

# A Ru/Zn synergism in extraction of ruthenium by calixarene phosphine oxides

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**Abstract** New calix[n]arenes ( $n = 4, 6$ ) grafted with different phosphine oxide metallocomplexing groups were synthesized and examined as extractants of the heterometallic Ru/Zn complexes. The calixarene macrocyclic effect and the Ru/Zn synergism in the extraction process were investigated. Size and conformation of the calixarene platform as well as electronic nature of substituents at phosphorus atom influence the extraction.

**Keywords** Calixarenes · Phosphine oxides · Ruthenium · Zinc · Complexes · Extraction

## Introduction

An increase in ecological safety in treatment of high level waste (HLW) generated by spent nuclear fuel is governed by recovery and separation of long lived radionuclides and platinum group metals before the waste vitrification or transmutation [1]. Different extractants were supposed for selective recovery of Cs and Sr (crown-ethers, chlorinated cobalt dicarbollide) [2], actinides and lanthanides (tributyl phosphate TBP, trialkyl phosphine oxides TAPO, carbamoyl phosphine oxides CMPO) [3], Pd and Ag (organic sulfides) [4]. Chemical linking of the extractants to macrocyclic platform of calixarene molecule increases

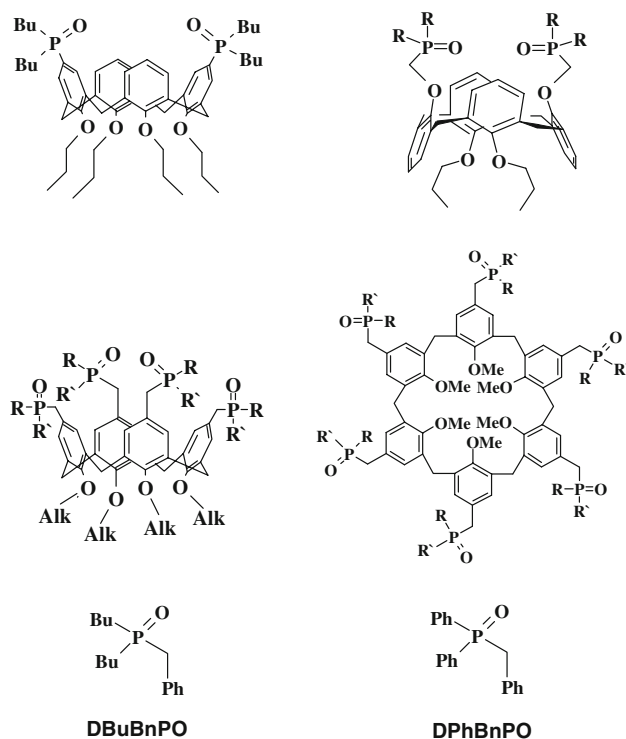
efficiency as well selectivity of the metal extraction due to the calixarene macrocyclic effect [5]. For example calix[4]arene (*1,3-alternate*) possessing 18-crown-6 residue two order of magnitude exceeds in efficiency and Cs/Na selectivity the traditional extractants in Cs extraction [6]. Similar results are observed in extraction of Ru by calix[8]arene grafted with eight dialkylamide complexing groups [7]. Placement of four carbamoyl phosphine oxide groups at the calix[4]arene platform gives a remarkable cooperative effect in extraction of actinides and lanthanides [8]. Calix[4,6]arenes possessing four of six sulfide groups are more two orders of magnitude effective than monodentate dialkylsulfides in extraction of Pd [9]. Therefore, the calixarene sulfides quantitatively recover Pd from HLW and separate the metal from Rh and Ru.

It should be noted that the extraction of Ru from HLW is restricted by existing of the metal as a variety of kinetically inert forms in the nitric–nitrous solutions. As result, the metal mainly remains in HLW after recovery of cesium, strontium, actinides and lanthanides [10]. Recently new method for ruthenium extraction was proposed [11]. The method consists in transformation of the different ruthenium forms into  $[\text{RuNO}(\text{NO}_2)_4\text{OH}]^{2-}$  form by the nitration of HLW solution. The form is effectively extracted by the organophosphorus compounds (TBP, TAPO, etc.) in the presence of non-ferrous transition metals [12]. The metals cause synergetic effect ( $\text{Zn}, \text{Cu} > \text{Co} > \text{Ni}$ ) in extraction of ruthenium up to three orders of magnitude due to formation of the Ru/M heterometallic complexes. In these complexes  $[\text{RuNO}(\text{NO}_2)_4\text{OH}]^{2-}$  is coordinated with  $(\text{ML})^{2+}$  by OH and  $\text{NO}_2$  bridging groups.

The synergism was also observed for extraction of Ru in the presence of Zn by the calix[4]arene bearing four phosphine oxide groups at the upper rim [13]. In this work,

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**Chart 1** Phosphorylated ligands used for ruthenium extraction

we investigated a relationship between structure of a series of the calixarene phosphine oxides (Chart 1) and the Ru/Zn synergetic effect in extraction of ruthenium.

