Pergamon

Tetrahedron Letters 40 (1999) 1613–1616

TETRAHEDRON
LETTERS

Syntheses of Some New Polyaminocarboxylate and CMPO Calix[4]arene Chelators for the Selective Extraction of Actinide Ions

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Received 30 July 1998; revised 10 December 1998; accepted 6 January 1999

Abstract: The syntheses of two new calix[4]arene derivatives designed for the selective liquid-liquid extraction of actinide ions have been achieved. The first, is a novel organic soluble calix[4]arene chelator **2** having four iminocarboxylate ligand moieties anchored to the lower rim. The second calix[4]arene derivative **3** that has been readily synthesized has four CMPO ligand groups tethered to the lower rim. Preliminary studies show that both **2** and **3** extract thorium(IV) more efficiently than europium(III) under acidic conditions into chloroform. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Supramolecular Chemistry; Calixarenes; Chelation; Actinides; Extraction

A variety of separation technologies and processes are currently being explored for the remediation of high level and transuranic radioactive waste[1]. In connection with these efforts, there is a need to develop efficient extracting agents to selectively remove various actinides such as plutonium and americium from process waste streams as well as from contaminated waters[2-4].

It is generally accepted that selective binding of chelators to tetravalent actinide ions can be achieved by taking advantage of their higher coordination number (8 or more) and more flexible coordination geometry relative to the smaller transition metals[5,6]. Calix[4]arenes[7,8] that are immobilized in the cone conformation present an ideal backbone for preorganization of the ligand groups on the same face of the molecule and hence for the construction of selective extractants for actinides. Recently, the synthesis of a calix[4]arene extractant for actinides having four CMPO (octyl(phenyl)N,N-diisobutylcarbamoyl methylphosphine oxide) like groups appended to the upper rim, has been disclosed[9-11]. The authors found that these calixarene derivatives were better extractants for actinides such as Np, Pu and Am than CMPO itself[9]. Another class of calixarene derivatives with phosphine oxide groups attached to the lower rim has been synthesized and shown to have high efficiency in the extraction of Th(IV) and Pu(IV) from simulated nuclear waste[12]. The syntheses and metal extraction properties of a number of calixarene based hydroxamate ligands for the selective extraction of actinide (IV) ions as well as uranyl ion have also been disclosed[13,14]. In this communication we would like to report the synthesis of two new extractants for actinides. The first is a novel organic soluble calix[4]arene chelator **2** having four iminocarboxylate ligand moieties anchored to the lower rim that is designed for the octadentate

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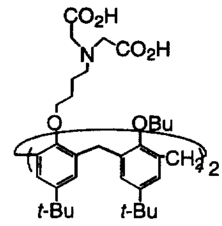
PII: S0040-4039(99)00070-2

coordination of an actinide ion. In parallel to this effort, we have also completed the first synthesis of a lower rim CMPO functionalized calix[4]arene **3**.



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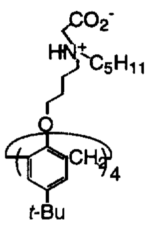

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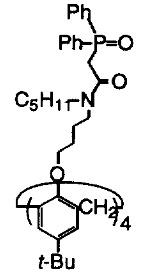

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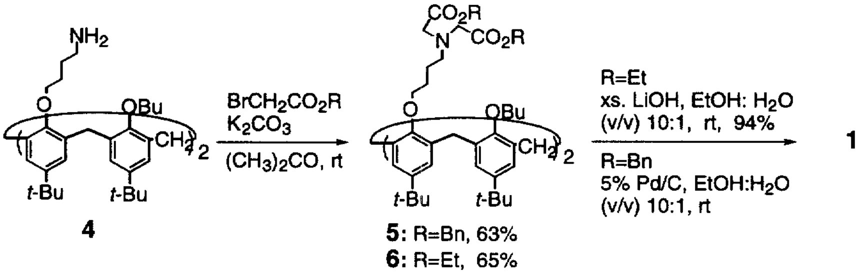
Water soluble aminocarboxylates such as ethylenediaminetetraacetate (EDTA) and diethylenetriaminepentaacetate (DTPA) are known to bind hard cations such as iron(III) and plutonium(IV) strongly and are potential plutonium sequestering agents[15]. DTPA is currently used as its calcium or zinc salt in the biodecorporation of plutonium or americium following accidental intake[16]; however, it is generally accepted that not all eight donor groups of the DTPA chelator can simultaneously bind the Pu^{4+} cation due to steric reasons[15]. In addition, the hydrophilic nature of this class of molecules excludes them from use in a liquid-liquid extraction remediation scheme. We envisioned that the incorporation of these ligands onto a calixarene platform should yield organic soluble analogs of these well known chelating agents.

