ChemComm

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COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 5595

Received 16th March 2013,
Accepted 29th April 2013

DOI: 10.1039/c3cc41965g

www.rsc.org/chemcomm

From elusive thio- and selenosilanoic acids to copper(I) complexes with intermolecular Si=E → Cu–O–Si coordination modes (E = S, Se)†

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The facile synthesis of the first stable selenosilanoic acid–base adduct LSi(=Se)OH(dmap) 3 (L = CH[C(Me)NAr]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$, dmap = 4-dimethylaminopyridine), the heavier analogue of the thiosilanoic acid adduct LSi(=S)OH(dmap) 1, is reported. Both adducts 1 and 3 react readily with MesCu (Mes = 2,4,6-trimethylphenyl) to form the novel dimeric Cu(I) complexes [LSi(=E)OCu]$_2$ (4: E = S; 5: E = Se) with unprecedented intermolecular Si=E → Cu–O–Si coordination modes. The latter are efficient pre-catalysts for the Cu(I)-mediated aziridination of styrene with PhI=N(Ts) (Ts = tosyl).

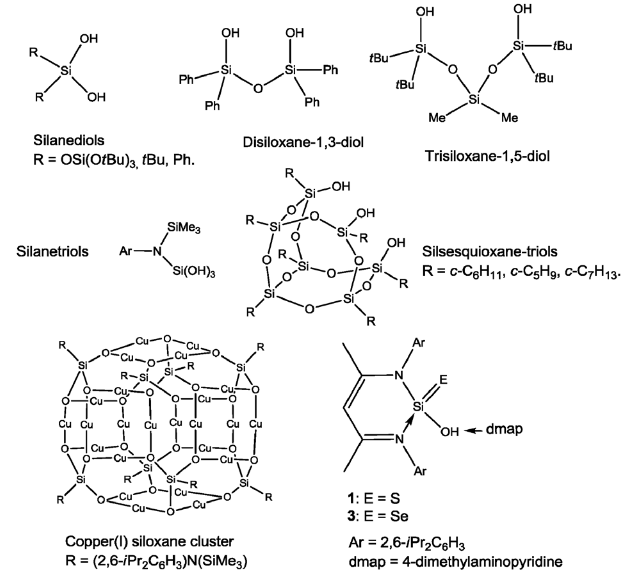

Chart 1

Using organic molecular defined species containing M–O–Si moieties as structural models for silica-supported metal/metal oxide catalysts has been proved to be a facile method to unravel the structure of a pre-catalyst as well as the mechanism of a catalytic reaction.[1] For example, the globular 56-membered copper(I) siloxane containing core made up of Cu–O–Si moieties (Chart 1), which is even soluble in organic solvents, could be prepared by the reaction of silanetriol with (MesCu)$_4$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$). This copper siloxane cluster is active for the Ullmann–Goldberg-type C–N coupling reaction,[2] and can serve as a structural and functional model for silica-supported copper (pre)catalysts. In order to better understand the structure–reactivity relationships of Cu–O–Si systems for various Cu-based chemical transformations, the synthesis of other types of Cu–O–Si containing compounds as structural and functional models for metallated terminal OH groups of silica surfaces is desired.

Organic silanols have been reported to form well defined M–O–Si type compounds including silanediols, disiloxane-1,3-diols, silanetriols, trisiloxane-diol and silsesquioxane-triols (Chart 1).[1a,b,3,4] As possible intermediates involved in silica synthesis through hydrolysis of suitable silicon(IV) starting materials under acidic conditions, silicic acids, SiO$_x$(OH)$_{4-2x}$, have not received much attention as precursors for the selective synthesis of M–O–Si compounds owing to their elusive nature. Likewise, organic silanoic acids RSi(=O)OH, the silicon analogues of carboxylic acids, represent elusive species which could only be studied at liquid nitrogen temperatures because of the presence of the highly polarized Si=O subunit which can undergo facile isomerisation or intermolecular head-to-tail polymerisation.[5] Recently, we reported the synthesis of the first isolable silanoic acid–base adducts, including the thiosilanoic system LSi(=S)OH(dmap) **1** (L = CH[C(Me)NAr]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$, dmap = 4-dimethylaminopyridine) which is stabilised *via* hydrogen bonding to the pyridine N atom of dmap (Chart 1).[6] With these compounds in hand it became possible to employ **1** as a building block for Si(=S)–O–M formation. Accordingly, we reported the formation and reactivity of an isolable monomeric Si(=S)–O–Mn(II) complex.[7] Herein, we report the unexpectedly facile synthesis of the first isolable selenosilanoic acid–base adduct LSi(=Se)OH(dmap) **3** (Chart 1), and the Cu-metallation reactions of **1** and **3** with (MesCu)$_4$ to give the novel dimeric LSi(=E)OCu complexes **4** (E = S) and **5** (E = Se) with unprecedented intermolecular Si=E → Cu–O–Si coordination modes. In addition, their ability to serve as efficient pre-catalysts

