In search of uranium terminal sulfide complexes

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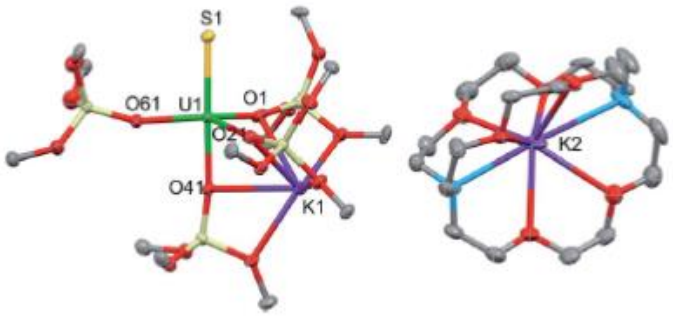
There has been renewed interest in uranium complexes with uranium-ligand multiple bonds (e.g. N, O, S), since such complexes could open up new reactivity and catalytic applications due to the large size of uranium ions and the involvement of *f* orbitals in uranium-ligand bonding. Also, they are of fundamental interest because they can be used to probe the nature of the bonding in actinide complexes. The list of well-characterised uranium terminal oxo complexes is growing but there are only a few uranium complexes bearing terminal sulfide ligands.[1-4] Sulfur-containing ligands are used in the selective extraction of actinides from nuclear waste, and this necessitates further studies into the nature of An–S bonds.

Different approaches have been used to prepare uranium(IV) terminal sulfide complexes. Hayton and co-workers treated a uranium(III) ylide adduct with 0.125 eq. of S_8,[1] while Meyer and coworkers deprotonated a uranium(IV) hydrosulfide complex.[3] Reductive cleavage of a uranium(IV) thiolate complex after treatment with Na(Hg) also yielded a uranium(IV) terminal sulfide complex.[2] Our group recently prepared a uranium(IV) terminal sulfide complex supported by bulky tris(tertbutoxy)siloxide ligands (L = $OSi(OtBu)_3$) (Fig. 1). This complex was prepared by first treating [KUL_4] with 0.5 eq. of $Ph_3P{=}S$. Then, 2.2.2-cryptand was added to abstract two of the potassium ions from the complex that is formed, $[SUL_4K_2]_2$, affording a new uranium(IV) terminal sulfide complex. [4]

The synthesis of uranium(V) terminal sulfide complexes more complicated than that of analogous uranium(IV) complexes, but our preparation of a uranium(IV) terminal sulfide complex supported by tris(tertbutoxy)siloxide ligands suggests that they could be suitable supporting ligands for a uranium(V) terminal sulfide complex.



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