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Communications

A Palladium(II) Selective Complexing Agent Based on the *all*-Homocalixarene Skeleton

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Being used for the extraction from an aqueous to an organic phase thiomorpholine substituted *all*-homocalix[6]arene 1 turns out to be more efficient and much more selective for Pd^{II} than the corresponding calix[6]arene 2 and a comparable open-chained compound 3.

Keywords: *All*-homocalixarene, calixarene, palladium, extraction properties

Calixarenes have been established as a versatile class of host compounds in the past two decades [1]. Cation selective derivatives can be obtained by attaching pendant arms on the lower rim [2]. Designing calixarenes for the coordination to transition metals often means modifying them with phosphorus [3], sulphur [4], or nitrogen donor [5] containing groups. Hitherto the combination of nitrogen and sulphur donor sites in the ligand arms has rarely been reported [6].

Calixarene based receptors usually differ by substituents or conformational properties but the modification of the skeleton has also been described, *e.g.*, the oxa- [7], thia- [8] and azacalixarenes [9] which contain CH_2—X—CH_2 (X = O, S, N) bridges.

A few years ago we reported on a new family of calixarenes, the *all*-homocalixarenes [10], which differ from the calixarenes in the substitution of the methylene by ethano bridges. Furthermore, they are conformationally more flexible and better soluble in organic solvents like CH_2Cl_2, $CHCl_3$, or toluene. *all*-homocalixarenes can be converted easily to molecular cation receptors analogous to known calixarene preparations without the need of separating any conformers. Because of their stable skeleton no ring cleavage despite of rigid experimental conditions occurs.

In this paper we report on the synthesis and the complexation properties of the six thiomorpholine-units containing *all*-homocalix[6]arene **1** [11] in comparison to the calix[6]arene analogues **2**. These receptor molecules are designed for the complexation of transition metals by their large

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flexible cavities and six identical pendant arms on the lower rim/intraannular positions. Each consists of hard donor sites – the carbonyl groups – and soft donor sites – the amide functionalities and sulphur centres. To increase the complexation kinetics, no bulky groups were attached to the upper rim/extraannular positions. Due to this electronical and sterical design of the host molecules the coordination to large thiophilic guest cations should be favoured. The ability to form different unimolecular coordination geometries is also important. So the square planar arrangement, *e.g.*, for Pd^{II} complexes, can be realized [12].

The synthesis of **1** was carried out as follows: an excess of 2-chloro-*N*-thiomorpholino-acetamide was added dropwise to a stirred suspension of *all*-homocalix[6]arene and Cs_2CO_3 in acetonitrile at room temperature and under argon atmosphere. The reaction mixture was refluxed for 72 h, then concentrated *in vacuo*. The solid brown residue was dissolved in CH_2Cl_2, washed with saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. After removal of the solvent the crude yellow product was washed several times with cold methanol to give pure **1** as small colourless crystals (mp. 132°C, MeOH-CH_2Cl_2) in 45% yield (Scheme 1).

The hexaamide **2** was readily prepared by reaction of thiomorpholine and 43,44,45,46,47,48-hexakis(chlorocarbonylmethoxy)calix[6]arene under base conditions as a microcrystalline colourless solid (mp. 168°C, MeOH-CH_2Cl_2) in 85% yield. We also tried an alternative convergent synthesis of **2** analogous to the formation of **1** starting from calix[6]arene and using anhydrous DMF instead of CH_3CN. In this case the target molecule **2** was obtained in only 37% yield due to the formation of many byproducts, such as rather alkylated calix[6]arenes.

The structures of **1** and **2** were fully characterised by ^1H and ^{13}C NMR spectroscopy, FAB/MALDI-TOF-MS and elemental analysis [13]. At room temperature the *all*-homocalixarene just as the calixarene is highly conformationally mobile, so no conformers could be observed and we obtained only one NMR signal for the ethano/methylene protons.

In the 400 MHz ^1H NMR spectrum in $CDCl_3$ **1** interestingly shows a pseudo-singlet resonance for the aromatic protons. The expected coupling pattern for the ABB' system did not appear. This could be explained by the collapsing chemical shifts of the H_A und H_B protons caused by electronic effects of the pendant arms and the ethano bridges. In contrast the substituted calixarene **2** shows the expected splitting pattern.

