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Calixarenes grafted with $Bu_2P(O)CH_2O$ binding groups at the narrow rim: synthesis, structure and extraction of heterometallic Ru/Zn complexes

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Abstract Calix[*n*]arenes (*n* = 4, 6) existing in the *cone*, *1,3-alternate* or *1,3,5-alternate* conformations and functionalized by two, four or six $Bu_2P(O)CH_2O$ groups have been synthesized by the alkylation of hydroxycalix[4,6]arenes with tosylate of dibutylhydroxymethylphosphine oxide. Their molecular and crystal structures as well as binding properties towards of heterometallic Ru/Zn complexes were investigated. Due to the "calixarene effect" the phosphine oxides are effective extractants for the Ru/Zn complexes.

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

Introduction

Ruthenium, existing in nitric-nitrous solutions in different nitrosoforms, is one of the most dangerous fission products

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of spent nuclear fuel [1]. Kinetic inertness of these forms in ligand substitution reactions results in weak ruthenium recovery both in PUREX process of main actinides recovery [2] and in the process of combined extraction of lanthanides and minor actinides by TOPO, CMPO [3] or "TOPO and CMPO-like" calixarenes [4, 5]. On the other hand transformation of ruthenium in $[RuNO(NO_2)_4OH]^{2-}$ form, dominating in weak acid solutions, allows extraction of Ru together with actinides and lanthanides by monodentate R_3PO [6] or macrocyclic calixarenes, upper rim modified with several R_2PO-groups [7], because of formation of heteronuclear Ru/M complexes in the presence of M^{2+} cations (Zn^{2+} and other). In this case ruthenium anion and PO-groups of extractant are coordinated to M^{2+} that neglects kinetic restrictions for ruthenium recovery.

In this work, we investigated the Ru/Zn extraction by the calixarenes **1-6** bearing dibutylphosphinoylmethoxy groups at narrow rim of macrocycle (Chart 1) and compared their properties with properties of Calix[4]arene **7** bearing the same groups at the wide rim as well as with monodentated complexant dibutylbenzylphosphine oxide **8**. According to [8] the narrow rim decorated calixarene phosphine oxides poorly extract relatively big lanthanides and actinides cations. We suppose that Zn^{2+} complexation by the lower rim PO-groups will be more preferable than lanthanides and actinides complexation. The fact can be interesting for selective recovery of ruthenium after nitration of HLW solutions and transformation of different ruthenium forms into $[RuNO(NO_2)_4OH]^{2-}$ [9].

Experimental

All reagents used were of standard pure grade. The NMR spectra were recorded on the Varian VXR-300 or the

Chart 1 Phosphorylated calixarenes used for extraction of heterometallic complexes

1

2, 3
R = Bu (**2**), R = Ph (**3**)

4, 5
R = H (**4**), R = t-Bu (**5**)

6
R= CH$_2$P(O)Bu$_2$

7

8

Varian Gemini-200 spectrometers with internal standard TMS and external standard 85% H$_3$PO$_4$. IR-spectra of solutions in DCE and extracts were recorded on IR-spectrometer Scimitar FTS 2000 in CaF$_2$ cells in the range of wavelengths 1,000–4,000 cm^{-1}. The measurement of diffraction was performed on a Nonius KappaCCD diffractometer. Structures were solved and refined using the programs SHELXS-97 [10] and SHELXL-97 [11]. Hydrogen atoms were calculated to their idealized positions and were refined as riding atoms.

Crystal data for **3**: C$_{60}$H$_{58}$O$_6$P$_2$, M = 937.00, colorless plate 0.10 × 0.35 × 0.50 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 22.8005(2), b = 10.9933(1), c = 21.6801(3) Å, β = 109.634(1)°, V = 5118.2(1) Å^3, Z = 4, D_c = 1.216 g/cm^3, F_{000} = 1984, MoKα radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 55.1°, 49628 reflections collected, 11721 unique (R_{int} = 0.047). Final $GooF$ = 1.09, R = 0.062, wR = 0.103, R indices based on 9,055 reflections with $I > 2\sigma$ (I) (refinement on F^2), 616 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.136 mm^{-1}.

Crystal data for **6**: C$_{96}$H$_{152}$O$_{12}$ P$_6$·4C$_2$H$_3$N·3.5H$_2$O, M = 1911.23, colorless block, 0.20 × 0.20 × 0.30 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 16.5253(2), b = 21.2883(3), c = 17.0116(3) Å, β = 109.935(1)°, V = 5626.0(1) Å^3, Z = 2, D_c = 1.125 g/cm^3, F_{000} = 2064, MoKα radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 46.4°, 71,

425 reflections collected, 7987 unique (R_{int} = 0.063). Final $GooF$ = 1.10, R = 0.073, wR = 0.156, R indices based on 5495 reflections with $I > 2\sigma$ (I) (refinement on F^2), 613 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.154 mm^{-1}. Cif-files containing complete information on structures were deposited to CCDC with numbers 784839 and 784840.

Calixarene phosphine oxides **2, 3** were synthesized in accordance with early described procedures [7].

5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26, 28-bis(dibutylphosphinoylmethoxy)calix[4]arene 1

A suspension of Calix[4]arene (**10**) (0.65 g, 1.00 mmol) and NaH (0.06 g, 2.5 mmol) in toluene (20 mL) was stirred at 80 °C for 1 h. Then Bu$_2$P(O)CH$_2$OTs (0.87 g, 2.2 mmol) was added and the resultant mixture was stirred at 80 °C for 48 h. Excess NaH was decomposed with MeOH (5 mL) and the solvent was evaporated in vacuo. The residue was taken up in CHCl$_3$ and washed with 1 N HCl aq. (50 mL) then with water (2 × 75 mL^2). The organic layer was dried with Na$_2$SO$_4$. After evaporation of the solvent, the solid residue was recrystallized from diethyl ether to give colorless crystals. Yield: 0.6 g, 65%; mp 247–250 °C. ^{1}H NMR, CDCl$_3$, δ: 0.85 (s, 18H, t-Bu), 0.96 (t, 12H, J = 7.5 Hz, P–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 1.34 (s, 18H, t-Bu), 1.51 (m, 8H, P–CH$_2$–CH$_2$–CH_2–CH$_3$), 1.81 (m, 8H, P–CH$_2$–CH_2–CH$_2$–CH$_3$), 2.03 and

2.17 (two m, 8H, P–CH_2–CH_2–CH_2–CH$_3$), 3.37 (d, 4H, J = 13.00 Hz, Ar–CH_{2eq}–Ar), 4.15 (d, 4H, J = 13.00 Hz, Ar–CH_{2ax}–Ar), 4.24 (d, J = 7.5 Hz, 4H, O–CH_2–P), 5.86 (s, 2H, Ar–OH), 6.67 (s, 4H, ArH–m), 7.13 (s, 4H, ArH–m); ^{31}P NMR (80.95 MHz, CDCl$_3$): δ 47.1. *Anal. Calc.* for C$_{62}$H$_{94}$O$_6$P$_2$, %: C 74.66; H 9.50; P 6.21. Found: %: C 74.76; H 9.30; P 6.21.

