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## Review

## Molecular actinide compounds with soft chalcogen ligands



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## Contents

1. Introduction .....	36
2. Complexes with chalcogen ligands as Lewis bases .....	36
3. Complexes with chalcogenolate ligands .....	36
3.1. Homoleptic chalcogenolates and their adducts .....	36
3.2. Heteroleptic chalcogenolate complexes .....	39
3.2.1. Inorganic chalcogenolate complexes .....	39
3.2.2. Organometallic chalcogenolate complexes .....	40
4. Complexes with anchored chalcogenolate ligands .....	44
4.1. Complexes with pyridine N-oxide thiolate, pyridine thiolate and pyrimidine thiolate ligands .....	44
4.2. Complexes with the 2-mercapto benzothiazolate ligand (SBT) .....	44
4.3. Thiametallacyclic complexes .....	45
4.4. Complexes with sulfenamido, thiohydroxamate, pyrazol-3-thione and thiosemicarbazone ligands .....	46
4.5. Complexes with imidodiphosphinochalcogenide ligands .....	47
4.6. Complexes with the bis(thiophosphinoyl)methanediide ligand .....	47
4.7. Complexes with phosphinine-based SPS pincer ligands .....	48
5. Chalcogenide complexes .....	48
5.1. Bridging chalcogenides .....	50
5.2. Terminal chalcogenides .....	52
5.3. Actinide chalcogenides in the gas phase .....	55
5.4. Actinide chalcogenides in solid state chemistry .....	55
6. Chalcogeno-carbamate, -phosphinate, -carbonate and -carboxylate complexes .....	55
6.1. Chalcogenocarbamate complexes .....	55
6.2. Chalcogenophosphinate complexes .....	56
6.3. Chalcogenocarboxylate and carbonate complexes and compounds resulting from carbon disulfide reactions .....	57
7. Conclusion .....	59
References .....	60

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## ABSTRACT

A comprehensive review of molecular actinide complexes with ligands containing soft donor chalcogen atoms (S, Se, Te), highlighting the more recent advances, is presented.

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## 1. Introduction

The chemistry of the molecular complexes of actinides (An), which was for a long time underdeveloped compared to the rest of the periodic table, has witnessed a speeding up of its historical process during the past three decades. A growing number of review articles have described these spectacular advances, which were favored by the use of new practical starting materials and were incited by the revealed existence of fundamental and fascinating aspects of actinide chemistry [1–9]. Actinide compounds definitely proved to be interesting for something else other than their oddness and their applications limited to nuclear industry, if necessary. The increasing number and variety of complexes, together with the improvement of spectroscopic and computational techniques, led to a better understanding of their structures, reactions and physicochemical properties.

In addition to the common experimental difficulties in handling air sensitive and radioactive compounds, the development of actinide complexes with sulfur, selenium and tellurium donor ligands suffered from the idea that the linkage between the hard metal and soft chalcogen atom would be disfavored. However, the efficiency of such ligands in the selective complexation and extraction of actinides was recognized early [10–14]. After this view of the hard-soft mismatch was conclusively invalidated, in particular with the synthesis of a range of stable uranium thiolate complexes, the actinide complexes with soft chalcogen ligands has significantly blossomed over the recent years. These complexes, which have been crystallographically characterized [15], are now 4 times more numerous than those reported before 1998, when the latest review on these compounds was published [16]. Also noteworthy is the number of such complexes with An–Se and An–Te bonds, 46 and 14, compared with 1 and 0 before 1998. And most interesting is the emergence of new chalcogen ligands for thorium, uranium and trans-uranium compounds, exhibiting unprecedented structures and reactions. A number of these complexes were synthesized with a series of actinide metals (Th, U, Np, Pu) and also with their lanthanide (Ln) analogues, allowing comparison of the bonding between the ligands and the 4f or 5f elements. The intent of this review is to give a comprehensive scope of the molecular actinide complexes with soft chalcogen ligands with highlights on the more recent advances.

## 2. Complexes with chalcogen ligands as Lewis bases

Such complexes with dative An ← E bonds and with no charge on the heteroatom remain less common and in most of these, the Lewis base is part of a multidentate ligand, so that coordination is favored by an entropic effect. The complexes are represented in Fig. 1.

Addition of tetrahydrothiophene (THT) to a toluene solution of the uranium(III) complex  $[U(C_5H_4Me)_3(THF)]$  gave the adduct  $[U(C_5H_4Me)_3(THT)]$  (**1**) in which the U–S distance is 2.986(5) Å [17]. The relative affinity of Lewis bases toward  $[U(C_5H_4Me)_3]$  showed that tertiary amines, ethers and thioethers are all roughly equivalent in donor capacity [18]. Treatment of  $[U(BH_3Me)_4]$  with THT and 1,2-bis(methylthio)ethane afforded  $[U(BH_3Me)_4(\mu-THT)]_2$  (**2**) and  $[U(BH_3Me)_4(MeSCH_2CH_2SMe)]$  (**3**), with U–S bond lengths of 3.18(2) and 3.06(1) Å, respectively [19,20].

Dimethyl sulfide coordinates to the An(IV) complexes  $[AnCp^*(\kappa^6(B_3cat)_6)(SMe_2)]$  (An = Th, U; Cp\* = η-C<sub>5</sub>Me<sub>5</sub>) (**4**) exhibiting a planar hexaaxo, trianionic, 15-membered macrocyclic ligand and resulting from reaction of  $[AnCp^*_2Me_2]$  and excess of catecholborane (HBCat) that contains 5% dimethyl sulfide [21].