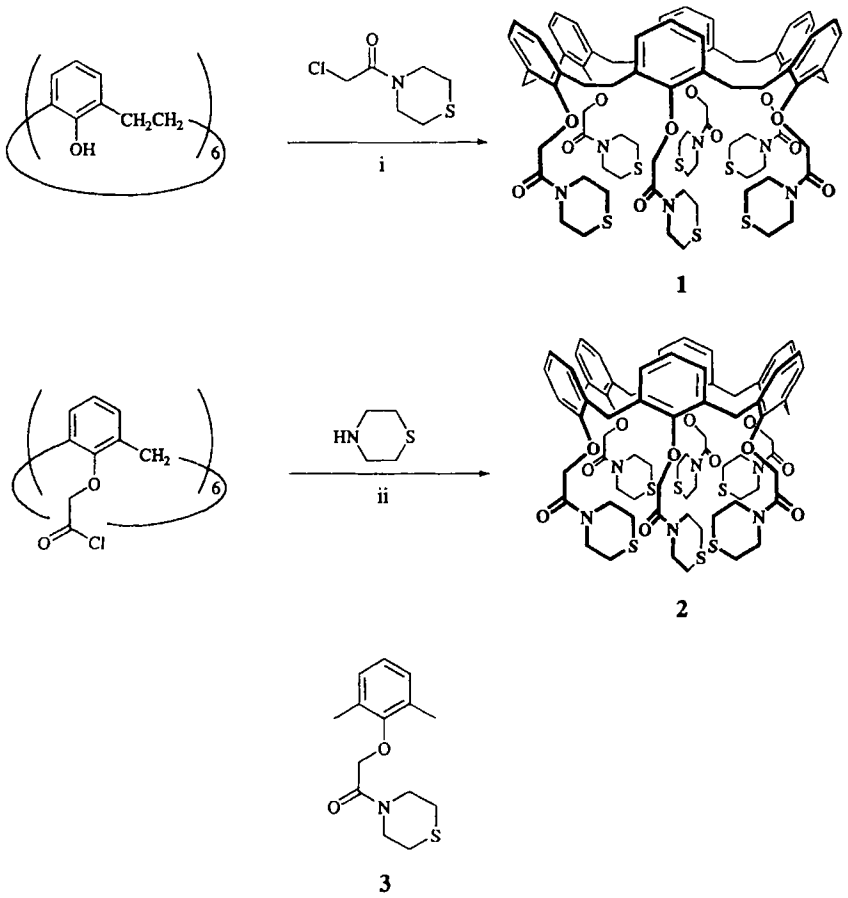
The complexation behaviors of **1** and **2** were investigated by liquid–liquid extraction measurements [14, 15]. Under the conditions chosen palladium chloride could be quantitatively transferred from an aqueous to an organic phase by both ligands (**1**: 99%; **2**: 97%). In addition a remarkable selectivity for palladium chloride could be observed for the *all*-homocalix[6]arene derivative. Other metal ions, such as barium or thallium, were practically not extracted (Fig. 1).

On the contrary the calix[6]arene derivative does not show such a selectivity. Extractabilities of 52% for Tl^I, 47% for Ba^{II} and 10% for Cs^I were found with this compound. These metal ions have an ionic radius comparable to the size of the cavity of **2**. Other alkaline and alkaline earth metal ions with smaller ionic radii were not extracted.

As expected the two ligands are also able, under other conditions, to extract quantitatively silver(I) ions, and the formation of 1:1-complexes in the organic phase could be observed [16]. Surprisingly both receptors show a very low affinity for the thiophilic mercury ions (3% and 5% for **1** and **2**, respectively).

For comparison extraction experiments were also carried out with the 'monomer' **3**. It is able to extract selectively palladium chloride from an aqueous to an organic phase, forming an 1:1-complex [16], but shows a significantly lower extraction efficiency of 16%.

Hitherto the composition of the palladium complexes with **1** and **2** has not been cleared up but 1:1-complexes should be formed as well. The



SCHEME 1 Reagents and conditions: i, Cs_2CO_3/CH_3CN, reflux, 3 d; ii, Et_3N, CH_2Cl_2, room temp., 1 d.

