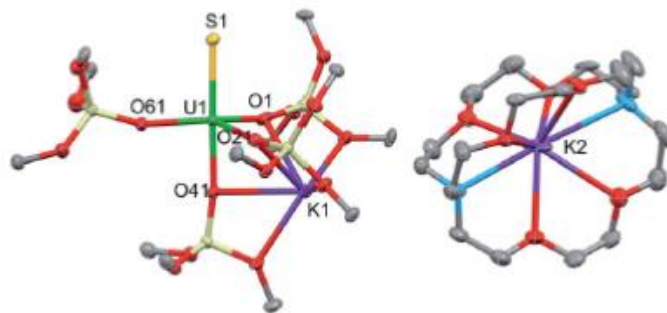


**In search of uranium terminal sulfide complexes**R. P. Kelly<sup>1</sup>, M. Falcone<sup>1</sup>, J. Andrez<sup>1</sup>, R. Scopelliti<sup>1</sup>, C. A. Lamsfus<sup>2</sup>, L. Maron<sup>1</sup>, M. Mazzanti<sup>1\*</sup><sup>1</sup>EPFL, <sup>2</sup>INSA, Toulouse

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 S<sub>8</sub>,[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)<sub>3</sub>) (Fig. 1). This complex was prepared by first treating [KUL<sub>4</sub>] with 0.5 eq. of Ph<sub>3</sub>P=S. Then, 2.2.2-cryptand was added to abstract two of the potassium ions from the complex that is formed, [SUL<sub>4</sub>K<sub>2</sub>]<sub>2</sub>, 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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[2] L. Ventelon, C. Lescop, T. Arliguie, P. C. Leverd, M. Lance, M. Nierlich and M. Ephritikhine, *Chem. Commun.* **1999**, 659.

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[4] J. Andrez, J. Pécaut, R. Scopelliti, C. E. Kefalidis, L. Maron, M. W. Rosenzweig, K. Meyer and M. Mazzanti, *Chem. Sci.* **2016**, *7*, 5846.