

METALLURGY OF RARE AND NOBLE METALS

Extraction of Noble Metals with Macrocyclic Compounds III: Extraction with Calyxarenes

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Abstract—The third and final part of a review on the extraction of noble metals by macrocyclic compounds, which is devoted to extraction with O-, S-, and N-containing calyxarenes with a generalization of references from 1978 to 2008, is presented. It is noted that no systematic investigations on the extraction of noble metals with calixarenes has been performed until now. Most works are qualitative and do not consider the regularities of the influence of the compositions of aqueous and organic phases and the properties of the extractant on the degree of metal extraction. The studied solutions are unlike production ones in regards to composition, and the chemical state of extracted ions in aqueous solutions is not always taken into account. It is emphasized that there is only fragmentary information on reextraction in the literature. The problem of the selectivity of extraction of noble metals with calixarene esters is discussed.

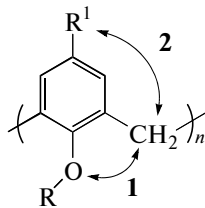
Keywords: noble metals, calyxarenes, hydrochloric acid solutions, extraction, reextraction.

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In the third and final section of our review on the extraction of noble metals by macrocyclic compounds [1, 2], we generalize the existing reference data on the extraction of platinum metals, gold, and silver with O-, S-, and N-containing calyxarenes.

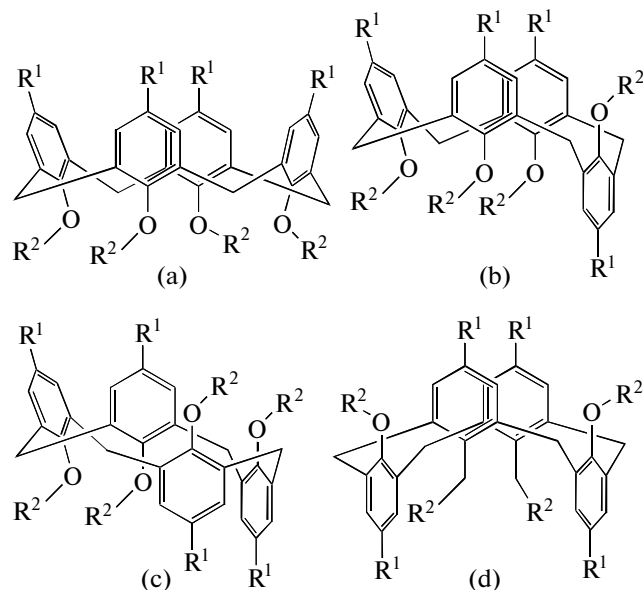
Calyxarenes are the products of the cyclic oligomerization of phenols with formaldehyde [3]. The term “calixarenes” was first suggested by Gutsche [4] and comes from the Latin “calyx” (cup) and “arene,” which reflects the special cuplike form of the molecule and points to the aromatic building block of this compound.

Calyx[n]arenes can exist in a multitude of conformations because of the absence of transannular interactions [5]:

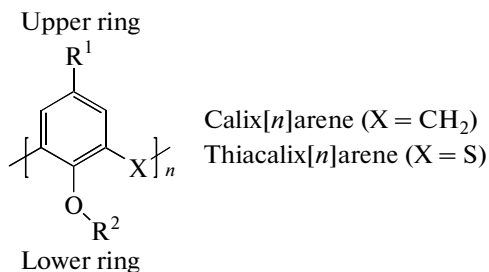


Here, **1** is the oxygen atom with the CH₂ group of a central ring and **2** is the substituting group in the *para* position with the CH₂ group of a central ring.

The main four conformations for calix[4]arenes are (a) the “cone,” (b) “partial cone,” (c) “1,2-alternate,” and (d) “1,3-alternate” [6]. They differ in regards to mutual arrangement with respect to the main plane of the macrocycle, which conventionally passes along the methylene bridges:



In the “cone” conformation, two cavities formed by substituents at the upper and lower rings, as well as the π cavity formed by arene fragments, can be distinguished for calixarenes:



Due to the cone structure of calixarenes, the size of the cavity of the upper ring is considerably larger than that of the lower one [4]. The different nature of these cavities (the upper cavity is hydrophobic, the lower cavity is hydrophilic, and the inner cavity is neutral) determines the possibility of including different types of “guests” into it, particularly, cations, anions, and neutral molecules. The variation in the number of arene fragments in calix[n]arenes leads to an increase in the number of possible conformations. For example, for calyx[6]arenes, the number of possible conformers is eight [7]. In the “cone” conformation of calyx[6]arene, two of the six opposite methylene bridges are directed inside the macrocycle, which leads to the existence of two cavities equivalent to the cavities in calyx[4]arene [8].

