ORIGINAL ARTICLE

Complexation and extraction of non-ferrous metals by calix[*n*]arene phosphine oxides

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Abstract The extraction of non-ferrous metal (M^{2+}) nitrates by the calix[4,6]arenes (L), bearing four or six phosphine oxide donor groups at the upper or at the lower rim, was quantitatively described in the form of $[M_n(NO_3)_{2n}L]$ ($n = 1$, 2) complexes. The extraction constants ($Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$) for the both types of L coincide with Irving-Williams sequence. Calix[4]arenes, phosphorylated at the lower (narrow) rim, provide better stability of ML complexes because of the best spatial fitting of M^{2+} by the donor groups. For the upper (wide) rim phosphorylated calix[4]arenes M_2L and ML_2 complexes are more stable. Unusual zwitterionic $[Co_2(NO_3)_4L]$ complex of the lower rim tetraphosphorylated calix[4]arene **1** was determined by X-ray structural analysis.

Keywords Calixarene · Phosphine oxide · Extraction · Zinc · Cobalt · Nickel · Copper · Zwitter-ion structure

Introduction

Calix[n]arenes functionalized by different donor groups are promising compounds for design of new highly selective extractants [1–4]. The switch from monodentate extractants to calixarene-based polydentate ligands increases a metal cation organic/water distribution ratio owing to a chelate effect of several donor groups spatially preorganized at the calixarene platform. In particular, transfer from carbamoyl phosphine oxides (CMPO) to "CMPO-like" calixarenes decreases for two orders the concentration of the extractant that is necessary to recover fission lanthanides and actinides [5]. The change of dialkylsulfides R_2S to calixarene thioesters increases the distribution ratio for palladium and silver and the extraction rate of palladium for 2–3 orders [6, 7].

Additional preference of calixarenes compared with the other macrocyclic compounds is the presence of two sites of modification (upper and lower rim). The different distance between donor groups placed at these sites can be used for additional tuning of spatial fitting between ligand and metal cation. With the same R_2PO-donor groups, calix[4]arenes modified at the upper (wide) rim extract relatively big lanthanide cations better than the lower (narrow) rim substituted analogues [8]. On the other hand, the opposite variation of distribution ratios was found for technetium extracted in the $HTcO_4$ form because the chelate coordination of H^+ by two proximal PO groups at the lower rim [8]. The difference in size of the rims also influences stoichiometry of complexes formed. The coordination number is systematically increased from the lower to the upper rim derivatives during the extraction of Am or Eu by "TOPO-like" calixarenes. [8]. According to [2] "CMPO-like" calix[4]arenes substituted at the lower rim, form complexes of 1:1 stoichiometry exclusively, while the upper rim substituted derivatives with the same donor groups form also M_2L complexes. X-ray analysis of the latter ones has shown that each metal atom is coordinated by two CMPO groups of calix[4]arene.

Earlier we have shown that the calixarenes phosphine oxides (L) are highly efficient in extraction of fission ruthenium from nitrated high level wastes (HLW) due to the formation of heterometallic $[Ru(NO)(NO_2)_4OHML]$

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complexes with non-ferrous metals ($M^{2+} = Co^{2+}$, Ni^{2+}, Zn^{2+}, Cu^{2+}) [9]. Strong synergetic effect (up to 10^3) is observed owing to coordination of ruthenium to M^{2+} cation by bridging OH and NO_2 groups. The calixarene tetraphosphine oxides increases distribution ratio for 10–40 times compared with monodentate Alk_3PO owing to chelate coordination of L to non-ferrous metal. In current article we compare the extraction and complexation of M^{2+} by different L, upper and lower rim functionalized, to validate the choice of optimal extraction system ($M(NO_3)_2$–L) for the recovery of Ru/M complexes.