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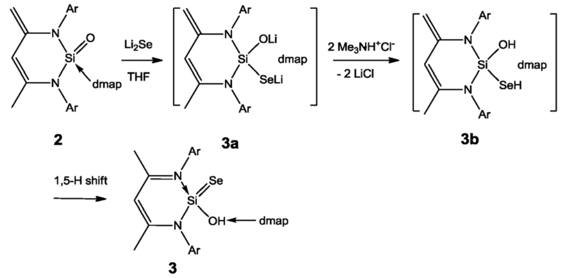
† Electronic supplementary information (ESI) available: Experimental details and crystal data and structure refinement for 3–5. CCDC 921657–921659. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc41965g



Scheme 1 Synthesis of compound **3**.

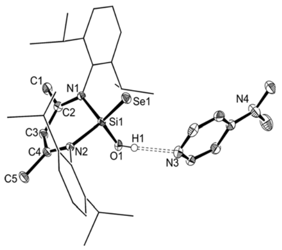
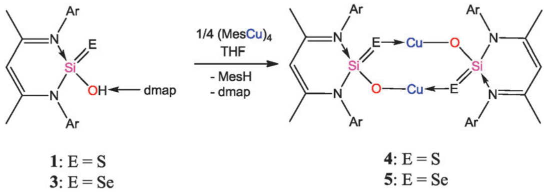


Fig. 1 Molecular structure of compound **3** in the solid state with the 50% probability level for the core structure. Hydrogen atoms (except for H1) and the *n*-hexane molecules are omitted for the sake of clarity.



Scheme 2 Syntheses of the Cu(I) complexes **4** and **5**.

in the aziridation of a C═C bond with PhI═N(Ts) has been demonstrated.

The thiosilanoic acid–base complex **1** is accessible from the reaction of the corresponding stable silanone complex L′Si(═O)(dmap) **2** (L′ = CH[C(Me)(C═CH$_2$)](NAr$_2$), Ar = 2,6-iPr$_2$C$_6$H$_3$) with H$_2$S at ambient temperature. Considering the toxicity of H$_2$Se, we attempted to synthesize the selenium congener of **1** with dilithium selenide as a selenium source, which can be obtained from the reaction of elemental selenium with lithium triethylhydridoborate in THF.[8] Treatment of the *in situ* prepared dilithium selenide with one equivalent of **2** in THF at −78 °C, followed by protonation with two molar equivalents of trimethylammonium chloride, leads to a clear yellow solution, from which compound **3** could be isolated in the form of yellow crystals in 75% yield (Scheme 1).

The strikingly stable compound **3** has very similar solubility properties to **1**. It is soluble in toluene, THF, chloroform, dichloromethane, marginally soluble in benzene but insoluble in *n*-hexane. It was fully characterised using multinuclear NMR spectroscopy, elemental analysis, mass spectrometry and IR spectroscopy, as well as single-crystal X-ray diffraction analysis. The high resolution electrospray ionization mass spectrometry (ESI-MS) shows the molecular ion peak at *m*/*z* 665.3138 [LSi(═Se)OH(DMAP) + H]$^+$ as the base signal. In the ^{1}H NMR spectrum in CDCl$_3$, the chemical shift of the ring proton in the γ-position of the β-diketiminate L is observed at δ = 5.73 ppm. This chemical shift is comparable to that observed for **1** (δ = 5.71 ppm). The proton of the OH group resonates at δ = 6.42 ppm in the same region as the proton resonance signals for the pyridine moiety of dmap. The ^{29}Si{^{1}H} resonance signal of **3** in CDCl$_3$ at δ = −25.5 ppm is low-field shifted compared to that of **1** (δ = −30.0 ppm), while its ^{77}Se{^{1}H} NMR spectrum exhibits a singlet at δ = −545.2 ppm, which is up-field shifted compared to those of the related selenosilanoic silylester diastereomers (δ = −384.8 and −401.3 ppm).[9]