Calixarenes are distinguished by their conformation activity, i.e., the possibility or impossibility of transitions occurring between the existing conformations. Conformationally rigid platforms are the calyx[4,6]arenes at $R^2 = H$, which are in the “cone” conformation both in the solution and in the solid state. The “cone” conformation is stabilized due to the formation of strong cyclic intramolecular hydrogen bonds on the lower ring of the macrocycle [9].

Flexible calyx[4]arenes ($R^2 = Me, Et$) are present in the solution in all possible conformations. As a rule, the dominant conformation is the transitive one between three other “partial-cone” conformations [10, 11]. The conformation equilibrium of these calixarenes is affected by such factors as the solvent polarity and its possibility of being involved into the macrocycle cavity, thereby stimulating a definite conformation, as well as the size of certain cations capable of being involved into the cavity. For example, for the calyx[4]arene ($R^1 = t-Bu, R^2 = Me$) in CD_2Cl_2 , the “cone” conformation is present in a larger percentage ($a/b/c/d = 20/75/5/<1$ than in $CDCl_3$ ($a/b/c/d = 4/85/8/3$) [12]. This is associated with the possibility of involving the molecule of the CD_2Cl_2 solvent into the conelike cavity; this leads to the stabilization of the cavity [12]. The Na^+ and Li^+ ions stabilize the “cone” conformation for the mentioned calyx[4]arene due to the interaction with the phenol atoms of oxygen of the

lower ring [5]. In the presence of the K^+ and Ag^+ cations, the “partial cone” and “1,3-alternate” conformations turn out to be the most favorable for the same calixarene due to the interaction of metal ions with benzene rings and phenol oxygen atoms [5].

The data on the extraction of noble metals by non-functionalized¹ calixarenes are limited since these elements are preferentially chalcophilic, and their complex formation with such calyx[n]arenes can occur due to the metal ions binding with the lower hydrophilic ring of the microcycle formed by the hydroxyl or ester groups.

Using NMR spectroscopy in organic solutions, the involvement of the $Ag(I)$ ions in the cavities of calyx[4]arene ($R^1 = H, R^2 = C_3H_7$) due to the π -cation² interaction [13] and calyx[4]arene ($R^1 = t-Bu, R^2 = C_3H_7$) is reliably established. This involvement is caused by the presence of bulk *tert*-butyl groups on the upper ring [14]. The location of $Ag(I)$ inside the cavity in the “cone” conformation is also confirmed by X-ray structural analysis.

Ohto et al. [15] studied the extraction of the $Ag(I)$ and $Pd(II)$ atoms from nitric acid solutions with calyx[4]arene ($R^2 = OCH_2COCH_3$) in chloroform. The possibility of separating the mentioned ions during extraction from solutions with the concentration $C_{HNO_3} < 1$ M is shown. The degree of recovery (E) of $Ag(I)$ is 90%, while palladium completely precipitates from the aqueous phase forming a black sediment of an indefinite composition ($C_{Ag(I)} = C_{Pd(II)} = 1 \times 10^{-4}$ mol/l, $C_{extr} = 3.3 \times 10^{-3}$ mol/l, the time of contacting between the phases in 72 h). As the C_{HNO_3} in the starting solution of $E_{Pd(II)}$ increases, and at $C_{HNO_3} = 10$ M, the degrees of recovery of $Ag(I)$ and $Pd(II)$ are more than 99%. It is also found [15] that, at $C_{HNO_3} < 1$ M, $Ag(I)$ is selectively extracted from solutions containing a 100-fold $Pd(II)$ excess. Consequently, calyx[4]arene ($R^2 = OCH_2COCH_3$) can be applied for the selective extraction of trace amounts of silver on the background of macroscopic amounts of $Pd(II)$ from nitric acid solutions. Based on the NMR ^1H spectra, it is concluded that $Ag(I)$ is coordinated with a molecule of the organic reagent over the oxygen atoms of carbonyl groups.

A review of the reference data showed that the N-containing calixarenes are investigated mainly to reveal the ability of the selective extraction of $Ag(I)$ from solutions containing ions of nonferrous metals.

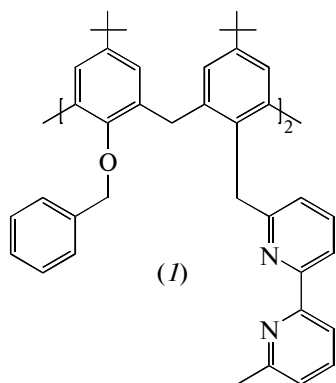
¹ We call the compounds containing no donor S and N atoms nonfunctionalized.

