

Synthesis and cation complexation of calix[4]azacrowns and a spirobiscalix[4]azacrown

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Received: 12 July 2011 / Accepted: 30 July 2011 / Published online: 31 August 2011
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Abstract The synthesis and complexation properties of three new derivatives, one spirobiscalix[4]azacrown (**1**) and two calix[4]azacrown (**2** and **3**), are reported. Complexation studies of the three ligands toward transition and heavy metal cations have been carried out and monitored by UV absorption spectrophotometry in acetonitrile. Mononuclear complexes were detected for all complexes, whereas binuclear species (M_2L) were also formed in the case of ligand **1** with Cu^{2+} and Pb^{2+} . The extraction properties of **1**, **2** and **3** toward Cu^{2+} , Zn^{2+} , Pb^{2+} , Ag^{2+} and Cd^{2+} are also reported. The results showed that complexation is the main factor affecting extraction with ligands **2** and **3**, while with ligand **1** it is not.

Keywords Calixarene · Calixazacrown · Complexation · Stability constant · Extraction

Introduction

Calixarenes have been widely exploited in all areas of supramolecular chemistry over the past three decades and chemists have synthesized many types of receptors based on them for complexing cations, anions and neutral molecules, both in solution and solid state [1, 2]. Since Ungaro and co-workers [3] first reported the selective binding of potassium (relative to sodium and lithium) by 1,3-calix[4]crown-5 ligands, the use of crown ethers covalently bound to calix[4]arenes has been studied extensively for selective extraction of complex cations [4]. Such calix-crown studies have been expanded to include calix[4]arene with modified crown structures. Among them, the family of calix[4]azacrowns refers to molecules combining calix[4]arene elements and polyaminoalkylene chains attached to the calixarenes via amido functions, which may also serve as both linking functions and chelating groups [5]. The amido functions arise from the method of preparation. The linkage of an azacrown unit onto a calix[4]arene is often conducted by coupling diacylchloride or dimethyl- or diethylester calix derivatives with a polyaminoalkylene diamino compound to give a bridged calix(aza)crowns [5]. The complexing properties of such derivatives have been reported. Calix(aza)crowns show low affinity for divalent (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) and trivalent (Sc^{3+} , Y^{3+} , In^{3+} , Gd^{3+} and Bi^{3+}) [6] metal cations, yielding complexes with various stoichiometries (including ML, M_2L and ML_2) [7]. After complexation of lanthanide ions (Eu^{3+} , Tb^{3+} , Nd^{3+} , Er^{3+} and La^{3+}), calix[4]azacrowns were used as molecular scaffold groups that could be used to generate visible and near-infrared luminescence [8]. In the crystal state, some calix[4]azacrowns have been shown to form tubular architectures, with the channels filled by methanol [9]. In

Dedicated to Professor Leonard F. Lindoy, a great chemist, on the occasion of his 75th birthday.

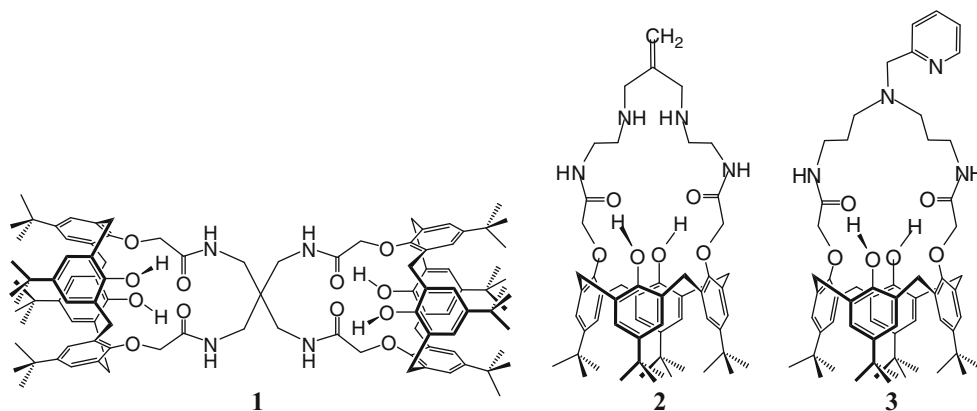
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the literature examples, the calixarene unit of various calix[4]azacrowns is intramolecularly bridged either by one bridge (at the 1,3-positions) or by two bridges (at the 1,2;3,4-positions).

Based on previous work [10], we now report the synthesis of a novel derivative of a double-calixazacrown, spirobiscalix[4]azacrown (**1**), in which two calix[4]arenes are connected via a spiro C-atom with the two calix[4]arene moieties in cone conformations [10–13]. We also report the synthesis of the two new calix[4]azacrowns (**2**) and (**3**). A comparative study of the liquid extraction and complexation properties of the three ligands conducted in acetonitrile is also presented.



