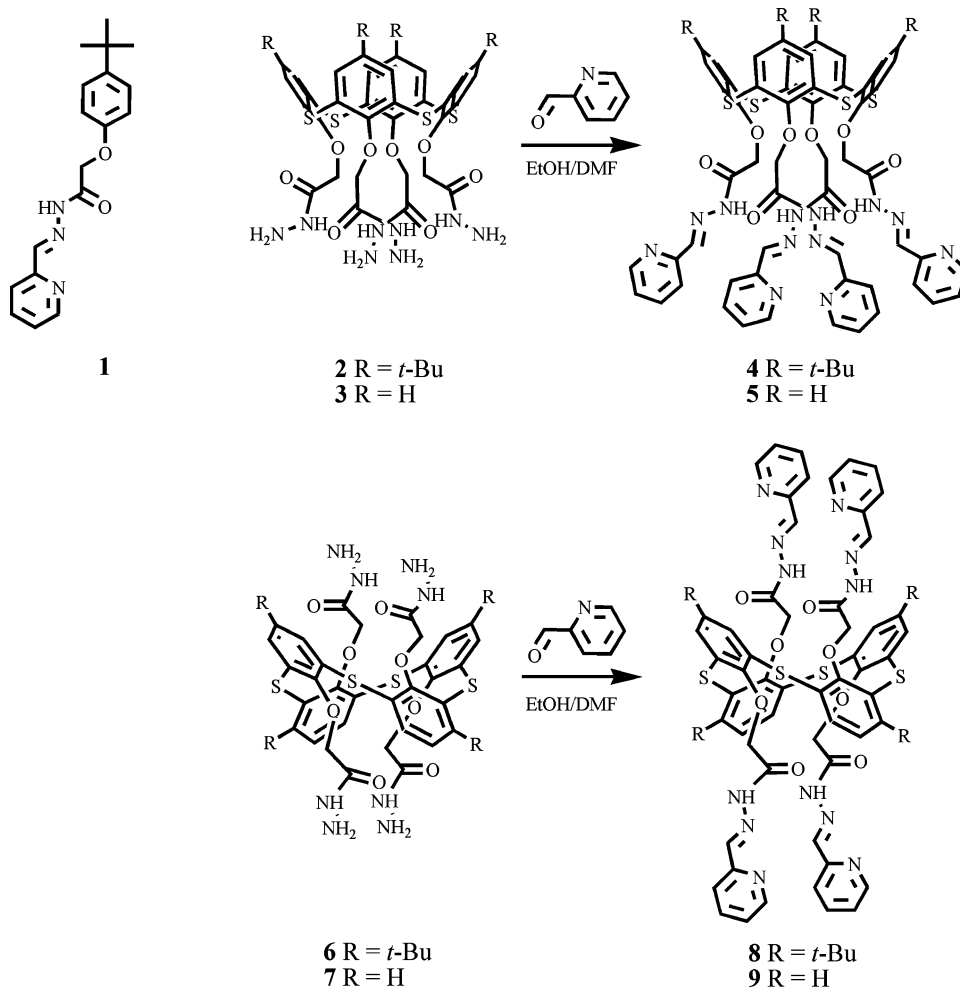
The synthetic routes and the structural formulae of the investigated compounds are shown in Fig. 1. The

hydrazones **1** [13], **4** [14], **8** and **9** [15] and tetrahydrazone calix[4]arene derivatives **2** [10], **3** [16], **6** [11] and **7** [16] were obtained as described by us earlier.

Preparation of 25,26,27,28-tetrakis[(2-pyridinylmethylidene)hydrazinocarbonylmethoxy]-2,8,14,20-tetrathiocalix[4]arene (cone-5)