² π -cation interaction is the interaction between the π -electrons of the benzene ring and metal cation.

Table 1. Structural formulas of azocalix[4]arenes 2–13

	R ²	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Notation	$-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Notation	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$	Notation
	R ¹		2		3		4
			5		6		7
			8		9		10
			11		12		13

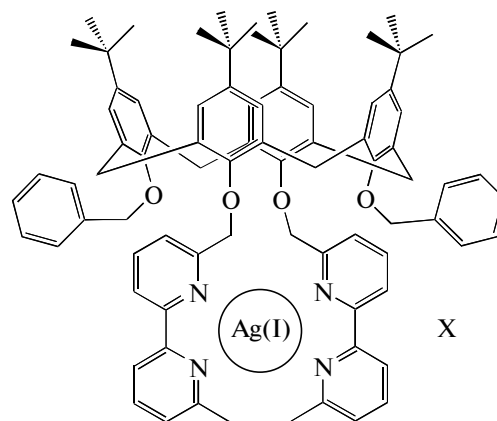
For example, calyx[4]arene with two 2,2'-bipyridil residues and two benzene substituents on the lower ring



is able to selectively extract Ag(I) from aqueous solutions [16].

The starting solutions were prepared by dissolving AgNO₃ and Pb(NO₃)₂ in water, and the molar ratio Ag(I)/Pb(NO₃)₂ varied from 1 to 1/10000. The Ag⁺ concentration was varied in the range of (8.8–0.10) × 10^{−3} mol/l, while that of lead was varied in the range of (8.7–838) × 10^{−3} mol/l. The extractant was a solution of reagent 1 in dichloromethane. The equilibrium in this system is attained for 15 min. It is found that even a 10000-fold excess of Pb(II) does not affect the degree of recovery of Ag(I), which is 95% on average in all experiments. After the treatment of the organic phase with the ammonia solution, reagent 1 can be used at the stage of extraction again. By using NMR ¹H spectroscopy, it is established that the complex formation

of reagent 1 with the Ag atom occurs over the pyridine nitrogen atoms:



This is indicated by the variations in the multiplicity of the signals of protons of the OCH₂-bipyridine and OCH₂C₆H₅ groups and their shift to the region of weak fields (3.92 and 4.14 ppm) compared with the spectrum of the starting compound (5.20 and 4.77 ppm).

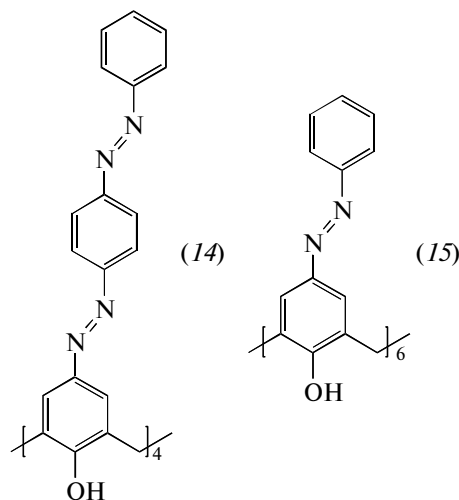
Azocalix[4]arenes 2–13 (Table 1) with the concentration of 1 × 10^{−3} mol/l in chloroform are suggested for the extraction of Ag(I), Co(II), Ni(II), and Cu(II) from individual solutions ($C_{\text{M(NO}_3)_2} = C_{\text{AgNO}_3} = 2 \times 10^{-5}$ mol/l) in picric acid [17]. The ratio of the volumes of the organic and aqueous phases O : A = 1, while contact time τ = 1 h. The results are presented in Table 2. It is evident from the tabulated data that all tested extractants are unable to selectively extract the ions of the abovementioned metals. The best extraction ability with respect to the latter is characteristic of

Table 2. Data on the extraction of Ag(I), Co(II), Ni(II), and Cu(II) ions by solutions of reagents 2–13 in chloroform ($C_{2-13} = 1 \times 10^{-3}$ mol/l)

Reagent	Degree of recovery of M^{n+} , %			
	Ag(I)	Co(II)	Ni(II)	Cu(II)
2	37	15	14	34
3	28	—	—	1
4	14	17	15	32
5	87	67	44	79
6	55	45	26	45
7	58	43	35	63
8	52	23	24	23
9	68	21	15	2
10	57	21	18	17
11	45	22	19	21
12	54	24	20	25
13	54	20	16	23

reagent 5. Ak et al. [17] assume that their experimental data can be interpreted taking into account the totality of parameters affecting the extraction ability of reagents 2–13: the correspondence between the sizes of the calixarene cavity and metal ions; the conformation mobility of the extractant molecules, which leads to a variation in the distance between the donor atoms of the extractant; steric factors; etc.

