Dalton Transactions

COMMUNICATION

Cite this: *Dalton Trans.*, 2017, **46**, 2415

Received 2nd January 2017,
Accepted 25th January 2017

DOI: 10.1039/c7dt00006e

rsc.li/dalton

Synthesis and structural study of new metallasilsesquioxanes of potassium and uranium†‡

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The first metallasilsesquioxanes comprising potassium and uranium have been synthesized and structurally characterized by single-crystal X-ray diffraction. $(Cy_7Si_7O_{12})_2K_6(DME)_4$ (2; Cy = cyclohexyl) is a centrosymmetric dimer, in which the two silsesquioxide ligands are interconnected by μ_3- and μ_4-bridging siloxide moieties. $(Cy_7Si_7O_{12})_2U^{VI}$ (3) represents the first metallasilsesquioxane complex of an actinide element, featuring a U atom that is coordinated by two tridentate silsesquioxide ligands in a distorted octahedral fashion. The different structural effects of the large metal atomic radii are discussed.

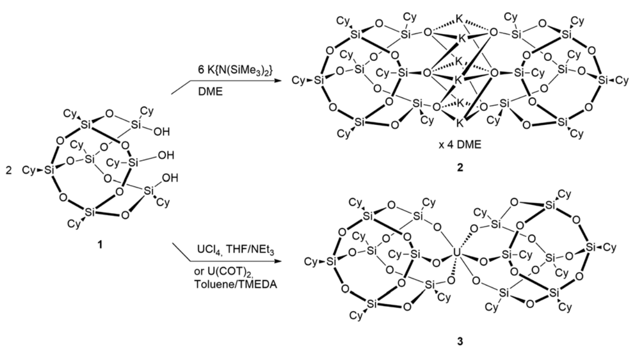
Introduction

Well-defined molecular metal siloxides (= metallasiloxanes) comprising M–O–Si functionalities attract significant interest due to their diverse practical applications.[1] Not only are metal siloxides excellent molecular models for silica-supported heterogeneous metal catalysts,[2] but they can also serve as precursors for new materials,[3] nanoparticles,[4] well-defined surface species,[5] and homogeneous catalysts.[6] Particularly useful and versatile precursors for a large variety of complex metal siloxides are incompletely condensed cubic silsesquioxane derivatives such as $Cy_7Si_7O_9(OH)_3$ (**1**, Cy = cyclohexyl). Silsesquioxanes like **1** have far-reaching structural similarities with β-tridymite and β-cristobalite, and metal complexes derived from **1** are therefore regarded as quite realistic molecular models for industrially important metal catalysts immobilized on silica surfaces.[7] Incompletely condensed silsesquioxanes have been shown to form stable complexes ("metallasilsesquioxanes") with virtually all metallic elements across the Periodic Table ranging from lithium through numerous early and late transition metals to rare-earth metals.[1,7,8] However, the "Periodic Table of Metallasilsesquioxanes"[7b] still has noticeable empty spaces mainly in Group 1 and actinide elements. In the case of alkali metals only a lithium compound has been reported earlier,[8b] while actinide silsesquioxides are unknown thus far. We report here the preparation and structural characterization of the first metallasilsesquioxanes of potassium and uranium. In this study we were interested in the structural influence of increasing metal atom radii. In particular, the structural effects of the exchange Li → K and W → U are discussed.

Synthesis and characterization

Potassium derivative $(Cy_7Si_7O_{12})_2K_6(DME)_4$ (2)

While the lithium silsesquioxide $(Cy_7Si_7O_{12})Li_3$ has already been structurally characterized,[8b] no molecular structures of heavier alkali metal derivatives have been published in the literature so far. Research in this field has probably been discouraged by a report by Feher *et al.* that treatment of **1** with 3 equiv. of NaO^tBu resulted in complete breakdown of the silsesquioxane cage.[8a] We now succeeded in the preparation of the first potassium silsesquioxide by deprotonation of the parent silsesquioxane $Cy_7Si_7O_9(OH)_3$ (**1**) with potassium hexamethyldisilazide in DME solution (Scheme 1). The resulting



Scheme 1 Preparation of the title compounds from the silsesquioxane **1**.

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† Dedicated to Professor Andrew Streitwieser on the occasion of his 90th birthday.