Experimental

Reagents and extraction technique

Nitrates of copper, zinc, nickel and cobalt were of standard pure grade ("Merck") and used without additional purification. Commercial m-nitro(trifluoromethyl)benzene (NTFB, "Rhodia") was treated sequentially with 5% NaOH, 5% HNO_3 and water (three cycles) and dried [10]. This diuent was chosen because of potential interest in radiochemical applications. It was shown earlier that use of NTFB and other fluorinated solvents could lead to the increase in both D values [11] and phase stability [12]. Calixarenes 1–5 (Scheme 1) were synthesized according to [8, 13, 14]. Solutions of extractants in NTFB were prepared from the precise weights.

Number of coordinating L molecules was determined by dilution method during the extraction from 0.25 M solution of metal nitrates in water at constant ionic strength (2 M $NaNO_3$). Isotherms of zinc extraction up to concentration

EXPERIMENTAL.

1-3

	X	n
1	t-Bu	1
2	H	1
3	H	3

4,5

	Y	Alk
4	CH_2	Pr
5	CH_2OCH_2	Bu

Scheme 1

of Zn^{2+} equal 1 M were examined at the constant concentration of nitrate-ions in water phase (2.5 M NO_3^-) maintained by sodium nitrate addition. For higher Zn^{2+} concentrations extraction was performed from the pure solutions of zinc nitrate. 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. Extracts were analyzed directly in flame or in graphite atomizer depending on the metal concentration. Equilibrium concentrations of metals in conjugated phases (C_M^{org}, C_M^{aq}) were used to determine distribution ratio ($D_M = C_M^{org}/C_M^{aq}$). Extraction constants were calculated by the least square procedure minimizing $\Sigma(C_M^{org,\ exp} - C_M^{org,\ calk})^2$. Microcalorimetric titration of $Zn(NO_3)_2$ (1.4 mmol/l) solution by solution of 1 (28.4 mmol/l) in methanol was performed with thermal activity monitor TAM 2277. Complexation constants and enthalpies ($\beta_{11} = (5.8 \pm 0.4) \cdot 10^4$ $\Delta H = -16.4 \pm 2.5$ kJ/mol, $\beta_{21} = (1.2 \pm 0.1) \cdot 10^7$ $\Delta H = -72.6 \pm 3.4$ kJ/mol) were calculated from experimental data by DIGITAM 4.1 program.

Synthesis of complex [$Co_2(NO_3)_4 \cdot 1$]

$Co(NO_3)_2$ $6H_2O$ (0.2 mmol) was stirred at room temperature in solution of 1 (0.1 mmol) in CH_2Cl_2 (3–5 mL) until complete dissolving of cobalt nitrate. After evaporation of the mixture to 1–1.5 mL the violet [$Co_2(NO_3)_4$*1] was precipitated by addition of $(C_2H_5)_2O$ (10–15 mL). The complex is well soluble in CH_2Cl_2, $CHCl_3$ and acetone and almost insoluble in heptane. Single crystal suitable for X-ray analysis was prepared by slow diffusion of heptane to the solution of complex in CH_2Cl_2 during 1–2 days. The complex crystallizes as solvate [$Co_2(NO_3)_4$*1] $(C_2H_5)_2O$ losing solvent molecules on air. IR(cm^{-1}): 792, 810—$\delta(NO_3)$; 1275, 1300—$v_s(ONO_2)$; 1479, 1513—$v_{as}(ONO_2)$; 1008, 1022—$v(N = O)$; 1123—$v(P = O)$.

For $C_{80}H_{132}P_4O_{20}Co_2N_4$

|			
Calc. without solvent (%)	C—56.1	H—7.71	N—3.28
Found (%)	C—56.2	H—7.78	N—3.19

Attempts to prepare the complex in NTFB by extraction procedure failed because of very high initial concentration of M^{2+} in water phase required to achieve 2:1 composition in organic phase. We also made some attempts to prepare complexes in NTFB by technique similar to described with other metals except of Co, but failed to obtain pure substances or single crystals suitable for X-ray analysis.

