Substituent control of potassium and rubidium uptake by asymmetric calix[4]-thiacalix[4]tubes

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Received 6th February 2006, Accepted 20th February 2006
First published as an Advance Article on the web 13th March 2006
DOI: 10.1039/b601709f

Herein we report on the synthesis and ionophore properties of the first asymmetric *p-tert*-butylcalix[4]-*p*-R-thiacalix[4]tubes **7a–c** (R = *t*-Bu, H, 1-adamantyl). The target compounds were obtained by the condensation of tosyloxyethoxy-*p-tert*-butylcalix[4]arene with the corresponding *p*-R-thiacalix[4]arenes in the presence of K_2CO_3 in acetonitrile. The complexation with sodium, potassium and rubidium iodides was studied in $CDCl_3$–CD_3OD (4 : 1) medium by means of ^1H NMR measurements. It was found that the ionophore properties of calixtubes **7a–c** are controlled by the character of the substituents at the upper rim of the thiacalix[4]arene fragment and it was shown that only the molecular tube **7c** with an adamantane-containing thiacalixarene unit is capable of quantitatively binding potassium (swiftly) and rubidium (slowly) cations.

Introduction

Selective recognition and extraction of alkali metals are currently interesting for researchers.[1] Recently biscalixarenes composed of two lower rim ethylene linked calix[4]arene moieties, calix[4]tubes **1** and **2** (Fig. 1), have attracted considerable interest due to their exceptional selectivity towards potassium over other group IA cations.[2] Calix[4]arene units in these compounds serve as size discriminatory filters for cations entering in a manner similar to that for tyrosine-based filters in cellular potassium ion channels,[3] and rates of complexation were found to depend on the character of the substituents at the upper rims of the calix[4]arene units.[2b,d]

The calix[4]tubes family has been extended with the symmetric thiacalix[4]tube **3**.[4] Due to the replacement of the methylene bridges with sulfur compound **3** possesses entrance filters and a molecular cavity of slightly larger size in comparison with the parent ligands **1** and **2**. However thiacalix[4]tube **3** was characterized also by considerably higher conformational flexibility resulting in poor binding ability and selectivity towards alkaline metal cations. Compounds **1** and **2** were also found to form complexes with silver(I)[5,2c] and thallium(I)[6] ions with a cation located within the oxygen donor cryptand-like enclosure or in the aromatic cavity of a calix[4]arene unit.

Being interested in further exploring chemistry of these ionophores we investigated new calix[4]tubes bearing calix[4]- and thiacalix[4]arene units simultaneously. In contrast to calix[4]tubes **1–3** these new ligands have different calixarene filters for cation entry. Moreover, the replacement of one thiacalix[4]arene fragment in heterocalix[4]tube **3** with a classical one should give heterotubes with a slightly smaller molecular cavity, higher rigidity and, consequently, different ionophore properties. In this paper we report on the synthesis of the first asymmetric *p-tert*-butylcalix[4]-*p*-R-thiacalix[4]tubes **7** (R = *t*-Bu, H, 1-adamantyl) and their complexation properties towards selected group IA metal cations (Na^+, K^+, Rb^+).

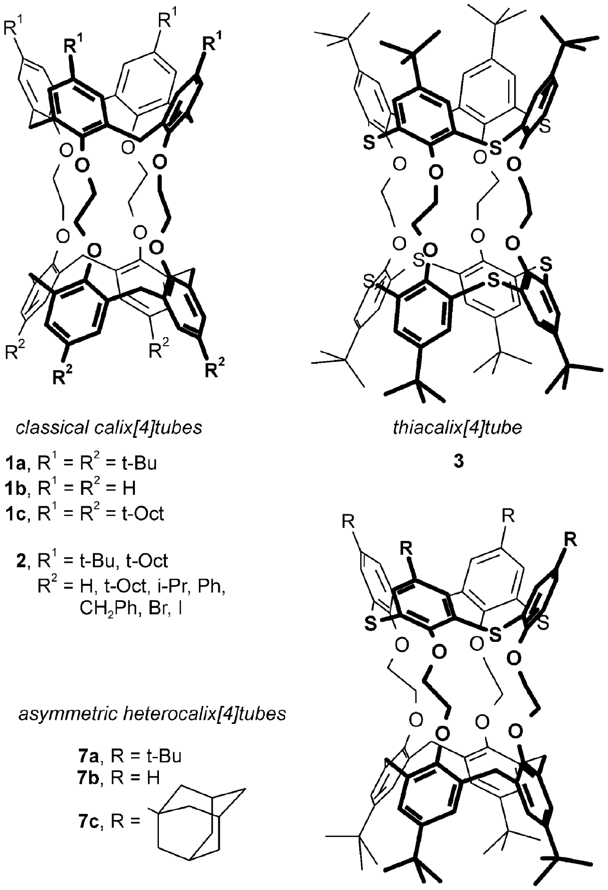

Fig. 1 Calix[4]tubes.