Solutions of azocalix[n]arenes 14 and 15 ($C_{14, 15} = 1 \times 10^{-3}$ mol/l) in chloroform were used as reagents to extract Ag(I), Co(II), and Cu(II) from aqueous media ($C_{M(NO_3)_2} = C_{AgNO_3} = 2 \times 10^{-5}$ mol/l) [18]:



It is established that compound (15) is inefficient as an extractant, because only silver(I) is extracted; $E_{Ag(I)} = 22\%$ in this case. The degrees of recovery of Ag(I), Co(II), and Cu(II) from the solution, in which the alkali metal ions Na(I) and K(I) with reagent 14 are included, are 74.6, 83.3, and 78.9%, respectively, while the Na(I) and K(I) ions are not extracted by this ligand. Deligos and Erdem [18] assume that, similarly to compounds 2–13, metal ions link to a molecule of reagent 14 due to the π -cation interaction between the metal cation and π electrons of the N=N groups.

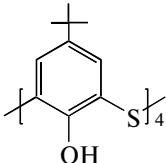
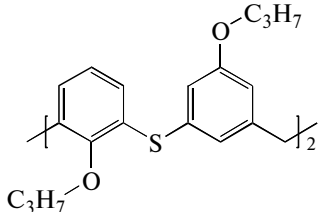
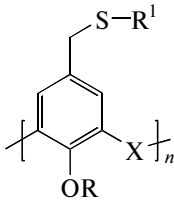
Bisheterocyclic calixarenes 16–19 and thiacalixarenes 20 and 21 were studied as the extractants of transition metals (Table 3) [19].

The starting solutions were aqueous (pH = 4.8) solutions of Cu(II) and Ag(I) chlorides ($C_M = 1 \times 10^{-4}$ mol/l)

Table 3. Structural formulas of calyx[4]arenes 16–19 and thiacalixarenes 20 and 21

			R ¹	R ²	R ³	X	Notation
			H	bpy	H	CH ₂	16
			H	btz	H	CH ₂	17
			btz	H	N ₂ Ph	CH ₂	18
			bpy	H	N ₂ Ph	CH ₂	19
			bpy	H	N ₂ Ph	S	20
			btz	H	N ₂ Ph	S	21

Table 4. Structural formulas of calyx[*n*]arenes 22–26

 <div>(22)</div>		 <div>(23)</div>			
	<i>n</i>	R	R ₁	X	Notation
	4	C ₃ H ₇	<i>p</i> -CH ₃ C ₆ H ₄	CH ₂	24 <i>a</i>
	4	C ₃ H ₇	CH ₃	CH ₂	24 <i>b</i>
	4	C ₃ H ₇	<i>n</i> -C ₄ H ₉	CH ₂	24 <i>c</i>
	6	CH ₃	<i>p</i> -CH ₃ C ₆ H ₄	CH ₂	25 <i>a</i>
	6	CH ₃	<i>n</i> -C ₄ H ₉	CH ₂	25 <i>b</i>
	4	H	<i>p</i> -CH ₃ C ₆ H ₄	S	26

and solutions of reagents ($C_{16-21} = 5 \times 10^{-4}$ mol/l) in dichloromethane (the ratio O : L = 1 : 5; $\tau = 12$ h).

It is established [19] that compounds 20 and 21 manifest the better extraction ability with respect to the mentioned ions under experimental conditions. The degrees of recovery of Cu(II) and Ag(I) with reagent 20 are 97 and 88%; with reagent 21 they are 81 and 85%; for other compounds, they were no higher than 50%. Unfortunately, researchers [17–19] had not studied the influence of the solvent and the acidity of the aqueous phase on the extraction of Ag(I), Co(II), Ni(II), and Cu(II), and they gave no interpretation of the influence that substituents in the upper and lower rings of calixarene have on the degree by which the mentioned ions are recovered. Data on reextraction, without which, as we have emphasized repeatedly, the application of the extraction method is problematic, are also absent.

Introducing sulfur-containing functional groups into the calixarene skeleton (upper or lower rings) opens up additional possibilities for the complex formation of calixarenes with noble metals. Compounds 22–26 (Table 4) were used for the recovery of Au(III) from hydrochloric acid media [20].

In practice, thiocalixarenes 22 and 23 do not recover Au(III) from a 3–6 M HCl solution irrespective of the conformation of the calixarene nucleus (1,3-alternate or cone), which coincides with the data [21] about the absence of the extraction of Au(III) with tiacalix[6]arene from 2 M HCl.