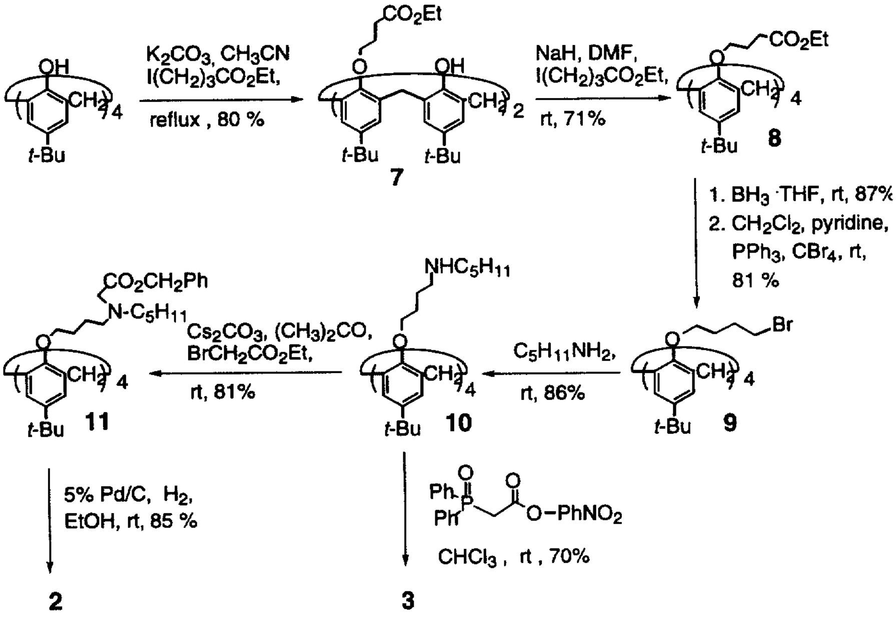
The first target chosen for synthesis was the EDTA analog **1** (scheme 1). Alkylation of the readily available diamine[17] with benzyl 2-bromoacetate or ethyl 2-bromoacetate in the presence of potassium carbonate gave **5** and **6** respectively in moderate yields after chromatographic purification. Attempts to obtain **1** by deprotection of the benzyl esters of **5** by conventional catalytic reduction failed, and led to the formation of a coarse precipitate that could not be readily separated from the catalyst.



Scheme 1

The tetraethylester **6** was then saponified with lithium hydroxide in aqueous ethanol. Subsequent acidification of the reaction mixture and extraction with chloroform gave only poor yields (<10%) of the desired di-iminodiacetic acid **1**. Subsequently, **1** was isolated as its tetra-lithium salt by filtration of the reaction mixture, after removal of the ethanol and dilution with water. Unfortunately, **1** did not have the desired solubility in organic solvents to be useful for a solvent extraction process (more surfactant like).

The tetraiminocarboxylate **2** was expected to be a more lipophilic extractant and capable of the desired octadentate coordination of the actinide ion. The synthetic route to **2** is shown in scheme 2. Dialkylation of t-butylcalix[4]arene with ethyl 4-iodobutyrate in the presence of potassium carbonate in refluxing acetonitrile gave the diester **7** in 80% yield. Further alkylation of **7** with ethyl 4-iodobutyrate in DMF at room temperature gave the tetraester **8** (cone conformer) in 71% yield after careful chromatography on silica gel.



Scheme 2

The tetraethylester **8** was then readily converted to the tetrabromide **9** in two steps (BH_3-THF and then PPh_3, CBr_4). Treatment of the tetrabromide **9** with excess amyl amine (neat) at room temperature gave the tetraamine **10** in good yields. The choice of amylamine in this reaction was to enhance the organic solubility of the target extractant **2**. The crude amine **10** was then reacted with benzyl 2-bromoacetate (Cs_2CO_3, acetone, rt) to yield the tetrabenzylester **11** in 81% yield. Hydrogenolysis of **11** led to the formation of tetraiminoacetic acid **2**, which was isolated as its zwitterion, in good yields[18].

The preparation of the lower rim CMPO analog **3** could also be easily accomplished from the tetraamine **10**. Coupling of tetraamine **10** with *p*-nitrophenyl(diphenylphosphoryl) acetate[9] gave the CMPO-calix[4]arene ligand **3** in good yield after chromatographic purification.

Results of some preliminary extraction studies[19] on calixarenes **2** and **3** are quite promising. At pH=1 and 2, the tetraiminocarboxylate **2** extracted about 62% and 96% of the Th^{4+} that was present from an aqueous solution (0.10M $NaNO_3$) into $CHCl_3$, respectively. In comparison, less than 2% of the available europium(III) was extracted under these conditions. The CMPO chelator **3** was also examined for its ability to extract thorium(IV) and europium(III) into $CHCl_3$ from a 4M $NaNO_3$/1%HNO3 aqueous solution (pH=0.33). Under these conditions, 90% of the Th^{4+} and only 13-14% of the available Eu^{3+} was extracted into the organic layer.