To a suspension of tetrahydrazone **3** (0.20 g, 0.25 mmol) in 6 mL EtOH and 6 mL DMF the picolinaldehyde (0.16 g, 1.5 mmol) was added. The reaction mixture was heated for 24 h at 40 °C. 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 a mixture of EtOH and DMF. Yield: 0.17 g (60%) as a white powder. Mp 182–184 °C. $^1\text{H NMR}$ (600.0 MHz, $\text{DMSO-}d_6$, 30 °C) δ : 4.65, 5.36 (br s, 8H, O–CH₂), 6.69, 6.84 (s, 4H, C(3)H in Ar–O), 7.40 (s, 4H, C(4)H in 2-Py), 7.45, 7.59 (s, 8H, C(3)H in Ar–O), 7.90 (s, 4H, C(5)H in 2-Py), 8.0, 8.67 (s, 4H, –N=C–H), 8.10 (s, 4H, C(6)H in 2-Py), 8.51, 8.59 (s,

Fig. 1 Synthetic routes and structural formulae of investigated compounds



4H, C(3)H in 2-Py), 10.28, 11.58 (s, 4H, NH). ^{13}C NMR (150.9 MHz, DMSO- d_6 , 30 °C) δ : 67.9, 69.1 (O-CH $_2$), 121.0, 121.3 (C(6) in 2-Py), 123.9, 125.3 (C(4) in Ar-O), 124.6, 125.0 (C(4) in 2-Py), 128.1, 129.2 (C(2) in Ar-O), 134.1, 134.7 (C(3) in Ar-O), 137.0, 137.4 (C(5) in 2-Py) 144.2, 149.8, 150.0 (-N=C-H), 148.4, 148.9 (C(3) in 2-Py), 153.1, 153.2 (C(1) in 2-Py), 157.7, 158.8 (C(1) in Ar-O), 163.6, 169.0 (C=O). IR (ν/cm^{-1} , Nujol): 3400, 3220 (νNH), 1692 ($\nu\text{C=O}$), 1537 (δNH). Elemental analysis calc. for C $_{56}$ H $_{44}$ N $_{12}$ O $_8$ S $_4$ (1141.28): C 58.93; H 3.89; N 14.73; S 11.24. Found: C 59.19; H 3.60; N 14.35; S 10.95. Mass spectrum (MALDI-TOF): $m/z = 1141$ [M + H] $^+$; 1163 [M + Na] $^+$; 1180 [M + K] $^+$.

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** was 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 ^1H and 150.864 MHz in ^{13}C experiments. Chemical shifts in ^1H and ^{13}C spectra were reported relative to the solvent as internal standard (DMSO $\delta(^1\text{H}) = 2.50$ ppm, $\delta(^{13}\text{C}) = 39.5$ ppm). Assignment was accomplished by means of 2D ^1H - ^{13}C HSQC and 2D ^1H - ^{13}C HMBC methods. The pulse programs of the NOESY, HSQC and HMBC experiments were taken from Bruker software library. A mass spectrum (MALDI) was detected on a Bruker Ultraflex III MALDI-TOF/TOF mass spectrometer.

Extraction procedure and measurements

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 $\lambda_{\text{max}} = 355$ 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. The percent of extraction was calculated as ratio $E\% = \alpha \times 100\% = 100 \times (A_0 - A_1)/A_0$. $E\%$ uncertainties are generally $\leq 2\%$. The log K_{ex} and n values were determined from the plot of logQ versus log[L] $_{\text{org}}$ where $Q = \alpha/z(1-\alpha)^z$ as described elsewhere [11, 12].

Results and discussion

Synthesis

We have shown earlier that the condensation of *cone* isomer of tetrahydrazide *tert*-butyl-tetrathiacalix[4]arene with aldehydes results in the formation of bisacetylhydrazone derivatives having the *N,N*-diacetylhydrazine intramolecular bridge. Only by using the picolinaldehyde as a reagent we have succeeded in obtaining the tetrahydrazone derivative of tetrathiacalix[4]arene in a “*cone*” isomeric form **4** [14, 17]. Now we have synthesized its analogue **5** which does not have *tert*-butyl groups at upper rim of calix[4]arene platform. The thin-layer chromatography (TLC) and MALDI-TOF mass-spectroscopy analysis of the reaction mixture has shown that beside the new *cone* isomer **5** no products with intramolecular *N,N*-diacetylhydrazine bridge are formed. The change of calix[4]arene platform structure from *cone* to *1,3-alternate* also provides the formation of desired tetrasubstituted products (compounds **8** and **9**) [15].