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Results and discussion

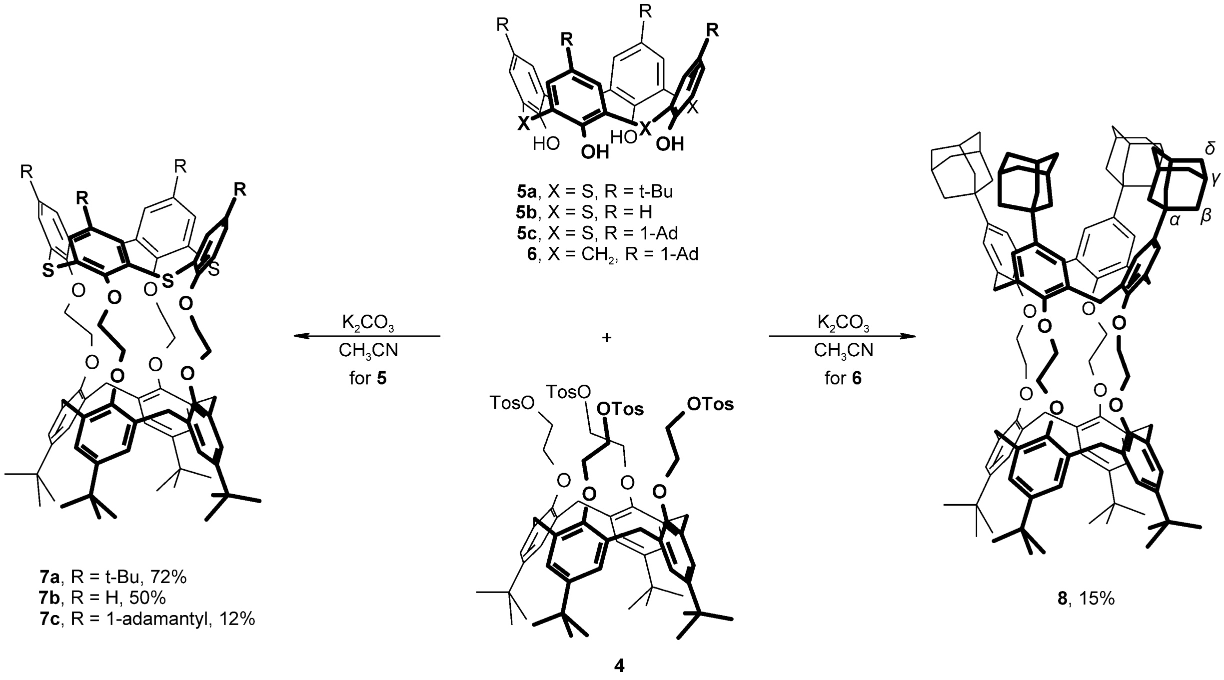
Synthesis and NMR structural determination

The synthesis of calix[4]-thiacalix[4]tubes **7a–c** was performed *via* the condensation reaction of known *p-tert*-butylcalix[4]arene tetratosylate **4**[7] with selected *p*-R-thiacalix[4]arenes **5a–c** (R = *t*-Bu,[8] H,[9] 1-adamantyl[10]) in the presence of K_2CO_3 in boiling acetonitrile (Scheme 1) according to the procedure developed for calix[4]tube preparations.[2a,b] These conditions were proved to be suitable for the synthesis of heterocalix[4]tubes **7** in moderate to good yield.

In order to clarify the influence of adamantane substituents at the calixarene upper rim on cation binding, classical calix[4]tube **8** derived from the *p*-(1-adamantyl)calix[4]arene **6**[11] and bis-calix[4]arene **1a** were also prepared.

All compounds synthesized were fully characterized by NMR (^{1}H, 1D NOE and ^{13}C) and mass spectrometry (ESI-MS). Since ^{1}H and ^{13}C NMR spectra (see Experimental section) contain doubled sets of resonance signals (excluding signals of methylene bridges), (thia)calix[4]arene units in heterotubes **7** as well as in asymmetric classical calix[4]tube **8** possess C_{2v} symmetry and are connected by ethylene linkers of two types (*trans* and *gauche*) in a manner described for known calix[4]tubes **1** and **2**.[2b]

The fact that formally C_4-symmetrical calix[4]tubes appear in spectra as less symmetrical ones (C_{2v}) was attributed to the conformational properties of the calixarene units forming the tube.[2b] Macrorings were proved to undergo *flattened cone* (C_{2v}) to *flattened cone* (C'_{2v}) interconversion which is slow on the NMR time-scale (Fig. 2). Rates of these motions were measured and k_{exch} in $CDCl_3$ were found to be ~1–3 s^{-1} (depending on the upper rim substituents) for classical tubes **1–2** at 328 K and close to



Scheme 1 Synthesis of heterotubes based on calix[4]arenes and thiacalix[4]arenes.