In a competitive study with equimolar quantities of ligand **3** and each of the two metal ions, 64% of the thorium (IV) and less than 3% of the europium(III) was extracted.

In conclusion, efficient synthetic routes for two new calixarene extractants for actinides that have useful organic solubility have been developed. Results from preliminary studies indicate that both ligands are efficient extractants for Th^{4+} over Eu^{3+}. Studies to understand the complexation/extraction properties of these ligands have been initiated and we also hope to include extraction studies with americium(III) and plutonium(IV). The full details of the syntheses and evaluation of these ligands as well as related analogs will be reported in due course.

Acknowledgments: This work was supported by the Waste-Management Education and Research Consortium of New Mexico and the Efficient Separations and Processing Crosscutting Program of the US-DOE. Dr. Hollie Jacobs is thanked for her insightful discussions and Dr. Gary Rayson and Mr. Patrick Williams are thanked for their assistance in the metal analysis.

References:

1. Gopalan, A.; Huber, V.; Jacobs, H. in *Waste Management from Risk to Remediation*, Bhada, R., Ed.; ECM Press: Albuquerque, 1994, pp. 227-246.
2. *Proceedings of the First Hanford Separation Science Workshop*, PNL-SA-21775, Pacific Northwest Laboratory, Richland, WA, July 23-25, 1991.
3. *Separations of f Elements*, Nash, K. L.; Choppin, G. R., Eds.; Plenum, NY, 1995.
4. Nash, K. L.; Choppin, G. R. *Sep. Sci. Tech.* **1997**, *32*, 255.
5. Raymond, K. N.; Garrett, T. M. *Pure Appl. Chem.* **1988**, *60*, 1807.
6. Raymond, K. N.; Smith, W. L. *Struct. Bond.* (Berlin) **1981**, *43*, 159.
7. For some recent reviews on calixarenes see Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713, and references cited therein. Also see reference 8.
8. Casnati, A. *Gazz. Chim. Ital.*, **1997**, *127*, 637.
9. Arnaud-Neu, F.; Böhmer, V.; Dozol, J. -F.; Grüttner, C.; Jakobi, R. A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M. -J.; Simon, N.; Vogt, W. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1175.
10. Delmau, L. H.; Simon, N.; Schwing-Weill, M. -J.; Arnaud-Neu, F.; Dozol, J. -F.; Eymard, S.; Tournois, B.; Böhmer, V.; Grüttner, C.; Musigmann, C; Tunayar, A. *Chem. Commun.* **1998**, 1627.
11. For resorcin[4]arene based CMPO cavitands see Boerrigter, H.; Verboom, W.; de Jong, F; Reinhoudt, D. N. *Radiochim. Acta.* **1998**, *81*, 39, and references 3 and 4 therein.
12. Malone, J. F.; Marrs, D. J.; McKervey, M. A.; O'Hagan, P.; Thompson, N.; Walker, A.; Arnaud-Neu, F.; Mauprivez, O.; Schwing-Weill, M.-J.; Dozol, J.-F.; Rouquette, H.; Simon, N. *J. Chem. Soc., Chem. Commun.* **1995**, 2151.
13. Dasaradhi, L.; Stark, P. C.; Huber, V. J.; Smith, P. H.; Jarvinen, G. D.; Gopalan, A. S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1187.
14. Araki, K.; Hashimoto, N.; Otsuka, H.; Nagasaki, T.; Shinkai, S. *Chem. Lett.* **1993**, 829, and references cited therein.
15. For a recent review on plutonium selective ligands see O'Boyle, N. C.; Nicholson, G. P.; Piper, T. J.; Taylor , D. M.; Williams, D. R.; Williams, G. *Appl. Radiat. Isot.* **1997**, *48*, 183.
16. Stradling, G.N. *Radiat. Prot. Dosim.* **1994**, *53*, 297, and references cited therein.
17. Dasaradhi, L.; Lambert, T.; Gopalan, A. S. unpublished results. The diamine **4** was synthesized in three steps from calix[4]arene in good yields (1. Iodobutane, K_2CO_3, DMF, 60 °C, 18 h, 85% 2. NaH, DMF, *N*-4-iodobutylphthalimide, rt, 18 h, 78%. 3. aq. $MeNH_2$, THF, reflux, 16 h, 91%).
18. The structural identity of all compounds has been established by ^{1}H and ^{13}C NMR, IR, and elemental analysis.
19. Equal volumes of aqueous solution containing the metal ion of interest and chloroform containing a fivefold molar excess of the ligand were contacted for 2 h at ambient temperature with gentle shaking. The layers were separated carefully by centrifugation and the metal concentration in the aqueous layer was determined by ICP analysis. The necessary control experiments were also performed in the absence of ligand.