It should be noted that to obtain the totally substituted *1,3-alternate* calix[4]arene isomers **8** and **9** a higher temperature is required than for the synthesis of the *cone* forms **4** and **5**. Obviously in the case of *1,3-alternate* structure the reaction centers are hindered by the phenyl rings and as a result the reaction rate decreases. The same peculiarity was also observed in the synthesis of hydrazide derivatives of calix[4]arene **2**, **3** and **6**, **7** [10, 11, 16].

Extraction studies

This work is focused on the ability of calix[4]arene tetrahydrazone derivatives to bind metal cations. The factors which determine the efficiency and selectivity of these receptors towards transition metal ions are herein emphasized. The usefulness of donor sites, the removal of *tert*-butyl groups from upper rim and the influence of calix[4]arene isomeric form on the receptor properties are considered. The affinity between metal ions and hydrazones has been estimated from the extraction data with the use of the methodology described in our previous works [11, 12].

It was established that the basic imine and pyridine nitrogen atoms in hydrazone molecules **1**, **4**, **5**, **8** and **9** induce the transfer of picric acid (HPic) from aqueous to organic phase even without metal ion participation (Fig. 2).

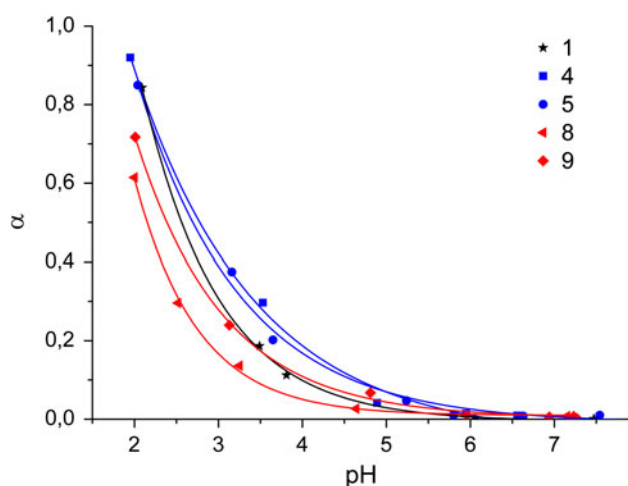
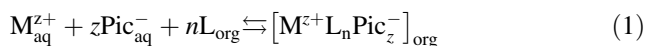


Fig. 2 The pH effect on HPic-transfer degree in the systems containing hydrazones (L) **1**, **4**, **5**, **8** and **9**. [HPic] = 2.5×10^{-4} M; $[L_1] = 4 \times 10^{-3}$ M; $[L_{4,5,8,9}] = 1 \times 10^{-3}$ M

The most effective HPic-transfer were proved to be the *cone* calix[4]arenes **4** and **5**. Taking into account this fact, all extraction experiments in the presence of metal ions have been carried out in a buffer at pH 6.0, where the transfer of picric acid ($\alpha < 0.02$) is negligible. In this case the extraction process can be described by Eq. 1:



where M^{z+} , Pic^- , L, $[M^{z+}L_n\text{Pic}_z^-]$ 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:

$$K_{\text{ex}} = \frac{[M^{z+}L_n\text{Pic}_z^-]_{\text{org}}}{[M^{z+}]_{\text{aq}} [\text{Pic}^-]_{\text{aq}}^z [L]_{\text{org}}^n} \quad (2)$$

The results of extraction for hydrazones are summarized in Figs. 3 and 4, Table 1.

It is clear seen that monohydrazone **1** recovers the transition and toxic metal ions from aqua solutions rather efficiently (Fig. 3a), particularly the Cu^{2+} (65%), Ag^+ (61%) and Hg^+ (25%) are especially well extracted. The integration of the hydrazone moieties into the calix[4]arene molecule increases the extraction efficiency of the compound. Thus, the tetrathiacalix[4]arenes **4**, **5**, **8** and **9** bind transition metal ions essentially better than the compound **1** (Fig. 3). At the same time the extraction of alkali ($E < 2\%$ for Li^+ , Na^+ , K^+ , Cs^+) and alkaline-earth ($E < 3\%$ for Ca^{2+}) ions was found to remain poor for them, similarly as it was observed in the case of **1**.