The opinion exists [22, 23] that the low extraction ability of sulfur atoms conjugated with the aromatic group is caused by a decrease in electron density at its donor atom. In addition, steric obstacles are possible for thiocalixarenes upon the coordination of Au(III) to bridge sulfur atoms.

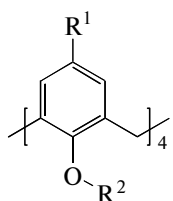
Thioester derivatives of calyx[4,6]arenes are arranged in the series 24*a* > 25*b* > 24*b* > 25*a* (Table 5) by their ability to extract Au(III) from sulfuric acid solutions during extraction.

With the same amount of sulfur atoms, the distribution coefficient of gold ($D_{\text{Au(III)}}$) increases as the size of calixarene increases upon the passage from calyx[4]arenethioesters to calyx[6]arenethioesters (25*b* > 24*b*, 25*a* > 24*a*). However, the substitution of bridge CH₂ groups in 24*a* by sulfur atoms, which also leads to an increase in the size of calixarene [21], is accompanied by a decrease in the degree of recovery of Au(III) for compound 26. Kostin et al. [20] assume that this can be caused by a decrease in the electron

Table 5. Data on the extraction of Au(III) ions from 3 M and 6 M HCl with solutions of sulfur-containing calixarenes in toluene ($C_{24a-24c, 26} = 5 \times 10^{-3}$ mol/l and $C_{25a, 25b} = 3.3 \times 10^{-3}$ mol/l)

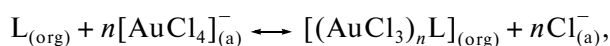
Calixarene	3 M HCl		6 M HCl	
	$E_{\text{Au(III)}}, \%$	$D_{\text{Au(III)}}$	$E_{\text{Au(III)}}, \%$	$D_{\text{Au(III)}}$
24 <i>a</i>	98.6	70	98.5	64
24 <i>b</i>	99.9	670	99.8	440
24 <i>c</i>	99.9	1670	99.9	890
25 <i>a</i>	99.1	107	98.9	92
25 <i>b</i>	99.9	1230	99.9	740
26	45.9	0.85	25.9	0.35

Table 6. Structural formulas of calyx[*n*]arenes 30–38

	R ¹	R ²	Notation
	H	CH ₂ CH ₂ SC(S)N(CH ₃) ₂	30
	<i>t</i> -Bu	CH ₂ CH ₂ SC(S)N(CH ₃) ₂	31
	H	CH ₂ CH ₂ SCH ₃	32
	<i>t</i> -Bu	CH ₂ CH ₂ SCH ₃	33
	<i>t</i> -Bu	CH ₂ CH ₂ SH	34
	<i>t</i> -Bu	CH ₂ CH ₂ C(O)C ₄ H ₉ S	35
	CH ₂ SCH ₃	H	36
	CH ₂ SCH ₃	CH ₃	37
	CH ₂ CH ₂ SC(S)N(CH ₃) ₂	CH ₃	38

density at donor sulfur atoms of the CH₂SR groups of the upper ring.

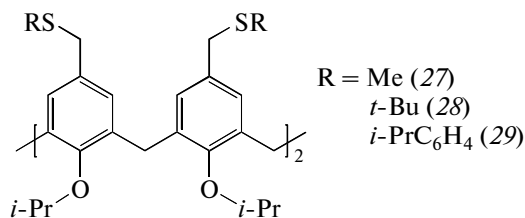
The stoichiometry of extraction is studied for calixarenes 24a–26c [24]. It is shown by the method of saturation of the extractant that the complexes with the ratio Au : L = 1 : 1, 2 : 1, 3 : 1, and 4 : 1 are formed in the organic phase for L = 24b and 24c, and Au : L = 1 : 1 and 2 : 1 are formed for L = 24a. Thus, Torgov et al. [24] come to the conclusion that extraction with these reactants can be described by the following equation:



where $n = 1-4$.

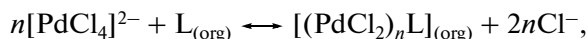
A decrease in the degree of recovery of Au(III) with an increase in the acidity of the aqueous phase from 3 to 6 M HCl can be interpreted qualitatively by the shift in equilibrium of the abovementioned reaction to the left due to the increase in the concentration of chloride ions in the aqueous phase [24].

Reactions of the complex formation of [PdCl₄]²⁻ ($C_{\text{Pd}} = 1 \times 10^{-4}$ mol/l) in the course of extraction with calyx[4]arenes 27–29



are studied in the concentration range of $1 \times 10^{-3} - 1 \times 10^{-5}$ mol/l. Calixarenes are functionalized on the upper ring in the toluene medium [25, 26].