A few complexes exhibit the actinide metal included in a crown thioether:  $[AnI_3(9-thiacrown-3)(MeCN)_2]$  (An = U, Pu) (**5**), which were prepared from  $[AnI_3(THF)_4]$  and 1,4,7-trithiacyclononane in acetonitrile [22,23], and  $[U(BH_4)_2(18-thiacrown-6)][BPh_4]$  (**6**), which was obtained from  $[U(BH_4)_2(THF)_5][BPh_4]$  and 18-thiacrown-6 in

tetrahydrothiophene [24]. The U–S distances in the iodide compound, which average 3.04(3) Å, are 0.04 Å shorter than the La–S distances in the isostructural lanthanum analogue, showing the presence of a stronger M–S interaction in the U(III) complex [22].

The first uranyl complex with a dative U←S bond,  $[UO_2Cl_2(meso-bis(trans-2-hydroxycyclohexyl) sulfide-OOS)]$  (**7**), was synthesized by adding the neutral terdentate ligand to  $[UO_2Cl_2 \cdot 3H_2O]$  [25]. A series of Schiff base ligands containing the donor  $(CH_2)_2-S-(CH_2)_2$  fragment were coordinated to the  $UO_2^{2+}$  cation: *N,N'*-bis(salicylidene)-1,5-diamino-3-thiapentane in complex **8** [26], the cyclic and acyclic binucleating ligands formed by condensation of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-thiapentane [27,28], or 2-dimethylacetal-4-chloro-6-formylphenol and bis(2-aminoethyl) sulfide [29]. In the heterobimetallic uranyl-nickel and uranyl-copper compounds,  $[UO_2\{4-ClC_6H_2(CHO)CH=NCH_2CH_2\}_2S]MCl_2$  (M = Ni, Cu) (**9**), the d transition metal is supposed to be tetracoordinated by the phenoxides acting as μ-alkoxy ligands and the two o-aldehyde groups [30].

Two pyrazolyl rings in dihydrobis(pyrazolyl)borates were replaced by two 2-mercapto-1-methylimidazolyl rings in order to obtain a softer ligand. Reaction of  $UI_3(THF)_4$  with  $M[H(R)B(tim^{Me})_2]$  (M = Li or Na) and TIBPh<sub>4</sub> in the molar ratio 1:2:1 afforded the cationic uranium(III) complexes  $[U\{H(R)B(tim^{Me})_2\}_2(THF)_3][BPh_4]$  (R = H or Ph) (**10**), in which the dihydrobis(thioimidazolyl)borate ligand,  $[H(R)B(tim^{Me})_2]$ , acts as a terdentate ligand to the metal center through the two thione sulfurs and one agostic hydrogen [31].

The lithium salt of the rigid NSN-donor proligand, 4,5-bis(2,6-*i*Pr<sub>2</sub>-anilino)-2,7-<sup>t</sup>Bu<sub>2</sub>-9,9-Me<sub>2</sub>-thioxanthene  $[H_2(TXA_2)]$  reacted with  $UCl_4$  to give  $[Li(DME)_3][U(TXA_2)Cl_3]$  (**11**), which was reduced by K(naphthalenide) into  $[U(TXA_2)(DME)_2Cl_2Li(DME)_2]$ . Theoretical calculations pointed to significantly greater covalency in U–SAr<sub>2</sub> versus U–OAr<sub>2</sub> bonding, in agreement with the acute C–S–U angles and uncommonly short U–S distances of 2.77(1) and 2.825(1) Å in the U(IV) and U(III) complexes [32].

Protonolysis of  $[ThCl(NR_2)_3]$  (R = SiMe<sub>3</sub>) with two equivalents of 2,2'-selenobis(4,6-<sup>t</sup>Bu<sub>2</sub>phenol),  $(H_2^A OsEO)$ , yielded the selenium bis(phenolate) complex  $[Th(^A OsEO)_2(THF)_2]$  (**12**) in which the Th–Se distances of 3.2306(5) and 3.3262(5) Å are longer than the sum of their effective ionic radii (Σ = 3.03). The interaction between the metal center and selenium atom was best described as a dative interaction rather than a covalent one [33].

## 3. Complexes with chalcogenolate ligands

### 3.1. Homoleptic chalcogenolates and their adducts

The first actinide thiolates  $[U(SR)_4]$  (R = Et, <sup>n</sup>Bu) were reported in 1956 by Gilman et al [34]. These homoleptic complexes were synthesized by protonolysis of the amide precursor  $[U(NEt_2)_4]$  with RSH and characterized by titration of the metal after hydrolysis. The samples were very sensitive to water or oxygen, they spontaneously burst into flames and burned vigorously when exposed to the open air. These features that were related to the mismatch between the hard uranium metal and the soft sulfur atom discouraged for a long time further studies on these compounds.

This situation changed in the early 1990s, after it was noted that the instability of the bonds between f elements and sulfur was more often presumed than actually proved [35]. The first homoleptic thiolate compound of an actinide to have been crystallographically characterized is the tetrakis(dithiolate) complex  $[Li_4(dme)_4U(edt)_4]$  (dme = MeOCH<sub>2</sub>CH<sub>2</sub>OMe, edt = SCH<sub>2</sub>CH<sub>2</sub>S) (**13**) (Fig. 2), which was synthesized by the reaction of  $UCl_4$  and  $Li_2edt$  in dimethoxyethane [36]. The NMR spectra showed that the dodecahedral solid-state structure is retained in the solution; the U–S distances corresponding to the sites A and B are 2.82(5) and 2.885(8) Å. More recently, treatment of  $UCl_4$  with  $Na_2dddt$  (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) in THF gave the unique example

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