The *cone* calix[4]arenes **4** and **5** are particularly effective towards Cu^{2+} and Ag^+ ions. The maximum of heavy

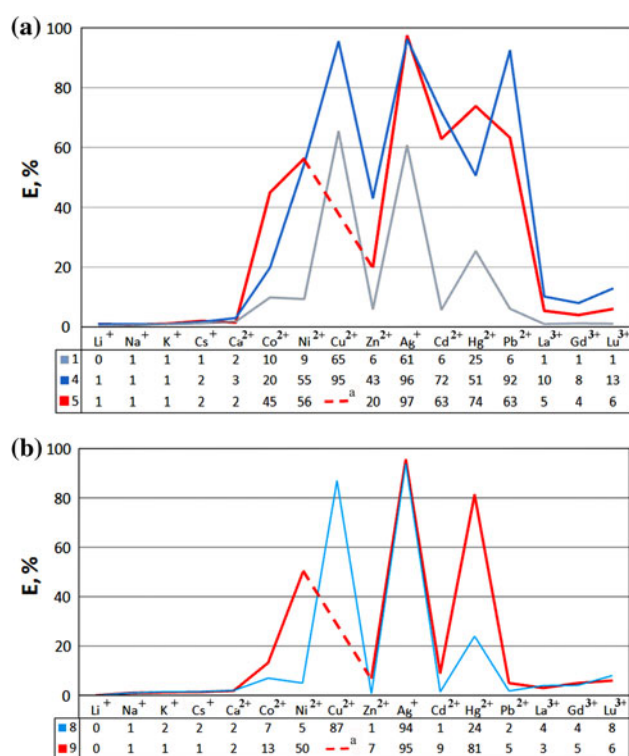
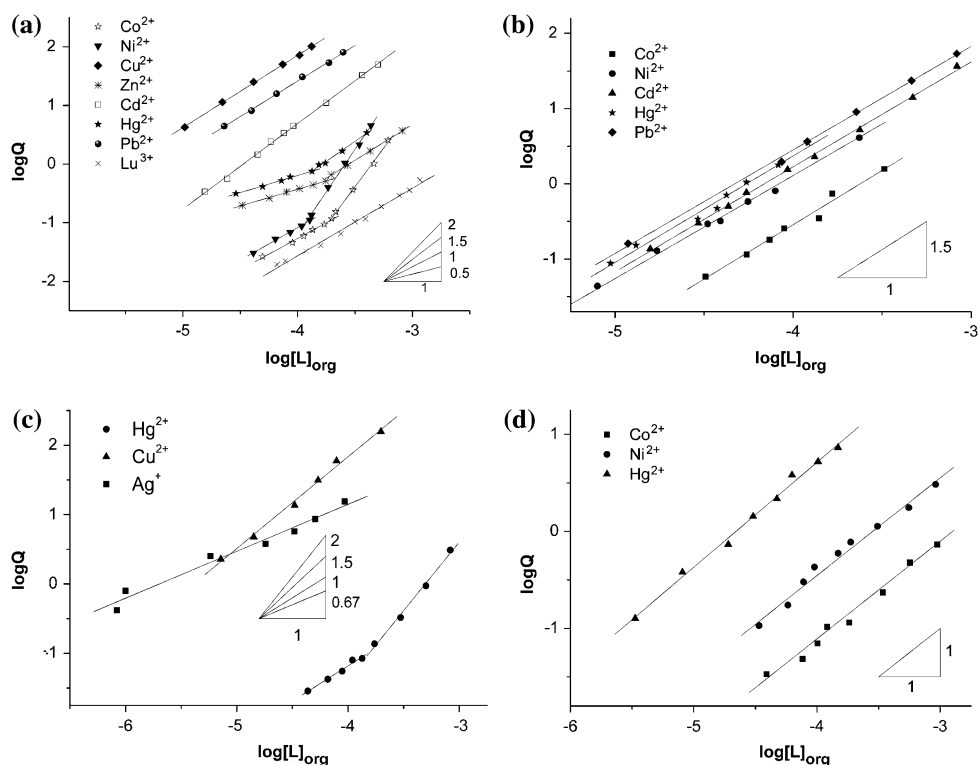