## Experimental

All reagents used were of standard pure grade. Complex  $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}]\cdot 2\text{H}_2\text{O}$  was synthesized by the method [14]. The synthesis of calixarenes **10**, **11**, **13–19** was described in [15]. The NMR spectra were recorded on the Varian VXR-300 or the Varian Gemini-200 spectrometers with internal standard TMS and external standard 85%  $\text{H}_3\text{PO}_4$ . IR—spectra of solutions were recorded on Specord M-80 spectrometer in 0.1–1 mm cells.

**5,11-Dibutylphosphinyl-25,26,27,28-tetrapropoxycalix[4]arene 2.** To a solution of dibromotetrapropoxycalixarene **1** (2.5 g, 3.33 mmol) in benzonitrile (10 mL) anhydrous  $\text{NiBr}_2$  (0.004 mmol) was added at 120 °C. To the mixture, iso-propyldibutyl phosphinite (1.43 g, 6.98 mmol) was added at stirring during 10 min. The reaction mixture was stirred at 180 °C within 1.5 h. The solvent was evaporated at reduced pressure (0.05 mmHg). The residue was solved in dichloromethane (100 mL) and washed with diluted  $\text{NH}_4\text{OH}$  to remove nickel (control by dimethylglyoxime) and after that—with water. The organic phase was dried with sodium sulfate and evaporated.

The residue was crystallized from acetonitrile. Compound **2** (1.12 g, 37%) was obtained as white crystals. M.p. 237–240 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz),  $\delta$ , ppm: 0.85 (t, 12H, J 7.5 Hz, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.15 (t, 12H, J 7 Hz, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.30–2.12 (m, 8H + 24H, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ , P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 3.21 (d, 4H, J 13.0 Hz,  $\text{ArCH}_{2\text{eq}}$ ), 3.66 and 4.10 (two t, 4H + 4H, J 7.5 Hz, O- $\text{CH}_2\text{-CH}_3\text{-CH}_2$ ), 4.48 (d, 4H, J 13.0 Hz,  $\text{ArCH}_{2\text{ax}}$ ), 5.99 and 7.46 (two d, 4H, J 7.2 Hz,  $\text{ArH-m}$ ), 6.13 (t, 2H, J 7.2 Hz,  $\text{ArH-p}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 120 MHz),  $\delta$ , 41.34 ppm. Calculated for  $\text{C}_{56}\text{H}_{82}\text{O}_6\text{P}_2$ , %: C, 73.65, H, 9.05, P, 6.78. Found, %: C, 73.31, H, 9.45, P, 6.96.

**25,27-Dipropoxy-26,28-bis(dibutylphosphinylmethoxy)calix[4]arene 4 (1,3-alternate).** To solution of dipropoxycalix[4]arene **3** (1.5 g, 2.95 mmol) in dry acetonitrile (50 mL) anhydrous cesium carbonate (2.4 g, 7.37 mmol) was added. The suspension was stirred 1 h at 70 °C. To the suspension formed  $\text{Bu}_2\text{P}(\text{O})\text{CH}_2\text{OTs}$  (2.55 g, 7.37 mmol) was added and the mixture was refluxed at stirring during 96 h. The acetonitrile was evaporated in vacuum and the residue was solved in chloroform. The chloroform solution was washed with HCl (10%), water and was dried by sodium sulfate. The residue was crystallized from carbon tetrachloride. Compound **4** (1.89 g, 75%) was obtained as white crystals. M.p. 220–222 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 0.99 (t, J 7.4Hz, 12H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.09 (t, 6H, J 7.4Hz, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.56–1.45 (m, 8H, P-( $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ )<sub>2</sub>), 1.79–1.6 (m, 8H, P-( $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ )<sub>2</sub>), 2.03–1.81 (m, 8H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$  and 4H, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 3.53 (d, 4H, J 12.8 Hz,  $\text{ArCH}_2\text{Ar}_{\text{eq}}$ ), 3.6 (d, 4H, J 13 Hz,  $\text{ArCH}_2\text{Ar}_{\text{ax}}$ ), 3.69 (t, 4H, J 7.4 Hz, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 4.1 (d, 4H, J 4.4Hz,  $\text{OCH}_2\text{P}$ ), 6.56 (t, 2H, J 7.7Hz,  $\text{ArH-p}$ ), 6.65 (t, 2H, J 7.7 Hz,  $\text{ArH}$ ), 7.03 (d, 4H, J 7.7 Hz,  $\text{ArH-m}$ ), 7.11 (d, 4H, J 7.7 Hz,  $\text{ArH-m}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$  120 MHz),  $\delta$ , 43.8 ppm. MS (CI)  $m/z$  857 ( $\text{M}^+$ , 100%). MM calculated 857.057. Calculated for  $\text{C}_{52}\text{H}_{74}\text{O}_6\text{P}_2$ , %: C 72.87; H 8.71; P 7.23. Found, %: C 73.04; H 8.73; P 7.21.