Experimental

Materials and physical measurement

All reagents and solvents for synthesis were commercial and used without further purification. The supporting electrolyte, Et_4NClO_4 , for the stability constant measurement was purchased from Acros and the other metal perchlorates from Fluka. All the reactions were performed under a N_2 atmosphere. TLCs were performed on Silica gel 60 F254 (Merck 1.05554.0001). SiO_2 (Geduran 1.11567) was used for column chromatography. ^1H NMR spectra were recorded at 300 K using a 300 MHz Bruker SY 200 spectrometer. Chemical shifts (δ) are quoted relative to the internal reference standard, tetramethylsilane (TMS). Coupling constants (J) are given in Hertz. MALDI TOF mass spectra were measured on a Biflex Bruker instrument. Melting points were measured using an electrothermal Buchi 535 melting point (Mp) apparatus and reported uncorrected. Microanalyses were carried out at the Service de Microanalyse de l'ULP in Strasbourg. *p*-*tert*-Butylcalix[4]arene 1,3-dimethylester [14, 15], 2,2-bis(aminomethyl)propane-1,3-diamine [16], 1,1-bis(2'-aminoethylaminomethyl)-ethene [17],

and *N*¹-(3-aminopropyl)-*N*¹-(pyridin-2-ylmethyl)propane-1,3-diamine [18] were all prepared by the literature methods.

The extraction experiments of metal picrates from water to dichloromethane were performed according to a procedure described in the literature [19, 20]. Equal volumes (5 mL) of neutral aqueous solution of metal picrate salts (2.5 mol L^{-1}) and CH_2Cl_2 solution (5 mL) of calixarene derivatives (2.5 mol L^{-1}) were mixed and magnetically shaken in thermoregulated water at 20 °C for 30 min and then left standing for 2 h in order to obtain a complete separation of the two phases. The concentration of metal picrate remaining in the aqueous phase was determined from the absorbance A at 355 nm. The percentage

extraction was determined from the following expression in which A_0 is the absorbance in UV/visible of the aqueous solution of a blank experiment without calixarene

$$\%E = 100(A_0 - A)/A_0$$

Preparation of **1**

1,3-Dimethylester *p*-*tert*-butyl calix[4]arene (595 mg, 0.75 mmol) and 2,2-bis(2-aminomethyl)propane-1,3-diamine (49 mg, 0.37 mmol) in $\text{C}_6\text{H}_5\text{CH}_3/\text{CH}_3\text{OH}$ (1/1, 20 mL) were refluxed with stirring for 20 h. The solvents were evaporated under reduced pressure and the residue was chromatographed on a silica column using $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (98/2) as eluent. Pure compound (**1**) was obtained as a white solid (100 mg, 31%). Mp = 215–216 °C. ^1H NMR (300 MHz) δ (ppm): 8.48 (t, $J = 5.0$ Hz, 4H, CONH), 7.90 (s, 4H, OH), 7.07 (s, 8H, ArH), 6.96 (s, 8H, ArH), 4.55 (s, 8H, ArOCH₂), 4.11 (d, $J = 14.0$ Hz, 8H, AB system, ArCH₂Ar), 3.87 (d, $J = 5.0$ Hz, 8H, CONHCH₂), 3.44 (d, $J = 14.0$ Hz, 8H, AB system, ArCH₂Ar) 1.27 (s, 36H, C(CH₃)₃), 1.06 (s, 36H, C(CH₃)₃). MW = 1590.14 calcd for $\text{C}_{101}\text{H}_{128}\text{N}_4\text{O}_{12}$. MALDI-TOF: $m/z = 1590.62$. Anal. calcd.: C, 76.30; H, 8.10. Found C, 76.17; H, 8.13.