The measurement of diffraction was performed on automatic diffractometer Bruker Nonius X8Apex CCD at
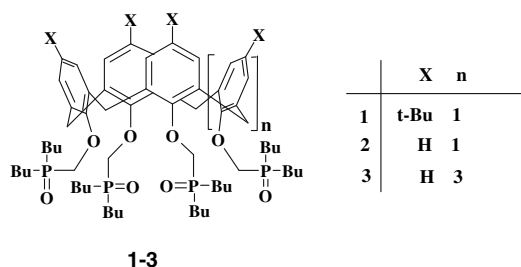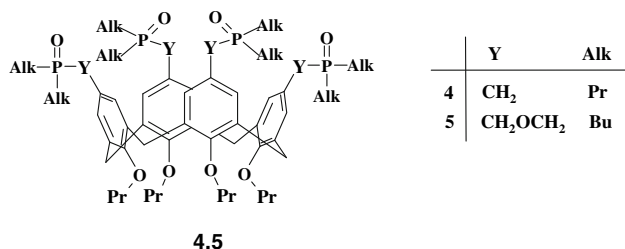
100 K (MoK$_\alpha$—radiation, graphite monochromator, φ,ϖ-scanning), crystal size—$0.46 \times 0.1 \times 0.08$ mm. Totally 16433 reflections were collected in the range of θ from 2 to 26°. The compound is crystallized in Pna2$_1$ space group ($a = 17.586(4)$, $b = 23.126(6)$, $c = 23.985(4)$ Å, $V = 9755.2(3)$ Å^3, $Z = 4$). The absorption was corrected by SADABS program [15]. Structure was solved by means of the direct methods and refined by full-matrix least-square techniques with the use of the program SHELXTL [15] with 9384 unique reflections ($I > 2\sigma(I)$). Hydrogen atoms were calculated to their idealized positions and were refined as riding atoms. Final calculation includes 1058 of structural parameters, $R = 0.067$ ($wR = 0.1519$) for $I > 2\sigma(I)$, $R = 0.1445$ ($wR = 0.1808$) for all reflections. CIF-file containing complete information on the structure was deposited to CCDC with number 738854.

Results and discussion

Extraction and complexation

Complexation and extraction of metals with functionalized calix[4]arenes is generally described by the set of forms with M:L = 1:1, 2:1, 1:2 [1, 2, 7]. Earlier we found that L with dialkylphosphine oxide groups at the upper rim during extraction forms in organic phase ML and ML$_2$ complexes with Ni, Co and Cu nitrates and ML and M$_2$L complexes with Zn nitrate [9]. According to the literature data for the lower rim grafted calix[4]arenes the ML complexes with two or more donor groups coordinated to a metal cation are mostly preferable [2].

The stoichiometry of Co, Ni, Cu and Zn nitrate complexes formed during extraction by calix[n]arenes 1–3 was determined from $\lg D = f(\lg C_L^0)$ dependencies at up to 10–20 fold molar excess of metal in respect to extractant. The slopes (n) of lines in these coordinates are close to unity (0.87–1.15) for all systems that confirms prevailing of ML form in extracts (Table 1, Fig. 1). Thus the extraction in these conditions is determined by the equation

$$M^{2+}_{(aq)} + 2NO^-_{3(aq)} + L_{org} = \left[M(NO_3)_2L\right]_{org} \quad (1)$$
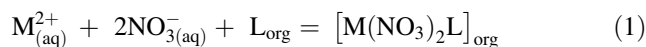
with equilibrium constant

$$K_{11} = C_M^{org} / \left(C_M^{aq} C_L^{org} \left(C_{NO3}^{aq}\right)^2\right) \quad (2)$$