The molecular structure of compound **3** is depicted in Fig. 1. It crystallizes in the triclinic space group $P\bar{1}$ with one *n*-hexane molecule lying about an inversion center. It is isotypic with **1**, with one dmap ligand connected to the selenosilanoic acid moiety through an O–H···N hydrogen bond. The Si1–O1 bond length of 1.619(2) Å is comparable to that of **1** (1.620(2) Å), whereas the Si(1)–Se(1) bond distance of 2.1348(7) Å is close to the Si═Se distance of a related selenosilanoic silyl ester (2.117(1) Å).[9] As expected, other metric parameters of **3** are akin to those of **1**.

Both compounds **1** and **3** were allowed to react with (MesCu)$_4$ (Mes = 2,4,6-trimethylphenyl) in the hope of producing the corresponding Cu(I) complexes **4** and **5**, respectively. (MesCu)$_4$ is known to serve as a smooth reagent for preparing Cu(I) complexes by deprotonation of amines and silanols.[2,3,10]

Accordingly, the reaction of compound **1** with $\frac{1}{4}$ molar equivalent of (MesCu)$_4$ was carried out in THF at −20 °C. The ^{1}H NMR spectrum of the resulting reaction mixture already shows the absence of the resonance signals of the OH group of **1** and those of (MesCu)$_4$ with concomitant liberation of dmap, indicating that the metallation of **1** was successful. Indeed, the desired compound **4** could be isolated from the reaction mixture as yellow crystals in 85% yield (Scheme 2). Single crystals of **4** suitable for X-ray diffraction analysis could be obtained in toluene solutions at 0 °C. The structure analysis revealed that the compound is a dimer with intermolecular Si═S → Cu–O–Si interactions (Fig. 2). The compound possesses C_2 symmetry and consists of a planar eight-membered Si$_2$O$_2$S$_2$Cu$_2$ ring with two *trans*-oriented β-diketiminato ligands L. The Cu centres are linearly coordinated by one oxygen and a sulfur atom of the neighbouring Si═S subunit. The Cu(1)···Cu(1A) distance of 2.8135(7) Å suggests a weak d^{10}···d^{10} interaction in this molecule.[11] The Si(1)–O(1) distance of 1.568(2) Å is significantly shorter than that in the precursor **1** (1.620(2) Å), whereas the Si(1)–S(1) bond length (2.0609(9)) is longer than that

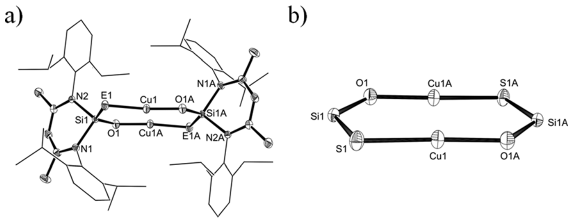


Fig. 2 (a) Molecular structures of compounds **4** (E═S) and **5** (E = Se) in the solid state with the 50% probability level for the core structure. Hydrogen atoms and the toluene molecules are omitted for the sake of clarity. Operation symmetry for all atoms labelled ''A'': $-x + 3/2, -y + 1/2, -z$ (**4**); $-x + 2, -y, -z$ (**5**); (b) representation of the eight-membered planar Si$_2$O$_2$S$_2$Cu$_2$ ring without substituents at silicon atoms.

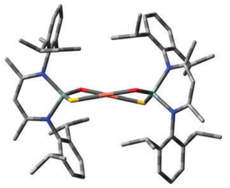


Fig. 3 Optimized structure for the proposed stereoisomer **4b**. Hydrogen atoms are omitted for the sake of clarity.

observed in **1** (1.993(1) Å), suggesting carboxylate-like π-conjugation in the SiSO moiety.[12]

