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Novel Exocyclic Ligands. Synthesis of Selenium Calix[4]arenes and Their High Extraction Selectivity for Ag^+†

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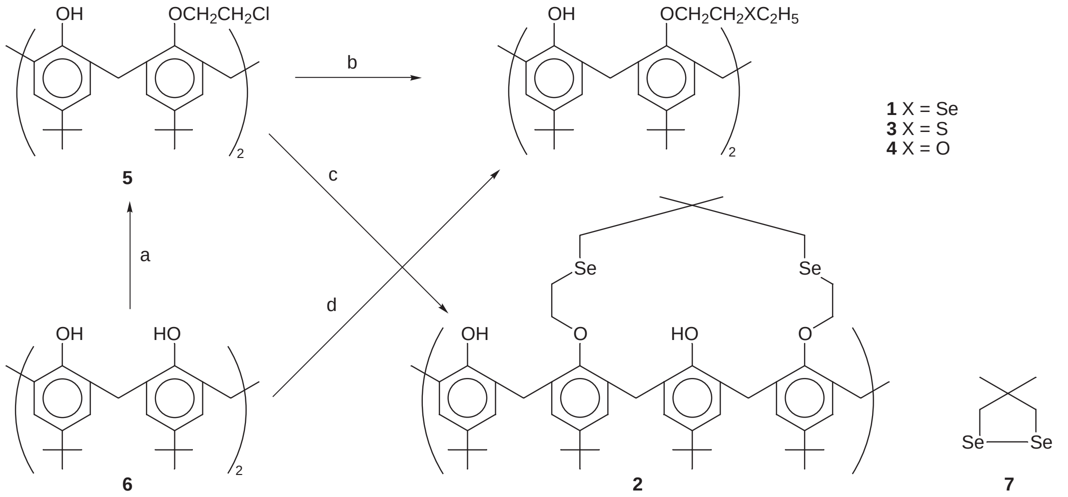
1,3-Lower rim selenium-containing calix[4]arenes are synthesized from 1,3-di(2-chloroethoxy)-*p-tert*-butylcalix[4]arene and corresponding diselenides, and found to possess high Ag^+ extraction selectivity.

Exocyclic ligands, *i.e.* macrocyclic compounds bearing functional side arm(s), *e.g.* lariat crown ethers, are of great interest. Some display special complexation and unique guest specificity *via* macroring–side arm cooperativity;[1,2] others serve as ditopic receptors, either for hard–soft metal ions or for cation–anions.[3] Furthermore, complexes in which the transition metals are coordinated to the side arms are famous supramolecular metallocatalysts, known for their shape-, regio- and stereo-selectivity due to the combination of the macrocyclic recognition and the metallic centers.[4] Many such ligands have been reported, *e.g.* exocyclic phosphine, sulfur, and nitrogen ligands.[1–6] Few exocyclic selenium ligands, however, have been synthesized[7,8] and no metal binding behaviors investigated, to our knowledge, although selenium ligands[9] including numerous macrocyclic hosts containing selenium atom(s) in the rings have been prepared and found to exhibit attractive binding properties toward heavy metal and transition metal cations.[7,10] Very recently we communicated the synthesis of the first calixselenacrown.[7] Liu *et al.* reported the synthesis of selenoether-modified β-cyclodextrins and their recognition properties for aliphatic alcohols. Continuing our interest in calix[4]arenes[5,6,11,12] and selenium ligands,[7,13] we have synthesized another new exocyclic selenium ligand based on calix[4]arene and for the first time investigated the metal binding behaviours of selenium calix[4]arenes.

The synthetic route is depicted in Scheme 1. Reaction of calix[4]arene **6** with 2-chloroethyl tosylate in K_2CO_3/acetone afforded calix[4]arene **5** in 68% yield,[14] which was further treated with ethyl selenide anion ($EtSe^-$) generated *in situ* by KBH_4 reduction on $(EtSe)_2$[15] to give selenium calix[4]arene **1** in 87% yield. Its structure was identified by ^1H NMR, FAB-MS and elemental analysis. The NMR spectrum indicated that the bridge methylene protons appeared in an AB pattern at δ 4.30 and 3.31 ($J = 13.0$ Hz), suggesting that compound **1** is in a cone conformation. Selenium calix[4]arene **2** was obtained from **5** and 4,4-dimethyl-1,2-diselenacyclopentane **7** in the same manner.[7] For comparison, the analogs of selenium calix[4]arene **1**, sulfur calix[4]arene **3** and oxygen calix[4]arene **4** in which selenium atoms of **1** were replaced by sulfur and oxygen atoms, respectively, were prepared by reacting calix[4]arene **1** with the corresponding alkylating reagents.[11,16]