It is noticed that the extraction of Pd(II) from potassium hydrochloric acid solutions with calyx[4]arenethioesters 27–29 is characterized by a high rate (the time of complete recovery of Pd(II) from chloride media is 2–3 min). The totality of the spectral data (electron spectroscopy and ¹³C NMR) corresponds to the presence of two forms of palladium in the organic phase. They are formed by the reaction



where L are reagents 27–29 and $n = 1, 2$.

Thus, the extraction of Pd(II) with calixarenethioesters 27–29 leads to the formation of complex PdCl₂L and (PdCl₂)₂L in the organic phase. Two chloride ions and two neighboring SR groups of calixarene are coordinated to each palladium atom.

The qualitative data obtained by Iordanov et al. [27–29] are referred mainly to the extraction of noble metals from the HNO₃ solutions by reagents 30–38 (Table 6).

Based on the electron absorption spectra of extracts of Au(III) and Pd(II) presented in the mentioned works, we can conclude that the extraction ability of sulfur-containing calixarenes is caused by the formation of the metal–sulfur bond.

The data on the extraction of ions of chalcophylic metals with solutions 30–38 with a concentration of 1×10^{-3} mol/l in chloroform and from 0.1 M HNO₃ ($C_M = 1 \times 10^{-3}$ mol/l; $\tau = 1$ min) are presented in Table 7.

Regardless of the location of sulfur atoms (upper or lower ring), the extraction of ions of noble metals with thiocarbamate derivatives ($R = CH_2CH_2SC(S)N(CH_3)_2$) can be arranged in the series Au(III) ≥ Pd(II) ≥ Ag(I).

Some regularities of extraction associated with the structure of extractants can be selected for the com-

Table 7. Data on the reextraction of the ions of transition metals with reagents 30–38 from nitric acid solutions ($C_{30-38} = 1 \times 10^{-3}$ mol/l)

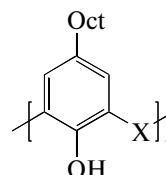
Reagent	Degree of extraction, %		
	Pd(II)	Au(III)	Ag(I)
30	100	97	60
31	100	100	74
32	63	99	97
33	70	100	65
34	41	100	60
35	31	8	39
36	63	97	14
37	100	100	<1
38	100	99	<1

pounds presented in Table 7. In calyx[4]arenes that are functionalized over the lower ring (30–33), the presence of bulk substituents on the upper ring weakly affects the extraction ability, since their arrangement on the upper ring only increases its cavity that does not participate in complex formation [30]. The change of conformation of the macrocycle upon switching from the calix[4]arene 33 cone to the flexible calix[4]arene partial cone affects only the extraction of Ag(I) and Pd(II), while the degree of recovery of Au(III) remains invariable. The stabilization of the cone conformation with an increase in the length of the alkyl radical on the lower ring of calyx[4]arene ($R^1 = \text{CH}_2\text{SCH}_3$, $R^2 = \text{Pr}$) leads to the practically quantitative recovery of Ag(I) [24].

High (97–100%) values of the degree of recovery of Au(III) for all extractants studied in [27–29] and the

absence of the data on distribution coefficients do not allow us to make any conclusions about any “structure–property” regularities. A decrease in $E_{\text{Pd(II)}}$ by thioester derivatives compared with dithiocarbamate ones (Table 7) is possibly associated with the necessity of a prolonged phase contact during extraction with calixarethioesters ($\tau > 1$ min).

For the extraction of Pd(II), Pt(II), Ru(III), Ag(I), Au(III), Co(II), Ni(II), and Cu(II) ($C_M = 1 \times 10^{-4}$ mol/l) from HNO_3 , the solutions of reagents 39–42 with the concentration of 5×10^{-4} mol/l in CHCl_3 are tested [31],

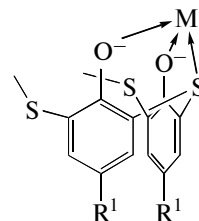


where $X = (39) \text{CH}_2$, $(40) \text{S}$, $(41) \text{SO}$, and $(42) \text{SO}_2$.

Aqueous and organic phases were in contact for 24 h; pH was controlled by the addition of NH_3 . Obtained results are generalized in Table 8.

The recovery of the mentioned ions takes place from weakly alkali and neutral media under conditions when the deprotonation of hydroxyl groups is possible [32], while extraction is absent in the acidic media.

There are reference structural data for complexes in which metal is coordinated over the lower ring of the macrocycle, i.e.,



In this case, metal coordinates both deprotonated phenol groups and bridge sulfur atoms [14].