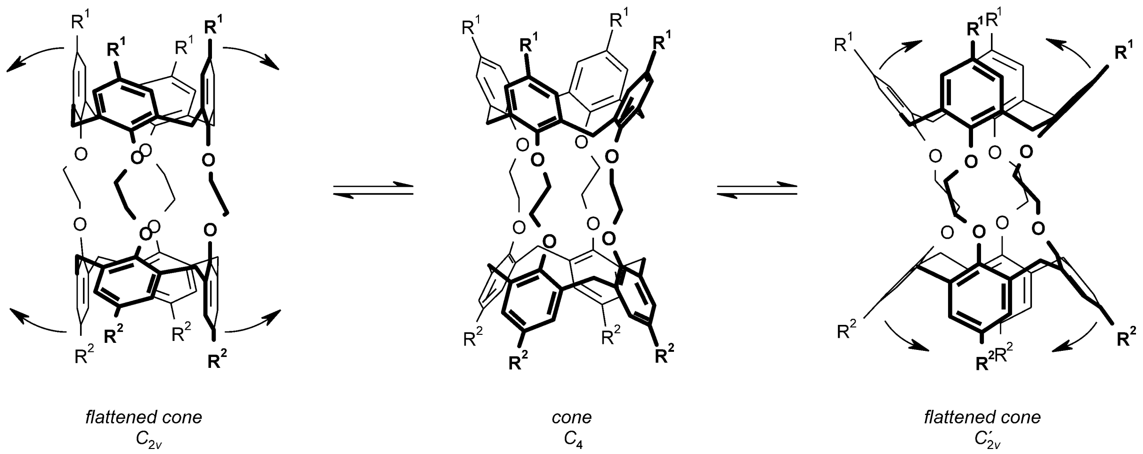


Fig. 2 Conformational interconversions in calix[4]tubes.

9 s^{-1} for thiacalixtube **3** at 273 K.[4] Such a difference characterizes the significant increase of conformational mobility of calix[4]tube molecules upon replacement of all ArCH$_2$Ar fragments with ArSAr motifs.

To investigate the mobility of the calix[4]tubes synthesized, dynamic and 2D EXSY NMR experiments were performed. Upon heating to 328 K in CDCl$_3$ ^{1}H NMR spectra of heterotubes **7** undergo line broadening which is most significant in the case of calixtube **7c** bearing adamantane groups at the upper rim of the thiacalixarene unit (Fig. 3). On the other hand the spectrum of classical tube **8** remains without remarkable changes. 2D EXSY NMR spectroscopy describes conformational mobility more or less quantitatively.[12] The exchange NMR experiments for aromatic protons were performed at 303 K and 328 K for tubes **7a,b** and **8**, and at 303 K for **7c** since the experiment should be applied before significant line broadening occurs. In all cases large exchange cross-peaks were observed proving the conformational interconversion takes place. The quantitative exchange data extracted from the spectra allow comparison of the mobility of the calix[4]tubes synthesized (the same experiment applied to classical tube **1a** at 328 K gave a k_{exch} value which is in good agreement with the published one[2b]).

It was found that the mobility of classical tube **8** is very close to that of tube **1a** and the k_{exch} was estimated to be ~1 s^{-1} at 328 K. At the same time k_{exch} for heterotubes **7** have the same values but at 303 K. EXSY experiments for **7a,b** performed at 328 K showed $k_{\text{exch}} \sim 2.5$ s^{-1}. Thus the internal mobility of heterotubes increases in the order **7b** ≈ **7a** < **7c**. Hence the obtained heterotubes **7** are more flexible than classical tubes (like **1** and **8**) but much more rigid in comparison with thiacalixtube **3**.

^{1}H NMR spectra of the newly synthesized compounds were also recorded in a CDCl$_3$–CD$_3$OD (4 : 1, v/v) mixture since the complexation of heterotubes with alkali cations was investigated in these solutions. We were surprised with the significant line broadening that occurred exclusively for adamantane containing heterotube **7c** (Fig. 3). On the other hand no notable line broadening was observed for adamantylated classical calix[4]tube **8** upon increasing the solvent polarity.

Thus the data reported showed that the dynamic properties of calix[4]tubes are significantly influenced both by the macroring type (classical of thiacalixarene) and by the structure of the upper rim substituents.

Complexation study

The exceptional complexation affinity and selectivity towards potassium cations over other alkali metals and barium is the most impressive property of calix[4]tubes **1** and **2**. In the present study we investigated the complexation between heterotubes **7** and Na$^+$, K$^+$, Rb$^+$ ions by means of ^{1}H NMR measurements. Classical calix[4]tubes **1a** and **8** were also tested in order to clarify the role of the thiacalixarene unit and the upper rim substituents in the ionophore behavior of heterotubes **7**.