**25,27-Dipropoxy-26,28-bis(diphenylphosphinylmethoxy)calix[4]arene 5 (1,3-alternate)** was synthesized similar to compounds **4** with the yield 77%. White crystals with m.p. 280–282 °C (from methanol).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.05 (t, 6H, J 7.4Hz, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.93–1.81 (m, 4H, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 3.39 (d, 4H, J 12.9Hz,  $\text{ArCH}_2\text{Ar}_{\text{eq}}$ ), 3.52 (d, 4H, J 2.9Hz,  $\text{ArCH}_2\text{Ar}_{\text{ax}}$ ), 3.61 (t, J 7.4Hz, 4H, O- $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 4.6 (d, 4H,  $J_{\text{HP}}$  3.7 Hz, O- $\text{CH}_2\text{-P}$ ), 6.22 (t, 2H, J 7.4 Hz,  $\text{ArH-p}$ ), 6.59 (t, 2H, J 7.4 Hz,  $\text{ArH-p}$ ), 6.65 (d, 4H, J 7.4 Hz,  $\text{ArH-m}$ ), 6.95 (d, 4H, J 7.4Hz,  $\text{ArH-m}$ ), 7.67–7.55 (m, 12H,  $\text{PPh}_2$ ), 7.95–7.88 (m, 8H,  $\text{PPh}_2$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 120MHz),  $\delta$ , 25.5 ppm. MS (CI)  $m/z$  937 ( $\text{M}^+$ , 100%). MM calculated 937.008. Calculated for  $\text{C}_{60}\text{H}_{58}\text{P}_2\text{O}_6$ , %: C 76.9; H 6.24; P 6.60. Found, %: C 77.13; H 6.38; P 6.37.

5,11,17,23-tetrakis-(diethylphosphinylmethyl)-25,26,27,28-tetrapropoxycalix[4]arene **9**. Mixture of tetrachloromethylcalix[4]arene **6** (1.59 g, 2.02 mol) and isopropyl-diethylphosphinite (9.78 g, 60.6 mmol) was stirred 2 h at 140 °C. The excess of isopropyl-diethylphosphinite was removed in vacuum. Solid residue was washed with hexane (3 × 25 mL) and dried in vacuum. Calixarene phosphine oxide **9** was obtained as colorless hygroscopic powder (2.06 g, 96%) with m.p. 254–256 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ, ppm: 0.92 (m, 36H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> + P(-CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 1.40 (m, 16H, P(-CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 1.81 (m, 8H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 2.66 (d, 8H, <sup>3</sup>J<sub>PH</sub> 13.8 Hz, ArCH<sub>2</sub>P), 3.02 and 4.31 (two d, 8H, <sup>2</sup>J 13.3 Hz, ArCH<sub>2</sub>Ar), 3.73 (t, 8H, <sup>2</sup>J 7.2 Hz, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 6.43 (s, 8H, ArH). <sup>31</sup>P ЯMP (CDCl<sub>3</sub>), δ, 50.05 ppm. Calculated for C<sub>60</sub>H<sub>92</sub>O<sub>8</sub>P<sub>4</sub>, %: C 67.68, H 8.70, P 11.67. Found, %: C 67.11, H 8.17, P 11.92.

5,11,17,23-Tetrakis(dibutylphosphinylmethyl)-25,26,27,28-tetrahexyloxy-calix[4]arene **12** was synthesized similar to compound **9** by the Arbuzov reaction of calixarene **7** with iso-propyldibutyl phosphinite. White powder (2.68 g, 86%) with m.p. 46–48 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ, ppm: 0.91 (m, 36H, O(-CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub> + P-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.35 (br. s, 48H, P(-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 1.49 (br. s, 24H, O(-CH<sub>2</sub>)<sub>2</sub>(-CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>), 1.87 (br. s, 8H, O-CH<sub>2</sub>-CH<sub>2</sub>(-CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>), 2.75 (d, 8H, <sup>3</sup>J<sub>PH</sub> 13.6 Hz, ArCH<sub>2</sub>P), 3.06 and 4.34 (two d, 8H, <sup>2</sup>J 13.46 Hz, ArCH<sub>2</sub>Ar), 3.82 (8H, <sup>2</sup>J 7.1 Hz, O-CH<sub>2</sub>(-CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>), 6.44 (c, 8H, ArH). <sup>31</sup>P NMR (CDCl<sub>3</sub>), δ, 42.59 ppm. Calculated for C<sub>88</sub>H<sub>148</sub>O<sub>8</sub>P<sub>4</sub>, %: C 72.49, H 10.23, P 8.50. Found, %: C 72.68, H 10.01, P 8.66.