‡ Electronic supplementary information (ESI) available: Full crystallographic data for **2** and **3**. CCDC 182419 and 1414135. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt00006e

moisture-sensitive crystalline product was identified as $(Cy_7Si_7O_{12})_2K_6(DME)_4$ (**2**) by single-crystal X-ray analysis, which revealed that the dimeric molecule is centrosymmetric (Fig. 1). In the crystal structure of compound **2**, one K atom (K1) is attached to the $(Cy_7Si_7O_{12})^{3-}$ ligand in a $\kappa O1,\kappa O2,\kappa O3$-chelating fashion and therefore occupies the missing edge of a cube-like Si_7K framework (Fig. 4a). The distorted tetragonal coordination of the central K atom is completed by a siloxide O atom of the symmetry-related $(Cy_7Si_7O_{12})^{3-}$ ligand (O1′). The remaining two K atoms in the asymmetric unit (K2, K3) are bonded to the silsesquioxide moiety only in a bidentate $\kappa O1,\kappa O2$ or $\kappa O1,\kappa O3$ mode, respectively, and are therefore situated above two adjoining Si_3K planes of the Si_7K cube. Coordinative saturation of these K atoms is each achieved by one siloxide O atom of the symmetry-related $(Cy_7Si_7O_{12})^{3-}$ ligand and one chelating DME ligand, resulting in a distorted pentagonal coordination geometry.

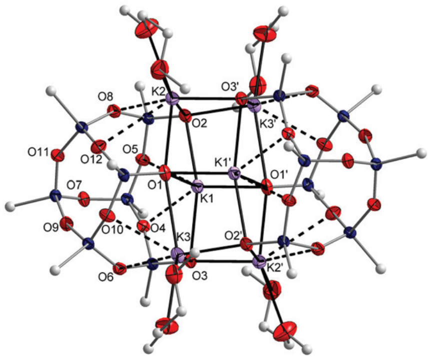

Fig. 1 Molecular structure of **2** in the crystal showing the atom-labeling scheme (displacement ellipsoids of K, Si and O drawn at the 50% probability level, H atoms and peripheral C atoms of the cyclohexyl groups omitted for clarity). Selected interatomic distances [pm] and angles [°]: K1–O1 278.4(3), K1–O1′ 263.2(3), K1–O2 274.4(3), K1–O3 284.0(3), K1⋯O4 273.0(3), K1⋯O5 295.6(3), K2–O1 284.4(3), K2–O2 268.3(3), K2–O3′ 262.8(3), K2⋯O8 317.7(3), K2⋯O12 330.3(3), K2–O13 280.4(4), K2–O14 297.2(4), K3–O1 317.8(3), K3–O2′ 262.1(3), K3–O3 274.5(3), K3⋯O6 318.0(3), K3⋯O10 308.8(3), K3–O15 280.1(3), K3–O16 295.4(3), O1–K1–O1′ 105.8(1), O1–K1–O2 86.0(1), O1–K1–O3 90.3(8), O2–K1–O3 164.6(1), O1′–K1–O2 101.9(1), O1′–K1–O3 93.4(1), O1–K2–O2 86.0(1), O1–K2–O3′ 93.4(1), O2–K2–O3′ 90.2(1), O1–K3–O3 84.3(1), O1–K3–O2′ 91.6(1), O2′–K3–O3 89.0(1), K1–O1–K1′ 74.2(1), K1–O1–K2 89.7(1), K1′–O1–K2 86.5(1), K1–O1–K3 86.8(1), K1′–O1–K3 78.8(1), K2–O1–K3 165.3(1), K1–O2–K2 94.1(1), K1–O2–K3′ 87.6(1), K2–O2–K3′ 90.3(1), K1–O3–K3 94.6(1), K1–O3–K2′ 86.7(1), K2′–O3–K3 88.8(1). Symmetry code: ′1 − *x*, 2 − *y*, 1 − *z*.

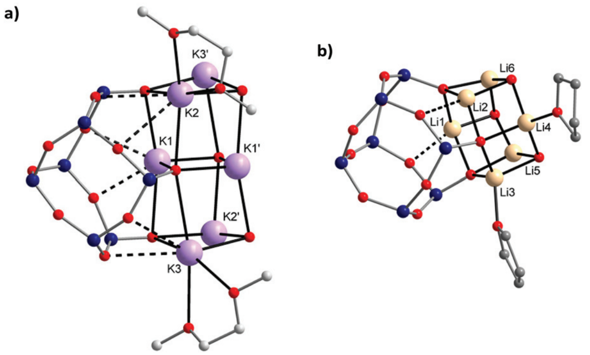

Fig. 2 Representation of the coordination sphere of the metal atoms in the potassium compound **2** (a) compared to those in the related lithium derivative $(Cy_7Si_7O_{12})_2Li_6(THF)_2$ (b).[8b]