General procedure for the synthesis of 25,26,27, 28-tetrakis- and 37,38,39,40,41,42-hexakis (dibutylphosphinoylmethoxy)-calix[4,6]arenes **4-6**

A suspension of Calix[n]arene (**9, 10** or **12**) (2.00 mmol) and NaH (3.00 mmol for each OH group) in toluene (60 mL) was stirred at 80 °C for 4 h. Then Bu$_2$P(O)-CH$_2$OTs (2.2 mmol for each OH group) was added and the resultant solution was stirred at 80 °C for 48 h. Excess NaH was decomposed with MeOH (20 mL) and the solvent was evaporated in vacuo. The residue was taken up in CHCl$_3$ and washed with 1 N HCl (60 mL) then with water (2 × 75 mL^2). The organic layer was dried with Na$_2$SO$_4$. After evaporation of the solvent, the solid residue was crystallized.

25,26,27,28-tetrakis(dibutylphosphinoylmethoxy) calix[4]arene **4**

White powder; yield 75%; mp 59–61 °C (Et$_2$O); ^{1}H NMR, CDCl$_3$ δ: 0.87 (t, 24H, ^{3}J$_{HH}$ = 7.2 Hz, P–CH$_2$–CH$_2$–CH$_2$–CH_3), 1.12–2.00 (m, 48H, P–CH_2–CH_2–CH_2–CH$_3$), 3.30 and 4.82 (two d, 8H, ^{2}J$_{HH}$ = 13.25 Hz, Ar–CH_2–Ar), 4.45 (s, 8H, O–CH_2–P(O)), 6.41-6.64 (m, 12H, ArH). ^{31}P NMR, δ: 45.3. *Anal. Calc.* for C$_{64}$H$_{100}$O$_8$P$_4$, % C 68.55, H 8.99, P 11.05. Found, % C 68.64, H 8.91, P 11.08.

5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis (dibutylphosphinoylmethoxy)calix[4]arene **5**

White powder; yield 70%; mp 142–143 °C (hexane); ^{1}H NMR, CDCl$_3$, δ: 0.87 (t, 24H, ^{3}J$_{HH}$ = 7.2 Hz, P–CH$_2$–CH$_2$–CH$_2$–CH_3), 1.1 (s, 36H, *t*-Bu), 1.25–1.70 (m, 48H, P–CH_2–CH_2–CH_2–CH$_3$), 3.28 and 4.98 (two d, 8H, ^{2}J$_{HH}$ = 13.25 Hz, Ar–CH_2–Ar), 4.61 (s, 8H, O–CH_2–P(O)), 6.76 (s, 8H, ArH); ^{31}P NMR, δ: 43.4. *Anal. Calc.* for C$_{80}$H$_{132}$O$_8$P$_4$, %: C 71.4, H 9.88, P 9.14. Found, %: C 71.38, H 9.64, P 9.06.

37,38,39,40,41,42-hexakis(dibutylphosphinoylmethoxy) calix[6]arene **6**

Colorless crystals; yield 65%; mp 100–102 °C (Et$_2$O); ^{1}H NMR, CDCl$_3$, δ: 0.82 (s, 36H, P–CH$_2$–CH$_2$–CH$_2$–CH_3), 1.0–2.1 (m, 72H, P–CH_2–CH_2–CH_2–CH$_3$), 3.98 (s, 12H, O–CH_2–P), 4.22 (s, 12H, Ar–CH_2–Ar), 6.6–7.2 (m, 18H, ArH). ^{31}P NMR, δ: 45.21. *Anal. Calc.* for C$_{96}$H$_{150}$O$_{12}$P$_6$, %: C 68.55, H 8.99, P 11.05. Found, % C 67.87, H 8.50, P 10.78.

5,11,17,23-tetrakis(dibutylphosphinoylmethoxymethyl)- 25,26,27,28-tetrapropoxycalix[4]arene **7**

To a solution of Bu$_2$P(O)CH$_2$OH (2.68 g, 14.00 mmol) in DMSO (40 mL) solution of KOH (0.78 g, 14.00 mmol) and H$_2$O (0.8 mL) was added. The resulting mixture was stirred for 1 h at room temperature, then chloromethylcalixarene **13** (2.5 g, 3.2 mmol) was added. The reaction mixture was heated at 60 °C for 24 h. The contents of the flask was cooled, neutralized with HCl and extracted by CHCl$_3$. The organic layer was washed with H$_2$O (2 × 75 mL^2) and dried with Na$_2$SO$_4$. After evaporation of the solvent, the viscous residue was washed with hexane and dried in high vacuum. Yield 90%. ^{1}H NMR, CDCl$_3$, δ: 0.86 (m, 36H, CH_3), 1.25–1.60 (m, 48H, P–CH_2–CH_2–CH_2–CH$_3$), 1.89 (d × t, 8H, O–CH$_2$–CH_2–CH$_3$), 3.56 (d, 8H, ^{3}J$_{PH}$ = 13.8 Hz, O–CH_2–P), 3.08 and 4.43 (two d, 8H, ^{2}J$_{HH}$ = 13.35 Hz, Ar–CH_2–Ar), 3.83 (t, 8H, O–CH_2), 4.18 (s, 8H, Ar–CH_2–O), 6.49 (s, 8H, ArH). ^{31}P NMR, CDCl$_3$, δ: 48.8. MS (CI) m/z 1423.8 (M$^+$, 100%). FW calc. 1409.83. *Anal. Calc.* for C$_{80}$H$_{132}$O$_{12}$P$_4$, %: C, 68.16; H, 9.44; P, 8.79. Found: %: C, 67.46; H, 9.84; P, 9.08.

Extraction procedures

To simulate the composition of real HLW after neutralization stage the extraction was carried out from fresh solution of Na$_2$[RuNO(NO$_2$)$_4$OH]·2H$_2$O in 2 M NaNO$_3$. Na$_2$[RuNO(NO$_2$)$_4$OH]·2H$_2$O was synthesized from RuCl$_3$ by the method [12]. Extractant solutions in purified *m*-nitro(trifluoromethyl)benzene (NTFB, "Rhodia") and 1,2-dichloroethane (DCE) were prepared from the precise weights. Upper rim modified calixarene with CH$_2$OCH$_2$-PO(Bu)$_2$ groups **7** and monodentate (Bu)$_2$(C$_6$H$_5$CH$_2$)PO (**8**) were investigated for comparison with lower rim derivatives. To achieve equilibrium, extraction was performed by the intensive stirring of equal volumes of organic and water phase during 30 min at 298 K. Analysis of equilibrium phases was carried out by atomic absorption spectroscopy (Hitachi Z-8000) with zeeman background correction. Equilibrium concentrations of metals in conjugated phases (C$_M^{org}$, C$_M^{aq}$) were used to determine distribution ratio for extraction from solutions containing only one metal (D$_{Ru}^0$, D$_{Zn}^0$) and extraction from solutions containing both metals (D$_{Ru}$, D$_{Zn}$). For calculation of synergic effect S$_{Ru}$ = D$_{Ru}$/(D$_{Ru}^0$ + D$_{Zn}^0$) and macrocyclic effect ME (ratio of D$_{Ru}$ for calixarene and **8**) values of D$_M$ were determined at the same permanent concentration of PO-groups. Stoichiometry of extraction was determined from logD–logC$_L$

to logD–logC$_{Ru(Zn)}$ dependencies at the constant concentration of nitrate-ions (2 mol/L) in water phase. Extraction constants were calculated by the least square procedure minimizing $\Sigma(C_{Ru}^{org, \, exp} - C_{Ru}^{org, \, calk})^2$ with relative uncertainties $\sigma_{\pm}$.