The experiments were performed as follows. The solution of calix[4]tube (1 μmol) in CDCl$_3$ (0.54 cm^3) was added to the NMR sample tube containing the appropriate metal iodide (50 μmol) in CD$_3$OD (0.135 cm^3). The sample was sonicated for 1 min and ^{1}H NMR spectra were recorded at various times (starting from 5 min after mixing). Since complexations are accompanied by the structural reorganization of the ligand molecules followed by the increase of symmetry from C_{2v} to C_{4v}, ion uptakes were measured directly by the integration of the NMR signals of complexes and free ligands. Selected results are presented in Table 1.

Initially complexation with potassium was studied. It was observed that the heterotube **7c** bearing adamantane groups formed the potassium complex quantitatively and swiftly (Fig. 4a,b), while the biscalixarene **7b** with an unsubstituted thiacalix[4]arene upper rim did not demonstrate any binding ability towards potassium ions. The heterotube **7a** with a *p-tert*-butylthiacalix[4]arene unit occupies the intermediate position: an equilibrium with ~35% of complex was found to be achieved in 1–2 h after mixing of the

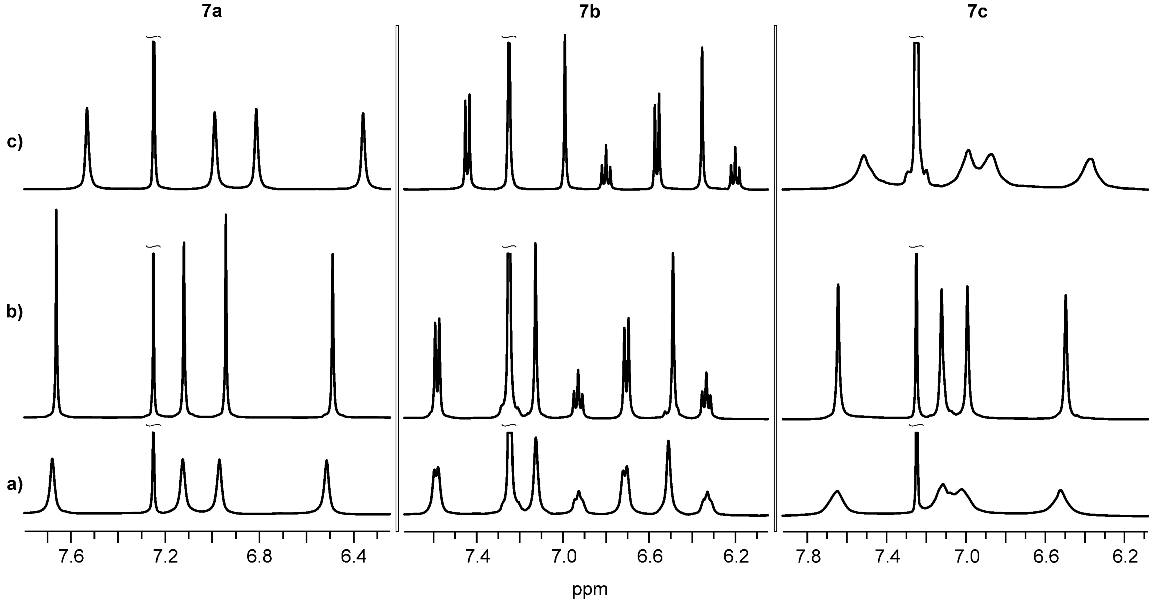


Fig. 3 Aromatic regions in ^{1}H NMR spectra of calixtubes **7**: (a) CDCl$_3$, 328 K; (b) CDCl$_3$, 303 K; (c) CDCl$_3$–CD$_3$OD (4 : 1), 303 K.

Table 1 Uptake (%) of alkali metal ions by calixtubes **1a**, **7** and **8**

		Tube				
Ion	Time	**1a**	**7a**	**7b**	**7c**	**8**
Na^+	144 h	0	0	0	0	0
K^+	10 min	100	22.1	0	100	100
	1 h		31.9	0		
	2 h		32.6	0		
Rb^+	10 min	1.6	1.0	0	13.3	4.9
	1 h	2.9	1.8	0	21.6	6.3
	12 h	6.8	5.2	0	42.4	8.9
	48 h	10.8	9.4	0	61.7	10.8
	144 h	15.7	15.0	0	83.1	12.6
	312 h				96.3	