Preparation of **2**

1,3-Dimethylester *p*-*tert*-butyl calix[4]arene (595 mg, 0.75 mmol) and 1,1-bis(2'-aminoethylaminomethyl)-ethene (64 mg, 0.37 mmol) in C₆H₅CH₃/CH₃OH (1/1, 25 mL) were stirred at room temperature for 48 h. The solvents were evaporated under reduced pressure and the residue was chromatographed on a silica column using CH₂Cl₂/CH₃OH (95/5) as eluent. Pure *p*-*tert*-butyl calix[4]arene vinylazacrown-7 (**2**) was obtained as a white solid (300 mg, 44%). Mp = 236–237 °C. ¹H NMR (300 MHz) δ (ppm): 8.73 (t, *J* = 5.0 Hz, 4H, CONH), 7.09 (s, 4H, ArH), 6.76 (s, 4H, ArH), 4.94 (s, 2H, C = CH₂), 4.55 (4H, ArOCH₂), 4.20 (d, *J* = 14.0 Hz, 4H, AB system, ArCH₂Ar), 3.56 (q, *J* = 6.0 Hz, 4H, CONHCH₂), 3.42 (s, 2H, OH), 3.36 (d, *J* = 14.0 Hz, 4H, AB system, ArCH₂Ar), 3.35 (t, *J* = 6.0 Hz, 4H, CONHCH₂CH₂NHCH₂), 2.85 (t, *J* = 6.0 Hz, 4H, CONHCH₂CH₂), 1.29 (s, 18H, C(CH₃)₃), 0.93 (s, 18H, C(CH₃)₃). MW = 901.23 calcd for C₅₆H₇₆N₄O₆. MALDI-TOF: *m/z* = 902.39. Anal. calcd.: C, 74.63; H, 8.50. Found C, 74.24; H, 8.42.

Preparation of **3**

1,3-Dimethylester *p*-*tert*-butyl calix[4]arene (397 mg, 0.50 mmol) and *N*¹-(3-aminopropyl)-*N*¹-(pyridin-2-ylmethyl) propane-1,3-diamine (56 mg, 0.25 mmol) in C₆H₅CH₃/CH₃OH (1/1, 15 mL) were stirred at room temperature for 72 h. The solvents were evaporated under reduced pressure and the residue was chromatographed on a silica column using CH₂Cl₂/CH₃OH (94/6) as eluent. Pure *p*-*tert*-butyl calix[4]arene pyridylmethylazacrown-6 (**3**) was obtained as a white solid (240 mg, 50%). Mp = 221–222 °C. ¹H NMR (300 MHz) δ (ppm): 8.50 (d, *J* = 5.0 Hz, 1H, pyH), 8.23 (t, *J* = 5.0 Hz, 2H, CONH), 7.65 (t, *J* = 5.0 Hz, 1H, pyH), 7.47 (d, *J* = 5.0 Hz, 1H, pyH), 7.14 (t, *J* = 5.0 Hz, 1H, pyH), 7.11 (s, 4H, ArH), 6.70 (s, 4H, ArH), 6.36 (s, 2H, OH), 4.50 (s, 4H, ArOCH₂), 4.16 (d, *J* = 14.0 Hz,

4H, AB system, ArCH₂Ar), 3.77 (s, 2H, pyCH₂), 3.49 (q, *J* = 6.0 Hz, 4H, CONHCH₂), 3.37 (d, *J* = 14.0 Hz, 4H, AB system, ArCH₂Ar), 3.67 (t, *J* = 6.0 Hz, 4H, CONHCH₂CH₂CH₂), 1.78 (q, *J* = 6.0 Hz, 4H, CONHCH₂CH₂), 1.31 (s, 18H, C(CH₃)₃), 0.88 (s, 18H, C(CH₃)₃). MW = 951.28 calcd for C₅₆H₇₆N₄O₆. MALDI-TOF: *m/z* = 952.39. Anal. calcd.: C, 75.75; H, 8.26. Found C, 75.24; H, 8.32.

Results and discussion

Overall stability constants, β_{xy}^C being the concentration ratio $[M_xL_y^{n+}]/[M^{n+}]_x[L]_y$ and corresponding to the general equilibrium:

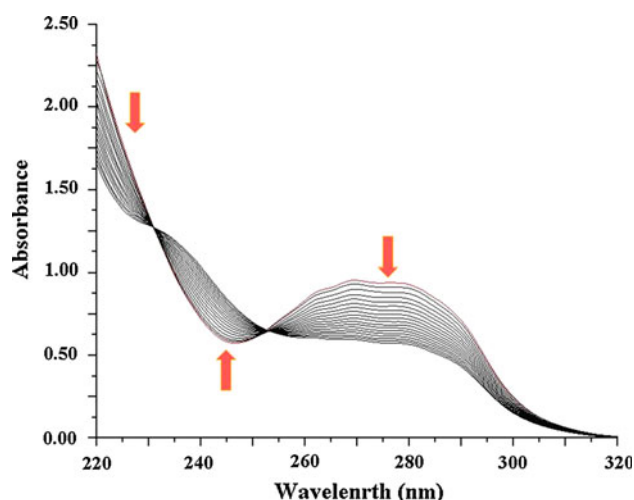
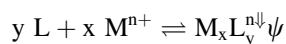


