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A neutral uranyl dimeric complex and remarkable extraction properties of a 1-acid 3-diethyl amide substituted calix[4]arene ligand

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The crystal structure of $[(UO_2)_2L_2]$ (L = 1-acid 3-diethyl amide substituted calix[4]arene) has been determined; the uranyl, lanthanide and heavy metal extraction properties of L and of a recyclable polymeric calix[4]arene based resin material are also described.

Motivated by major economic and environmental considerations the selective extraction of uranium from sea water and radioactive nuclear waste is a topic of intense current interest.[1,2] Many tailor-made ligands (uranophiles) have been designed to perform this operation at the molecular level, some of which have utilised the calixarene framework.[2] In order to achieve the desired commercial viability, the ideal receptor must display a remarkable specificity and this may be achieved by taking into account many of the co-ordinating particularities of the uranyl cation (UO_2^{2+}). One of these key features is the ability of the UO_2^{2+} ion to accommodate from four to six oxygen donor ligands in an equatorial pseudo-planar arrangement.[3–5] We report here the novel crystal structure of a neutral uranyl dimeric complex and the remarkable and efficient extraction properties of a 1-acid 3-diethyl amide substituted calix[4]arene ligand L.[6]

The addition of $UO_2(OAc)_2{\cdot}2H_2O$ to L in acetonitrile† gave crystals of the uranium complex (Scheme 1) suitable for X-ray crystallographic determination.‡ The structure is a centrosymmetric dimer and is illustrated in Fig. 1. Each uranium atom is bonded to the two oxygen atoms in axial positions at 1.78(1) Å to make up the linear uranyl group. In the equatorial plane the uranium is bonded to only four oxygen atoms in an approximate plane (maximum deviation from the UO_4 least squares plane is 0.13 Å). The uranium is bonded to one phenolic oxygen at the bottom rim of the calixarene, one amide oxygen atom and to two acid oxygen atoms from different acid groups. These acid groups from the two adjacent calixarenes form together an eight-membered centrosymmetric ring of the type (U–O–C–O–U–O–C–O–).

It is interesting that this UO_4 equatorial plane is approximately perpendicular to the plane of the methylene groups of the calixarene (angle of intersection 87.2°). The four U–O bond distances are all different with the shortest bond to the phenolic oxygen at the bottom rim [U(1)–O(250) 2.162(7) Å]. The amide oxygen distance [U(1)–O(353)] is 2.379(9) Å while distances to the two acid oxygen atoms are [U(1)–O(154)] 2.321(8) and [U(1)–O(153^I)] 2.403(9) Å. This irregularity of distance is concomitant with considerable variation in the *cis* O–U–O angles in the equatorial plane being 108.3(3) for O(154)–U–O(250), 92.5(3) for O(250)–U–O(353), 76.1(3) for O(353)–U–O(153^I) and 83.3(3)° for O(153^I)–U–O(154). It seems likely that these variations are due to the steric constraints of the ligand.

Computer modelling calculations had demonstrated that the uranyl ion could not fit into the calixarene so that the uranyl axis was coincident with the calixarene axis and the uranium bonded to the four oxygens at the bottom rim in an equatorial plane. It is interesting that the recent crystal structure[2b] of a uranyl complex with calix[6]arene also shows dimer formation with two uranyls sandwiched between two calix[6]arenes and the uranyl axes perpendicular to the calixarene axes. In that structure the equatorial planes are made up of two oxygen atoms from each calixarene.

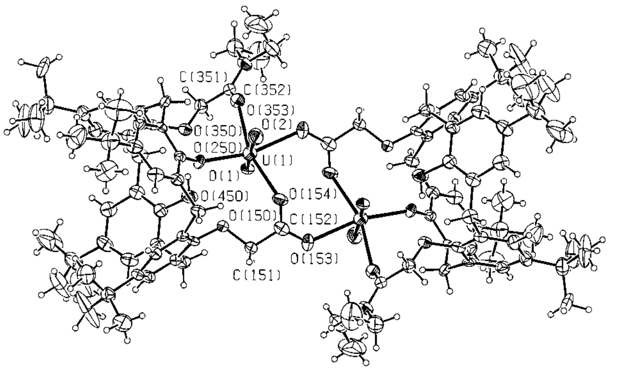
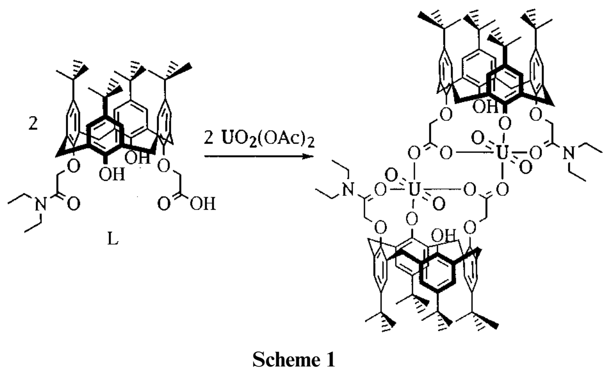


Fig. 1 Structure of the $[(UO_2)_2L_2]$ dimer. Selected bond lengths (Å): U(1)–O(250) 2.162(7), U(1)–O(154) 2.321(8), U(1)–O(353) 2.379(9), U(1)–O(153^I) 2.403(9). Symmetry element I −*x*, −*y*, −*z*.