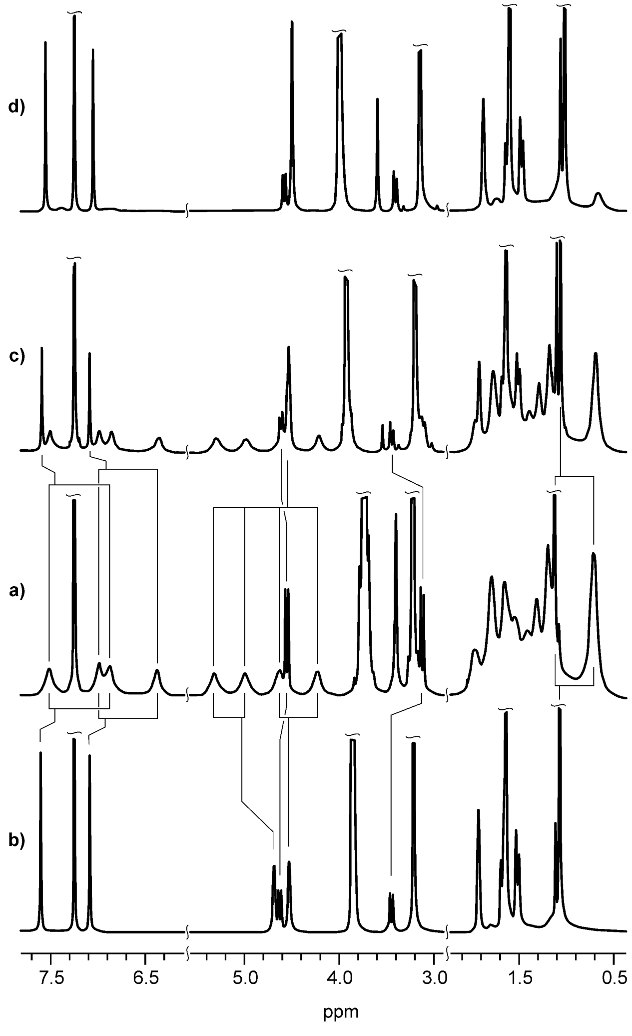


Fig. 4 ^{1}H NMR spectra of **7c** and its mixtures with KI and RbI in $CDCl_3$–CD_3OD (4 : 1): (a) pure **7c**; (b) **7c** + KI, 10 min; (c) **7c** + RbI, 1 h; (d) **7c** + RbI, 312 h.

components. At the same time calix[4]tubes **8** and **1a** complexed potassium ions quantitatively in less than 5 min demonstrating that the replacement of *tert*-butyl groups with 1-adamantyl ones did not change the ionophore properties of classical tubes.

Then the complexation of calix[4]tubes with sodium and rubidium iodides was investigated. The data presented in Table 1 show that calix[4]tubes **1a**, **7** and **8** do not form any NMR detectable sodium complexes even within several days.

At the same time remarkable results were obtained for rubidium uptake. Classical tubes **1** and **2** with various substituents at the upper rim are known to bind rubidium cations slowly and far from quantitatively.[2a,b,d] Similarly the new classical tube **8** bearing adamantane fragments was found to be ineffective in complexation with rubidium. According to the data presented in Table 1 calixarene **8** has more or less the same binding affinity as known tube **1a**. Rubidium ion uptake by *tert*-butylthiacalix[4]arene based heterotube **7a** is comparable with that for classical tubes **1a** and **8**, while the removal of the thiacalixarene upper rim substituents in the case of **7b** resulted in complete loss of ionophore activity towards alkaline metals. Suddenly, slow (for several days) but almost quantitative rubidium uptake followed by C_{4v} symmetrical complex formation was observed for heterotube **7c** (Fig. 4a,c,d).

These data indicate that ligand **7c** containing an adamantane substituted thiacalix[4]arene unit possesses unique ionophore properties. The reasons could be explained in terms of the earlier suggested axial mechanism of complexation between calix[4]tubes and metal cations.[2b] According to this mechanism the ion upon complexation passes into the molecular tube through one of the calixarene gates (routes A, D, Fig. 5a) to be located between eight ether oxygen atoms. The increase of the gate size upon the replacement of the classical calixarene unit with a thiacalixarene one allows the rubidium cation (as well as sodium and potassium ones) to pass easily into the cryptand-like cavities of ligands **7** by route A. The efficiency of complexation is influenced also by the ability of the calix[4]tube to hold the complexed ion inside the internal cavity, or by the difficulty for the guest to leave the host molecule (routes B, C). The rise of potassium and rubidium uptake

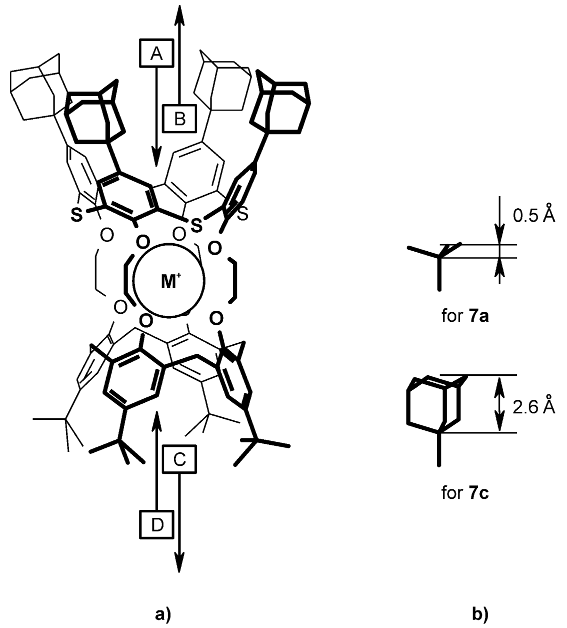


Fig. 5 (a) Possible routes for **7c**·M^+ complex formation/decomposition according to the axial mechanism (see text for notation). (b) 'Lipophilic layer thickness' for *tert*-butylated and adamantylated upper rims of calixtubes **7**.