Water saturated solutions of **5** in DCE were prepared after 30 min stirring with distilled water and centrifugation. Ru/Zn extracts used for IR were prepared on the base of solution of **4** and **5** in DCE, compositions of extracts are given in Table 3.

Quantum chemical calculations

The structures of the calix-Zn–Ru (calix = **1**, **5** and **6**) complexes have been obtained in semi-empirical quantum mechanics PM3-tm calculations using the SPARTAN'08 program. Experimental X-ray structures of uncomplexed calixarenes were used for the model building of the complexes.

Results and discussion

Synthesis

Calix[4]arenes **1**, **4**, **5** in the *cone* conformation bearing two or four CH$_2$P(O)Bu$_2$ functional groups at the narrow rim capable to form a chelate with a metal cation were synthesized by the alkylations of the calixarenes **9**, **10** phenolic groups by tosylate of hydroxymethyldibutylphosphine oxide in the presence of NaH (toluene, 80 °C) (Scheme 1).

The stereochemical outcome of the alkylation process is highly controlled by metal cation [13]. The reaction of 25,27-dipropoxycalix[4]arene **11** with tosylates of hydroxymethyldibutyl(diphenyl)phosphine oxide in the presence of cesium carbonate in refluxing acetonitrile produces calixarene bis-phosphine oxides **2**, **3** possessing the *1,3-alternate* conformation [7] (Scheme 2).

Calix[6]arene **6** bearing six dibuthylphosphinoylmethoxy groups was synthesed similarly to Calix[4]arenes **4**, **5** by the reaction of hydroxycalix[6]arene **12** with tosylate of
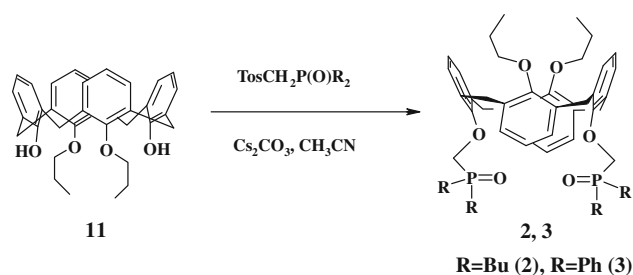
Scheme 2 Synthesis of calixarenes **2**, **3**

hydroxymethyldibutylphosphine oxide in the presence NaH (toluene, 80 °C) (Scheme 3).

Calix[4]arene **7** in the *cone* conformation bearing four CH$_2$OCH$_2$P(O)Bu$_2$ functional groups at the upper rim was synthesized by the alkylation of the hydrohymethyldibutyl-phoshine oxide by chloromethylcalixarene **13** in the presence of super base system DMSO/KOH (24 h, 60 °C) (Scheme 4).

Stereochemistry

A conformation of the Calix[n]arenes macrocyclic platform was determined by the analysis of signals pattern of ArCH$_2$Ar methylene linkers in the ^{1}H NMR spectra. The two doublets of AB spin system with $\Delta\delta$ 0.78–1.50 ppm (^{2}J$_{HH}$ = 13.5 Hz) for axial and equatorial protons of the ArCH$_2$Ar methylene links in the ^{1}H NMR spectra confirm the *cone* conformation of calixarenes **1**, **4**, **5**, **7** [14].

The ^{1}H NMR spectra of Calix[4]arenes **2,3** existing in the *1,3-alternate* conformation also possess AB spin system of the methylene groups with ^{2}J$_{HH}$ = 13.2 Hz. However, their $\Delta\delta$ parameter is equal 0.1 ppm [15]. The *1,3-alternate* conformation of calixarene **3** is also observed in solid state as revealed by single crystal X-ray analysis (Fig. 1).

The two pairs of facing one another aromatic rings of calixarene **3** macrocycle are rotated towards the macrocyclic cavity due to the repulsion of the two big diphenylphosphinylmethoxy groups and consequently, the dipropoxy substituents are also pushed away of the cavity. The dihedral
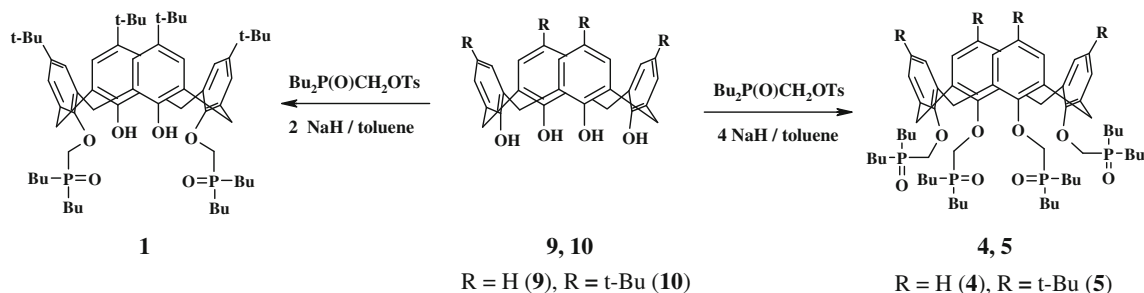
**Scheme 1** Synthesis of calixarenes **1**, **4**, **5**

Scheme 3 Synthesis of calixarene **6**

R= CH₂P(O)Bu₂

12   **6**
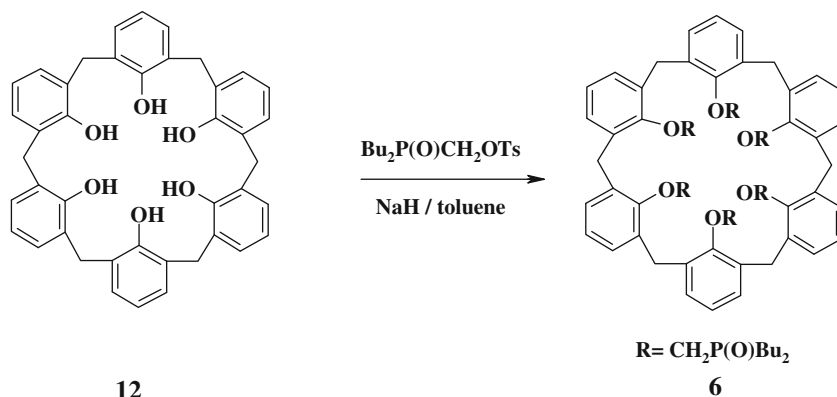
Scheme 4 Synthesis of calixarene **7**