## Extraction procedure

Solutions of the extractants in *m*-nitro(trifluoromethyl)benzene were prepared from exact weights. To simulate the composition of the real HLW after neutralization stage the extraction was carried out from fresh solution of Na<sub>2</sub>[RuNO(NO<sub>2</sub>)<sub>4</sub>OH] in 2 M NaNO<sub>3</sub>. The technique of the extraction and the method of determination of ruthenium or zinc content in aqueous or organic phases were described in [12]. On the base of initial (C<sub>i</sub><sup>0</sup>) and equilibrium concentrations the partitions coefficients were calculated both for separate extraction of ruthenium (D<sub>Ru</sub><sup>0</sup>) or zinc (D<sub>Zn</sub><sup>0</sup>) metals and for their combined extraction (D<sub>Ru</sub> and D<sub>Zn</sub>). The macrocyclic effects (ME) of the calixarene extractants were defined as the ratio of ruthenium partition coefficients for the calixarene extractants and the modeling compounds at the equal concentration of PO groups. The synergic effects (S<sub>Ru</sub>) were calculated as follows: S<sub>Ru</sub> = D<sub>Ru</sub> / (D<sub>Ru</sub><sup>0</sup> + D<sub>Zn</sub><sup>0</sup>).

## Results and discussion

### Synthesis of calixarenes

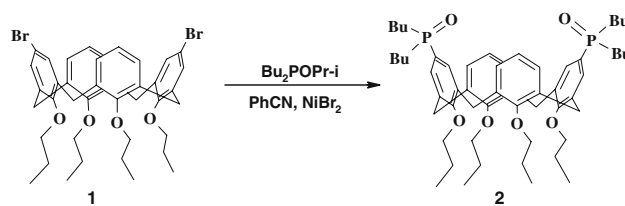
In order to investigate the relationship “structure-extraction properties” a series of the calix[4,6]arenes bearing two, four or six P=O binding groups connected with the calixarene platforms by different manners was synthesized.

Calix[4]arene **2** bearing two dibutylphosphinyl groups at the distal *para*-positions of benzene rings capable to form chelate complexes with metal cations was synthesized by the nickel catalyzed Arbuzov reaction of 5,11-dibromotetrapropoxycalix[4]arene **1** with isopropyl-dibutyl phosphinite in boiling benzonitrile (Scheme 1) similar to [16].

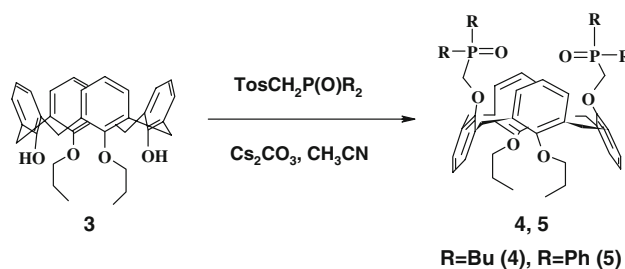
The reaction of 25,27-dipropoxycalix[4]arene **3** with tosylates of hydroxymethyldibutyl(diphenyl)phosphine oxides in the presence of cesium carbonate in refluxing acetonitrile produces calixarene bis-phosphine oxides **4, 5** possessing the 1,3-*alternate* conformation (Scheme 2). The stereochemical outcome of the alkylation process is highly controlled by cesium cation [17].

Calix[4]arenes **9–16** and calix[6]arenes **17–19** [9] bearing four or six P=O groups capable to cooperatively bind the metal cation were synthesized by the Arbuzov reaction of tetrakis- or hexakis(chloromethyl)tetraalkoxy-calix[n]arenes **6–8** with an excess of isopropyl ester of appropriate P(III)-acid by method [18] (Scheme 3).

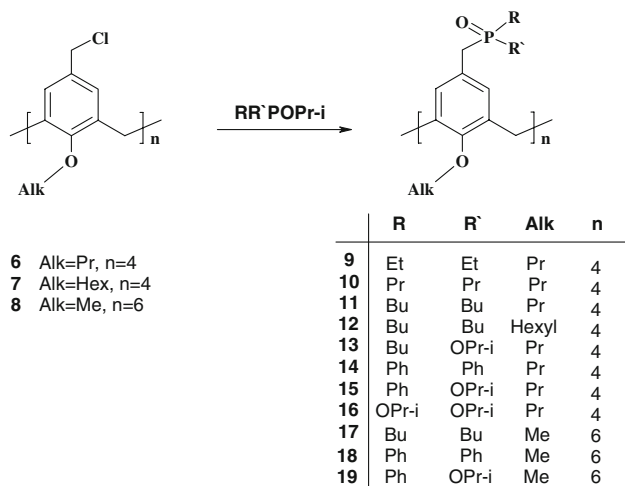
A conformation of the calix[n]arenes macrocyclic platform was determined by the analysis of signals pattern of ArCH<sub>2</sub>Ar methylene linkers in the <sup>1</sup>H NMR spectra. The



Scheme 1 Synthesis of calixarene **2**



Scheme 2 Synthesis of calixarenes **4, 5** in alternate conformation



**Scheme 3** Synthesis of calixarenes 9–19

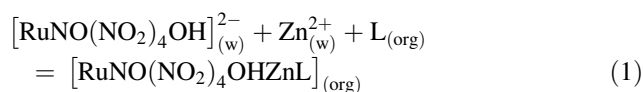
spectra of the  $C_{2v}$  symmetrical cone shaped calix[4]arenes **2**, **9–16** possess two doublets of AB spin system of the axial and equatorial protons of the methylene groups with  $^2J_{HH} = 13.2$  Hz and  $\Delta\delta$  parameter of the protons 1.4 ppm [19].

