Subtleties with Sulfur: Calixarenes as Uranophiles**

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Evidence that support of donor atoms on a calixarene scaffolding might provide selectivity in the binding of U^{VI}, putatively as UO_2^{2+},[1] has led to interest in establishing the coordination mode of uranium in such species.[2] Early work[3, 4] on the synthesis of UO_2^{2+}-specific ligands, so-called "uranophiles",[5, 6] presumed that ligands providing essentially planar pentagonal or hexagonal donor atom arrays would be most apposite, given that such geometries, common in UO_2^{2+} complexes, are not well known for other metal ions.[7] This argument was advanced[1] as a possible explanation of selective binding of UO_2^{2+} by a number of (water-soluble) calix[6]arene derivatives, though the focus was more on the geometry than the dimensions and nature of the donor set. Indeed, the suggestion that six phenoxide donors might be involved seems at variance with the known chemistry of UO_2^{2+} with alkoxide ligands,[8] where only four such ligands are found in species of near-octahedral symmetry. True U^{VI} alkoxides, $[U(OR)_6]$, are known[8] but are not stable under the conditions used to form uranyl ion/calixarene complexes by solvent extraction, though there may be exceptional formation of such species by a calix[6]arene ligand. Significantly, however, the recent structural characterization of a pyridine-stabilized U^{VI} derivative of *p-t*Bu-calix[6]arene[9] shows two ligand molecules are required to give octahedral coordination, each of which functions as a tridentate donor in a 1,2,3-*alternate* conformation.

In crystal structures of UO_2^{2+} complexes of calixarenes with only phenoxide donors, a maximum of four equatorial phenoxide groups is found.[2] Trigonal coordination is seen in the complex of the expanded calixarene, *p-t*Bu-hexahomotrioxa-calix[3]arene,[10] suggesting a different possible approach to the synthesis of uranophiles to that based on attaining unusual, high-coordination geometries, though it is not known if this complex is more stable than those obtained with *p-t*Bu-dihomooxacalix[4]arene,[11] *p-t*Bu-calix[6]arene[12] or *p-t*Bu-calix[7]arene,[13] which display approximately square-planar coordination. (In the complex of *p-t*Bu-calix[5]arene,[14] a phenol OH unit functions as a fifth donor in a strongly distorted pentagonal-planar array.) It may be that the determinant of UO_2^{2+} bonding to calixarenes, regardless of selectivity, is the optimal U−O(phenoxide) separation; data from structures of U^{VI} compounds with unrestricted (unidentate) alkoxide ligands provide an estimate of about 2.2 Å as the "ideal" such distance.[2] Here, we present structures for the hitherto uncharacterized UO_2^{2+}/calix[4]arene system and the UO_2^{2+} complex of *p-t*Bu-tetrathiacalix[4]arene. These illustrate how quite subtle changes in ligand geometry can drastically alter the form of complexes. In the first case, the structure is that of the uranyl ion complex of calix[4]arene itself,[15a] the smallest methylene-bridged calixarene. In the second case, the structures of two different solvates[15b,c] of the UO_2^{2+} complex of *p-t*Bu-tetrathiacalix[4]arene,[16] which is apparently generally superior to its CH_2-bridged analogue as a metal binding agent. Structural evidence shows that, at least in some cases, this should be associated with coordination of the thiaether sulfur atoms.[17, 18] Paradoxically, the UO_2^{2+} complex structures are the first of a diversity determined by us in which there is no metal−S interaction.