Fig. 3 Extraction percentages ($E\%$) of metal picrates from water into CHCl_3 at 25°C by (a) hydrazone **1**, *cone*-**4**, *cone*-**5** and (b) *1,3*-*alternate*-**8** and **9**. pH 6.0; [HPic] = 2.5×10^{-4} M, $[M^{z+}] = 1 \times 10^{-2}$ M, $[L_1] = 1 \times 10^{-3}$ M, $[L_{4,5,8,9}] = 2.5 \times 10^{-4}$ M. ^a $E\%$ was not determined due to formation of precipitate

toxic metals recovery by macrocycle **4** is shifted from Hg^{2+} to Pb^{2+} in comparison with the compounds **1** and **5**. The macrocycle **4**, in contrast to the monoanalogue **1**, demonstrates a rather notable extraction ability towards f-ions ($E \sim 8\text{--}13\%$, Fig. 3a), which achieves $\sim 26\text{--}38\%$ at the extractant concentration 1×10^{-3} M. The removal of *tert*-butyl groups from calix[4]arene framework leads to the decreasing of f-ions extraction efficiency ($E \sim 4\text{--}6\%$ for **5**, Fig. 3a). Meanwhile, the extraction yield for Co^{2+} (from 20% for **4** to 45% for **5**) and Hg^{2+} (from 51% for **4** to 74% for **5**) significantly goes up. Thus, the calix[4]arene **5** can separate d-ions from alkali, alkaline-earth and f-ions more selectively than its more rigid *tert*-butyl analogue **4**.

The extraction efficiency of *1,3*-*alternate* isomers **8** and **9** is lower than for their *cone* analogues **4** and **5**. A small extraction yield is observed for f-ions ($E < 4\text{--}8\%$ for **8** and $E < 3\text{--}6\%$ for **9**). However, the selectivity of the recovery of Cu^{2+} , Ag^+ and Hg^{2+} metal ions becomes substantially higher. Thus, the selectivity of Cu^{2+} recovery ($E(\text{Cu}^{2+})/E(\text{Me}^{n+})$) in the case of tetrahydrazone **8** relative to Co^{2+} , Ni^{2+} and Zn^{2+} equals ~ 12 , 17 and 87, respectively. The selectivity values $\text{Hg}^{2+}/\text{Pb}^{2+}$ and $\text{Hg}^{2+}/\text{Cd}^{2+}$ are ~ 12 and ~ 24 . In the case of Ag^+ ion these values become considerably higher. The removal of *tert*-butyl groups from

Fig. 4 Log Q versus log [L]_{org} for some metal ions extracted by *cone-4* (a), *cone-5* (b), 1,3-*alternate-8* (c) and 1,3-*alternate-9* (d) in CHCl₃. [HPic] = 2.5 × 10⁻⁴ M, [M^{z+}] = 1 × 10⁻² M, pH 6.0



tetrathiacalix[4]arene framework leads to the improvement of their extraction efficiency for d-ions. The appreciable increase of $E\%$ is especially observed for Ni²⁺ (from ~5% for **8** to ~50% for **9**) and Hg²⁺ (from ~24% for **8** to ~81% for **9**) ions.

The sequence (Co²⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺) of extraction efficiency values for investigated hydrazones **4**, **5** and **9** is in accordance with Irving–Williams order for the relative stability of complexes formed by the first transition series of metal ions [18]. However, the yield of Cu²⁺ recovery by the compounds **5** and **9** could not be estimated correctly at the concentration of macrocycle 2.5 × 10⁻⁴ M, because of a precipitation in the solutions. The Irving–Williams order for the compound **8** is disturbed: the extraction efficiency for the Ni²⁺ ion ($E \sim 5\%$) was found to be lower than for Co²⁺ ($E \sim 7\%$).

The stoichiometry of extracted complexes and the extraction constants have been determined from log Q versus log [L]_{org} plots (see Experimental section) for the most extractable metal ions (Fig. 4). The determination of these values in the case of low extraction yields (α) is not correct. Therefore, the extraction constants of calix[4]arenes **8** and **9** for some metal ions represented in the Table 1 have been evaluated on the basis of α values and the proposed complex stoichiometry.