As a result of the bridging coordination, each of the three siloxide O atoms O1–O3 is part of an almost planar K_2O_2 ring. These three K_2O_2 rings are interconnected by additional K–O contacts vertical to the ring planes, resulting in a closed K_6O_6 framework that consists of two plane-linked K_4O_4 heterocubanes (Fig. 2a). While the formation of K_4O_4 cubes is a typical structural motif for potassium compounds with oxygen anions,[9] the K_6O_6 motif in compound **2** is unique to our knowledge. The solid state structure of **2** is therefore considerably different from that of the previously reported lithium derivative $(Cy_7Si_7O_{12})_2Li_6(THF)_2$,[8b] where the central Li_6O_6 framework is composed by only two Li_2O_2 rings that are edge-linked by two separated LiO units (Fig. 2b). The structure of compound **2** is obviously supported by two additional K–O contacts per K atom to adjacent Si–O–Si bridges within the silsesquioxane backbone. The central K atom (K1) exhibits a low-symmetrical [4 + 2] coordination, while the ligand sphere of K2 and K3 can be described as [5 + 2]. The structural influence of the supporting Si–O–Si coordination is therefore higher than in the lithium analog.[8b] This finding meets the expectation in view of the larger ionic radius of potassium. In compound **2**, the central siloxide O atom of the K_6O_6 cage (O1) adopts a μ_4-bridging coordination, while the coordination of the siloxide moieties O2 and O3 can be described as μ_3-bridging. The coordination environment around the O atoms is strictly trigonal-bipyramidal (O1) or trigonal-pyramidal (O2, O3), respectively, and consequently an sp^2 hybridization can be assigned to those O atoms. This model fits well to the finding that the apical K–O bonds are significantly longer than the equatorial K–O bonds (*e.g.* K2–O2 268.3(3) pm, K2–O3′ 262.8(3) pm and K2–O1 284.4(3) pm). Taken the example of K2, it can consequently be assumed that the shorter bonds to O2 and O3′ are each formed by an sp^2 electron pair, while a p electron pair contributes to the longer bond to O1. By contrast, in the lithium derivative all siloxide O atoms are surrounded by one Si atom and three Li atoms in an almost tetrahedral fashion and are therefore certainly sp^3-hybridized. The preference of an sp^2-hybridization of the ligating atom against an sp^3-hybridization was frequently observed in amides of the heavier alkali metals.[10] This effect is usually explained with the high ionic character of the M–N bond, so that a more s-rich hybridization of the N atom is energetically more beneficial. In potassium alkoxides and siloxides, the change from an sp^3- to an sp^2-hybridization of the O atom has been observed in much fewer cases.[9,11] The occurrence of this phenomenon in compound **2** can possibly be explained in a similar manner to potassium amide compounds, even though additional theoretical calculations would be necessary to gain insight into the bonding situation.

Uranium(VI) complex $(Cy_7Si_7O_{12})_2U$ (3)

Since silsesquioxides of actinide metals are completely unknown so far, we were interested in the preparation of uranium complexes of the $(Cy_7Si_7O_{12})^{3-}$ ligand. In a first attempt to prepare a uranium(IV) derivative, the silsesquioxane **1** was treated with anhydrous uranium(IV) chloride in THF in the presence of triethylamine. Recrystallization of the reaction mixture from *n*-pentane afforded the unexpected uranium(VI) species **3** as a colorless crystalline solid in 52% yield (*cf.* Scheme 1).