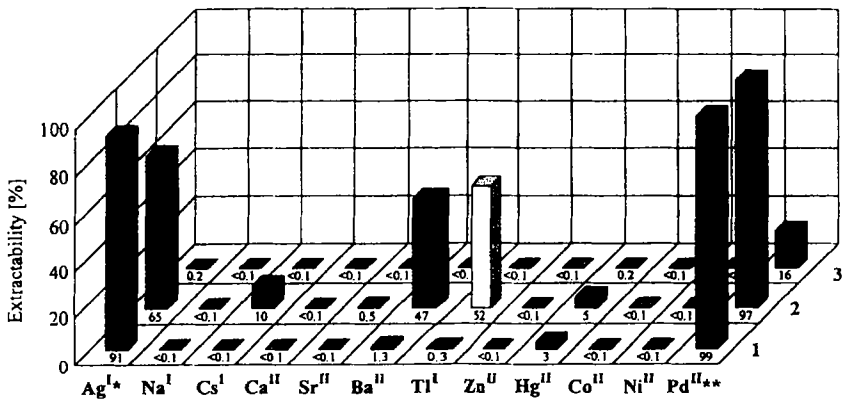


FIGURE 1 Extraction properties of different metal ions with the thiomorpholino-substituted ligands **1**, **2** and **3**. *Experimental conditions*: $[MCl_n]$ or $[M(NO_3)_n] = 1 \times 10^{-4}$ M, pH = 5.2 (NaOAc/HCl buffer); [picric acid] = 5×10^{-3} M; 30 min shaking time; *: $[AgNO_3] = 1 \times 10^{-4}$ M, pH = 5.2 (Mes/NaOH buffer); [picric acid] = 5×10^{-3} M; 30 min shaking time; **:$[PdCl_2] = 1 \times 10^{-4}$ M, pH = 5.2 (NaOAc/HCl buffer); 2 hours shaking time; For all metals: [ligand] = 1×10^{-3} M, $CHCl_3$.

formation of 1:1-complexes of Ag^{I}, Hg^{II}, Ba^{II} and Tl^{I} with ligand **2** and Ba^{II} with ligand **1** could be observed in the organic phase [16].

Studies of the extraction kinetics with Pd^{II} were also carried out and a significant acceleration of the extraction rate of the calixarenes **1** and **2** could be observed in contrast to **3**.

Due to its formation of stable palladium complexes **1** is an interesting, highly selective phase-transfer host [17]. Comparative liquid–liquid extraction experiments using the calixarene ligand **2** show that the selectivity towards Pd^{II} cations is remarkably increased by the less rigid and larger cavity of the *all*-homocalixarene ligand.

In conclusion designing host systems based on *all*-homocalixarene-like expanded calixarenes is an important alternative route to improve the selectivity of host-guest systems.

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[13] Selected data: **1**, ^{1}H NMR ($CDCl_3$) δ 6.57 (s, ArH, 18 H), 4.38 (s, OCH_2, 12 H), 3.81 (br t, NCH_2, 12 H), 3.69 (br t, NCH_2, 12 H), 2.94 (s, $ArCH_2$, 24 H), 2.61 (br t, SCH_2, 12 H), 2.59 (br t, SCH_2, 12 H). Elemental analysis: Calc. for $C_{84}H_{102}N_6O_{12}S_6 \cdot 1CH_2Cl_2$: C, 61.32; H, 6.30; N, 5.04. Found: C, 61.33; H, 6.38; N, 4.84%. **2**, ^{1}H NMR ($CDCl_3$) δ 6.80 (d, ArH, 12 H), 6.72 (t, ArH, 6 H), 4.46 (s, OCH_2, 12 H), 4.06 (br t, NCH_2, 12 H), 3.81 (s, $ArCH_2$, 12 H), 3.46 (br t, NCH_2, 12 H), 2.57 (br t, SCH_2, 12 H), 2.32 (br t, SCH_2, 12 H). Elemental analysis: Calc. for $C_{78}H_{90}N_6O_{12}S_6 \cdot 1CH_2Cl_2 \cdot 1H_2O$: C, 59.57; H, 5.99; N, 5.22. Found: C, 59.60; H, 5.99; N, 5.52%.

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