In the graphs of extraction dependences for calix[4]arene **4** with Co²⁺, Ni²⁺, Zn²⁺ and Hg²⁺ (Fig. 4a) and for **8** with Hg²⁺ (Fig. 4c) two regions can be clear observed. The

regions with an excess of cation and with an excess of ligand are attributed to the different types of stoichiometry for predominantly extracted species. The *cone* thiacalix[4]arene **4** forms the complexes (M^{z+}:L) of 1:1 with all metal ions except for Cd²⁺ (See Fig. 4a and Table 1). In case of insufficiency of the ligand the binuclear complexes 2:1 for the Zn²⁺ and Hg²⁺ metal ions are formed. An excess of ligand leads for the Co²⁺ and Ni²⁺ complexes to the bis-ligand 1:2 stoichiometry. The selectivity in the series of d-elements (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) with compound **4** achieves three orders of magnitude ($K_{\text{ex}}(\text{Cu}^{2+})/K_{\text{ex}}(\text{Co}^{2+}) = 10^{3.2}$ for the complex 1:1). The extraction constant for Pb²⁺ (10^{11.9}) is two orders higher than for Hg²⁺ (10^{9.5}).

The graph dependence log Q versus log [L]_{org} for Cd²⁺ has a linear character with the slope $n \sim 1.5$. The similar results were also obtained with the use of the acetate salt of Cd²⁺ instead of chloride one and the use of tris(hydroxymethyl)aminomethane–HCl as a buffer. This fact demonstrates that these anions do not affect the complex formation process in organic phase. It could be proposed that in both cases the formation of a binuclear complex with 2:3 stoichiometry is obviously realized, when one ligand molecule acts as a bridge. The removal of *tert*-butyl groups from calix[4]arene framework leads to the similar binuclear 2:3 complexes of tetrahydrazone **5** with the Co²⁺, Ni²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ ions.

The 1,3-*alternate* structure of calix[4]arene is well-adapted for the formation of mono- as well as binuclear

Table 1 Extraction constants and stoichiometry of metal complexes with tetrahydrazones **4**, **5**, **8** and **9**

Cation	Metal:ligand stoichiometry	log K_{ex}			
		<i>Cone-4</i>	<i>Cone-5</i>	<i>1,3-alt-8</i>	<i>1,3-alt-9</i>
Co ²⁺	1:1	8.3 ± 0.2	–	–	8.5 ± 0.5
	2:3	–	10.8 ± 0.5	–	–
	1:2	13.0 ± 0.6	–	–	–
Ni ²⁺	1:1	9.0 ± 0.3	11.2 ± 0.7	–	9.2 ± 0.3
	2:3	–	–	–	–
Cu ²⁺	1:1	11.5 ± 0.3	^a –	–	^a –
	2:3	–	–	12.8 ± 0.2	–
Zn ²⁺	2:1	6.8 ± 0.2	–	–	–
	1:1	9.1 ± 0.4	–	–	–
Ag ⁺	3:2	^b –	^b –	5.9 ± 0.2	^b –
	1:1	–	–	–	–
Cd ²⁺	1:1	–	–	6.6 ^c	7.6 ^c
	2:3	11.7 ± 0.1	11.4 ± 0.1	–	–
Hg ²⁺	2:1	7.3 ± 0.2	–	–	–
	1:1	9.5 ± 0.3	–	8.5 ± 0.3	11.2 ± 0.2
	2:3	–	11.6 ± 0.3	–	–
Pb ²⁺	1:2	–	–	12.1 ± 0.4	–
	1:1	11.9 ± 0.4	–	6.7 ^c	7.2 ^c
La ³⁺	2:3	–	11.6 ± 0.1	–	–
	1:1	12.3 ± 0.2	–	–	–
Gd ³⁺	1:1	12.5 ± 0.2	–	–	–
Lu ³⁺	1:1	12.0 ± 0.2	–	–	–