The  $^1H$  NMR spectra of calixarenes **4**, **5** existing in the *1,3-alternate* conformation also possess AB spin system of the methylene groups with  $^2J_{HH} = 13.2$  Hz. However their  $\Delta\delta$  parameter is equal 0.1 ppm [20].

In contrast to the calix[4]arenes, calix[6]arenes **17–19** are conformationally mobile due to free rotation of the benzene rings through the macrocyclic annulus [21]. The signals of the methylene links protons and the benzene ring protons in the  $^1H$  NMR spectra as well as the signals of phosphorus atoms in the  $^{31}P$  NMR spectra of the calix[6]arenes are displayed as sharp peaks at room temperature.

## Extraction

All phosphorylated calixarenes as well as the modeling monodentate extractants **DBuBnPO** or **DPhBnPO** poorly extract the ruthenium  $[RuNO(NO_2)_4OH]^{2-}$  form as well as Zn cations from water solution (Table 1). However the compounds effectively extract the Ru/Zn heterometallic complexes. The sequence of the partition coefficients  $D_{Ru} > D_{Zn}^0 > D_{Ru}^0$  is observed for all extractants and determined by the synergetic effect of heterometallic complex formation:



with equilibrium constant

**Table 1** The partition coefficients  $D$ , synergetic effects  $S$  and macrocyclic effects  $ME$  in the metals extraction from the water solution into *m*-nitro(trifluoromethyl)benzene

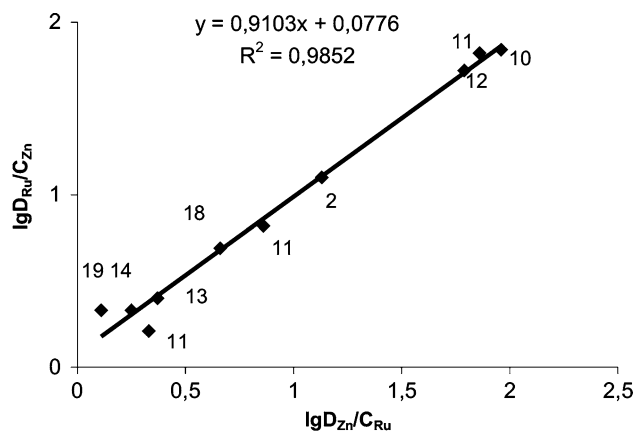
Extractant, L	$C_L, M$	$D_{Ru}$	$D_{Ru}^0$	$D_{Zn}^0$	$S_{Ru}$	ME	$lgK_{1,1,1}$
<b>2</b>	0.02	3.1	0.027	0.009	86	1.4	–
<b>4</b>	0.02	0.08	0.0002	0.0012	55	–	2.92
<b>5</b>	0.02	0.005	0.0002	0.0003	10	–	–
<b>9</b>	0.01	14.9 <sup>a</sup>	0.0047	0.0044	–	–	–
<b>10</b>	0.01	16.0	0.0103	0.024	470	7.4	4.40
<b>11</b>	0.01	16.0	0.011	0.022	485	7.4	4.70
<b>12</b>	0.01	12.7	0.013	0.014	480	5.9	4.18
<b>13</b>	0.01	0.63	0.0003	0.0029	197	–	2.51
<b>14</b>	0.01	0.67	0.02	0.002	25	22.0	2.41
<b>15</b>	0.01	0.34	0.0042	0.0012	60	11.0	2.15
<b>16</b>	0.01	0.13	0.0008	0.0008	81	–	1.72
<b>17</b>	0.0067	26.6	0.01	0.02	750	12.0	–
<b>18</b>	0.0067	1.2	0.034	0.001	34	39.0	3.12
<b>19</b>	0.0067	0.53	0.0059	0.0014	70	17.0	2.38
<b>DBuBnPO</b>	0.04	2.2	0.0052	0.0021	300	–	2.33
<b>DPhBnPO</b>	0.04	0.03	0.005	0.002	4.4	–	0.49

Concentrations:  $Na_2[RuNO(NO_2)_4OH] 6 \times 10^{-3}$  M,  $Zn(NO_3)_2 0.25$  M and  $NaNO_3 2$  M

<sup>a</sup> During the extraction precipitates are formed on the interphase.  $D_{Ru}$  was estimated from ruthenium content only in water phase

$$K_{1,1,1} = C_{Ru}^{opr} / C_{Ru} C_{Zn} C_L \quad (2)$$

The formation of the heterometallic Ru/Zn complexes of Ru:Zn:L = 1:1:1 composition is confirmed by the equality  $D_{Ru}/C_{Zn} = D_{Zn}/C_{Ru}$  (the line slope equal 1 on Fig. 1) according to the equilibrium constant. The stoichiometry was also confirmed by dilution and saturation methods and by the independence of  $D_{Ru}$  on the initial ruthenium concentration. Extraction constants  $K_{1,1,1}$  defined for some calixarenes describe interphase ruthenium distribution in