upon the increase of the thiacalixarene upper rim substituent lipophilicity and bulkiness is concerned, perhaps, with higher shielding of the cation complexed from polar solvent molecules (methanol) resulting in higher complex stability. The comparison of the so-called 'lipophilic layer thickness' (the distance between the first carbon atom of the substituent and the plane passing through the outermost ones) shows that for 1-adamantyl groups this parameter is 5 times higher than for *tert*-butyl groups (Fig. 5b).

We also compared chemical shift values changes in the ^{1}H NMR spectra of ligands **7a,c** and **8** upon the complexation with potassium and rubidium. For all the calix[4]tubes low-field shift deviations of calixarene signals (aromatic, ArCH$_2$Ar, upper rim substituent) were observed (+0.07 to +0.43 ppm). However a significant difference in the behavior of OCH$_2$ signals was found. While a high-field shift change (−0.24 ppm) was observed for **8**, in ligands **7** the signals of OCH$_2$ groups connected to the classical calixarene units are slightly unshielded (+0.04 to +0.11 ppm) and the signals of methylene groups connected to the thiacalixarene units are significantly shielded (−0.48 to −0.58 ppm for potassium complexes and −0.65 to −0.66 ppm for rubidium complexes). Apparently these features of molecular tubes are concerned with a displacement of electronic density of the ligand towards the molecule equatorial plane caused by the close proximity charge of the complexed metal ion, and with the dissymmetry of heterotubes **7** due to the presence of bridging sulfur atoms in the thiacalixarene fragment.

Conclusions

The asymmetric heterotubes **7** constructed from calix[4]- and thiacalix[4]arene units have been synthesized and their complexation properties towards group IA metal cations (Na$^+$, K$^+$, Rb$^+$) have been studied. It was revealed that the type of upper rim substituents in the thiacalix[4]arene units of ligands **7a–c** (R = H, *t*-Bu, 1-adamantyl) influences significantly the metal uptake. Fast and effective complexation of *p*-(1-adamantyl)thiacalix[4]-*p*-*tert*-butylcalix[4]tube **7c** was observed only for potassium ions. At the same time this compound is the first ligand of this group of biscalixarenes which is capable of binding rubidium ions completely, although the complexation rate is slower than that for potassium ions. Since the adamantane containing classical tube **8** does not possess such unusual complexation properties, it could be concluded that this results from the unique combination of calixarene filter size and high cation-shielding ability of adamantane substituents in ligand **7c**.

Experimental

^{1}H, ^{13}C, 1D NOE, 2D EXSY and temperature-dependent NMR spectra were recorded on a Bruker Avance 400 spectrometer with the solvent signals as internal reference. The labeling of adamantane carbon atoms for signal attribution in ^{13}C NMR spectra of **7c**, **8** is indicated in Scheme 1. ESI mass spectra were recorded on an Agilent 1100 LC/MS instrument. Melting points are uncorrected. Chemicals were commercial grade and used without further purification. Solvents were purified and dried according to standard procedures. *p*-*tert*-Butylcalix[4]tube **1a**,[2a] tetra(tosyloxyethoxy)-*p*-*tert*-butylcalix[4]arene **4**,[7] *p*-*tert*-butylthiacalix[4]arene **5a**,[8] *p*-H-thiacalix[4]arene **5b**,[9] *p*-(1-adamantyl)thiacalix[4]arene **5c**[10] and *p*-(1-adamantyl)calix[4]arene **6**[11] were prepared according to the published procedures.

General procedure for the synthesis of calix[4]tubes 7a–c, 8

A suspension of tetrakis[(4-methylphenyl)sulfonyloxyethoxy]-calix[4]arene **4** (0.15 mmol), *p*-substituted thiacalix[4]arene **5a–c** or 1-adamantylcalix[4]arene **6** (0.162 mmol), and K$_2$CO$_3$ (0.1 g, 0.75 mmol) in acetonitrile (25 cm^3) was heated at reflux for 120 h. After cooling the solvent was removed under reduced pressure and the residue was triturated with a hot ethanol–water mixture (4 : 1). The crude product was separated by filtration, dried and purified by column chromatography (silica gel, hexane–chloroform (2 : 1)) to give calix[4]tubes as white solids.