^a The extraction constant was not evaluated because of precipitation

^b The stoichiometry was only defined by using the Job plot

^c The extraction constant was evaluated from extraction yield for complex stoichiometry 1:1

complexes. The Cu²⁺ ion forms with tetrathiacalix[4]arene **8** the binuclear 2:3 complexes characterized by a high extraction constant ($K_{ex} = 10^{12.8}$), whereas the Hg²⁺ cation forms only mononuclear complexes 1:1 and 1:2 in the investigated concentration range. For the *1,3-alternate* isomer **9** all graphs have the slope $n \approx 1$ (Fig. 4d), which indicates the formation of only mononuclear 1:1 complexes with Co²⁺, Ni²⁺ and Hg²⁺ metal ions. This fact can be caused by a negative allosteric effect, when the structural change induced by the metal coordination on the one side of molecule does not favor binding of the second metal on the other side [19–21]. The removal of *tert*-butyl groups from the calix[4]arene results in a sharp increase of the extraction constant for the 1:1 complex with Hg²⁺ ($K_{ex9}(\text{Hg}^{2+})/K_{ex8}(\text{Hg}^{2+}) = 10^{2.7}$). The selectivity for the Hg²⁺ metal ion relative the toxic Cd²⁺ and Pb²⁺ becomes very excellent achieving four orders of magnitude ($K_{ex9}(\text{Hg}^{2+})/K_{ex9}(\text{Cd}^{2+}) = 10^{3.6}$ and $K_{ex9}(\text{Hg}^{2+})/K_{ex9}(\text{Pb}^{2+}) = 10^{4.0}$). In the case of **8** this selectivity was not above two orders of the extraction constant value ($K_{ex8}(\text{Hg}^{2+})/K_{ex8}(\text{Cd}^{2+}) = 10^{1.9}$ and $K_{ex8}(\text{Hg}^{2+})/K_{ex8}(\text{Pb}^{2+}) = 10^{1.8}$).

The attachment of *tert*-butyl groups on calix[4]arene platform decreases the flexibility of these compounds. The increased rigidity of the molecular receptor and as a result

the preorganization of donor groups can promote the high efficiency and selectivity of metal ions binding. Indeed, this phenomenon was observed when the metal ions were being coordinated by quite small ester and amide groups incorporated on calix[4]arene framework, where ether and carbonyl oxygen atoms closely located to macrocycle platform have formed the binding sites [22, 23]. In the case of the rather large acetylhydrazone fragments the binding centers are obviously formed by donor atoms which are remote from the calixarene skeleton. The decrease of the flexibility of calix[4]arene platform and the steric difficulties provided by *tert*-butyl groups in *1,3-alternate* isomer **8** prevent the effective coordination of metal ions by this compound in comparison with compound **9**.

The high extraction efficiency of Ag⁺ ion recovery by hydrazones **4**, **5**, **8**, **9** and the visible precipitation for **4**, **5** and **8** during the extraction experiment did not permit to obtain accurate data for the stoichiometry and the extraction constants. The precise definition of stoichiometry of formed Ag⁺ complexes was carried out in H₂O/CHCl₃ phases by the Job plots. The extraction yields reached the maxima at 0.5 for **4**, **5**, **9** and 0.6 mol fractions of Ag⁺ for **8** (Fig. 5). This fact clearly indicates that Ag⁺ forms complexes of 1:1 and 3:2 (M^{z+}/L) stoichiometry, respectively. The obtained result

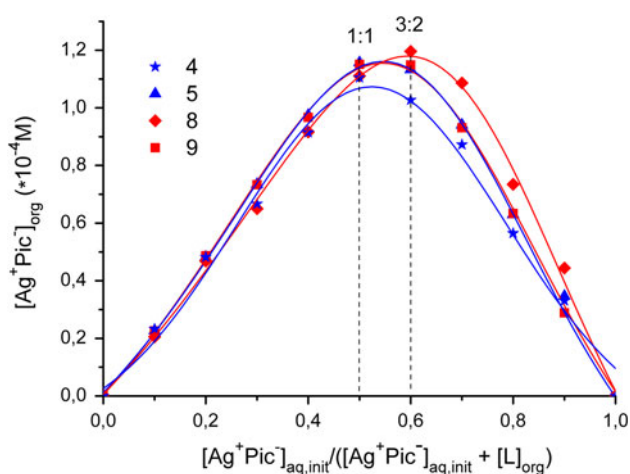


Fig. 5 Job plots for Ag^+Pic^- extracted by *cone-4*, *cone-5*, *1,3-alternate-8* and *1,3-alternate-9*. $[\text{HPic}]_{\text{aq}} + [\text{L}]_{\text{org}} = 2.5 \times 10^{-4} \text{ M}$, $[\text{M}^{z+}] = 1 \times 10^{-2} \text{ M}$, pH 6.0