Scheme 1

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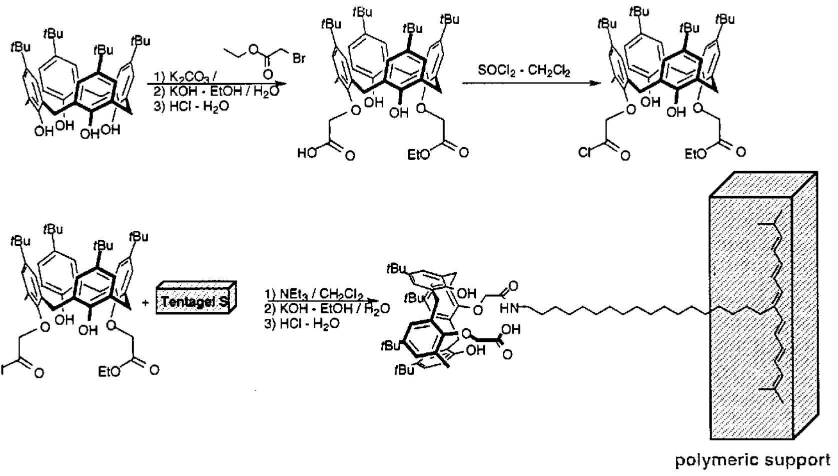
† A solution of $UO_2(OAc)_2{\cdot}2H_2O$ (0.025 g, 5.9×10^{-5} mol) in acetonitrile was added to a stirred solution of L (0.05 g, 5.9×10^{-5} mol) in acetonitrile. Slow evaporation of the resulting solution gave red crystals (45 mg, 70% yield). Reproducible elemental analytical results could not be obtained because of the presence of variable amounts of included solvent, which is a well documented feature of calixarene chemistry.

‡ Crystal data: $[(UO_2)_2L_2]{\cdot}10MeCN{\cdot}2MeOH$, $C_{126}H_{170}N_{12}O_{20}U_2$, *M* 2648.80, triclinic, space group $P\bar{1}$, $a = 12.350(9)$, $b = 12.765(12)$, $c = 23.67(3)$ Å $\alpha = 94.643(10)$, $\beta = 97.523(10)$, $\gamma = 110.143(10)°$, $T = 293$ K, $U = 3441(6)$ Å^3, $Z = 1$, $\mu = 2.41$ mm^{-1}, $D_c = 1.278$ g cm^{-3}, reflections collected 7941, $R1 = 0.0711$, $wR2 = 0.1934$ for 5998 data with $I > 2\sigma(I)$. CCDC reference number 186/1086. See http://www.rsc.org/suppdata/dt/1998/2783/ for crystallographic files in .cif format.



Scheme 2

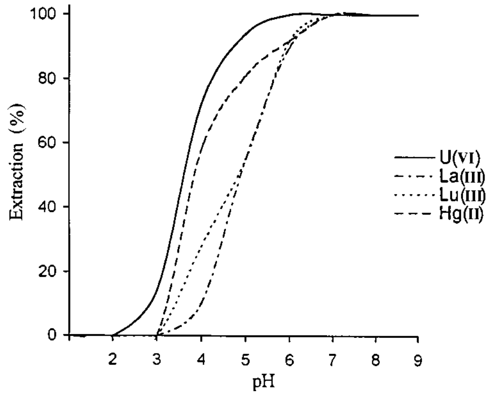


Fig. 2 Percentage of UO_2^{2+}, La^{3+}, Lu^{3+} and Hg^{2+} (0.4×10^{-3} mol dm^{-3}) extracted by L (9.6×10^{-3} mol dm^{-3}) in dichloromethane in the presence of citrate (1.2×10^{-3} mol dm^{-3}) at 293 K as a function of pH.

Uranyl extraction experiments and those of a variety of other selected metals were carried out using an aqueous phase of metal nitrate (0.4×10^{-3} mol dm^{-3}) at differing pH values with citrate buffer and the extractant dichloromethane solvent phase containing L at a concentration of 9.6×10^{-3} mol dm^{-3}. After 1 h of rapid mixing of solutions, inductively coupled plasma atomic emission spectral (ICP-AES) analysis was used to determine the concentrations of metal in the respective phases. The extraction results as a function of pH displayed in Fig. 2 clearly show that *quantitative* extraction of uranyl, lanthanum, lutetium and mercury occurs at pH values $\geqslant 6$. This may be attributed to the calix[4]arene's unique, lower rim, coordination environment forming neutral metal cation complexes which in combination with the ligand's lipophilic exterior results in a remarkably efficient extracting reagent.† Crystal structure determinations have previously shown L to form neutral dimeric and monomeric complexes with lanthanum and lutetium respectively.[6] It is noteworthy that washing the organic phase with 1 mol dm^{-3} nitric acid releases the extracted metal and allows calixarene re-use. Indeed recycling the calixarene ligand ten times did not result in any decline in extraction performance. Fig. 3 shows the preliminary extraction results at physiological pH with an extended range of metals which reveal L selectively extracts UO_2^{2+}, La^{3+}, Lu^{3+}, Hg^{2+}, Sr^{2+}, Pb^{2+}, Bi^{3+} quantitatively, and to a lesser extent Y^{3+}, Ag^{+}, and is a poor extractant for Group 1, 2 and transition metals.

