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Synthesis and characterization of nitro derivatives of Calix[4]arene as an effective removal agents for Co^{2+} and Pb^{2+} Ions

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Abstract: Synthesis of several derivatives of nitro calix[4]arenes and their effects on the absorption capability toward Co^{2+} and Pb^{2+} ions was studied. The synthesized receptors have been characterized by ^{1}HNMR, ^{13}CNMR and FTIR.

Keywords: Nitro calix[4] arenes, Ion Receptor, Removal agents, Co^{2+}, Pb^{2+}.

Introduction

Calix[4]arenes have attracted considerable interest as building blocks for constructing selective host molecules [1]. Upper rim functionalized compounds can be obtained in a multi-step procedure from suitably substituted precursors [2]. Two or tetra nitro groups at the upper rim have also been prepared by a stepwise synthesis. After reduction these compounds are important starting materials for molecular receptors based on calixarenes [3].

The control of cation-binding ability of calixarenes has been the subject of more recent investigations. The calixarenes structure itself can behave as a soft donor group through its phenyl group π electrons, and this has been demonstrated by applications as selective ligands in ion selective electrodes [4–24].

In this paper, tetra-nitro and di-nitro calixarene have been prepared and characterized by various spectroscopy techniques. The ion selectivity of prepared receptors have been investigated by Uv-Vis spectroscopy method toward the Co^{2+} and Pb^{2+} Ions.

Results and discussion

The cone conformation of 5,11,17,23-tetra tert-butyl-25,26,27,28-tetra butyloxy calix[4]arene (**b**) reacts with 63% HNO_3 in a mixture of dichloromethane and glacial acetic acid in -10°C to afford tetra-nitro calix(4)arene (**c**) in 90% yield. Compared to the published procedure [11], the present method offers both milder reaction conditions and an improved yield. Treatment of (**b**) with 63% HNO3 in dichloromethane and in presence of glacial acetic acid in 0°C, afforded the dinitro compounds (**c**) and (**d**) in a ratio of 3:2. Compounds (**c**) and (**d**) could be differentiated by their ^{1}H NMR spectra. According to the symmetry of their structures, the protons of the methylene groups between the phenol moieties of (**c**) appear as a pair of doublets, and those of **d** indicating a central plane of symmetry appear as three pairs of doublets [6].

Spectroscopic studies of receptors (c) and (d) towards metal cations:

It is well known that the cation binding ability and selectivity upon complexation with calix[4]arene and its derivatives are influenced by many factors, such as the ion surface charge density, spatial arrangement of the donor atoms, size-fit relationship between cation and calix[4]arene, as well as the cooperative binding of the appended side-arms, and so on [8-10]. In this work, it is considered that the induced three-dimensional cavity of the parent calixarene platform and the attached side arms upon complexion play an important

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role in cation binding ability and selectivity. For investigation of binding ability of **b,c** and **d** towards cation ions Co^{2+} and Pb^{+2} were selected for their size capability with synthesized receptors **c** and **d**. Spectral titrations were performed in acetone / water (90:10 /V:V) solution. The metal nitrates did not show any significant absorption in the scanned spectral range. Typical UV spectral changes by addition of Co^{2+} and Pb^{+2} to **b,c** and **d** solutions are shown in **Figure 2-7**. Absorbance of Host **3** in λ=340 nm was increased with increasing the concentration of Co^{2+} and Pb^{+2} ions. Fig 2 and **c** show the binding interactions of **c** with Co^{2+} and Pb^{+2} respectively. Fig 4 and 5 illustrates the dependence of absorbing variations of **d** with Co^{2+} and Pb^{+2} concentrations. Fig 6 and 7 show the absorbing variations of **b** with Co^{2+} and Pb^{+2} concentrations.

According to Fig 8 the removal capability of receptor **c** Pb^{+2} ions is very good. The UV spectra of compounds **b,c** and **d** in the presence of Pb^{+2} ion can be concluded that the receptor **c** has been the selective. In Figure 9, the **c** receptor is removed of the Co^{2+} ion, but receptors **b, c** and **d** are not much different from each other.

Experimental

All the reagents were purchased from Merck Company. NMR spectra were recorded on a Bruker AM-500 spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on Bruker Tensor 27 and Perkin –Elemer model IFS 25, V-vis. spectra were obtained on a T90 UV-visible spectrophotometer, PG Instrument ltd.

Preparation of p-Tert-butyl calix[4]arene (a):

Parent calix[4]arene was synthesized according to the Literature [3]. mp=342 – 344 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) *1.21* (s, 36 H), 3.51(d, 4H, J=12.8 Hz), 4.24 (d, 4H, J=12.8Hz), 7.05(s, 8H), 10.34 (s, 4H); ^{13}CNMR (125 MHz, $CDCl_3$) δ(ppm) 30.5, 32.4, 34.0, 126.1, 128.2, 144.5, 146.8 ; IR, ν(cm^{-1}) = 3155.