13   **7**
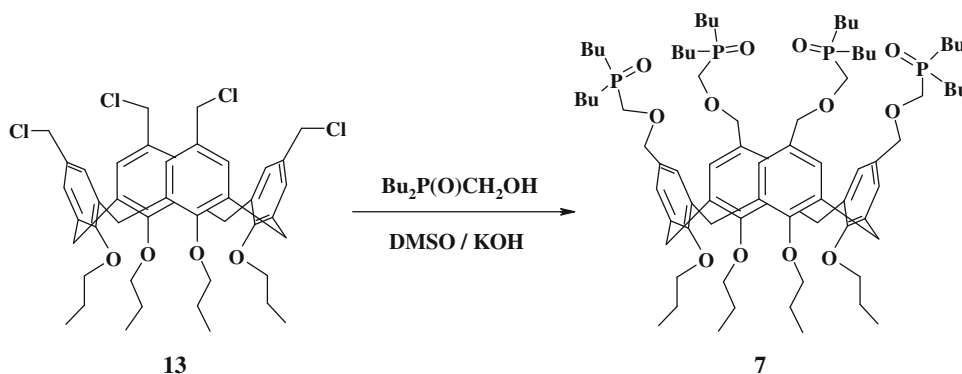
Fig. 1 Ortep drawing of calixarene **3** with atom numbering. Thermal displacement ellipsoids are drawn with 50% probability
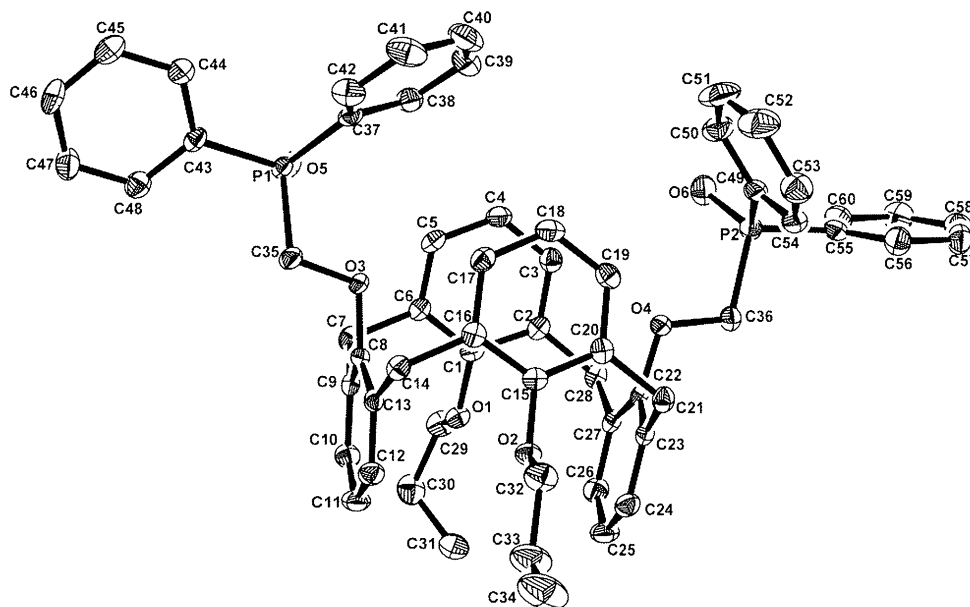
angles are 16.4° and 12.5° between the propoxy and diphenylphosphinylmethoxy substituted aromatic rings, respectively. The molecules are arranged in columns along *c* axis and those form layers parallel to *bc* plane (Fig. 2).

In Calix[6]arene **6** due to fast (in the NMR time scale) rotation of the aromatic fragment through the large inner

circular space of the macrocycle the proton signals of the methylene links in the macrocyclic core are manifested in the ¹H NMR spectra as broadened singlets at room temperature [16].

Calix[6]arenes can exist as 8 conformers (*cone, partial cone, 1,2-alternate, 1,3-alternate, 1,4-alternate, 1,2,3-alternate,*
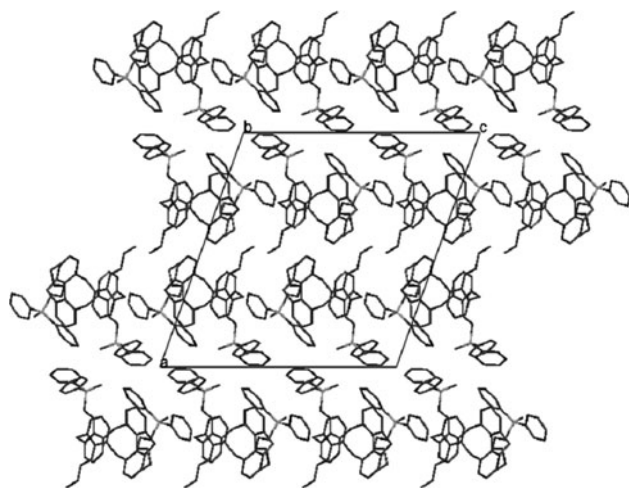
Fig. 2 Packing diagram of **3**

1,2,4-alternate, 1,3,5-alternate), having different orientation of the aromatic rings relatively to the main plane of the macrocycle, which is defined by the carbon atoms of the six methylene bridges [17].

According to the X-ray crystallographic study, the molecule of **6** exists in a centrosymmetrical *1,3,5-alternate* conformation as a complex with two water molecules (Fig. 3, left). In this conformation the two opposite aromatic rings form the angles of 29.4° with the main plain of the macrocyclic ring defined as an plane through CH_2 bridges between the aromatic moieties, whereas the two pairs of others rings are form the angles of 63.4 and 61.8° to the same main plane. The dihedral angles between the pairs of the

neighboring aromatic rings are 95.0°, 77.0° and 96.3°. According to the Gutsche's nomenclature [18] this conformation can be described as (uo, u, d, do, d, u). The two pairs of the distal dibutylphosphine oxide groups are linked by the P=O···H–O–H···O=P hydrogen bonds with two water molecules (Fig. 3, right). The third pair of phosphine oxide groups is not hydrogen bonded.

The packing of molecules in the crystal is shown in Fig. 4. Infinite columns are formed in the crystal along the crystallographic *a* axis which is held together by weak intermolecular forces. Between the molecules of **6** a large cavity is formed, in which four acetonitrile molecules (two symmetrically independent and two generated through the crystallographic center of symmetry) is included. The fifth molecule is disordered through the center of symmetry and is located in intermolecular channels formed along *c* axis.

