Subtleties with Sulfur: Calixarenes as Uranophiles

Abstract

Evidence that support of donor atoms on a calixarene scaffolding might provide selectivity in the binding of UVI, 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 UVI 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 pyridinestabilized UVI derivative of p-tBu-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.

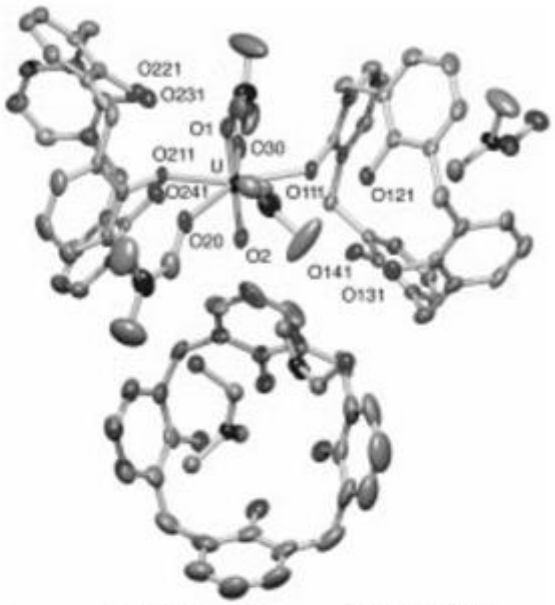

Figure 1. Structure of $[UO_2\{(calix[4]arene-H)(dmf)\}(calix[4]arene-H)(dmf)_{2.7}(dmso)_{0.3}]\cdot[calix[4]arene(dmf)]\cdot 1/2\,DMF$. U–O(1,2; 111,211; 10,20,30) 1.753(3), 1.755(3); 2.358(3), 2.396(3); 2.399(3), 2.400(3), 2.368(3) Å. O···O distances in the calixarene (cyclically from O(m11): 2.747(4), 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 between the six-membered rings and the relevant O_4 planes: m = 1 ($\chi^2 = 10^6$; deviations from the average plane: δ(Om1) 0.181(4), −0.189(4), 0.208(4), −0.196(4); δ(U) 2.382(3) Å): 63.1(1), 39.8(1), 72.0(1), 49.4(1)°; m = 2 ($\chi^2 = 6\times10^3$; δ(Om1) 0.129(4), −0.160(4), 0.154(4), −0.157(4); δ(U) 2.229(3) Å): 64.0(1), 40.0(1), 70.0(1), 55.8(1)°; m = 3 ($\chi^2 = 53$; δ(Om1) 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)°.