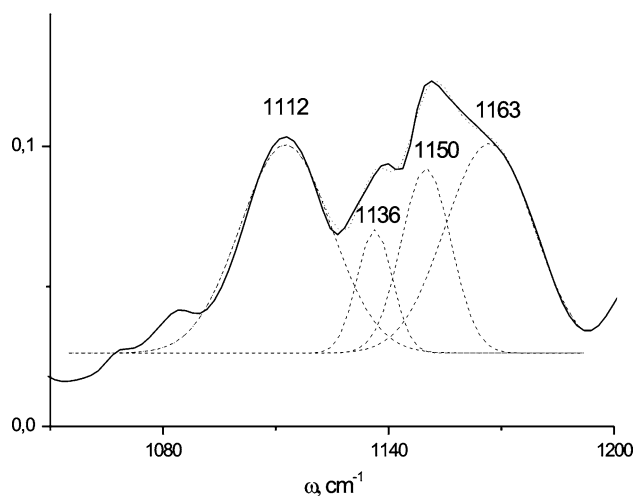


**Fig. 1** The correlation  $LgD_{Ru}/C_{Zn}$  versus  $LgD_{Zn}/C_{Ru}$  in extraction of the Ru/Zn heterometallic complexes by calixarenes **2**, **10–14**, **18**, **19**

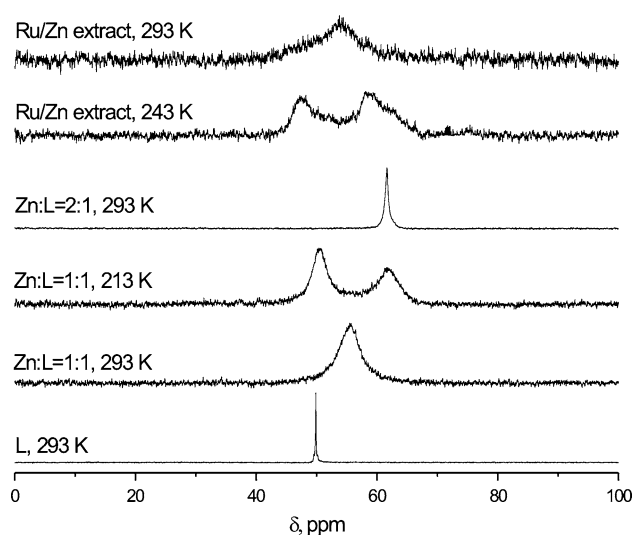
the range of Ru and L concentrations from  $10^{-3}$  to  $3 \times 10^{-2}$  M with errors no more than 10%. Earlier the structure of extracting Ru/Zn species with monodentate  $R_3PO$  was characterized in solution by IR and EXAFS spectroscopy [12, 13]. We found that phosphine oxide molecules are coordinated only to zinc cation, Zn–Ru bonding being provided by bridging  $\mu$ -OH and bidentate(N,O)—nitrogroups. The structure of triphenyl phosphine oxide complexes was confirmed also by X-ray analysis [22]. Because the IR-spectra in the range of NO, OH and  $NO_2$  vibrations are similar for heterometallic complexes with monodentate  $R_3PO$  and calixarene phosphine oxides, we suppose that ruthenium coordination sphere remains the same. The difference is concerned with the various type of ligand coordination—monodentate coordination of two-three molecules of  $R_3PO$  and polydentate coordination of L. The latter was determined by IR and  $^{31}P$ -NMR spectroscopy.

In the range of PO-stretching vibrations IR spectra of Ru/M complexes with L = **10** are superposition of four vibration bands: 1163 and  $1150\text{ cm}^{-1}$  are assigned to vibrations of free PO-groups, while 1136 and  $1112\text{ cm}^{-1}$  should be assigned to coordinated PO-groups (Fig. 2). The integral intensity in the range  $1090\text{--}1190\text{ cm}^{-1}$  is proportional to concentration of **10** and weakly depends on the metal concentration, so we suppose that the vibration band intensities for free and coordinated PO-groups are approximately similar. The share of coordinated PO-groups calculated as  $\alpha_{\text{coord}} = (I_{1136} + I_{1112})/\Sigma I$  is close to 0.5, that corresponds to the coordination of two PO-groups of calix[4]arene phosphine oxide **10** to  $Zn^{2+}$  cation.

