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Selenium speciation and preconcentration by a novel diammoniumcalix[4]arene

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Abstract

The synthesis of a diammoniumcalix[4]arene is reported and its ability to extract Se(VI) and not Se(IV) is demonstrated. This property is used to selectively preconcentrate trace amounts of Se(VI). © 1999 Published by Elsevier Science Ltd. All rights reserved.

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Selenium is an element which is both toxic and essential depending on its chemical form and concentration. In aqueous samples, it can exist at least under two oxidation states, selenite (Se(IV)) and selenate (Se(VI)).[1] While the separation of both selenite and selenate has been extensively described in the literature, quantification of selenium at trace levels often requires a derivatization or a preconcentration step.[2] A wide range of methods is proposed for Se(IV): a selective derivatization can be performed, e.g. hydride generation,[3] formation of piazselenols[4] and numerous extractants have been investigated such as pyrrolidinedithiocarbamate [5–7] or dithizone,[7,8] which allow a selective extraction of Se(IV) over Se(VI). As these methods can only be applied to Se(IV), Se(VI) concentration was often determined by a difference between total and Se(IV) amounts.

Calixarenes provide unique platforms to build molecular receptors and despite the popularity of ammoniums in matters of anion recognition, only a few studies focused on the use of ammoniumcalixarenes for that purpose.[9]

In the present note, we report the synthesis of diammoniumcalix[4]arene derivative **3** and demonstrate its ability to selectively concentrate Se(VI) over Se(IV) under their anionic form.

Synthesis of **3**: The synthesis of **3** is illustrated on Scheme 1. Calixarene derivative **1** was prepared in a 72% yield by reaction of *p-tert*-butylcalix[4]arene with 2.1 equiv. of 4-bromobutyronitrile in the presence of K_2CO_3 in refluxing acetonitrile for 5 days. Dicyanocalix[4]arene **1** was reduced by 10 equiv. of $LiAlH_4$

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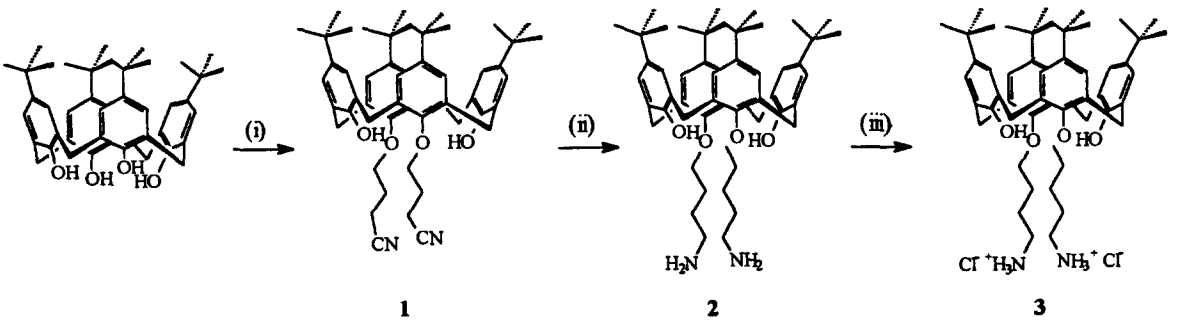
in refluxing diethyl ether for 5 h to give the diaminocalix[4]arene derivative **2** in a 90% yield. Compound **2** was then converted into the hydrochloride form **3**. Products **1–3** have been fully characterized.[10]



Scheme 1. Synthetic pathway to **3**. (i) $Br(CH_2)_3CN/K_2CO_3$/acetonitrile; (ii) $LiAlH_4$/diethyl ether; (iii) HCl/dichloromethane

Solvent extraction of Se(VI): Extraction of Se(VI) from a 10^{-2} mol L^{-1} chloride medium were carried out at 25°C by magnetically stirring the aqueous phase with a chloroform phase containing ligand **3** for 30 min.[11] Selenium concentrations in both phases were then determined using ICP/AES (inductively coupled plasma/atomic emission spectrometry). The influence of pH (Table 1) and ligand concentration (Fig. 1) were investigated in order to determine the optimal conditions.

