Silsesquioxane Chemistry, 5. Retention of the Cu₄O₄ core upon formation of the first copper(I) silsesquioxane from tetrameric copper(I)-t-butoxide

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Abstract

The first copper(I) silsesquioxane derivative, Cu₄O₄[CY₃Si₃O₄(OSiMe₃)₄]₂ (4) was prepared by reacting tetrameric copper(I)-t-butoxide, (CuO/BU₄)₄ (3), with the monosilylated silsesquioxane precursor CY₃Si₃O₄(OH)₄(OSiMe₃)₂ (2) in a 1:2 molar ratio. An X-ray diffraction study revealed the presence of a centrosymmetric dimer. A slightly puckered Cu₄O₄ ring forms the central part of a complex structure comprising nine eight-membered inorganic ring systems.

PACS: Silsesquioxanes; Metallasilsesquioxanes; Copper(I)-t-butoxide; Copper(I) silsesquioxane

1. Introduction

The chemistry of metallasilsesquioxanes receives considerable current interest [1,2] as these Si/O cage structures can be regarded as small soluble fragments of silica. Incompletely condensed silsesquioxanes such as CY₃Si₃O₄(OH)₄ (1) share structural similarities with β-cristobalite and β-tridymite and are thus quite realistic models for the silanol sites on silica surfaces [3–7].

In recent years numerous main group, transition metal, and lanthanide complexes derived from 1 have been prepared [4–6]. It is now generally accepted that such metal-silsesquioxanes are suitable models for heterogeneous silica-supported transition metal catalysts. Moreover, it has turned out that certain metallasilsesquioxanes, especially those of titanium and vanadium, are valuable catalysts themselves e.g. in the metathesis, polymerization, and epoxidation of alkenes [8]. In contrast, very little is known about silsesquioxane derivatives of the late transition metals, and notably Group 11 derivatives are completely absent. In this contribution we report the formation of the first copper(I) silsesquioxane derivative involving a remarkable transfer of the intact central Cu₄O₄ unit in tetrameric copper(I)-t-butoxide.

2. Experimental

2.1. General information

The reaction was carried out in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents (diethyl ether and toluene) were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer System 2000. NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer (¹H 400 MHz, ¹³C 101 MHz, ²⁹Si 79.5 MHz). Chemical shifts are re-
ported in ppm and referenced to residual solvent resonances (H, 13C) or an internal standard (H, 29Si: TMS = 0 ppm). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. Melting and decomposition points were measured on an Electrothermal IA 9100 apparatus. X-ray diffraction data were collected with a Bruker CCD instrument. The following starting materials were prepared according to literature procedures: Cy-Si-O,Si(OH), (1) [2], Cy-Si-O,Si(OH),OSiMe) (2) [2,9], and (CuOrBu), [10].

2.2. Preparation of Cu,O,[Cy-Si-O,Si(OSiMe),] (4)

A solution of freshly prepared (CuOrBu), (3, 0.27 g, 1.98 mmol) in diethyl ether (30 ml) was added via syringe to a solution of 2 (1.00 g, 0.96 mmol) in toluene (50 ml). The mixture was stirred for 20 h at room temperature and concentrated in vacuo to a total volume of ca. 20 ml. Cooling to 0°C for 2 d afforded 0.55 g (49%) 4 as colorless rod-shaped crystals which were dried under vacuum. M.p. 262°C (dec.). No characteristic fragments were detected in the CI MS spectrum. IR (KBr, ν (cm⁻¹)): 2923 (vs), 2850 (s), 1448 (m), 1347 (vw), 1236 (vw), 1266 (m), 1196 (s), 1111 (vs br), 1038 (s), 999 (m), 933 (w), 895 (m), 847 (m), 825 (w), 755 (w), 669 (vw), 638 (vw), 567 (w), 513 (m), 459 (w), 415 (w). 'H NMR (400.13 MHz, CD, 25°C): δ 2.16 (m, 30H, Cy–CH₂); 1.73 (m, 72H, Cy–CH₂); 1.30 (m, 38H, Cy–CH₂); 1.02 (m, 14H, Cy–CH); 0.75–0.32 (m, 18H, OSiMe) ppm. 13C NMR (100.62 MHz, CD, 25°C): δ 28.9–26.8 (m, Cy–CH₂); 25.7–23.8 (m, Cy–CH); 4.1–1.9 (m, OSiMe) ppm. 29Si NMR (79.49 MHz, CD, 25°C): δ 8.5 (OSiMe); −60.6, −61.0 (Si–O–Cu); −67.5, −71.2 (Si–O–Si) ppm. Anal. Calc. for C₉H₁₇₂Cu₃O₄Si₁₆ (2341.89): C, 46.16; H, 7.40. Found: C, 45.45; H, 7.00%.