There is only one line (47.4 ppm at 293 K) in  $^{31}P$ -NMR-spectrum of extractant **10** related to free PO-groups



**Fig. 2** IR-spectrum of Ru/Zn extract with **10** in the field of PO stretching vibrations and its decomposition to gaussian lines (dash lines)



**Fig. 3**  $^{31}P$ -NMR spectra of calixarene **10**, zinc complexes with various molar ratio and Ru/Zn extract.

(Fig. 3). This line does not split but slightly moves ( $<0.7$  ppm) with decrease in temperature to 213 K. To assign the signals of coordinated PO-groups organic solutions containing only  $Zn(NO_3)_2$  and L without ruthenium were characterized. NMR-spectrum of the solution with molar ratio Zn:L = 2:1 also has only one line at the room temperature (61.58 ppm). The line is substantially shifted from free ligand and corresponds to coordinated PO-groups. The decrease in temperature results in splitting of the signal to two lines (64.02 and 61.8 ppm) because of the decrease in the rate of conformation exchange “flattened cone”—“flattened cone” after the coordination of L to zinc atoms. Structural analysis of similar complexes of cobalt and nickel  $[M(NO_3)_2]_2L$  shown that each metal atom is bidentate-coordinated by two PO-groups of calix[4]arene phosphine oxide **10**[15c].

$^{31}P$ -NMR spectrum of solution with Zn:L = 1:1 have only one wide line at the room temperature (maximum—53.9 ppm) typical for exchange processes. The line width shrinks with the heating to 308 K, while decrease in temperature results in two signals (61.7 and 50.5 ppm). These regularities can be explained by the exchange « $PO_{\text{coord}}$ » — « $PO_{\text{free}}$ ». The share of coordinated PO-groups estimated from equation  $\delta_{\text{exch}} = \delta_{\text{coord}}X_{\text{coord}} + \delta_{\text{free}}(1 - X_{\text{coord}})$  lies in the range 0.42–0.56 ( $T = 293\text{--}308\text{ K}$ ) that agrees with the coordination of two PO-groups to zinc atom.

NMR spectrum of extract with molar ratio Ru: Zn:L = 1:1:1 have very broad exchange band at 293 K (maximum  $\approx 55$  ppm), located practically in the middle between signals of free (47.4 ppm) and coordinated (61.6 ppm) PO-groups. Decrease in temperature results in two wide bands ( $\approx 48$  ppm and  $\approx 59$  ppm) because of the « $PO_{\text{coord}}$ » — « $PO_{\text{free}}$ » exchange freezing. Therefore we



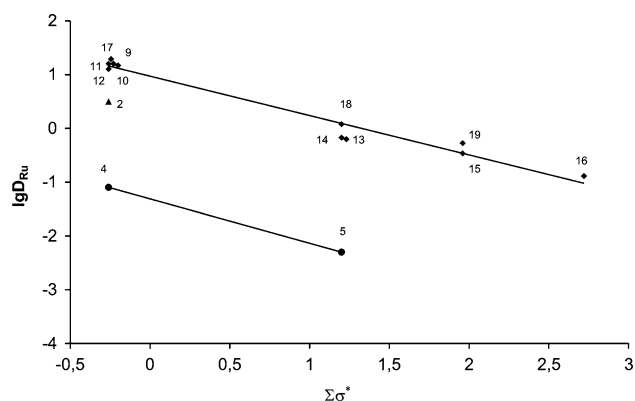
suppose that only two PO-groups are coordinated to  $Zn^{2+}$  in heterometallic complex  $[RuNO(NO_2)_4OHZnL]$  similar to solution with  $Zn:L = 1:1$ .

Totally all spectral data (IR and  $^{31}P$ -NMR) adjust each other and shows that in both heterometallic complexes and  $[Zn(NO_3)_2]_nL$  complexes calix[4]arene phosphine oxide **10** is a bidentate ligand to each zinc atom. At the same time, when ratio  $Zn:L$  is equal to 1:1 fast exchange between coordinated and free PO-groups takes place. We suppose that namely chelate formation after bidentate coordination of L provides macrocyclic effect for calix[4]arene phosphine oxides.

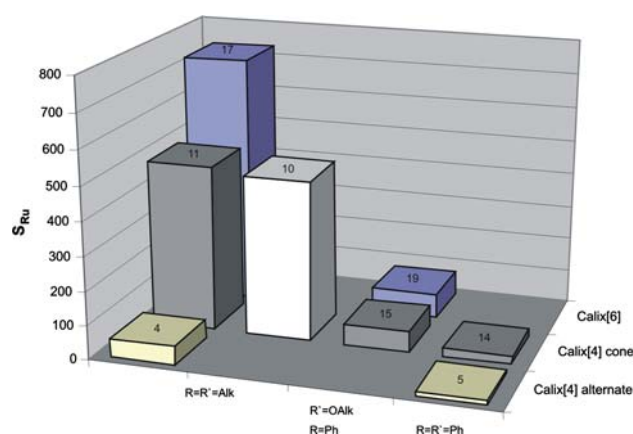
The distribution coefficients of the heterometallic complexes  $D_{Ru}$  as well as the calculated synergetic effect  $S_{Ru}$  and calixarene macrocyclic effect ME strongly depend on substituents at phosphorus atom, size and conformation of the calixarene platform, spacer between phosphorus atom and the platform.