The structure of the stoichiometric unit of the UO_2^{2+}/calix[4]arene complex is shown in Figure 1. Ignoring the

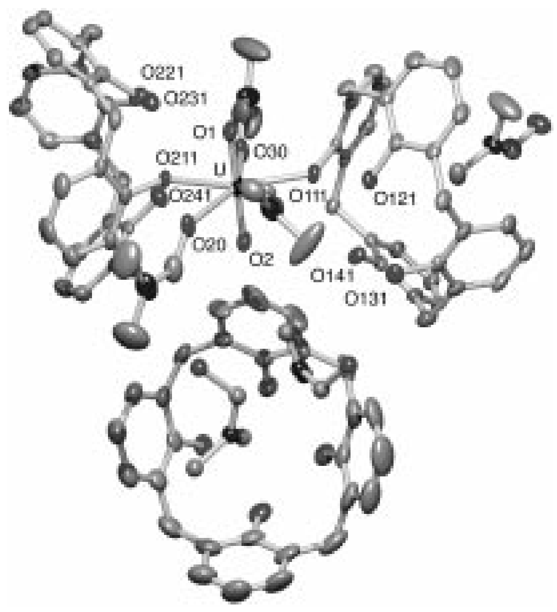

Figure 1. Structure of $[UO_2\{(\text{calix[4]arene}-H)(\text{dmf})\}(\text{calix[4]arene}-H)(\text{dmf})_{2.7}(\text{dmso})_{0.3}]\cdot[\text{calix[4]arene(dmf)}]\cdot 1/2\,\text{DMF}$. U−O(1,2; 111,211; 10,20,30) 1.753(3), 1.755(3); 2.358(3), 2.396(3); 2.399(3), 2.400(3), 2.368(3) Å. O$\cdots$O distances in the calixarene (cyclically from O(m11): 2.747(4), 2.779(4), 2.912(4), 2.691(4), ($m = 1$); 2.718(4), 2.740(4), 2.978(4), 2.732(4) ($m = 2$); 2.658(5), 2.678(5), 2.626(5), 2.663(5) Å ($m = 3$). C_6 dihedral angles betweeen the six-membered rings and the relevant O_4 planes: $m = 1$ ($\chi^2 = 10^4$; deviations from the average plane: $\delta(On1)$ 0.181(4), −0.189(4), 0.208(4), −0.196(4); $\delta(U)$ 2.382(3) Å): 63.1(1), 39.8(1), 72.0(1), 49.4(1)°; $m = 2$ ($\chi^2 = 6\times10^3$; $\delta(On1)$ 0.129(4), −0.160(4), 0.154(4), −0.157(4); $\delta(U)$ 2.229(3) Å): 64.0(1), 40.0(1), 70.0(1), 55.8(1)°; $m = 3$ ($\chi^2 = 53$; $\delta(On1)$ 0.014(4), −0.017(5), 0.018(5), −0.015(4) Å): 54.8(2), 60.0(2), 52.6(2), 55.0(2)°.

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disorder associated with the mixture of neutral, unidentate (solvent) ligands present, the cause of earlier failures to isolate complexes, principally of *p*-*t*Bu-calix[4]arene but also of calix[4]arene, may lie in the limited interaction with the calixarene suggested by its mere unidentate coordination. Although influenced by hydrogen bonding involving residual phenolic protons, the 1,3-oxygen atom separation is less than twice the "ideal" U−O(phenoxide) distance (4.4 Å). Thus, if the observed conformation is an indicator of that adopted by the fully deprotonated ligand, envelopment of UO_2^{2+} by provision of four "equatorial" phenoxide donors may not be possible. For a simple calixarene[19] with pendent donors (cf. some biological systems[20]) variable donor atom separation can result from tilting of the units to which they are attached.[21] Here, however, it seems a sufficient tilt to span UO_2^{2+} is energetically too demanding. The relatively long U−O(phenoxide) bonds indicate that when full deprotonation of a calixarene is not achieved, hydrogen bonding with residual phenolic units may reduce the donor strength of formal phenoxide donors.