Extraction constants K_{11}, determined with fixed $n = 1$, decrease in the sequence $Zn^{2+} \geq Cu^{2+} > Co^{2+} > Ni^{2+}$ for extractant 1 (Fig. 1a; Table 1) and $Zn^{2+} > Co^{2+} > Ni^{2+}$ for extractant 2 (Fig. 1b; Table 1). The sequence coincides with the data obtained earlier for calixarene 4 with four dipropylphosphine oxide groups at the upper rim [9] and is determined mainly by the nature of cation (Irving-Williams sequence). Comparison of zinc and cobalt extraction by 1, 2 and 4 showed that the change of modification site from the upper to the lower rim leads to moderate increase of ML stability, the difference between extraction constants is no more than 0.7 logarithmic unit. Change of para-t-butyl group in 1 to hydrogen atom in 2 results in decrease of extraction constants of cobalt, nickel and zinc. The largest change was found for nickel, the extraction constant decreases for more than one order of magnitude. According to [2] for lanthanide and actinide extraction, dealkylation of

Table 1 Parameters of extraction of non-ferrous metals with calixarene phosphine oxides 1–5

L	M^{2+}	$\lg D = f(\lg C_L^0)$			Isotherms		
		n	K_{11}	K_{21}	K_{11}	K_{21}	$\lg K_d + 0.6$
1	Zn^{2+}				$(5.8 \pm 0.4)\ 10^4$ [a]	$(1.2 \pm 0.1)\ 10^7$ [a]	-1.8
1	Zn^{2+}	1.00	2.9 ± 0.1		3.0 ± 0.2	$(7.1 \pm 0.6)\ 10^{-3}$	-2.5
1	Cu^{2+}	1.15	1.5 ± 0.2				
1	Co^{2+}	0.91	$(1.5 \pm 0.1)\ 10^{-1}$				
1	Ni^{2+}	0.98	$(4.0 \pm 0.2)\ 10^{-2}$				
2	Zn^{2+}	0.97	1.7 ± 0.12				
2	Co^{2+}	0.87	$(3.7 \pm 0.2)\ 10^{-2}$				
2	Ni^{2+}	1.02	$(2.5 \pm 0.2)\ 10^{-3}$				
3	Zn^{2+}	0.96	$(6.0 \pm 0.1)\ 10^{-1}$				
4 [7]	Zn^{2+}	0.95	1.01		1.1 ± 0.2	$(8.5 \pm 0.9)\ 10^{-3}$	-1.6
4 [7]	Cu^{2+}	1.22	0.26	2.8			
4 [7]	Co^{2+}	1.20	$3.1\ 10^{-2}$	2.0			
4 [7]	Ni^{2+}	1.61	$7.6\ 10^{-3}$	0.6			
5	Zn^{2+}	0.84	$(3.6 \pm 0.3)\cdot10^{-1}$		$(3.9 \pm 0.8)\ 10^{-1}$	$(1.2 \pm 0.3)\ 10^{-3}$	-1.5