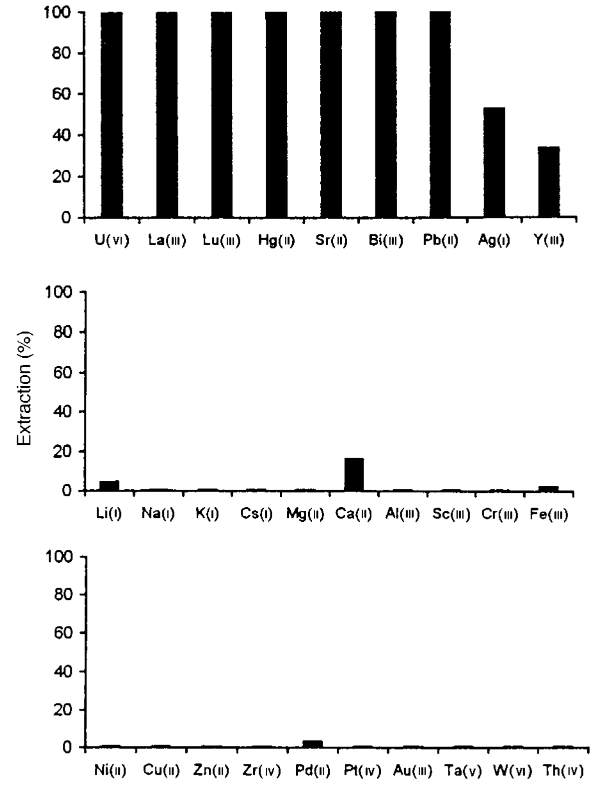


Fig. 3 Percentage extraction of metal ions (0.4×10^{-3} mol dm^{-3}) in the presence of citrate (1.2×10^{-3} mol dm^{-3}) in dichloromethane at 293 K. The pH value of the aqueous phase was 7.0 ± 0.1.

In order to further test the potential commercial viability of this calixarene based extractant this ligand design was successfully attached to a Tentagel S NH_2 resin polymer using the synthetic route shown in Scheme 2. Elemental analysis of the resulting material suggested a loading of 0.24×10^{-3} mol of calix[4]arene ligand per gram of resin. Aqueous solutions of uranyl nitrate were passed through the resin material and quantitative extraction was observed over the range pH 4–9. The preliminary results of passing actual low level nuclear waste are also very exciting. The resin selectively extracts uranyl at concentrations as low as ppb levels and on addition of nitric acid uranyl can be removed and the resin recycled without any diminution in extraction efficiency. Modelling calculations show the uranyl dimeric structure is still possible with the polymeric attachment. Studies are in progress to elucidate whether the *solution* formation of the dimeric uranyl L complex is crucial to the efficient extraction of the actinide either with L or the polymeric calix[4]arene based resin material.

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§ Preliminary ^1H NMR solution binding studies reveal L forms an empirical 1 : 1 stoichiometric complex with UO_2^{2+} in CD_2Cl_2 solution. Obviously this result does not prove or disprove whether the dimeric 2 : 2 structure is retained in solution.

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References

1 P. Thuéry, N. Keller, M. Lange, J.-D. Vignier and M. Nierlich, *New J. Chem.*, 1995, **19**, 619 and refs. therein.

2 (*a*) P. Thuéry and M. Nierlich, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1997, **27**, 13; (*b*) P. Thuéry, M. Lance and M. Nierlich, *Supramol. Chem.*, 1996, **7**, 183; Y. Kubo, S. Maeda, M. Nakamura and S. Tokita, *J. Chem. Soc., Chem. Commun.*, 1994, 1725; T. Nagasaki and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1063; S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *J. Am. Chem. Soc.*, 1987, **109**, 6371.

3 W. G. Van der Sluys and A. P. Sattleberger, *Chem. Rev.*, 1990, **90**, 1027.

4 P. Guilbaud and G. Wipf, *J. Phys. Chem.*, 1993, **97**, 5685.

5 P. H. Walton and K. N. Raymond, *Inorg. Chim. Acta*, 1995, **240**, 593; T. S. Franczyk, K. R. Czerwinski and K. N. Raymond, *J. Am. Chem. Soc.*, 1992, **114**, 8138.

6 P. D. Beer, M. G. B. Drew, A. Grieve, M. Kan, P. B. Leeson, G. Nicholson, M. I. Ogden and G. Williams, *Chem. Commun.*, 1996, 1117.

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