A pH of 2.6 was found to be a good compromise to keep Se(VI) under an anionic form and to prevent the deprotonation of ligand **3**. For this pH, an increase of ligand **3** concentration up to 4×10^{-4} M was shown to allow the quantitative extraction of 5×10^{-5} mol L^{-1} Se(VI).

Table 1
Influence of pH on selenium extraction using a [ligand 3]/[Se] ratio of 10

pH	% extraction of Se(VI)
2.6	97
3.0	93
4.5	90
7.6	0

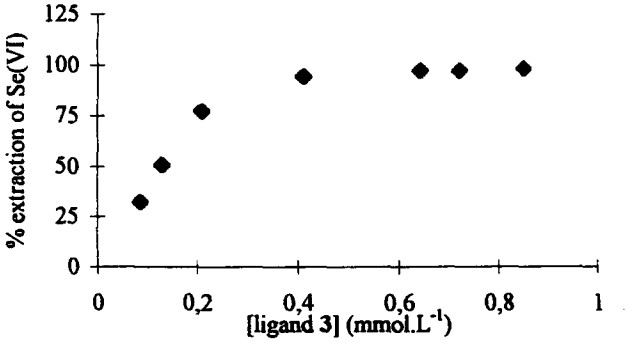


Figure 1. Influence of ligand concentration on the extraction of 5×10^{-5} mol L^{-1} Se(VI) from a 10^{-2} mol L^{-1} chloride medium at pH 2.6 by $CHCl_3$ containing ligand **3**

The extraction of Se(VI) from a mixture containing both Se(VI) and Se(IV) was performed. The analysis of the different extraction phases by ionic chromatography demonstrated that a quantitative extraction of Se(VI) was obtained at pH 2.6 for a [ligand 3]/[Se] ratio greater than 12 whereas nearly no extraction of Se(IV) is noticed (Fig. 2).