[a] Complexation constants determined from calorimetric titration in methanol

Fig. 1 Determination of stoichiometry of extracting complexes: (**a**) **1** with Zn, Co, Ni, Cu, (**b**) **1**–**3** with Zn and Co
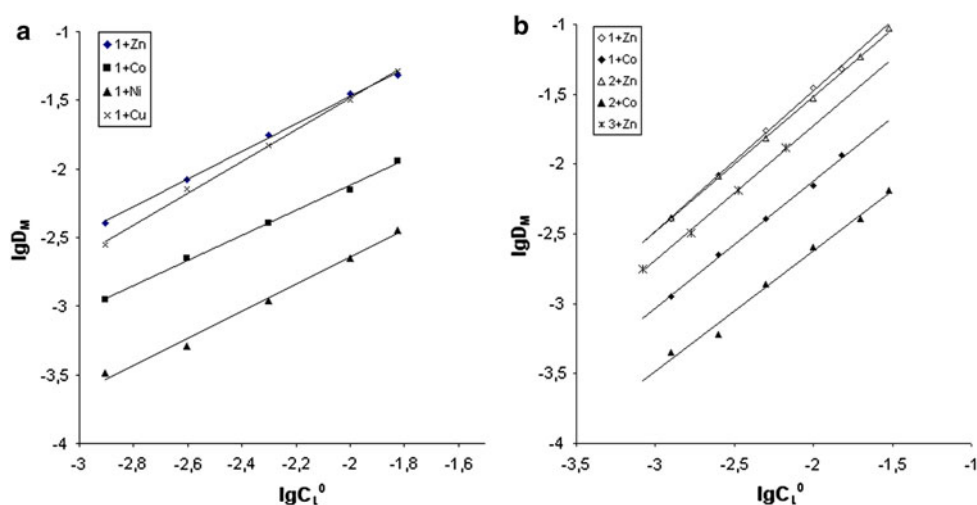
the upper rim can lead to the increase in extraction properties of functionalized calix[n]arenes in case of TOPO-like calixarenes or to the decrease in recovery for CMPO-like calixarenes. The most probable reason for that is the change of sterical rigidity of the ligand. For extraction of large cations Eu^{3+} and Am^{3+} (ionic radii is equal to 0.95 and 0.97 Å [16]) by R_2PO-grafted calixarenes the increase in D_M can be related to the increase in distance between PO-groups and diminishing of calixarene cavity after removal of bulky substituents. During the extraction of smaller cations Co^{2+}, Ni^{2+}, Zn^{2+} (ionic radii are from 0.65 to 0.74 Å [16]) the lability of calixarene plays a negative role and most strongly influences the distribution coefficients of smallest cations of cobalt and nickel.

The calixarene ligands sterical rigidity plays an important role in the extraction processes. This is confirmed by the increase of extraction constant for stereochemically rigid calix[4]arene **2** compared to flexible calix[6]arene **3**. Calixarene **4** with short CH_2 spacer between calixarene scaffold and PO groups is also more effective compared to **5** bearing longer CH_2OCH_2 one.

In saturation region the ratio $C_{Zn}^{org}:C_L^0$ is more than unity both for **4, 5** and for **1** bearing the same donor groups on the upper and the lower rim [9] (Fig. 2). The fact is determined by the presence of binuclear form, the share of M_2L is increasing with the increase of metal concentration in feeding phase (Fig. 3). The isotherms of zinc extraction in all three cases are satisfactorily described by two equilibriums:

$$nM_{(aq)}^{2+} + 2nNO_{3(aq)}^- + L_{org} = \left[M_n(NO_3)_{2n}L\right]_{org} \quad (3)$$
$$n = 1, 2$$
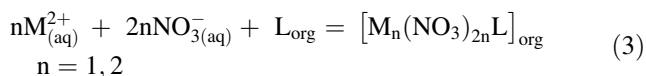
with the corresponding extraction constants K_{11} и K_{21} (Table 1). Values of K_{11}, determined from extraction isotherms coincide with the data obtained from $lgD = f(lgC_L^0)$ dependencies in the limits of errors. In the field of
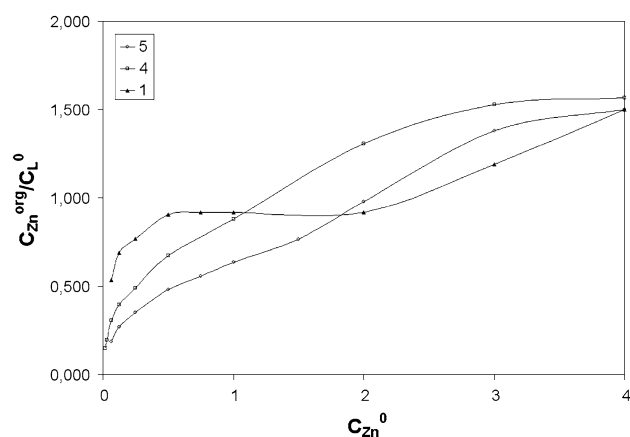