We observed a similar oxidation of uranium from the +IV to the +VI oxidation state with a disiloxanediolate ligand earlier,[12] which might be traced back to a formal oxygen transfer from the siloxane cage, as it was discussed elsewhere.[13] Surprisingly, compound **3** was also obtained from the reaction of compound **1** with uranocene, $U^{IV}(COT)_2$ (COT^{2-} = cyclooctatetraenyl), in a toluene/TMEDA mixture (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Recrystallization from *n*-hexane yielded crystals of the composition **3**·TMEDA·*xn*-hexane, which were suitable for X-ray structure determination (Fig. 3). It is worth mentioning that both the bulk material and the single-crystals are colorless, which is in agreement with our previous observations on uranium(VI) siloxide compounds.[12] Compound **3** is a rare example of a binary $(Cy_7Si_7O_{12})_2M$-type species, where two tridentate silsesquioxide ligands are attached to one metal atom. Thus the U atom is coordinated by six siloxide O atoms in an almost octahedral fashion, and consequently the $(Cy_7Si_7O_{12})_2U$ molecule comprises two cube-shaped Si_7U cages with a mutual U corner (Fig. 4b). The coordination environment around the U atom is therefore very similar to other uranium(VI) siloxides and silicates, *e.g.* $U\{Ph_2Si(OSiPh_2O)_2\}_2\{(Ph_2SiO)_2O\}$[12] and $K_4CaUSi_4O_{14}$.[14] The formation of distinct U–O single bonds rather than a bridging coordination of the siloxide moieties in compound **3** can be expected since U^{6+} is a highly polarizing cation which prefers a more covalent bonding situation. In view of the high steric bulk and the high negative charge of the $(Cy_7Si_7O_{12})^{3-}$ ligand, this structure type should generally be preferred for very large metal ions in a high oxidation state (especially +6). The molecular structure of compound **3** is thus very similar to that of the related tungsten(VI) derivative.[15] However, the range of O–M–O(*cis*) coordination angles in **3** is 83.9(1)–94.6(1)°, which is significantly larger than that in the tungsten complex, where the coordination polyhedron is a nearly perfect octahedron (O–W–O(*cis*) 89.7(6)–90.3(6)°).[15] The same hypothesis applies to the range of Si–O–M angles, which is 136.0(1)–170.0(2)° in compound **3** and only 162(1)–165(1)° in the tungsten analog. This finding can be interpreted such that the W^{6+} ion fits perfectly into the coordination pocket of the tridentate $(Cy_7Si_7O_{12})^{3-}$ ligands, while the U^{6+} ion might be little too large. Thus the metal atom in compound **3** should be coordinatively not as saturated as in the W complex, and consequently the chance to attach an additional ligand to it can be expected to be higher. However, it is worth mentioning that there are no meaningful U⋯N interactions in the crystalline TMEDA solvate of **3** (min. U⋯N 412(1) pm).

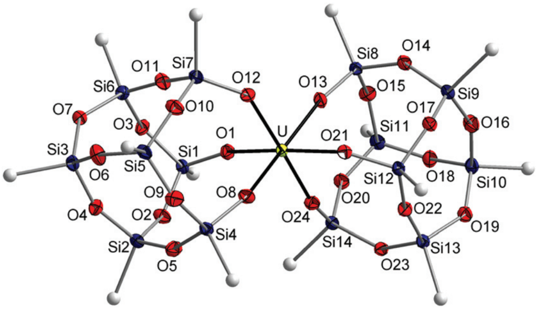

Fig. 3 Molecular structure of **3** in the crystal showing the atom-labeling scheme (displacement ellipsoids of U, Si and O drawn at the 50% probability level, H atoms and peripheral C atoms of the cyclohexyl groups omitted for clarity). Selected bond lengths [pm] and angles [°]: U–O1 212.0(2), U–O2 210.8(2), U–O3 216.8(2), U–O13 208.5(2), U–O14 211.1(2), U–O15 226.8(2), O1–U–O2 92.0(1), O1–U–O3 90.8(1), O1–U–O13 86.3(1), O1–U–O14 94.0(1), O1–U–O15 174.1(1), O2–U–O3 86.9(1), O2–U–O13 93.6(1), O2–U–O14 172.8(1), O2–U–O15 90.5(1), O3–U–O13 177.1(1), O3–U–O14 88.9(1), O3–U–O15 94.6(1), O13–U–O14 90.9(1), O13–U–O15 88.3(1), O14–U–O15 83.9(1), U–O1–Si1 163.3(1), U–O2–Si4 161.2(2), U–O3–Si7 139.9(1), U–O13–Si14 150.9(2), U–O14–Si8 170.0(2), U–O15–Si12 136.0(1).

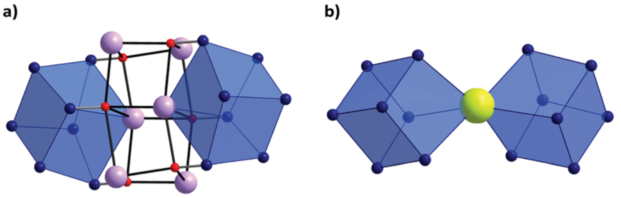

Fig. 4 Interconnection of the two cube-shaped Si_7M frameworks in the title compounds: by bridging siloxide moieties in compound **2** (M = K; a), by a mutual M corner in compound **3** (M = U; b).

Conclusions

The crystal structures of the novel metallasilsesquioxanes $(Cy_7Si_7O_{12})_2K_6(DME)_4$ (**2**) and $(Cy_7Si_7O_{12})_2U$ (**3**) have been determined and the structural effects of the formal exchange Li → K and W → U have been discussed. It was shown that the effect of an increasing metal ionic radius is basically different in both cases. In the potassium compound **2**, the metal's coordination number is increased by (i) the highly bridging coordination of the siloxide moieties under switching the oxygen's hybridization from sp^3 to sp^2 and (ii) the supporting coordination of Si–O–Si bridges. In the case of the uranium compound **3**, none of these effects were observed. Instead, the coordination octahedron around the metal atom becomes more unsymmetrical, which indicates coordinative unsaturation.