The composition of **4** has been confirmed by multinuclear NMR spectroscopy, elemental analysis and IR spectroscopy. The solubility of **4** is similar to that of precursor **1**. Unexpectedly, two sets of resonances for the β-diketiminato ligand L appear in the ^{1}H NMR spectrum with a ratio of 1 : 0.62 as indicated by the integrals of the resonances from the ring proton in the γ-position of L at $\delta = 5.55$ and 5.49 ppm, respectively. Accordingly, the ^{29}Si{^{1}H} NMR spectrum reveals two close signals at $\delta = -38.0$ and -39.1 ppm, respectively. The two sets of resonances suggest the presence of two stereoisomers of **4** (**4a** and **4b**) in chloroform solutions. Indeed this is substantiated by the results obtained from diffusion ordered spectroscopy (DOSY) experiments, revealing identical diffusion coefficients for these two species (see ESI†) and thus the same molecular size and composition, respectively. In other words, dissociation of **4** in chloroform solutions can be excluded. As expected, the two stereoisomers can be interconverted as shown using variable ^{1}H NMR spectroscopy. Cooling of a $CDCl_3$ solution of **4** to 230 K changes the ratio of signal sets of **4a** and **4b** from 1 : 0.62 at ambient temperature to 1 : 0.42 (see ESI†). In the solid state ^{29}Si NMR spectrum of **4** in crystalline form, there is only one resonance signal at $\delta = -41.6$ ppm, whereas in the spectrum of the fine powder two signals are observed ($\delta = -41.6$ ppm and -38.7 ppm) (see ESI†), this suggests that **4a** holds a structure as shown in Fig. 2 with two ligands L in the *trans*-position. We inferred that the other stereoisomer **4b** preserves the C_2 symmetry of **4a** but the two ligands L are now *cis*-oriented. However, this is ruled out by the results of DFT calculations, which revealed that the proposed *cis* isomer is least favoured. Instead the DFT calculations suggest a twisted $Si_2O_2S_2Cu_2$ core structure also with C_2 symmetry as a stereoisomer which is only 5.5 kJ mol^{-1} less stable than **4a** (Fig. 3 and ESI†).

Similar to the synthesis of **4**, compound **5** could be obtained by the reaction of **3** with $(MesCu)_4$ in THF (Scheme 2). Compound **5** has been fully characterized by multinuclear NMR spectroscopy, elemental analysis, IR and mass spectroscopy, and X-ray crystallography. Akin to the situation of **4**, there are two stereoisomers present in $CDCl_3$ solutions as shown by the ^{1}H, ^{13}C, ^{29}Si NMR spectra as well as ^{1}H-DOSY experiments (see ESI†).

Single-crystals of **5** in the triclinic space group $P\bar{1}$ could be obtained in toluene solutions. The X-ray diffraction analysis revealed that **5** and **4** are isotypic (Fig. 2). Akin to the structure of **4**, compound **5** is a dinuclear copper(I) complex with both copper centers coordinated by O and Se atoms. A linear geometry of the O–Cu–Se connection with an angle of 172.07(7)° is observed. The Cu(1)···Cu(1A) bond distance of 2.9271(8) Å is slightly longer than that in compound **4** (2.8135(7) Å). This can be explained by the longer Si–Se distance (2.2011(9) Å) compared to that of the Si–S bond (2.0609(9) Å) in **4**.

It has been shown that Cu(I) complexes can be efficiently applied as pre-catalysts in metal-catalyzed nitrene-transfer reactions if the Cu(I) centre is efficiently chelate coordinated.[13] In a preliminary study the catalytic ability of compounds **4** and **5** in the nitrene-transfer reaction (aziridation) of a C═C bond has been evaluated. The catalytic reactions were carried out by using styrene and PhI═N(Ts) (Ts = tosyl) as a nitrene source in the presence of 2.5 mol% of **4** and **5**, respectively, in CH_2Cl_2 at ambient temperature. The resulting yields of the *N*-tosyl-2-phenylaziridine product [85% (**4**) and 87% (**5**)] are similar to a reported result.[13a] It is generally considered that a Cu(I)–nitrene species is the active component for the aziridination reaction.[13b] Thus, it is reasonable to assume that the dimeric Cu(I) complexes react initially with PhI═N(Ts) to form the corresponding Cu(I)–nitrene intermediates, which are capable of facile nitrene-transfer to the C═C bond of styrene.

In summary, using dilithium selenide as a selenium source, the first isolable selenosilanoic acid–base adduct **3** has been synthesized which is isostructural with the thiosilanoic acid–base adduct **1**. Facile reaction of **1** and **3** with $\frac{1}{4}$ molar equivalents of $(MesCu)_4$ led to the unprecedented dimeric copper(I) complexes **4** and **5**. Both complexes exist in two stereoisomeric forms in chloroform solutions and verify the novel Si═E → Cu–O–Si structural motif in Cu(I) siloxane chemistry. In addition, compounds **4** and **5** can act as reliable pre-catalysts in aziridination of styrene with PhI═N(Ts).

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