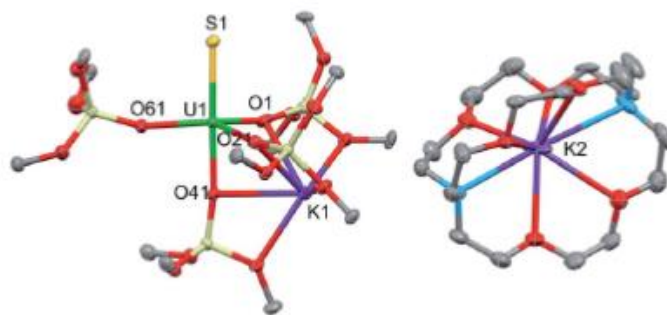


In search of uranium terminal sulfide complexesR. P. Kelly¹, M. Falcone¹, J. Andrez¹, R. Scopelliti¹, C. A. Lamsfus², L. Maron¹, M. Mazzanti^{1*}¹EPFL, ²INSA, Toulouse

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 S₈,[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 [KUL₄] with 0.5 eq. of Ph₃P=S. Then, 2.2.2-cryptand was added to abstract two of the potassium ions from the complex that is formed, [SUL₄K₂]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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