Fig. 1 Changes in the absorption spectrum of ligand **3** upon addition of Pb(ClO₄)₂ in acetonitrile; the ligand concentration was **3**: 4.0 × 10⁻⁵ mol L⁻¹, 0 ≤ *R* ≤ 1.4; concentration of NEt₄ClO₄ = 0.01 mol L⁻¹

Table 1 Logarithm of stability constants (log β_{xy}) for transition and heavy metal cations in acetonitrile (*T* = 25 °C and *I* = 10⁻² mol L⁻¹)

Cations	Ligand 1		Ligand 2		Ligand 3	
	M:L	log β _{xy}	M:L	log β _{xy}	M:L	log β _{xy}
Cu ²⁺	2:1	9.62 ± 0.09	1:1	4.63 ± 0.01	1:1	5.76 ± 0.05
Ni ²⁺	1:1	6.02 ± 0.05	1:1	4.44 ± 0.01	1:1	4.25 ± 0.05
Zn ²⁺	1:1	5.68 ± 0.05	1:1	4.75 ± 0.10	1:1	4.38 ± 0.04
Pb ²⁺	2:1	8.82 ± 0.07	1:1	5.64 ± 0.05	1:1	5.32 ± 0.08
Hg ²⁺	a	a	1:1	4.23 ± 0.03	1:1	3.78 ± 0.03
Cd ²⁺	a	a	1:1	4.59 ± 0.03	1:1	3.65 ± 0.05
Ag ⁺	a	a	1:1	5.28 ± 0.01	a	a

^a Only small spectral changes observed

(where M^{n+} = metal cation concentration, L = ligand concentration)

They have been determined in acetonitrile by UV/vis spectrophotometry at 25 °C, with the ionic strength maintained at 0.01 mol L⁻¹ by Et₄NClO₄.

The absorption spectra of each ligand (at 4×10^{-5} mol L⁻¹) in acetonitrile with increasing concentration of different metal ions (see Table 1) were recorded between 250 and 295 nm. Figure 1 illustrates the complexation of Pb²⁺ with ligand 3. Generally the metal ion to ligand ratio, R , did not exceed ten and the equilibrium was quasi-instantaneous for all systems. Addition of the respective metal ions to the ligand showed, on the whole, sufficient change in the spectra to allow the analysis of the resultant data using the program “Letagrop” [21]. The log $\beta_{xy}\psi$ values given in Table 1 correspond to the arithmetic means of at least three independent experiments.

The UV absorption spectra of 1, 2, and 3 in acetonitrile were in general dominated by a structured band between 250 and 295 nm. This corresponds to the $\pi \rightarrow \pi^*$ transitions of the aromatic moieties. Upon addition of metal perchlorates, the spectra in most cases showed distinct changes (Fig. 1) accompanied by two isosbestic points (232 and 253 nm).

Table 1 lists the stability constant (log β_{xy}) data for the transition and heavy metal complexes. The data are in accord with the formation of mononuclear species by the three ligands, except that Cu²⁺ and Pb²⁺ form complexes of 1:2 (M:L) stoichiometry with ligand 1. The absence of observable spectral changes for some examples was taken as indicative of the formation of very weak complexes (log $\beta_{xy} \leq 1$). Despite the presence of two cavities, ligand 1 forms mononuclear species with Ni²⁺ and Zn²⁺, suggesting that the inclusion of the first cation induces a rearrangement of the two cavities that disadvantages the second inclusion. Nevertheless the two mononuclear complexes are both quite stable ($\beta_{11} \approx 10^6$). In contrast, the complexation of Cu²⁺ and Pb²⁺ by ligand 1 forms a binuclear species (M₂L), indicating that each crown cavity is suitable for coordination of these metal ions. It seems that one metal ion is possibly coordinated by an amide group as well as by oxygens from the calixarene backbone. The metal complexation in acetonitrile for ligands 2 and 3 shows somewhat unexpected relatively strong binding for Hg²⁺, Cd²⁺ and Ag⁺. While the complexation of these cations with ligand 1 was not observed, Pb²⁺ formed a binuclear complex which was only ten times less stable than the Cu²⁺ binuclear complex. Compared to spirobiscalix[4]azacrown (1), the calix[4]azacrowns (2) and (3) formed only mononuclear complexes with all cations although Ag⁺ does not seem to be complexed by ligand 3. The stabilities of 1:1 complexes formed with ligand 2 show a comparable affinity for the present transition metals ($10^{4.44} < \beta_{11} < 10^{4.75}$). Although the

Table 2 Extraction percentages (%E)^a for the selected transition and heavy metal picrates (Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺ and Pb²⁺) from water into dichloromethane, at 20 °C