Preparation of 5,11,17,23-tetra tert-butyl-25,26,27,28-tetra butyloxy calix[4]arene (b)

To a suspension of 3 g (4.62 mmol) of **(a)** in 180 ml of dry DMF was added 3 g of NaH which washed with hexane (2×15 ml) .The reaction mixture was stirred for 45 min at 60 °C. then 30 ml (238 mmol) of butyl bromide was added and allowed to stirrer at 80 °C for 24h. The reaction mixture was poured into 1800 ml of water and extracted with 400 ml of CH_2Cl_2. The organic layer was separated, washed with water twice and dried over Na_2SO_4. The solvent was removed by evaporation. To leaving a residue was added methanol to precipitate the products. The solid was recrystallized from CH_2Cl_2-MeOH to give white crystals of **(b)**. (86%) mp:160-162 ˚C , ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 0.92 (36H, s, $C(CH_3)_3$), 0.96(12H, t, J=15 Hz), 1.38(8H, m), 1.81(8H, t, J=10 Hz), 3.30(4H, d, J=15Hz), 3.9 (8H, m, CH2), 4.48 (4H, d, J=20 Hz), 7.56 (8H, s, ArH) ; ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm) 14.3, 19.5, 0.5, 32.5, 34.0, 76.3, 125.4, 133.8, 142.3, 161.0 ;FTIR (KBr)ν = 2956, 1462, 1122 cm^{-1}.

Preparation of 5,11,17,23-tetra nitro-25,26,27,28-tetra butyloxy calix[4]arene (c)

To a solution of 3g (12.9 m mol) **(b)** in dichloromethane (50mL) and glacial acetic acid (100 mL) 63% HNO_3 (50 mL) was added drop wise at -10°C in 40 min and the reaction mixture was stirred at room temperature for 20h and poured into water (500 mL). The organic layer was extracted with dichloromethane and was separated, washed with water twice and dried over Na_2SO_4. The solvent was removed by evaporation. To leaving a residue was added methanol to precipitate the products. The solid was recrystallized from CH_2Cl_2-MeOH to give yellow crystals of 3. (90%) mp>220˚C , ^{1}H- NMR (500 MHz, $CDCl_3$) δ (ppm) 0.96 (12H, t, J=15 Hz), 1.38 (8H,m), 1.81 (8H, t, J=10 Hz), 3.30 (4H, d, J=15 Hz), 3.9 (8H, m, CH_2), 4.48(4H, d, J=20 Hz), 7.56 (8H, s, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm) 14.3, 19.5, 31.5, 32.5, 76.3, 124.4, 135.8, 143.3, 162.0 ; FTIR,ν=1006, 1202, 1343, 1460, 1519 cm^{-1}.

Preparation of 5,11-dinitro-17,23-di tert-butyl-25,26,27,28-tetra butyloxy calix[4]arene (d):

To a solution of 3g (12.9 mmol) **(b)** in dichloromethane (50mL) and glacial acetic acid (50 mL), 63% HNO_3 (25 mL) was added at 0 °C in 10 min and the reaction mixture was then stirred at room temperature for 20h and poured into water (500 mL). The organic layer was extracted with dichloromethane and was separated, washed with water twice and dried over Na_2SO_4. The solid was recrystallized from CH_2Cl_2-MeOH to give yellow powder of c and d. For resolutions d was purified by column chromatography of the mother liquors (silicagel, CH_2Cl_2, n-hexane, 1:5); yield 40%, mp>260˚C, ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 0.96 (18H, t, J=5 Hz) , 1.40 (12H,m), 1.51 (8H, m), 3.15 (4H, t, J=40 Hz), 3.81 (8H, m), 4.38 (4H, t, J=40 Hz), 6.63 (2H, s, ArH) , 6. 72 (2H, s, ArH) , 6.63(2H, s, ArH) , 7.71(2H, s, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm) 14.4, 14.8, 15.2, 15.4, 15.7, 16.1, 30.5, 31.0, 32.4, 32.8, 33.5, 75.7, 76.0, 124.4, 135.8, 137.2, 143.3, 145.4, 162.0, 122.3, 123.4, 125.1, 125.4, 159.1 ; FTIR, ν = 1207, 1340, 1457, 1521cm^{-1}.

UV-Vis Spectroscopic measurements:

The absorbing measurements were performed by UV-Vis titration experiments using a stable concentration of hosts and a varying guest concentration. All of the spectral titrations were performed in acetone / water (90:10 /V:V) solution. 4 mL solution of the host **b, c** or **d** (10^{-3} M) was titrated with stepwise addition of the metal cation solution (10^{-2} M). The initial and final absorbances of the host were recorded before and after titration. For both hosts **b,c** and **d** the data were collected over the range 300–400 nm. The ion removal by receptors can be calculated according equation 1.

Equation 1: $E\% = 1 - A/A_0 \times 100$

Where A_0 and A are the initial and final absorbance of the host before and after the titration, respectively. Fig 10 shows the extent of E% of receptors toward Co^{2+} and Pb^{+2}.

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