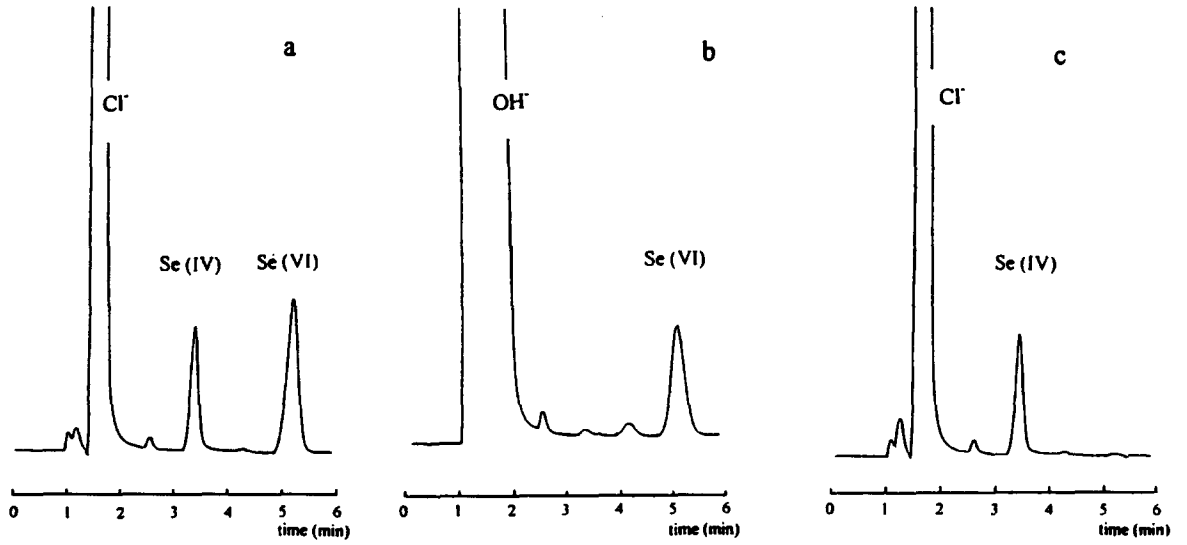


Figure 2. Chromatogram of: (a) initial mixture of 4.96×10^{-5} mol L^{-1} Se(VI) and 9.58×10^{-5} mol L^{-1} Se(IV) in a 10^{-2} mol L^{-1} chloride aqueous phase; (b) organic phase after extraction by 5.44×10^{-4} mol L^{-1} ligand **3** and stripping with 0.1 mol L^{-1} NaOH (c) aqueous phase after extraction by 5.44×10^{-4} mol L^{-1} ligand **3**

Using these conditions, preconcentrations of Se(VI) were performed by recirculating 500 mL of an aqueous phase containing Se(VI) through 25 mL of organic phase containing 5.5×10^{-4} mol L^{-1} of ligand **3** during 5 h at 25°C (Table 2).

Table 2
Determination of trace Se(VI) concentrations by ICP/AES after preconcentration using ligand **3**

Theoretical Se(VI) concentration in the initial solution (mol.L^{-1})	Se(VI) concentration found in the initial solution (mol.L^{-1})[a]
$6.2.10^{-6}$	$(6.3\pm0.4).10^{-6}$
$9.9.10^{-7}$	$(10.7\pm0.6).10^{-7}$
$5.5.10^{-7}$ [b]	$(5.3\pm0.4).10^{-7}$

[a] average of 3 determinations

[b] in presence of $6.4.10^{-7}$ mol.L^{-1} Se(IV)

Extraction of Se(VI) by ligand **3** was proved to be an efficient way to quantify this species at trace levels. Further studies on the extraction of other oxoanions by ligand **3** are currently under investigation.