Cation	Ligand		
	1	2	3
Cu ²⁺	5.1	48.7	70.1
Zn ²⁺	1.3	49	4
Ag ⁺	15	53.4	30.5
Cd ²⁺	20.5	48.3	23.8
Pb ²⁺	5.5	55.6	33

^a Standard deviation σ_{N-1} of the mean of n experiments: 0.05–0.1

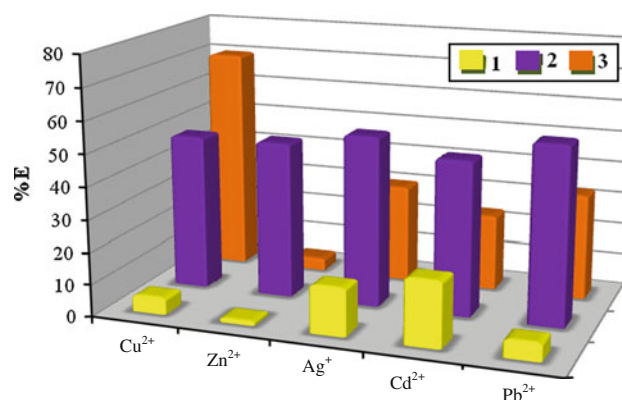


Fig. 2 Extraction diagram corresponding to Table 2

complexation of heavy metal ions is characterized by a selectivity for Pb²⁺ followed by Ag⁺ ($S_{Pb^{2+}/Hg^{2+}} = 14$). The stability of Hg²⁺ and Cd²⁺ are comparable to the metal ions. Concerning ligand 3, the selectivity profile is similar to ligand 1 and shows particular affinity toward Cu²⁺ and Pb²⁺, while weak interaction was revealed towards Hg²⁺, Cd²⁺ and Ag⁺. This weak interaction towards heavy metal cations could probably be improved by the introduction of soft donor atoms or by increasing the cavity size of the azacrown. According to the literature [7], the introduction of a pyridylmethyl moiety onto the secondary nitrogen of bis(amino)propylamine causes a significant change in the complexing properties of this ligand leading to a bis-ligand species with particular transition metals, but not with the copper, which forms a binuclear species. The pyridyl group is also able to coordinate the metal cation and promotes formation of the 1:1 stoichiometry.

Extraction percentages (%E) for transition and heavy metal picrates (Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺, Pb²⁺) from water by (1–3) into dichloromethane at 20°C (employing neutral pH) are reported in Table 2 (Fig. 2). The results yield an estimation of the extraction abilities of these ligands towards the above metal cations.

The three ligands have different extraction behaviour. Ligand **1** is a generally poor extractant with best extractability being toward Ag^+ and Cd^{2+} (with a %E of 15 and 20.5, respectively). These results do not parallel the complexation results since these two cations were not observed to be complexed. This result shows that complexation is not the major driving force for the extraction of these two metals observed with ligand **1**.

However compound **2** extracts the five cations with approximately the same %E ($48.7 < \%E < 55$). This result is in good agreement with those from the complexation study showing that the extraction is governed by complexation in these cases contrary to ligand **1**.

Ligand **3** shows enhanced selectivity for Cu^{2+} with a high extraction level of 70%. Excellent selectivity over Zn^{2+} , for which the extraction percentage is very low 4%, followed by Cd^{2+} with 24% and Ag^+ and Pb^{2+} with about 30% is observed. The affinity for Cu^{2+} was also observed in the complexation study. The extraction behaviour for ligand **3** almost parallels the observed complexation behaviour, except towards Ag^+ , for which no spectral changes were observed.

Conclusion

In general terms the present results give evidence for complexation selectivity towards Cu^{2+} and Pb^{2+} across all three ligands. Ligand **1** with the smallest cavity formed the most stable mononuclear species with Ni^{2+} and Zn^{2+} compared to ligands **2** and **3**. Ligand **1** showed the highest overall selectivity compared to its homologues, yielding a M_2L complex with copper from the transition metal series and lead from the heavy metal series. These complexation selectivities can be possibly rationalized in terms of the rigidities of the macrocycle cavities. From the extraction study we can conclude that complexation is the main factor influencing the extraction abilities of ligands **2** and **3**, however, the profiles for complexation and extraction do not fully coincide. This latter observation may reflect the effect of ion pairing in the case of ligand **1**, or may suggest more complicated processes occurring at the interface (water/dichloromethane) that can yield unexpected complexation/extraction behavior.

Acknowledgments This research was supported by the National Research Foundation of Korea (Grant 2010-00275) and Kosin University (2010).

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