Extraction

Earlier data shows that influence of ligand structure on the extraction of metals by lower rim grafted calixarene phosphine oxides is different for diphenyl- [4] and dialkylderivatives [8]. For the first group at fixed acidity (1 M HNO_3) de-*tert*-butylation of upper rim leads to the increase in metal (Th, Eu, alkaline and alkaline earth metals) recovery, while lengthening of spacer in lower rim decreases recovery of all metals except Th. For the second group in the range of acidity 0.1–3.0 M HNO_3 dealkylation does not influence the extraction of Am and Eu but slightly decrease the recovery of Pd and Tc. Lengthening of spacer in this case results in

Fig. 3 Molecular structure of Calix[6]arene **6**, conformation of the macrocyclic skeleton (*left*), complex with two water molecules (*right*)
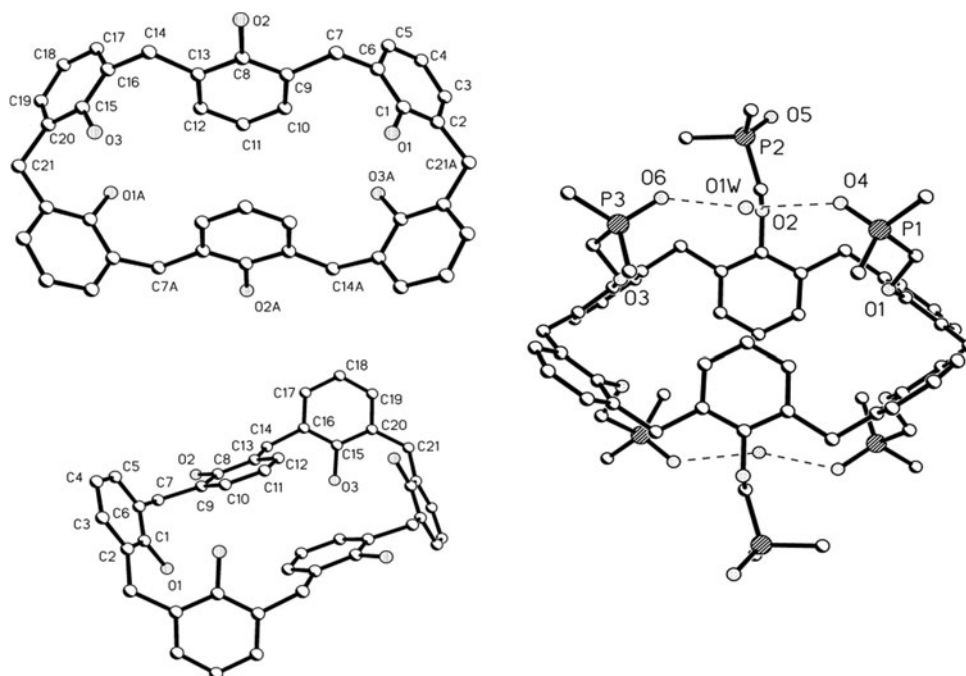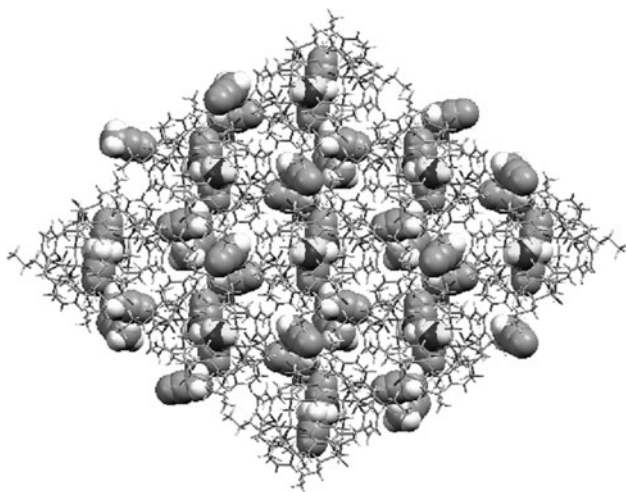
Fig. 4 Molecular structure of the Calix[6]arene **6** as 1:2 complex with water; crystal structure viewed along *a* axis–solvent (water and acetonitrile molecules) shown in space filling mode
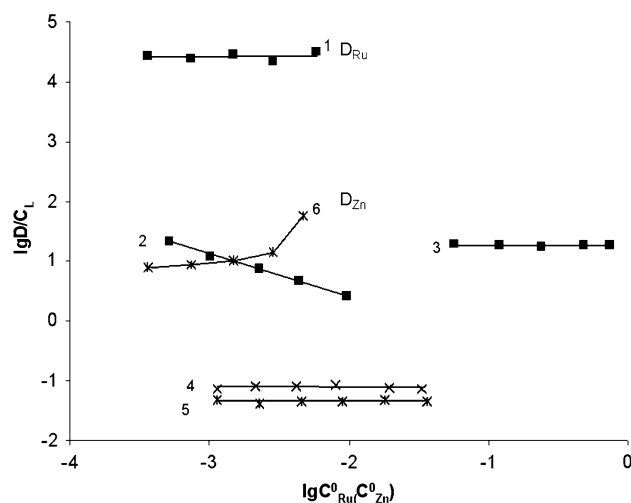

Fig. 5 Influence of Ru (*1,2,4,5,6*) and Zn (*3*) concentrations during separate extraction of Ru (*2,4,5*) and Zn (*3*) and during combined extraction (*1, 6*) by calixarene **5** (*1,2,3,6*), FOR (*4*) and CMPO (*5*). Extractant concentrations in NTFB (mol/L): **5**: 0,01, FOR and CMPO: 0,3. Water phase: 2 M NaNO$_3$

increase in D$_{Am(Eu)}$ for more than one order, similar to change of functionalization site from lower to upper rim. Regularities of Ru/Zn complexes extraction from nitrate solutions by calixarenes **1**, **4–6** are differ from both groups.

Extraction of heterometallic Ru/Zn complexes

Comparison of separate and combined extraction of [RuNO(NO$_2$)$_4$OH]$^{2-}$(An^{2-}) and Zn(NO$_3$)$_2$ by solutions of **1, 4–6** indicate interference of metals (Table 1). Similar to upper rim modified macrocycles [7], under the condition optimal for Ru recovery (C$^0_{Zn}$ >> C$^0_{Ru}$) for all extractants D$_{Ru}$ >> D$^0_{Ru}$ > D$^0_{Zn}$ and values of S$_{Ru}$ are equal to 10^2–10^3. Concentration of Zn in organic phase and zinc distribution ratio (D$_{Zn}$ > D$^0_{Zn}$, Table 1) also increase when ruthenium is added to the water phase. Moreover at the constant concentration of Zn (0.25 mol/L) values of D$_{Ru}$ are constant in the range of initial ruthenium concentration 0.4–6.0 mmol/L, while D$_{Zn}$ grows proportionally C$^0_{Ru}$ (Fig. 5), that is typical for coextraction systems.