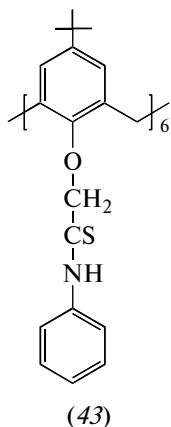
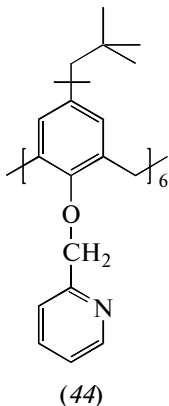
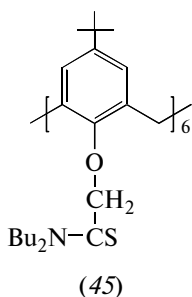
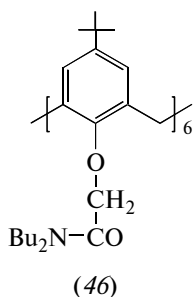
Table 8. Data on the extraction of Pd(II), Pt(II), Ru(III), Ag(I), Au(III), Co(II), Ni(II), and Cu(II) ions by reagents 39–42 in chloroform ($C_{39-42} = 5 \times 10^{-4}$ mol/l)

Reagent	Degree of recovery, %, at pH							
	0.05 M HNO_3	9.9	3.3	5.9	1.0 M HNO_3	8.0	8.0	8.0
	Pd(II)	Pt(II)	Ru(III)	Ag(I)	Au(III)	Co(II)	Ni(II)	Cu(II)
39	14	9	3	6	21	2	0	6
40	73	1	5	99	31	98	99	91
41	92	3	68	—	38	99	64	10
42	15	4	0	—	12	9	2	4

Table 9. Data on the extraction of Au(III) and Pd(II) ions by reagents 47 and 48 ($C_{47, 48} = 4 \times 10^{-3}$ mol/l)

Ligand	Degree of extraction, %			
	Extraction		Reextraction	
	Au(III)	Pd(II)	Au(III)	Pd(II)
47	92.8	82.5	92.9	66.5
48	94.5	57.6	94.6	57.6

In [33], the extraction of the $[\text{AuCl}_4]^-$ complex by reagents 43–46 is investigated:

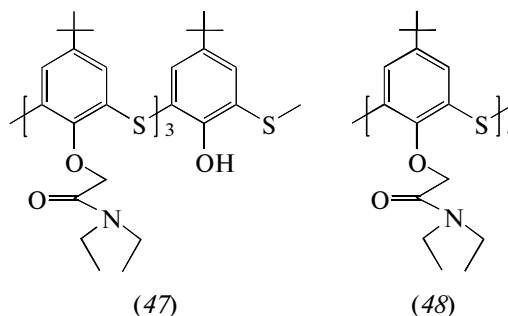


The solutions of compounds 43 and 45 ($C_{43, 45} = 3 \times 10^{-3}$ mol/l) in chloroform recover Au(III) from the 0.01 M HCl solutions, while ligands 44 and 46 ($C_{44, 46} = 5 \times 10^{-3}$ mol/l) do this with $C_{\text{HCl}} > 1$ M (i.e., under the conditions of protonation of reagents) higher than 99%. The time sufficient to qualitatively recover Au(III) is 5 min, and the ratio B : O = 1. Gold(III) is extracted in the form of the following complexes: (43) ($[\text{AuCl}_3 \cdot \text{LH}^+ \cdot \text{L}]$), (44) ($[\text{AuCl}_4]^- \cdot \text{LH}^+$), and (45) ($[\text{AuCl}_4]^- \cdot \text{LH}^+ \cdot \text{L}$).

Belhamel et al. [33] investigated the selectivity of reagents 43–46 with respect to Au(III). It is shown that solutions of reagents 44 and 45 with the concentration of 5×10^{-5} mol/l in chloroform quantitatively recover Au(III) from the solution containing 14 mg/l Au(III) and 0.1 mol/l Co(II), Ni(II), Pd(II), and Fe(III) in 1 M HCl, while the recovery of other metals is <7%. It was also suggested to reextract Au(III) from the organic phase with the thiourea solution in HCl

(43, 45) or in water (44, 46) [33]. In this case, recovery into the aqueous phase >99.9% Au(III) is attained for one step of reextraction.