Experimental section

General

All operations were carried out under an inert argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled under argon according to common procedures. The silsesquioxane **1**[16] and U(COT)$_2$[17] were prepared as described earlier. K[N(SiMe$_3$)$_2$] was obtained from HN(SiMe$_3$)$_2$ and KH. **Safety notes**: Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10^9 years. All manipulations and reactions of uranium compounds should be carried out in monitored fume hoods or gloveboxes in a laboratory equipped with α-counting equipment.

Synthesis of potassium complex 2

Silsesquioxane **1** (2.00 g, 2.05 mmol) was added to a solution of K[N(SiMe$_3$)$_2$] (1.30 g, 6.52 mmol) in DME (150 ml) and the resulting clear solution was stirred for 12 h at r.t. During this time a colorless crystalline precipitate was formed, which was filtered off and dried *in vacuo*. Yield: 2.00 g (77%). Single crystals suitable for X-ray structure determination were obtained from the mother liquor at 5 °C. Elemental analysis: calcd for $C_{100}H_{194}K_6O_{32}Si_{14}$ (**2**): C 47.35%, H 7.71%; found C 46.89%, H 7.42%. IR (KBr): 2917(vs), 2849(vs), 2666(m), 1616(w), 1447(s), 1347(w), 1325(w), 1271(m), 1195(s), 1063(vs), 931(m), 893(s), 848(s), 823(s), 734(s), 650(m), 579(w), 514(s), 471(s), 415(m) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6, 25(2) °C): 0.83–1.11 (m, 14H; Si–C*H*), 1.28–2.17 (m, 140H; CH_2), 3.19 (s, 24H; OCH_3), 3.33 (s, 16H; OCH_2) ppm. ^{13}C{^{1}H}-NMR (100 MHz, C_6D_6, 25(2) °C): 24.0–25.5 (3 × s; Si–*C*H), 27.8–29.0 (8 × s; *C*H$_2$), 58.6 (s; O*C*H$_3$), 71.8 (s; O*C*H$_2$) ppm.

Synthesis of uranium(VI) complex 3

(i) Compound **1** (1.74 g, 1.78 mmol) was added to a solution of UCl$_4$ (0.68 g, 1.78 mmol) in THF (80 ml) and triethylamine (0.75 ml, 5.41 mmol). The green mixture was stirred overnight at r.t. and the colorless precipitate was then filtered off. The solvent was removed *in vacuo* and the solid residue was recrystallized from *n*-pentane at 4 °C, yielding a colorless polycrystalline solid. Yield: 1.01 g (52%). M.p. 278–282 °C. Elemental analysis: calcd for $C_{84}H_{154}O_{24}Si_{14}U$ (**3**): C 46.29%, H 7.12%; found C 46.26%, H 7.17%. IR (KBr): 2923(vs), 2849(vs), 1617(w br), 1448(m), 1396(w), 1355(w), 1326(w), 1267(w), 1196(s), 1107(vs br), 1039(s), 1027(2), 999(m), 924(s), 895(s), 848(m), 824(w), 756(w), 739(w), 641(w), 581(w), 514(s), 466(m), 412(m) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6, 25(2) °C): 0.52 (m br, 14H; Si–C*H*), 0.52 (m br, 14H; Si–C*H*), 1.31–1.78 (m br, 140H; CH_2) ppm. ^{13}C{^{1}H}-NMR (100 MHz, C_6D_6, 25(2) °C): 24.5–25.3 (2 × s; Si–*C*H), 27.3–28.9 (7 × s; *C*H$_2$) ppm.

(ii) Compound **1** (1.30 g, 1.34 mmol) was added to a suspension of U(COT)$_2$ (0.30 g, 0.67 mmol) in toluene (50 ml) and TMEDA (2 ml). The mixture was stirred overnight at r.t. and then refluxed for 5 h. Volatiles were removed *in vacuo* and the solid residue was extracted with *n*-hexane (150 ml). The pale-green extract was reduced to approx. 15 ml and then stored at 4 °C, whereby a colorless crystalline precipitate of **3**·TMEDA·*xn*-hexane was obtained within a few days. Filtering off and drying *in vacuo* yielded the solvent-free compound **3**. Yield: 0.90 g (58%). Elemental analysis: calcd for $C_{84}H_{154}O_{24}Si_{14}U$ (**3**): C 46.29%, H 7.12%; found C 44.63%, H 7.69%.

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