In contrast, in the analogue of *p*-*t*Bu-calix[4]arene in which the CH_2 bridge is replaced by S, the macrocycle expansion of about 0.5 Å per "edge", which is defined by the distance between two adjacent bridging atoms, is apparently sufficient to allow accommodation of the needs of UO_2^{2+}. A 1:1 complex is readily obtained, the synthesis being insensitive to the presence of water, whereas with *p*-*t*Bu-calix[4]arene—and to a certain extent with calix[4]arene—the basic conditions employed lead to the ready precipitation of $UO_2(OH)_2$ through traces of water present in "dry" solvents.[2] The structure of the thiacalixarene complex is shown in Figure 2. The coordination geometry of uranium is similar to that in each uranium center of the dinuclear UO_2^{2+} complex with *p*-*t*Bu-calix[6]arene and is close to a regular octahedral form, as in $UO_2(OR)_4$ complexes. Interestingly, the insertion of one UO_2^{2+} oxygen atom into the calixarene cavity does not prevent the inclusion of solvent molecules. The UO_2^{2+}–oxygen bond lengths are significantly shorter than in the corresponding calix[4]arene species, which perhaps reflects more effective charge donation in the equatorial plane by the four phenoxide donors.

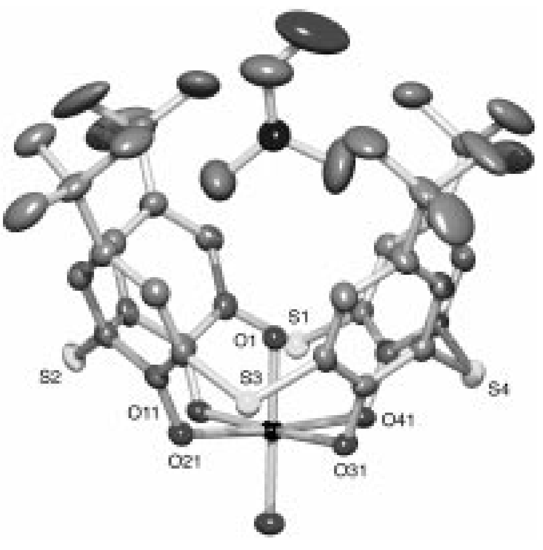

Figure 2. Structure of $[UO_2\{(p\text{-}t\text{Bu-tetrathiacalix[4]arene} - 4\,H)(dmf)\}]\cdot 2\,DMF$ array, projected quasi-normal to the cone axis, and showing the included DMF molecule. U−O(1,2; 11−41) 1.788(2), 1.804(2); 2.300(2), 2.230(2), 2.293(2), 2.241(2) Å. Dihedral angle between the six-membered rings and the O_4 plane ($\chi^2 = 5 \times 10^2$; $\delta(On1)$ (alternately) ±0.024(2); $\delta(U)$ 0.077(1) Å): 64.29(7), 59.98(7), 63.89(7), 62.05(7)°. While the U−O distance for the MeCN/DMSO solvate lie within 3σ (σ = standard deviation) of the value of the DMF solvent (exception: U−O(21) 2.260(4) Å), the C_6–O_4 dihedral angles are appreciably larger (67.2(2), 64.4(2), 67.8(2), 64.6(2)°), suggesting that inclusion of the "larger" DMF ligand is accommodated by "flattening" of the cone.

Experimental Section

$[HNEt_3]_2[UO_2\{(p\text{-}t\text{Bu-tetrathiacalix[4]arene} - 4\,H)(MeCN)\}]\cdot ca.\ 1.7\,DMSO$: *p*-*t*Bu-Tetrathiacalix[4]arene · $CHCl_3$ (0.11 g, 0.13 mmol) was dissolved in DMSO (1.5 mL) containing NEt_3 (0.1 mL) and mixed with a solution of $[UO_2(dmso)_5](ClO_4)_2$ (0.10g, 0.13 mmol) in DMSO (1.5 mL). Vapor diffusion of MeCN into this deep red solution in a closed vessel over three days provided large, red plates. A single crystal was selected for structure determination, and the residual solid was collected by filtration, washed with MeCN, and air-dried (100 mg, 56 %). Elemental analysis indicated some loss of DMSO from the bulk relative to the single crystal: calcd (%) for $[(CH_3CH_2)_3NH]_2[UO_2\{(C_{40}H_{44}O_4S_4)(MeCN)\}]\cdot C_2H_6SO$: C 51.32, H 6.54, N 3.21, S 12.23; found: C 51.4, H 6.0, N 3.2, S 11.2; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.10$ (s, *t*Bu), 1.49 (t, Me, NEt_3), 1.55 (s, MeCN), 2.57 (s, DMSO), 3.26 (q, CH_2, NEt_3), 7.62 (s, aryl-H); IR (KBr): $\tilde{\nu} = 3429$ (NH), 2693 (CH), 826, 797 cm^{-1} (U=O).