Fig. 2 Isotherms of Zn extraction by calixarene phosphine oxides **1, 4, 5**

mononuclear form ML domination ($C_{Zn}^0 < 1$ M) D_{Zn} increases in the sequence **4** < **5** < **1** similar to the change of K_{11}. In the region $C_{Zn}^0 > 2$ M the share of binuclear form changes from 20 to 60% (Fig. 3) and sequence of D_{Zn} is partially inverted (**1** < **4** < **5**) coinciding with the change of M_2L fraction in material balance.

The difference between K_{11} and K_{12} is determined by solvation energy of additional "$Zn(NO_3)_{2(aq)}$" fragment and by the change of solvation energy from calixarene phosphine oxide to extracting complexes. To estimate the contribution of the latter factor, the constants of disproportionation in organic phase excluding solvation in water phase were calculated:

$$2\left[M(NO_3)_2L\right]_{org} = \left[M_2(NO_3)_4L\right]_{org} + L_{org} \quad (4)$$
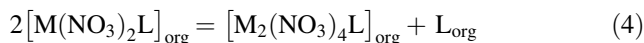
$$lgK_d = lgK_{21} - 2lgK_{11} \quad (5)$$

According to Bjerrum [17] this value can be described as a sum of statistic factor ($lgS = -0.6$) and residual effect (ligand effect). The last is determined in our case by the
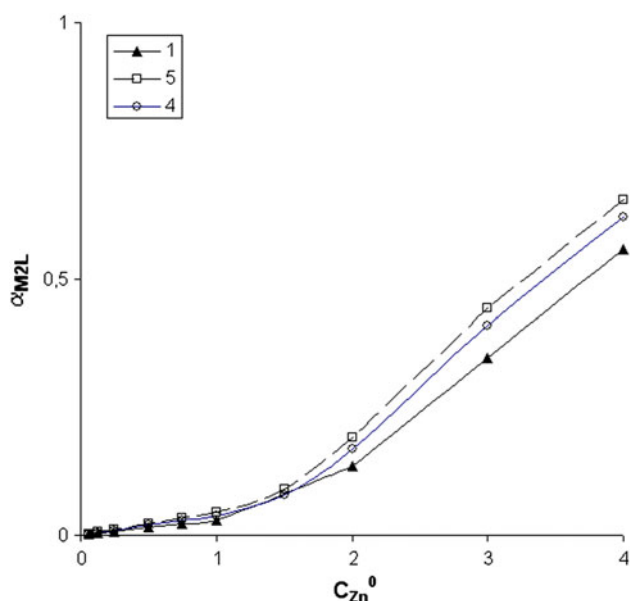
Fig. 3 The share of binuclear form M_2L during the extraction of Zn by calixarenes **1, 4, 5** depending on the initial metal concentration

change of calixarene molecule after coordination of the first $Zn(NO_3)_2$ fragment. The negative logarithmic value of the ligand effect for all three compounds implies that coordination of the first zinc atom results in unfavorable change of L hindering further formation of M_2L complex. It has to be noted that for the lower rim grafted calixarene **1** K_d value is the lowest that means the highest stability of ML form.

To compare the extraction data with the results of calorimetric titration in one-phase system (Fig. 4), we have estimated distribution of $Zn(NO_3)_2$ in the system pure NTFB/water. For initial $Zn(NO_3)_2$ concentrations in water phase 2 M and 4 M values of D_{Zn} are equal $1.9 \cdot 10^{-6}$ and