Heterotube 7a. Yield 72%, mp > 350 °C. δ_H(400 MHz; CDCl$_3$) 7.66 (4 H, s, *thia*-ArH), 7.12 (4 H, s, *class*-ArH), 6.94 (4 H, s, *thia*-ArH), 6.49 (4 H, s, *class*-ArH), 5.43 (4 H, m, OCH$_2$), 5.07 (4 H, m, OCH$_2$), 4.79 (4 H, m, OCH$_2$), 4.66 (4 H, d, *J* 12.76 Hz, ArCH$_2$Ar), 4.35 (4 H, m, OCH$_2$), 3.25 (4 H, d, *J* 12.76 Hz, ArCH$_2$Ar), 1.33 (36 H, s, *t*-Bu), 0.85 (18 H, s, *thia*-*t*-Bu) and 0.82 (18 H, s, *class*-*t*-Bu). δ_C(100 MHz; CDCl$_3$) 160.93, 158.32, 156.12, 152.92, 145.86, 145.67, 144.53, 144.30 (ArC), 135.42, 134.10 (ArCH), 133.42, 131.92, 131.04, 127.88 (ArC), 125.47, 124.66 (ArCH), 73.96, 73.45, 73.17, 72.56 (OCH$_2$), 34.32, 34.07, 33.83, 33.58 (*C*(CH$_3$)$_3$), 32.01 (ArCH$_2$Ar), 31.75, 31.44, 31.10 and 30.85 (C(*C*H$_3$)$_3$). ESI-MS *m/z* 1496.6 ([M + Na]$^+$, 100%), 1495.7 (99), 1497.7 (55) for C$_{92}$H$_{112}$NaO$_8$S$_4$ (1495.7).

Heterotube 7b. Yield 50%, mp > 350 °C. δ_H(400 MHz; CDCl$_3$) 7.58 (4 H, d, *J* 7.83 Hz, *thia*-ArH), 7.13 (4 H, s, *class*-ArH), 6.93 (2 H, t, *J* 7.83 Hz, *thia*-ArH), 6.71 (4 H, d, *J* 7.83 Hz, *thia*-ArH), 6.49 (4 H, s, *class*-ArH), 6.33 (2 H, t, *J* 7.83 Hz, *thia*-ArH), 5.36 (4 H, m, OCH$_2$), 4.97 (4 H, m, OCH$_2$), 4.59 (4 H, d, *J* 12.63 Hz, ArCH$_2$Ar), 4.33 (4 H, m, OCH$_2$), 3.25 (4 H, d, *J* 12.63 Hz, ArCH$_2$Ar), 1.32 (18 H, s, *t*-Bu) and 0.82 (18 H, s, *t*-Bu). δ_C(100 MHz; CDCl$_3$) 161.96, 158.60, 156.10, 152.64, 144.69, 144.37 (ArC), 135.58 (ArCH), 135.38 (ArC), 134.92 (ArCH), 132.88, 131.75, 129.13 (ArC), 125.57, 124.70, 123.11, 122.55 (ArCH), 73.45, 73.01, 72.77, 72.42 (OCH$_2$), 34.08, 33.57 (*C*(CH$_3$)$_3$), 31.80 (ArCH$_2$Ar), 31.72 and 31.05 (C(*C*H$_3$)$_3$). ESI-MS *m/z* 1271.8 ([M + Na]$^+$, 100%), 1272.6 (83), 1273.4 (39) for C$_{78}$H$_{80}$NaO$_8$S$_4$ (1271.5).

Heterotube 7c. Yield 12%, mp > 350 °C. δ_H(400 MHz; CDCl$_3$) 7.64 (4 H, s, *thia*-ArH), 7.13 (4 H, s, *class*-ArH), 6.99 (4 H, s, *thia*-ArH), 6.49 (4 H, s, *class*-ArH), 5.45 (4 H, m, OCH$_2$), 5.11 (4 H, m, OCH$_2$), 4.75 (4 H, m, OCH$_2$), 4.67 (4 H, d, *J* 12.63 Hz, ArCH$_2$Ar), 4.35 (4 H, m, OCH$_2$), 3.25 (4 H, d, *J* 12.63 Hz, ArCH$_2$Ar), 2.20–1.35 (60 H, m, AdH), 1.33 (18 H, s, *t*-Bu) and 0.83 (18 H, s, *t*-Bu). δ_C(100 MHz; CDCl$_3$) 161.25, 158.65, 156.06, 153.01, 146.05, 145.83, 144.44, 144.28 (ArC), 135.43, 134.15 (ArCH), 133.33, 131.98, 130.73, 127.72 (ArC), 125.42, 124.64 (ArCH), 74.14, 73.51, 73.12, 72.66 (OCH$_2$), 43.46, 42.68 (AdC$^\beta$), 36.81, 36.57 (AdC$^\delta$), 35.88, 35.44 (AdC$^\alpha$), 34.06, 33.58 (*C*(CH$_3$)$_3$), 32.08 (ArCH$_2$Ar), 31.75, 31.10 (C(*C*H$_3$)$_3$), 29.04 and 28.79 (AdC$^\gamma$). ESI-MS *m/z* 1808.9 ([M + Na]$^+$, 100%), 1808.1 (78), 1809.9 (64) for C$_{116}$H$_{136}$NaO$_8$S$_4$ (1807.9).