Table 1 Separate and combined extraction of [RuNO(NO$_2$)$_4$OH]$^{2-}$ and Zn(NO$_3$)$_2$ from nitrate solutions. Concentrations: Ru-6 mmol/L, Zn(NO$_3$)$_2$-0,25 mol/L, NaNO$_3$-2 mol/L

L	C$_L$ (mol/L)	D$_{Ru}$	D$^0_{Ru}$	D$_{Zn}$	D$^0_{Zn}$	S$_{Ru}$	ME
1	0.02	6.6	0.028	–	0.003	210	3.1
4	0.01	13.1	0.008	0.027	0.02	470	6.1
5	0.01	31.9	0.016	0.036	0.028	720	14.7
6	0.007	13.8	0.003	–	0.010	1030	6.4
7	0.01	19.5	0.059	0.028	0.018	253	9.0
8	0.04	2.2	0.005	–	0.002	300	1.0

In the extraction of Am and Eu D$_{upper}$/D$_{lower}$ = 60– 300 for calixarenes with the same R$_2$PO donor groups in different sites [8]. In contrast to that, values of D$_{Ru}$, synergic (S$_{Ru}$) and macrocyclic (ME) effect are of the same order for Calix[4]arenes with four PO-groups in lower (**4, 5**) or upper (**7**) rim. Presence of t-Bu-groups in the *para*-position of **5** increases D$_{Ru}$, ME and S$_{Ru}$ compared with dealkylated **4** (Table 1). For Calix[4]arene phosphine oxides increase in the number of Bu$_2$PO groups from two (**1**) to four (**5**) results in growth of D$_{Ru}$ (from 6.6 to 31.9), S$_{Ru}$ (from 210 to 720) and ME (from 3.1 to 14.7). Stereochemically flexible Calix[6]arene **6** with six Bu$_2$PO-groups has the same D$_{Ru}$ value as **4** but bigger values of S$_{Ru}$. Thus, extraction of Ru/Zn complexes by lower rim phosphorylated Calix[4]arenes has two distinctive features: close values of D$_{Ru}$ for upper (**7**) and lower (**4**) rim derivatives and increase of D$_{Ru}$ after alkylation of upper rim from **4** to **5**. According to [7] at the acidity 0.1–1.0 M HNO$_3$ distribution values of Am and Eu for **4** is equal to 0.01–0.02 allowing principal ability of separate ruthenium recovery with separation coefficient higher than 10^3. Possible reason for that is the different ionic radii of cations Eu^{3+} and Am^{3+}(0.95–0.97 Å) and Zn^{2+} cation (0.7 Å), coordinated by calixarene phosphine oxides in Ru/Zn complex.

Synergic effect in investigated systems is determined by formation of heterometallic Ru/M complexes with acyclic [6] and macrocyclic [7] phospine oxides. To describe interphase distribution of ruthenium in the presence of excess of Zn(NO$_3$)$_2$ and high concentration (2 M) of NO$_3^-$ we investigate equilibriums of two competing processes

$$Zn_w^{2+} + [RuNO(NO_2)_4OH]_w^{2-} + nL_{org}$$
$$= [RuNO(NO_2)_4OHZnL_n]_{org} \tag{1}$$
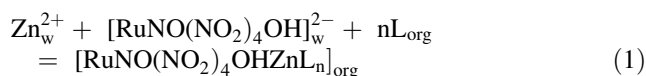
with equilibrium constants

$$K_{11n} = C_{Ru}^{org}/C_{Ru}C_{Zn}C_L^n \quad n = 1, 2 \tag{2}$$

and

$$nZn_w^{2+} +^- 2nNO_{3w} + L_{org} = [M_nL(NO_3)_{2n}]_{org} \tag{3}$$
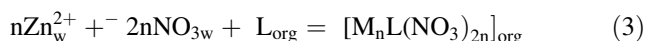
with

$$K_{0n1} = C_{Zn}^{org}/(C_{Zn})^2(C_{NO_3})^{2n}C_L \tag{4}$$

Stoichiometry of metal forms in organic phase was determined by extraction techniques. In the extraction of zinc nitrate according to Eq. 4 slopes of bilogarithmic dependencies are close to unity (0.88–1.03) for extractants **4–6** in the range of C_L from 10^{-3} to $3\cdot10^{-2}$ mol/L (Fig. 6). Thus the only form with composition $[ZnL(NO_3)_2]$ present in organic phase beyond of saturation with $Zn(NO_3)_2$, binuclear form $[Zn_2(NO_3)_4L]$ is essential only in conditions of complete saturation of L by metal similar to [19]. In contrast to that for the combined Ru/Zn extraction slopes of $logD_{Ru}–logC_L$ lines are systematically higher than unity (1.43–1.62), that corresponds to the formation of complexes with different Ru:L stoichiometry equal 1:1 or 1:2. Ratio $[Zn]_{org}/[Ru]_{org}$ rises with increase in C_L (Fig. 7) at the constant composition of water phase because of competition process (3). Still all trends (Fig. 7) tends to unity with decrease in initial concentration of L that corresponds to the formation of complex with Zn:Ru = 1:1. This ratio is also confirmed by linear equation $logD_{Ru}/C_{Zn} = 1.104\cdot logD_{Zn}/C_{Ru}-0.223$ with slope close to unity which results from (2) and valid for all extractants when organic phase is close to saturation with Ru ($C_L \approx C_{Ru}^{org}$).

Monomeric state of both complex forms is confirmed by independence of D values on initial concentration of metals
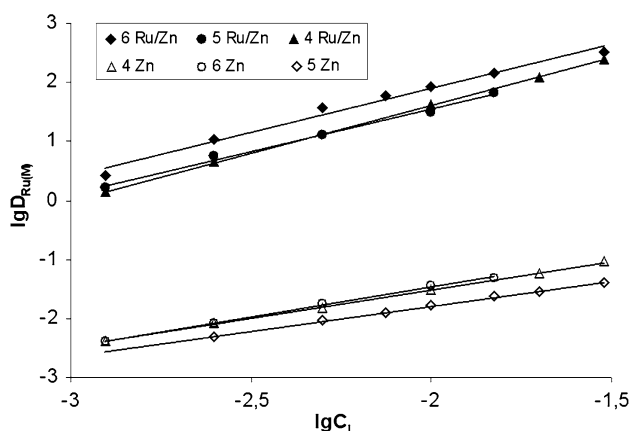
Fig. 6 Dependencies $logD_M–logC_L$ during extraction of zinc nitrate and heterometallic Ru/Zn complexes by solutions of **4–6** in NTBF
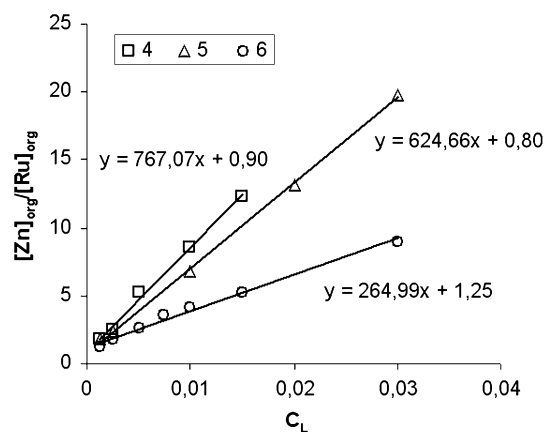
Fig. 7 Determination of Zn/Ru ratio in extracts with **4–6**. Initial water phase: Ru: 0,001 mol/L, Zn(NO₃)₂: 0,25 mol/L, NaNO₃: 2 mol/L