$[HNEt_3]_2[UO_2\{(p\text{-}t\text{Bu-tetrathiacalix[4]arene} - 4\,H)(dmf)\}]\cdot 2\,DMF$: *p*-*t*Bu-Tetrathiacalix[4]arene · $CHCl_3$ (0.10 g, 0.19 mmol) was dissolved in DMF (3 mL) containing NEt_3 (0.1 mL) and mixed with a solution of $[UO_2(NO_3)_2(OH_2)]\cdot 5\,H_2O$ (0.17 g, 0.20 mmol) in DMF (3 mL). The deep orange-red solution formed was placed in a closed vessel for three days, which led to deposition of large red plates. A specimen was removed for the X-ray work and the bulk was isolated as above (100 mg, 73 %). Elemental analysis indicated partial desolvation: calcd (%) for $[CH_3CH_2)_3NH]_2[UO_2\{(C_{40}H_{44}O_4S_4)(C_3H_7NO)\}]\cdot C_3H_7NO$: C 52.08, H 6.78, N 4.19, S 9.59; found C 51.6, H 6.6, N 3.7, S 9.7; IR (KBr): $\tilde{\nu} = 3430$ (N−H), 2957, 2651, 2489 (C−H), 833, 796 cm^{-1} (U−O).

$[UO_2\{(calix[4]arene - H)(dmf)\}(calix[4]arene - H)(dmf)_{2.7}(dmso)_{0.3}]\cdot[calix[4]arene(dmf)]\cdot 1/2\,DMF$: Calix[4]arene (106 mg) was dissolved in DMF (2 mL) containing ~1 M methanolic NMe_4OH solution (0.5 mL) and mixed with a solution of $[UO_2(dmso)_5](ClO_4)_2$ (220 mg) in DMF (1 mL). The deep red-orange solution formed was placed in a vapor diffusion cell along with 2-propanol. A heterogeneous deposit of colorless and orange material was obtained. On extended standing (1 year) of this mixture, an orange crystal appropriate for an X-ray study was removed, whose structure modeled the composition given above.