2.3. X-ray structure determination of Cu,O,[Cy-Si-O,Si(OSiMe),] (4)

Recrystallization of 4 from a minimum amount of hot toluene afforded colorless single crystals of the toluene solvate 4·2C₆H₆·C₁₀H₁₆Cu₆O₄Si₄Si₁₆. M = 2526.14, triclinic, space group P1 (no. 2), a = 14.058(2), b = 15.116(3), c = 18.198(3) Å, α = 104.97(1), β = 103.89(1), γ = 112.15(1), V = 3204.69 Å³, Z = 1, D = 1.309 g cm⁻³; F(000) = 1344, μ = 0.87 mm⁻¹; crystal dimensions: 0.79 × 0.64 × 0.19 mm; T = 0.49, 1.00, α scan mode, 2θ = 51.6°; monochromated Mo–Kα radiation, λ = 0.71073 Å, temperature = 173(2) K. A hemisphere of absorption corrected (SADABS) area detector diffractometer data (Bruker AXS CCD System) (18035 reflections) were merged to give 11925 unique (Rint = 0.030) used in the last-squares refinement (SHELXL 97) [11] on F². wR²(all data) = 0.194, R1 (conventional) = 0.066. S = 1.04.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 141154. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

The reaction of the monosilylated silsesquioxane derivative 2 with tetrameric copper(I)-t-butoxide was carried out in diethyl ether/toluene solution at room temperature according to Scheme 1.

![Scheme 1](image)

The main preparative advantage of employing copper(I)-t-butoxide as starting material is the fact that it is a salt-free route giving only t-butoxide as volatile by-product. A simple crystallization procedure directly from the concentrated reaction mixture afforded the new copper(I) silsesquioxane complex 4 in the form of colorless rod-like crystals. With 49% the isolated yield was fairly low due to the very high solubility of 4 even in non-polar organic solvents, which can be traced back to the presence of fourteen cyclohexyl groups in the periphery of the molecule. Besides diethyl ether and THF compound 4 also dissolves freely in toluene, hexane, and pentane. While the solid material is apparently air-stable for several days, solutions of 4 are very susceptible to oxidation and rapidly turn green upon contact with air.

The molecular structure of 4 was elucidated by an X-ray diffraction study, since information provided by the usual combination of spectroscopic data and elemental analysis is fairly limited. In the solid state compound 4 forms centrosymmetric dimers interconnected through a central eight-membered Cu₄O₄ ring (Fig. 1). This results in a complex overall structure comprising nine eight-membered inorganic ring systems.
Fig. 1. Structure of 4 in the crystal. Selected interatomic distances [pm] and bond angles [°]: Cu1–Cu2 2.6409(8), Cu1–Cu2a 2.6854(10), O7–Cu2 1.838(3), O7–Cu1 1.865(3), O14–Cu2 1.833(3), O14–Cu1 1.876(3), Si4–O7 1.626(3), Si5–O14a 1.628(3), O14a–Cu1–O7 169.9(1), O7–Cu2–O14 174.5(1), Cu1–O7–Cu2 91.0(1), Cu2–O14–Cu1a 94.1(1), Cu2–Cu1–Cu2a 129.2(2), Si4–O7–Cu2 119.6(2), Si5a–O14–Cu1a 109.9(2), Si5a–O14–Cu2 130.7(2).

The starting material copper(I)-t-butoxide (3) is self-assembled in the solid state as a tetramer containing a central nearly planar eight-membered Cu–O ring [12]. A related planar tetrameric structure has also been reported for tetra(trimethylsilylmethyl)copper(I), (Me3SiCH2)4Cu, whereas for tetrameric copper(I) trimethylsiloxide, (Me3SiO)4Cu, a heterocubane structure has been proposed [14]. With 185.3(3) pm the average Cu–O distance within the Cu–O ring is virtually identical with that in 4 (184.5(10) pm). However, the eight-membered Cu–O ring in 4 is slightly more puckered than that in the t-butoxide as demonstrated by O–Cu–O angles of 169.9(1)° and 174.5(1)° as compared to values of 172.1(5)° and 176.8(5)° in 3. It has been noted in the literature that copper is rarely found as a constituent in naturally occurring silicate minerals [15] and that the tendency of forming structures containing Cu–O–Si units is fairly low [16]. Prominent examples of such compounds include the trimethylsiloxide cluster Cu12O2(OSiMe3)14 [16] and several unusual copper complexes derived from cyclopolsiloxanulates (e.g., [(PhSiO2)6Cu6{(PhSiO2)6}6]6EtOH, K2[(EtSiO2)6Cu4{(EtSiO2)6}44nBuOH, and Na2[(PhSiO2)12Cu4{(8nBuOH)}17–21]. Compound 4 is the first example of a copper complex containing silsesquioxane cages as ligands.

4. Conclusions

The main conclusion to be drawn from this work is summarized in Scheme 1: The formation of the novel copper(I) silsesquioxane 4 upon treatment of tetrameric copper(I)-t-butoxide with the difunctional silsesquioxane precursor 2 involves retention of the central Cu4O4 unit. The product, Cu4O4[Cy3Si3O4(OSiMe3)]2 (4), represents a novel type of copper siloxanolate. In view of the synthetic value of copper(I)-t-butoxide [10] it can be expected that 4 will turn out to be a useful reagent for the preparation of other metal-silsesquioxane derivatives.

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References