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10. General: Melting points, Büchi 500. ^{1}H NMR, Bruker SY200 (δ in ppm, J in Hz). FAB (+), VG-Analytical ZAB HF. Elemental analysis were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg and at the Service Central d'Analyse of the CNRS. Preparation of **1**: *p-tert*-butylcalix[4]arene (5.01 g, 7.72 mmol), 4-bromobutyronitrile (2.42 g, 16.35 mmol) and K_2CO_3 (1.29 g, 9.31 mmol) were refluxed in acetonitrile (90 mL) for 5 days under a nitrogen atmosphere. After evaporation of acetonitrile, the residue was solubilized in CH_2Cl_2 (300 mL) and acidified with 1N HCl pH ~1. The organic phase was dried over $MgSO_4$ and concentrated. The residue was treated with methanol to yield to 1,3-dicyanocalix[4]arene **1** (4.32 g) as a white solid. Analytical data of compound **1**: mp >300°C. ^{1}H NMR (200 MHz, $CDCl_3$) 7.43 (s, 2H, ArO*H*), 7.05 (s, 4H, Ar*H*), 6.86 (s, 4H, Ar*H*), 4.17 (d, J=13.0, 4H, ArCH_2Ar, AB system), 4.10 (t, J=6.0, 4H, ArOCH_2), 3.38 (d, J=13.0, 4H, ArCH_2Ar, AB system), 3.05 (t, J=7.0, 4H, CH_2CH_2CN), 2.34 (qu, J=6.0, 4H, $ArOCH_2CH_2$), 1.28 (s, 18H, C_4H_9), 1.00 (s, 18H, C_4H_9). Anal. found: C, 80.03; H, 8.24. Calcd for $C_{52}H_{66}N_2O_4$: C, 79.76; H, 8.49. FAB (+) MS, *m/z*, 783.23 (MH^+). Preparation of **2**: dicyanocalix[4]arene derivative **1** (1.01 g, 1.3 mmol) was reduced by $LiAlH_4$ (0.45 g, 12.53 mmol) in refluxing diethyl ether (50 mL) for 5 h under a nitrogen atmosphere. The solvents were then evaporated and the residue was solubilized in CH_2Cl_2. A saturated LiOH solution (2 mL) was added and the organic phase was dried over $MgSO_4$. After filtration and evaporation of the solvent to dryness, the 1,3-diaminocalix[4]arene **2** (0.93 g) was recovered as a white solid. Analytical data of compound **2**: mp 168–169°C. ^{1}H NMR (200 MHz, $CDCl_3$) 7.58 (broad s, 2H, ArO*H*), 7.05 (s, 4H, Ar*H*), 6.81 (s, 4H, Ar*H*), 4.27 (d, J=13.0, 4H, ArCH_2Ar, AB system), 3.99 (t, J=6.0, 4H, ArOCH_2), 3.31 (d, J=13.0, 4H, ArCH_2Ar, AB system), 2.87 (t, J=7.0, 4H, $CH_2CH_2NH_2$), 2.06 (qu, J=6.0, 4H, $ArOCH_2CH_2$), 1.85 (qu, J =6.0, 4H, $CH_2CH_2NH_2$), 1.63 (broad s, 4H, NH_2), 1.29 (s, 18H, C_4H_9), 0.97 (s, 18H, C_4H_9). Anal. found: C, 76.68; H, 8.86. Calcd for $C_{52}H_{74}N_2O_4 \cdot H_2O$: C, 77.19; H, 9.47. FAB (+) MS, *m/z* 791.6 (MH^+). Preparation of **3**: diaminocalix[4]arene derivative **2** (0.100 g, 0.166 mmol) was dissolved in CH_2Cl_2 (50 mL). The solution was acidified with concentrated HCl, pH ~1 and magnetically stirred for at least 1 h. The organic phase was dried over molecular sieves and 1,3-diammoniumcalix[4]arene **3** was quantitatively obtained as a white solid after evaporation to dryness. Analytical data of compound **3**: mp 267–268°C. ^{1}H NMR (200 MHz, $CDCl_3$) 8.37 (broad s, 6H, NH_3^+), 7.09 (broad s, 2H, ArO*H*), 7.03 (s, 4H, Ar*H*), 6.72 (s, 4H, Ar*H*), 4.24 (d, J =13.0, 4H, ArCH_2Ar, AB system), 3.94 (t, J =6.0, 4H, ArOCH_2), 3.30 (d, J =13.0, 4H, ArCH_2Ar, AB system), 3.21 (t, J =7.0, 4H, $CH_2CH_2NH_3^+$), 2.17–2.00 (m, 8H, $ArOCH_2CH_2CH_2$), 1.27 (s, 18H, C_4H_9), 0.91 (s, 18H, C_4H_9). Anal. found: C, 70.85; H, 8.95; N, 3.27; Cl, 7.61. Calcd for $C_{52}H_{76}N_2O_4Cl_2 \cdot H_2O$: C, 70.80; H, 8.91; N, 3.18; Cl, 8.04. FAB (+) MS, *m/z* 791.4 (MH^+–2HCl).
11. Solvent extraction procedure: 5 mL of a 10 mM chloride aqueous phase containing $Na_2SeO_4 \cdot 10H_2O$ (5×10^{-5} mol L^{-1}) and/or $Na_2SeO_3 \cdot 5H_2O$ (5×10^{-5} mol L^{-1}) and 5 mL of a chloroform phase containing **3** (8×10^{-5}–8.5×10^{-4} mol L^{-1}) were magnetically stirred for 30 min at 25.0±0.2°C. Prior to extraction, the pH of the aqueous solution was adjusted to the desired value by an HCl/NaCl mixture so that the total chloride concentration was kept equal to 10 mmol L^{-1}. After separation, the pH was measured using a potentiometer and a glass electrode (reference:Ag/AgCl). Both phases were separated and aliquots were analyzed by ICP/AES (JY 138) at 196 nm. Prior to analysis, the organic phase (3 mL) was stripped using an aqueous solution containing 0.1 mol L^{-1} NaOH (3 mL) in order to deprotonate the ammonium and recover selenium in the aqueous phase.