Table 2 Extraction constants for $ML_n(NO_3)_2$ and $[RuNO(NO_2)_4OHML_n]$

L	M²⁺	$[ML_n(NO_3)_2]$				$[RuNO(NO_2)_4OHML_n]$			
		n	$logK_{011}$	$logK_{021}$	$\sigma_\pm$	n	$logK_{111}$	$logK_{112}$	$\sigma_\pm$
4	Zn	0.969	0.29	–	0.06	1.62	4.94	7.04	0.07
5	Zn	1.01	0.47	−2.13	0.08	1.43	4.64	7.11	0.12
6	Zn	0.86	−0.46	−4.1	0.07	1.49	4.72	5.96	0.07
7	Zn	0.84	−0.41	−2.84	0.13	1.51	4.62	6.25	0.15

(lines 1 and 3 on Fig. 5). Calculated constants K_{0n1} and K_{11n} (Table 2) describe distribution of zinc nitrate and Ru/Zn complexes with discrepancies no more than 12%. Mononuclear complexes with one molecule of L dominate in all extraction systems. Fraction of $[RuNO(NO_2)_4OHZnL_2]$ becomes essential (40% or more) only at 20-fold excess of L, fraction of binuclear $[Zn_2(NO_3)_4L]$ form in the extraction of zinc overlaps 40% only in saturated extracts when equilibrium concentration of free ligand is less than 1% of total ligand content.

Earlier we established that in Ru/M complexes with monodentate R_3PO [6] or with upper rim phosphorylated calixarenes [7] extractant molecules are coordinated to Zn cation, while Ru–Zn bounding is provided by bridging OH and NO_2-groups of ruthenium anion. Similar structure of Ru/Zn complexes with Calix[4]arene phosphine oxides **4** and **5** is indirectly confirmed by IR-spectra of extracts (Table 3). In the range of $\nu(PO)$ two new bands arise (1,136 and 1,109 cm⁻¹) that are absent in spectra of pure ligands (both in dry organic solution and in organic solution saturated by water) and can be assigned to PO-groups coordinated to metal. Intensities of the bands correlate with the concentration of Ru/Zn complex in extract. The band of nitrosogroup vibration (1902 cm⁻¹) is slightly shifted from

**Table 3** Main bands in IR-spectra of heterometallic extracts

L(C_L, M)	C_{Ru} (M)	Band assignment					
		$\nu(H_2O)^a$	$\delta(H_2O)$	$\nu(NO)$	$\nu_s(NO_2)$	$\nu_{as}(NO_2)$	$\nu(PO)$
4 (0.02)	0.017	3382	1607	1902	1338 (1)	1406 (1)	1167
					1300 (2)	1463 (2)	1136
							1111
	0.097	3383	1607	1902	1340 (1)	1406 (1)	1167
					1298 (2)	1463 (2)	1136
							1109
5 (0.02)	0.016	3383	1609	1902	1338 (1)	1404 (1)	1165
					1300 (2)	1466 (2)	1136
							1111
	0.095	3381	1609	1902	1338 (1)	1406 (1)	1165
					1300 (2)	1465 (2)	1136
							1109

[a] Maximum of wide band

$\nu(NO)$ in spectrum of anion (1877 cm^{-1}) [6] because of trans-influence during interaction of Zn^{2+} with OH-group of An^{2-}. Vibration bands $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$ in spectra of extracts are splitted in two pairs corresponding non-equivalent nitrogroups (Table 3). Similar to complexes with monodentate R$_3$PO, vibrations NO$_2$(1) with bigger difference ν_{as}–ν_s were assigned to bridging nitrogroups, while vibrations of NO$_2$(2) were assigned to terminal groups, not coordinated to Zn^{2+}.

Hydration and association of calix[4]arene phosphine oxides

Similar to mononuclear R$_3$PO, calixarene phosphine oxides weakly recover anionic form [RuNO(NO$_2$)$_4$OH]$^{2-}$ (Table 1). However, dependence of D$_{Ru}^0$ on initial ruthenium concentration is different for these two classes of PO-containing extractants. In case of CMPO or R$_3$PO D$_{Ru}^0$ is constant in the range of C$_{Ru}$ from 3 to 20 mmol/L (Fig. 5) because of formation of monomeric ionic pairs with coordination of extractant to aquated Na$^+$ cation [6]. In contrast to that D$_{Ru}^0$ decreases with the increase of initial ruthenium concentration for the extraction by **5** (Fig. 5). As long as ruthenium form in water solution does not change the fact can be described by decrease in activity of extractant because of association of **5** in organic phase with participation of water molecules. Indeed, the process

$$2Na_w^+ + [RuNO(NO_2)_4OH]_w^{2-} + nL_{org} + mH_2O$$
$$= \{Na_2L_n(H_2O)_m[RuNO(NO_2)_4OH]\}_{org}, \quad (5)$$
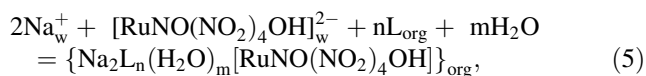
describes experimental line 2 on (Fig. 5) with one efficient constant K$_{Ru}$ = C$_{Ru}^{org}$/C$_{Ru}^w$C$_{Na}^2$(C$_L$−nC$_{Ru}^{org}$)^n. At the constant ionic force (2 M NaNO$_3$) average association number n is equal 9.8 and logK$_{Ru}$ = 18.5. According to previous data Calix[n]arenes with hydrophilic groups (SO$_3$H, P=O, NH$_2$) can form micellar associates in extraction processes due to

the formation of hydrogen bonds with water molecules [20] or participate in formation of mixed micelles with additional surfactants [21]. It is appropriate to mention here that hydrogen-bonded water molecules are present in solid phase of Calix[6]arene phosphine oxide **6** (Fig. 3).

Indirect confirmation of association of calixarene **5** was obtained from IR spectra of its solutions in DCE saturated with water. Two narrow bands (3,591 and 3,676 cm^{-1}) are present in spectrum of pure DCE saturated with water in the field of stretching vibrations of H$_2$O, that should be assigned to water molecules dissolved in DCE (spectrum 1, Fig. 8). IR-spectra of water saturated solutions of calixarene **5** in DCE exhibits additional wide absorption band with maximum near 3,400 cm^{-1} and increase in intensity of absorption in 3,650–3,670 cm^{-1} (spectrum 2, Fig. 8). Subtraction of "moist DCE" spectrum from spectra of
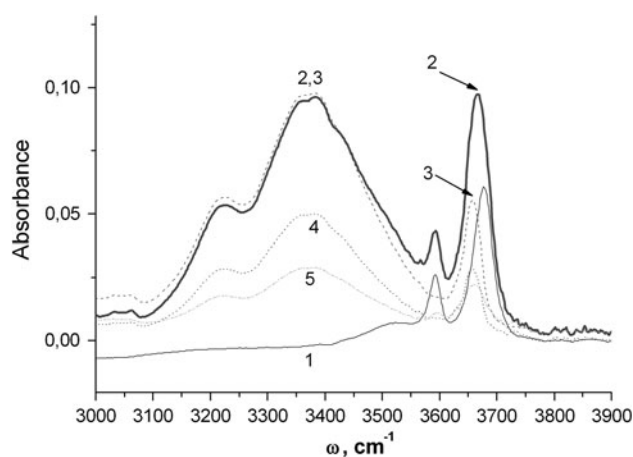
Fig. 8 *1* IR-spectrum of water saturated DCE, *2* IR-spectrum of 0,032 M **5** in DCE, saturated with water. IR-spectra of water saturated solutions of **5** in DCE after subtraction of spectrum (*1*), concentration of **5** is equal 0.032 M (*3*), 0.016 M (*4*), 0.0092 M (*5*)