The affinities of selenium calix[4]arenes and the analogs toward metal ions were evaluated by solvent extraction using a chloroform–water biphasic system. The results are summarized in Table 1. Selenium calix[4]arenes and the sulfur analog showed very high Ag^+ extraction selectivity (the extractabilities of **1**, **2** and **3** are 95, 77 and 90%, respectively) among the tested cations (Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}), while the oxygen analog **4** exhibited very low affinity for all cations as expected. This reveals that the chalcogen atoms play an important part in complexing with Ag^+, which was supported by ^1H NMR experiments. When an excess of CF_3SO_3Ag was added to a solution of selenium calix[4]arene



Scheme 1 *Reaction conditions*: (a) $ClCH_2CH_2OTs$, K_2CO_3, acetone; (b) $(EtSe)_2$, KBH_4, NaOH; (c) **7**, KBH_4, NaOH; (d) $BrCH_2CH_2XC_2H_5$ (X = S, O), K_2CO_3, acetone

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Table 1 Extraction (%) profile of calixarene hosts **1**–**4**[a]

Host	Extractability (%)	
	Pb^{2+}	Ag^{+}
1	1	95
2	1	77
3	1	90
4	0	2

[a] $CHCl_3$ phase (5.0 ml) [host] = 1.0×10^{-4} M. Aqueous phase (5.0 ml); [metal nitrate] = 0.01 M, [picric acid] = 3.0×10^{-5} M. The extractability for Co^{2+}, Cu^{2+} and Ni^{2+} with all hosts was 0%.

1 in $CDCl_3-CD_3CN$ (10:1) the methylene protons neighboring the selenium atoms were shifted downfield most significantly ($\Delta\delta = 0.478$, 0.483 ppm), demonstrating that selenium atoms are involved in the complexation. Noteworthy is that the chalcogen calix[4]arenes possessed very low affinity towards Pb,$^{2+}$ whose size is similar to that of Ag^+. The high preference for Ag^+ over Pb^{2+} is seldom observed with thiacrowns and azacrowns.[2] An important point is that a considerable decrease of Ag^+ affinity was observed with calixselenacrown **2** when compared with **1**, although Ag^+ is extracted preferentially by **2**. This may be attributed to an unfavorable size-fit or entropy change for **2** upon complexation as observed with thiacrown ethers.[17] Finally, selenide **1** showed a slightly greater Ag^+ extractability than the sulfide **3**. This is consistent with selenium ligands possessing slightly stronger complexation ability than sulfur analogs.[9]

In conclusion, selenium calix[4]arenes can be synthesized from alkylating groups containing calix[4]arenes (*e.g.* **5**) and diselenides in a straightforward way, and they exhibit high remarkably high Ag^+ selectivity. These features make them very promising candidates for further application such as in recovery of Ag^+ from industrial waster water and detection of Ag^+.

Experimental

Synthesis of Selenium Calix[4]*arene* **1**.—A mixture of $(EtSe)_2$ (0.93 g), NaOH (0.52 g), KBH_4 (0.65 g) and alcohol (30 ml) was stirred under argon and heated to 70°C until the solution became colorless. A solution of calix[4]arene **5** (3.30 g) in THF was added dropwise in 30 min and refluxed for 8 h. All the solvent was evaporated and the residue partitioned between dichloromethane and water. The organic layer was separated and the aqueous layer extracted with dichloromethane. The combined organic layer was dried, filtered and distilled to dryness. The remained solid was recrystallized from Pr^iOH to give white powder **1** in 87.0% yield, mp 144–146°C (Pr^iOH). ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS) δ 7.01 (s, 4 H, ArH), 6.90 (s, 2 H, ArOH), 6.88 (s, 4 H, ArH), 4.30, 3.31 (d, AB, 8 H, $J = 13.0$ HZ, $ArCH_2Ar$), 4.06 (t, 4 H, $ArOCH_2$), 3.06 (t, 4 H, $OCCH_2Se$), 2.70 (q, 4 H, $SeCH_2CH_3$), 1.48 (t, 6 H, CH_3), 1.20, 0.92 (s, 36 H, t-Bu); (Found: C, 67.75; H, 7.85 calc. for $C_{52}H_{72}O_4Se_2$; C, 67.97; H, 7.84%); FAB-MS, *m/z* 891, $(M-C_2H_5)^+$.

Extraction Experiment.—A chloroform solution of a calixarene and an aqueous solution of metal nitrate and picric acid were placed in a stopped tube, shaken for 3 min and then allowed to stand for 10 h in a water bath (27 ± 0.1°C). The concentration of picrate anion in the aqueous phase was determined by UV-VIS spectroscopy monitoring at 356 nm. The extractability was calculated according to eqn. (1)

$$\text{extractability (\%)} = ([\text{Pic}]_0 - \text{Pic}])/\text{Pic}]_0 \times 100 \qquad (1)$$

where $[\text{Pic}]_0$ is the initial concentration of picrate in the aqueous phase (1.0×10^{-5}) and [Pic] that in the aqueous phase after extraction. All experiments were performed in duplicate or triplicate.

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