The extractants investigated can be divided in two families according to substituent nature at the PO groups. The first family consists of calixarenes **2**, **4**, **9–12**, **17** and **DBBnPO** bearing alkyl groups at the phosphorus atom. The second family consists of calixarenes **5**, **13–16**, **18**, **19** and **DPhBnPO** bearing phenyl or/and alkoxy groups at phosphorus. For the both families the identical sequence of partition coefficients  $D_{Ru} > D_{Zn}^0 > D_{Ru}^0$  is observed confirming the Ru/Zn synergism in the extraction.

The extraction ability of the phosphorylated calixarenes decreases in the sequence  $Alk_2P(O) > AlkPhP(O) > Alk(AlkO)P(O) > Ph_2P(O) > (AlkO)_2P(O)$  in accordance with increase in electronegativity of the substituents at phosphorus atom. For the Ru/Zn extraction logarithms of  $D_{Ru}$  correlate with the sum of Kabachnik-Taft parameters [23] of the substituents:  $\lg D_{Ru} = -0.7497\Sigma\sigma - 1.953$  (Fig. 4). The similar dependence was observed for the separate zinc extraction ( $D_{Zn}^0$ , Table 1), though zinc



**Fig. 4** The correlation of the partition coefficients  $D_{Ru}$  versus Kabachnik-Taft parameters of substituents in calixarenes **2**, **4**, **5**, **9–19**



**Fig. 5** The synergic effect  $S_{Ru}$  in extraction of the Ru/Zn heterometallic complexes by calixarenes **4**, **5**, **10**, **11**, **14**, **15**, **17**, **19**

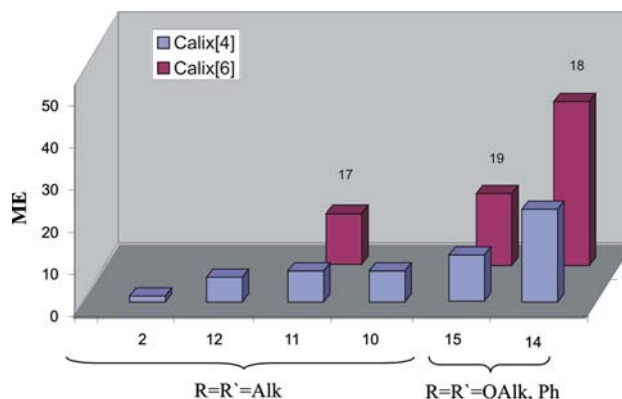
distribution coefficients are two-three orders lower than for Ru/Zn complexes.

For the cone shaped calixarenes the synergetic effects  $S_{Ru}$  (Fig. 5) have the same trend as  $D_{Ru}$  one. The  $S_{Ru}$  values are rather high ( $10^2$ – $10^3$ ) for the first calixarene family and are lower ( $10$ – $10^2$ ) for the second family.

In contrast to the synergetic effect  $S$  the macrocyclic effect ME for  $Ph_2P(O)$  derivatives ( $10$ – $40$ ) higher than for  $Alk_2P(O)$  derivatives ( $3$ – $20$ ) (Fig. 6).

Alkyl size at phosphorus atom practically does not influence the extraction. Increase in the alkyl size at the lower rim also does not influence  $D_{Ru}$  parameter, however it improves the phase stability in the extraction by calixarene **12**.

Increase in the number of  $Bu_2P(O)$  groups from two ones connected directly with the macrocyclic upper rim of calix[4]arene (compound **2**) to four groups connected by methylene spacer (compound **11**) increases the partition coefficient  $D_{Ru}$  from 3 to 16, the synergetic effect  $S$  from 90 to 480 and the macrocyclic effect ME from 1.47 to 7.4 (Table 1).



**Fig. 6** The macrocyclic effect ME in extraction of the Ru/Zn heterometallic complexes by calixarenes **2**, **10–12**, **14**, **15**, **17–19**

The cone shaped calix[4]arene **2** with two Bu<sub>2</sub>P(O) groups directly linked to the *para*-positions of the distal benzene ring is more effective extractant than 1,3-alternated calix[4]arene **4** possessing the groups connected by CH<sub>2</sub>O spacer. Change of Bu<sub>2</sub>P(O) groups in calixarene **4** on Ph<sub>2</sub>P(O) groups (compound **5**) decreases D<sub>Ru</sub> parameter.

Conformationally mobile calix[6]arenes **17–19** bearing six Bu<sub>2</sub>P(O), Ph<sub>2</sub>P(O) or Ph(PrO)P(O) binding groups exceed the stereochemically rigid cone shaped calix[4]arenes **11,14,15** possessing four same groups in partition coefficients D<sub>Ru</sub> (Table 1), synergic effects S (Fig. 3) and macrocyclic effects ME (Fig. 4) (**17** > **11**, **19** > **15**, **18** > **14**).

In conclusion, calix[4,6]arenes functionalized at the *para*-positions of the macrocyclic platform with four of six dialkylphosphine oxide binding groups due to the calixarene macrocyclic effect effectively extract heterometallic Ru/Zn complexes from nitric acid solution. Taking into account ability of the calixarene phosphine oxides to extract americium [24], the compounds can be used for combined recovery of the metals from HLW.

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