Zaghbani et al. [34] suggested compounds 47 and 48 for the extraction of Au(III) and Pd(II):

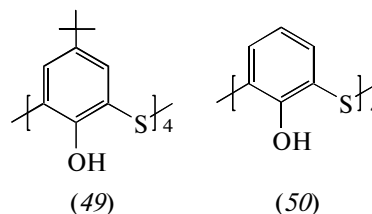


Solutions of Au(III) or Pd(II) ($C_M = 1 \times 10^{-4}$ mol/l) in 0.02 M HCl were used as the starting aqueous phases. A solution of reagents 47 and 48 ($C_{47, 48} = 4 \times 10^{-3}$ mol/l) served as the extractant; the ratio O : A = 1 : 2. Recovery of Au(III) is approximately identical in both cases (Table 9), while for Pd(II) it increases with the use of less substituted ligand 47.

The interaction between the chlorocomplex of Pd(II) and the organic ligand proceeds via the formation of ion pairs with protonated nitrogen atoms. Moreover, when Pd(II) interacts with ligand 47, phenol groups also participate in the complex formation [35]. In the case of $[\text{AuCl}_4]^-$, the extraction ability is independent of the number of functional groups on a lower ring. Ye et al. [35] explain this experimental fact by that the $[\text{AuCl}_4]^-$ ions are bound by calixarenes 47 and 48 over only one nitrogen atom.

For the recovery of extracted Au(III) and Pd(II) ions from the organic phase, a 0.5 M solution of thiourea in 1 M HCl was suggested as the reextractant [34]. It is evident from Table 9 that the recovery of Au(III) into the aqueous phase is more than 92% in both cases. During the reextraction of Pd(II) from the organic phase with the use of extractant 47, 16% Pd(II) remain in the extract. This is explained [34, 36] by the fact that, with the use of compound 47 with three amide groups, the hydroxyl group of the lower ring also participates in the complex formation; this group rather strongly coordinates the metal ion and thereby promotes a decrease in the efficiency of reextraction.

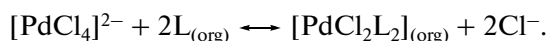
For the extraction of Au(III), Pd(II), and Pt(IV), reagents 49 and 50 are suggested:



The solutions of Au(III), Pd(II), or Pt(IV) ($C_M = 1 \times 10^{-4}$ mol) in 0.02 M HCl were used as starting aqueous phases; the solution of reagents 49 and 50 ($C_{49, 50} = 1 \times 10^{-3}$ mol/l) in chloroform served as extractant [36]; the O : A ratio = 1 : 2 and $\tau = 24$ h.

It was established that the mentioned compounds extract only Pd(II), the degree of its recovery is 30% (49) and 100% (50). Belhamel et al. [31] assume that the $[\text{PdCl}_4]^{2-}$ ion is coordinated with ligands by sulfur atoms. The reason for such behavior of thiacalixarenes 49 and 50 with respect to the $[\text{PdCl}_4]^{2-}$ ion should apparently be sought after in different conformation mobility of reagents, which differ in the presence (49) or absence (50) of bulk *tert*-butyl groups on the upper ring. The fact that, at the mentioned HCl concentration, there can be aquachlorocomplexes of platinum metals in the solution is not taken into account in [36].

According to [37], during the extraction of Pd(II) with compounds 49 and 50, metal–sulfur bonds are formed, and this process is described by the equation



As the HCl concentration increases from 0 to 2 M, a decrease in the degree of recovery of Pd(II) is observed right up to its complete suppression.

Fontas et al. [36] suggest to carry out the reextraction with the 0.5 M solution of thiourea in 1 M HCl; in this case, 83% of Pd(II) is recovered into the extract.

CONCLUSIONS

Thus, a generalization and analysis of the presented reference data on the extraction of noble metals with macrocyclic compounds (podands, crown-compounds [1, 2], and calixarenes) allow us to make the following conclusions:

(i) similarly to the extraction of noble metals by podands and crown compounds, the number of works devoted to an investigation of the extraction properties of calixarenes is small; they are mainly qualitative and do not consider the regularities of the influence that the composition of aqueous and organic phases or the properties of extractant have on the degree of recovery of metal;

(ii) optimal conditions for the recovery of noble metals in the course of extraction with macrocyclic compounds are attained by varying the conditions by which the process is carried out, such as the acidity of the aqueous phase, the nature of the counter ion, and the solvent;

(iii) the chemical state of the recovered ions in the solutions is not always taken into account;

(iv) the data on reextraction of noble metals from organic phases obtained during the extraction with podands, crown-compounds and calixarenes, without which the application of the extraction method of recovery is problematic, are extremely fragmentary.

In general, we can state that the data on the extraction of noble metals with macrocyclic compounds are mainly uncoordinated, and this circumstance indicates wide prospects for further scientific research and practical applications. Everything mentioned above and the data [1, 2] assume the possibility and necessity of widening the circle of investigations into extraction with macrocyclic compounds containing other donor atoms, first and foremost nitrogen and sulfur atoms, in addition to oxygen.

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