calixarene solutions result in complete disappearance of vibration band at 3,591 cm^{-1} (spectrum 3–5, Fig. 8). In the field 3,650–3,660 cm^{-1} new absorption band is revealed (3,657 cm^{-1}) shifted from water vibration in DCE solution (3,676 cm^{-1}). Intensity of wide band at 3,400 cm^{-1} is strictly proportional to concentration of **5** in concentration range 0.92–3.2 mmol/L with molar absorption coefficient $\varepsilon = 5.8 \pm 0.1$ L/(mol·mm). On the contrary absorbance at 3,567 cm^{-1} weakly changes from A = 0.022 ($C_L =$ 0.92 mmol/L) to A = 0.027 (C_L = 1.6 mmol/L). Further increase in concentration to 3.2 mmol/L result in proportional increase in absorption (A = 0.055). These facts can be explained by the presence of two types of water molecules in organic solutions of **4** saturated with water, that is typical for reverse micelles formation [22, 23]. Vibration band at 3,400 cm^{-1} absent in spectrum 1 (Fig. 8) can be assigned to water molecules (**I**) hydrogen-bonded with PO-groups, concentration of these molecules and intensity of corresponding band being proportional to C_L. Interactions between PO-groups and water is also reflected in shift of v(PO) frequency from 1.169 (dry solution of L) to 1,159 cm^{-1} (water saturated solution). Absorption band at 3,657 cm^{-1} close to vibration of water dissolved in DCE without L can be assigned to water molecules of type **II**. Possibly it can be bulk water inside micellar associates $L_n(H_2O)_m$, which volume depends on concentration of L.

On the other hand the description of Zn and Ru/Zn extraction and independence of D values on metal concentration (Fig. 5) does not require assumption of association. These facts indicate elimination of associates $L_x(H_2O)_y$ and in agreement with spectral changes. Comparison of spectra of Ru/Zn extracts and solutions of L in water-saturated DCE shows that the intensity of vibrations at 3,400 cm^{-1} (type **I**) decreases with the growth of metal concentration that is explained by substitution of water **I** by Zn cations. It is remarkable that vibrations of water at 3,657 cm^{-1} (type **II**) completely disappear in spectra of extracts, probably indicating destruction of associates.

Molecular modeling of the calixarene Ru/Zn complexes

To gain microscopic insight into the structure of extracted species we perform modeling studies using semi-empirical PM3-tm calculations for different calixarenes to elucidate the possible influence of calixarene structure on the extraction efficiency. In all cases Zn cation is coordinated by oxygen atoms of calixarene PO-groups and NO$_2$ (OH)-groups of [RuNO(NO$_2$)$_4$OH]$^{2-}$, calculated Zn–O distances are about 1.9–2.0 Å that is typical for Zn complexes with O-donors. Particular coordination patterns of Zn^{2+} depend on the number of donor centers of the ligand (Fig. 9). Tetrahedral coordination of Zn^{2+} by two P=O groups of the calixarene, and O(OH) and O(NO$_2$) atoms of the Ru-anion

(Fig. 9a) was detected for all three calixarenes (**1, 5, 6**). For bidentate calixarene **1** no other modes of Zn coordination was observed. In case of tetradentate Calix[4]arene **5** two coordination patterns have been found in addition to Fig. 9a. In these forms three PO-groups are located in the first coordination sphere of Zn^{2+} while ruthenium anion can be coordinated through two (Fig. 9b) or one (Fig. 9c) bridging group. Fourth PO group of **5** does not participate in coordination at all. It is remarkable that such calixarene coordination to M^{2+} is very close to coordination pattern, earlier found in complexes of **5** with cobalt nitrate [24]. For hexadentate Calix[6]arene **6** coordination patterns of Zn (Fig. 9a, b, d) is similar to Calix[4]arene **5**.

In general calculations shows that during the formation of Ru/Zn complexes with lower rim functionalized calixarenes the tetrahedral coordination of Zn is most typical (Fig. 9a, c, d). Ruthenium anion can be coordinated to Zn^{2+} by bridging OH (Fig. 9c), NO$_2$ (Fig. 9d) or both groups (Fig. 9a, b) similar to coordination in [(Ph$_3$PO)$_3$ZnRuNO(NO$_2$)$_4$OH] [25]. Number of PO-groups taking part in the coordination does not exceed 3 even for hexadentate Calix[6]arene **6**, possibly because of steric restrictions.

Conclusion

Calix[4]arenes with alkyl phosphine oxide groups in the lower rim are found to be more efficient for recovery of heterometallic Ru/Zn complexes compared with both
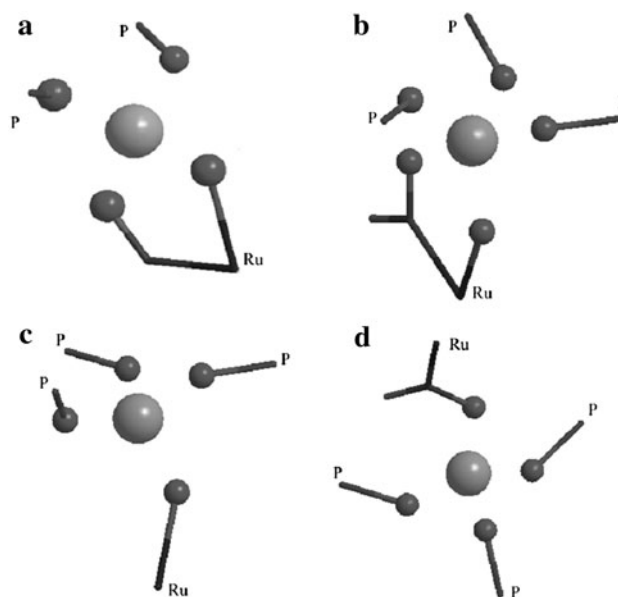
Fig. 9 Coordination modes of Zn^{2+} in heterometallic complexes with calixarenes **1,5,6** according to PM-3 calculations. Zinc cation and closest oxygen atoms are designated as spheres

monodentate phosphine oxides and the upper rim modified Calix[4]arenes. The fact can be explained by optimal spatial fitting between donor groups in the lower rim to small Zn^{2+} cation. Calix[4]arene **5** can be recommended for selective recovery of ruthenium from weak acidity HLW, containing Am^{3+} and Eu^{3+} which distribution ratios does not exceed 0.05 in similar conditions [8].

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