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[15] Crystal structure analyses: a) $[UO_2\{(calix[4]arene-H)(dmf)\}(calix[4]arene-H)(dmf)_{2.7}(dmso)_{0.3}]\cdot[calix[4]arene(dmf)]\cdot 1/2\,DMF$: $C_{100.2}H_{108.2}N_{5.2}O_{19.5}S_{0.3}U$, $M_r = 1945.0$; monoclinic, space group *C*2/*c*, $a = 29.970(3)$, $b = 18.180(3)$, $c = 33.802(3)$ Å, $\beta = 97.073(2)°$, $V = 18277$ Å^3; $Z = 4$; $\rho_{calcd} = 1.413\ g\,cm^{-3}$; crystal dimensions: $0.22 \times 0.14 \times 0.10$ mm; $\mu_{Mo} = 18.6\ cm^{-1}$; 89915 measured reflections (Bruker AXS CCD diffractometer, $T \approx 153$ K, monochromatic $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), multiscan absorption correction (min./max. transmission = 0.60/0.84; $2\theta_{max} = 58°$) gave 23359 unique reflections ($R_{int} = 0.037$), of which 13875 were considered observed ($F > 4\sigma(F)$), refinement on $|F|$ (anisotropic thermal parameter refinement for non-H atoms, $(x, y, z, U_{iso})_H$ included constrained at estimates, phenolic hydrogen atoms located in difference maps), $R = 0.043$, $R_w = 0.043$ (statistical weights).[15d] b) $[HNEt_3]_2[UO_2\{(p\text{-}t\text{Bu-tetrathiacalix}[4]arene-4H)(dmf)\}]\cdot 2\,DMF$: $C_{61}H_{97}N_5O_9S_4U$, $M_r = 1410.8$; monoclinic, space group $P2_1/n$, $a = 12.309(2)$, $b = 21.524(3)$, $c = 25.719(3)$ Å, $\beta = 103.828(2)°$, $V = 6616$ Å^3; $Z = 4$; $\rho_{calcd} = 1.416\ g\,cm^{-3}$; crystal dimensions: $0.40 \times 0.20 \times 0.20$ mm; $\mu_{Mo} = 26.4\ cm^{-1}$; min./max. transmission = 0.51/0.72; 72054 measured reflections, of which 16139 were independent ($R_{int} = 0.027$) and 13760 observed ($F > 4\sigma(F)$); $R = 0.025$, $R_w = 0.037$.[15d] c) $[HNEt_3]_2[UO_2\{(p\text{-}t\text{Bu-tetrathiacalix}[4]arene-4H)(MeCN)\}]\cdot \sim 1.7\,DMSO$: (isomorphous with the DMSO adduct) $C_{57.46}H_{89.38}N_3O_{7.73}S_{5.73}U$, $M_r = 1367.7$; $a = 11.6912(7)$, $b = 21.612(1)$, $c = 25.543(2)$ Å, $\beta = 101.275(1)°$, $V = 6329$ Å^3; $Z = 4$; $\rho_{calcd} = 1.435\ g\,cm^{-3}$; crystal dimensions: $0.45 \times 0.40 \times 0.15$ mm; $\mu_{Mo} = 28.0\ cm^{-1}$; min./max. transmission = 0.48/0.72; 69598 measured reflections, of which 15779 were independent ($R_{int} = 0.044$) and 11866 observed ($F > 4\sigma(F)$); $R = 0.050$, $R_w = 0.053$. Determination c) is less auspicious than b), since the Et_3NH^+ ion is disordered, with (concomitant) generally higher "thermal motion" throughout; the DMF solvate is disordered.[15d] d) The structures were solved using the Xtal3.6.1 software package (*Xtal3.6.1 System* (Eds.: S. R. Hall, D. J. du Boulay, R. Olthof-Hazekamp), University of Western Australia, **1999**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-147758, CCDC-147759, and CCDC-147760. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Isolation of a Highly Persistent Diphosphanyl Radical: The Phosphorus Analogue of a Hydrazyl[**]

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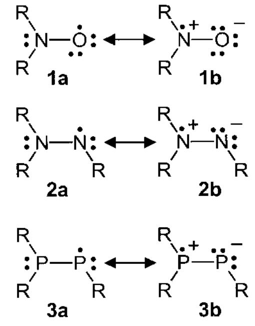
Despite the enormous importance of radicals in both chemical reactions and biological processes, very few organic free radicals have been isolated.[1, 2] Notable exceptions are nitroxides **1** and hydrazyls **2**, in which the unpaired electron is localized on a nitrogen center.[3] These stable radicals, which are described by the resonance structures **a** and **b** (Scheme 1), are applied as contrast agents, molecular markers, and reporters for molecular movements (spin labels).[4] Considerable effort has been invested in the synthesis of stable free radicals localized on phosphorus, the closest homologue to nitrogen.[5–9] Indeed, this element consists of only one isotope, ^{31}P, with a nuclear spin of ½ giving rise to a hyperfine coupling which is much larger than with the nitrogen isotope ^{14}N. This property is particularly interesting for spin-labeling experiments, since the anisotropy (orientation dependence) of the hyperfine coupling with ^{31}P would provide detail concerned



Scheme 1. Resonance structures **a** and **b** of nitroxide **1**, hydrazyl **2**, and diphosphanyl **3**.

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