$4.6 \cdot 10^{-6}$. Using values of K_{11} and K_{12} and the average value of $K_{Zn} = D_{Zn}/(C_{NO3})^2 = 4.2 \cdot 10^{-7}$ complexation constants β_{11} and β_{12} for formation of $Zn(NO_3)_2L$ and $Zn_2(NO_3)_4L$ in NTFB were calculated ($\beta_{11}^{NTFB} = K_{11}/K_{Zn} = 7.14 \cdot 10^6$, $\beta_{12}^{NTFB} = K_{21}/K_{Zn}^2 = 4.02 \cdot 10^{10}$). Values of β_{11}^{NTFB}, β_{12}^{NTFB} are 2–3 orders higher than complexation constants in methanol (Table 1), mainly because of the worse solvation of zinc nitrate in weak polar NTFB. At the same time values of K_d depend only on the solvation of calixarene and its complexes with $Zn(NO_3)_2$ and change insignificantly from methanol to NTFB. Increase in K_d from NTFB to methanol by a factor of five may be determined by greater polarity of M_2L compared with ML and, therefore, by better solvation in polar solvent.

Structure of complexes

We have shown earlier that in 1:2 stoichiometry complexes of **4** with nickel and cobalt nitrates each metal atom is coordinated in similar way by two proximal PO-groups of the upper rim and two nitrate-anions [18]. In contrast to that in 1:2 complex of calixarene **1** the lower rim PO groups demonstrate two different types of cobalt coordination (Fig. 5).

Coordination environment of Co1 atom is formed by three oxygen atoms of phosphoryl groups of **1** and by two oxygen atoms of nitrate-ion. Distances Co1-O(P) vary in the range 1.941 (3)–2.004(4) Å that is approximately equal to the same lengths in complex with L = **4**. Nitrate anion has asymmetric coordination mode: bond length Co1-O112 is equal 2.000(3) Å, while the second oxygen atom (O111)
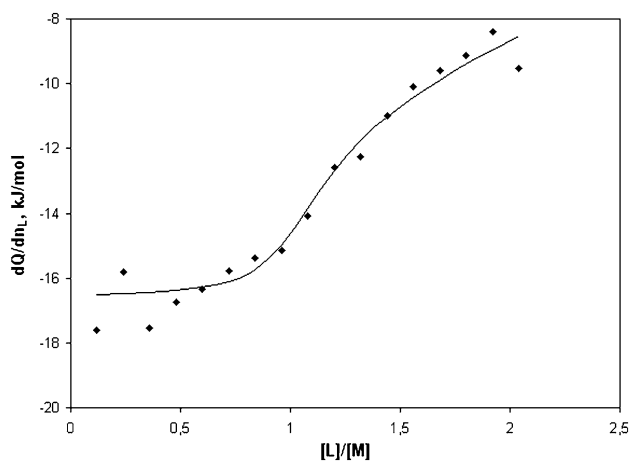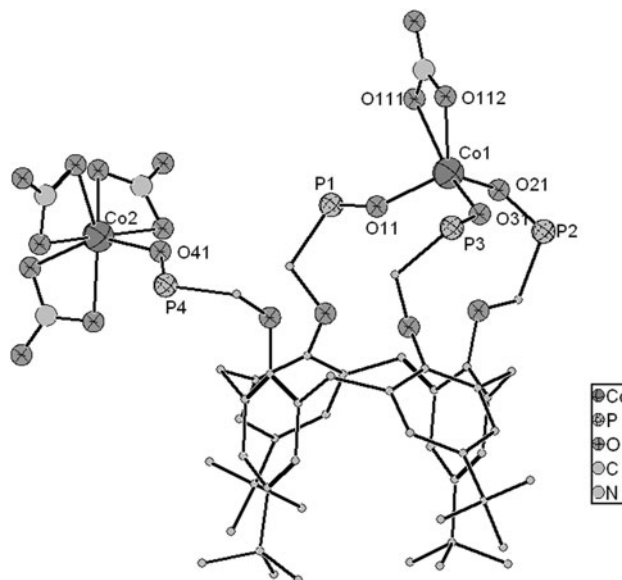