for **8** is in accordance with the data for complex stoichiometry determined from $\log Q$ versus $\log [\text{L}]_{\text{org}}$ plot dependences ($K_{\text{ex}8}(\text{Ag}^+) = 10^{5.9}$) (See Fig. 4c and Table 1).

Taking into account a high binding ability of investigated compounds it could be expected a participation of both pairs of pyridinyl hydrazone fragments in the coordination of the Ag^+ ions. Indeed, the formation of three-nuclear complexes in the case of tetrahydrazone **8** testifies to the participation of acetylhydrazone groups located on opposite sides of calix[4]arene platform in a coordination process. Although the presence of *tert*-butyl groups in the structure of *1,3-alternate* isomer would obviously hinder the bi-ligand coordination of metal ion. This factor is a main reason of abnormally low extraction efficiency by tetraacetylhydrazone derivative of *tert*-butylthiacalix[4]arene ($\sim 6\%$) in contrast to its *de-tert*-butyl analogue ($\sim 83\%$) [16]. However, the extraction yields of compounds **8** and **9** are similar (Fig. 5). Probably this is due to the coordination of “soft” Ag^+ ion by the “soft” pyridine nitrogen atoms which are quite distant from the macrocyclic platform. Thus, it would be reasonable to expect for **9** the participation of both pairs of hydrazone groups in Ag^+ ion binding.

Unfortunately, the extraction data analysis cannot distinguish between the formation of 1:1 or $n:n$ complex stoichiometry. Therefore, the formation of polymer complexes in the case of compound **9** could be also proposed. The precipitation during the extraction experiment with this compound indirectly indicates on this assumption. The possible structure of polymer complex Ag^+ with *1,3-alternate* calix[4]arene **9** is presented in Fig. 6. In this case the coordination of Ag^+ ion is accomplished by all hydrazone groups of calix[4]arene **9** with the realization of effective 1:1 complex stoichiometry.

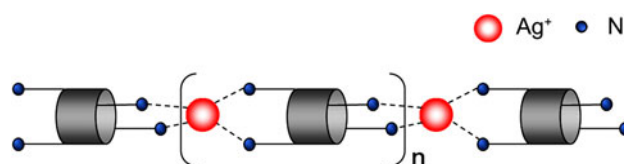


Fig. 6 The proposed structure of a polymer Ag^+ complex with *1,3-alternate-9*

Conclusion

The ion extraction ability of receptors based on calix[4]arene derivatives **4**, **5**, **8**, **9** and their monomer structural block **1** has been studied. The obtained data have demonstrated that the incorporation of hydrazone fragments into the calix[4]arene platform increases considerably the extraction efficiency. The change of calix[4]arene platform structure from *cone* to *1,3-alternate* results in the improvement of extraction selectivity of the compounds towards d-metal ions. The Cu^{2+} , Ag^+ and Hg^{2+} ions are found to be recovered most selectively. The removal of *tert*-butyl groups in the case of *1,3-alternate* isomer **9** promotes an increase of its extraction efficiency for the most toxic Hg^{2+} metal ion more than three times. The selectivity of the Hg^{2+} recovery relative to the toxic Cd^{2+} and Pb^{2+} becomes very excellent, achieving four orders of magnitude K_{ex} . Moreover, the *cone* calix[4]arene **5** in contrast to its *tert*-butyl analogue **4** demonstrates a high preference for d-ions not only relatively alkali and alkaline-earth ones, but also f-metals. This peculiarity of metal recovery process can be successfully utilized in a practice for the preconcentration and group separation of d-ions in the presence of high content of other metal ions.

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