Classical tube 8. Yield 15%, mp > 350 °C. δ_H(400 MHz; CDCl$_3$) 7.10 (4 H, s, *t*-Bu-ArH), 7.07 (4 H, s, Ad-ArH), 6.54

(4 H, s, Ad-ArH), 6.49 (4 H, s, *t*-Bu-ArH), 5.17 (8 H, m, OCH_2), 4.60 (4 H, d, *J* 12.63 Hz, $ArCH_2Ar$), 4.58 (4 H, d, *J* 12.63 Hz, $ArCH_2Ar$), 4.39 (8 H, s, OCH_2), 3.26 (8 H, br d, *J* 12.63 Hz, $ArCH_2Ar$), 2.12–1.35 (60 H, m, AdH), 1.32 (18 H, s, *t*-Bu) and 0.82 (18 H, s, *t*-Bu). δ_C(100 MHz; $CDCl_3$) 157.08, 157.03, 155.88, 155.78, 144.87, 144.73, 144.46, 144.33, 135.17, 135.12, 131.95, 131.80 (ArC), 125.47, 125.01, 124.77, 124.41 (ArCH), 72.92, 72.52 (OCH_2), 43.87, 42.99 (AdC^{β}), 37.07, 36.85 (AdC^{δ}), 35.68, 35.16 (AdC^{α}), 32.53, 32.26 ($C(CH_3)_3$), 31.74, 31.05 ($C(CH_3)_3$), 29.30 ($ArCH_2Ar$), 29.25 and 28.99 (AdC^{γ}). ESI-MS *m/z* 1753.0 ($[M + K]^+$, 100%), 1752.0 (77), 1754.0 (66) for $C_{120}H_{144}KO_8$ (1752.1).

Acknowledgements

This work was financially supported by the Russian Foundation for Basic Research (grants 04-03-32782, 05-03-32845).

References

1 (*a*) A. Ikeda and S. Shinkai, *Chem. Rev.*, 1997, **97**, 1713; (*b*) P. Beer, P. Gale and Z. Chen, *Adv. Phys. Org. Chem.*, 1998, **31**, 1; (*c*) X. Zhang, R. Izatt, J. Bradshaw and K. Krakowiak, *Coord. Chem. Rev.*, 1998, **174**, 179.

2 (*a*) P. Schmitt, P. Beer, M. Drew and P. Sheen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1840; (*b*) S. Matthews, P. Schmitt, V. Felix, M. Drew and P. Beer, *J. Am. Chem. Soc.*, 2002, **124**, 1341; (*c*) J. Budka, P. Lhotak, I. Stibor, V. Michlova, J. Sykova and I. Cisarova, *Tetrahedron Lett.*, 2002, **43**, 2857; (*d*) S. Matthews, V. Felix, M. Drew and P. Beer, *Org. Biomol. Chem.*, 2003, **1**, 1232; (*e*) M. Makha, P. Nichols, M. Hardie and C. Raston, *J. Chem. Soc., Perkin Trans. 1*, 2002, 354; (*f*) A. Notti, S. Occhipinti, S. Pappalardo, M. Parisi, I. Pisagatti, A. White and D. Williams, *J. Org. Chem.*, 2002, **67**, 7569.

3 D. Dougherty, *Science*, 1996, **271**, 163.

4 S. Matthews, V. Felix, M. Drew and P. Beer, *New J. Chem.*, 2001, **25**, 1355.

5 V. Felix, S. Matthews, P. Beer and M. Drew, *Phys. Chem. Chem. Phys.*, 2002, **4**, 3849.

6 S. Matthews, N. Rees, V. Felix, M. Drew and P. Beer, *Inorg. Chem.*, 2003, **42**, 729.

7 P. Cobben, R. Egberink, J. Bomer, P. Bergveld, W. Verboom and D. Reinhoudt, *J. Am. Chem. Soc.*, 1992, **114**, 10573.

8 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971.

9 Y. Higuchi, M. Narita, T. Niimi, N. Ogawa, F. Hamada, H. Kumagai, N. Iki, S. Miyano and C. Kabuto, *Tetrahedron*, 2000, **56**, 4659.

10 E. Shokova, V. Tafeenko and V. Kovalev, *Tetrahedron Lett.*, 2002, **43**, 5153.

11 A. Khomich, E. Shokova and V. Kovalev, *SYNLETT*, 1994, 1027.

12 C. Perrin and T. Dwyer, *Chem. Rev.*, 1990, **90**, 935.