Fig. 4 Differential curve of calorimetric titration in methanol of $Zn(NO_3)_2$ (1.41 mM) by **1** (0.028 M): experimental data (points) and calculated data (line)

Fig. 5 Structure of $[Co_2(NO_3)_4 \, \mathbf{1}]$ complex. All hydrogen atoms and butyl substituents at phosphorus atoms are omitted for clarity

is 2.354(3) Å distant from Co1. Thus the closest environment of Co1 is distorted tetrahedron (O11, O21, O31, O112) with angles between Co–O bonds in the range 101.3(1)–120.4(1)°, supplemented with O111 on one of the faces. Co2 atom is surrounded by six oxygen atoms of three nitrate ions and one oxygen atom of the fourth PO-group of calixarene, thus having rather unusual for Co^{2+} heptacoordinated mode. Bond length Co2-O41 is equal 2,018(4) Å, that is 0.05 Å greater than average distance Co1-O(P). Nitrate anions are coordinated more symmetrically than in case of Co1: the difference between shortest (2.157(3) Å) and longest (2.236(5) Å) Co2-O(N) distance is lower than 0.1 Å. Bond lengths $N-O_{coord}$ (1.245–1.308 Å) are systematically longer than $N-O_{free}$ (1.215–1.217 Å) for all nitrate-ions. The whole molecule $[Co_2(NO_3)_4$ **1**] represents a zwitter-ionic structure with positively charged fragment $Co1(NO_3)^+$ and negatively charged $Co2(NO_3)_3^-$, intra-(8,687 Å) and shortest intermolecular (8,816 Å) distances Co1-Co2 being very close. Such zwitter-ionic structure should be more polar than the similar complex of the upper rim modified calixarene **4**. That change in polarity corresponds well with the decrease in K_d from **4** to **1** in weakly polar NTFB and with an increase in K_d for **4** from NTFB to more polar methanol due to enhancement of solvation of the polar M_2L form.

Symmetry of calixarene scaffold is close to C_{2v} (*flattened cone* conformation) both for **1** and **4** complexes. Planes of two from four arene rings are almost normal to [C4] plane including carbon atoms of methylene bridges Ar–**CH₂**–Ar (interfacial angles are equal to 81.6, 81.4 for the complex with L = **4** and 76.1 and 83.3 for complex with L = **1**). Two other benzene rings in respect to [C4] are at angles 140.5, 136.6 (L = **4**) or 134.7, 130.3 (L = **1**). Average angles between arene rings planes and [C4] are slightly lower for the complex with calixarene **1** modified on the narrow rim thus leading to the decrease in inner cavity volume compared with L = **4** modified on the wider upper rim.

Two types of nitrate groups (symmetric and asymmetric coordination) are also registered in IR-spectra. Each band of NO_3^- vibrations appear as asymmetric doublet with intensities corresponding to different number of NO_3^- coordinated to different cobalt atoms. The only band of PO stretching vibrations $\nu(PO) = 1123$ cm^{-1} confirms the coordination of all PO-groups.

Generally, the results obtained show that calix[4]arenes grafted at the lower rim with four phosphine oxide groups form most stable 1:1 complexes with M^{2+} due to the proximity of donor groups and better geometrical fitting ligand-cation. That is why lower rim functionalized L provide better recovery of M^{2+} in the field of ligand excess. At the same time the upper rim grafted calix[4]arene tetra-phosphine oxides are more inclined to formation of 1:2 and 2:1 complexes. Earlier we have shown that during the extraction of Ru/M complexes by monodentate R_3PO and upper rim grafted calixarenes ruthenium fragment coordinates to M^{2+}, sequences of recovery for M^{2+} and Ru/M complexes coinciding (Zn^{2+}, $Cu^{2+} > Co^{2+} > Ni^{2+}$) [9, 10, 19]. Therefore we can expect that lower rim grafted L will demonstrate the best recovery of Ru/Zn complexes and this system can be investigated for ruthenium extraction from HLW.

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