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Synthesis and structures of novel tetra- and pentanuclear copper sandwich-like metallasiloxanes with pyridine ligands

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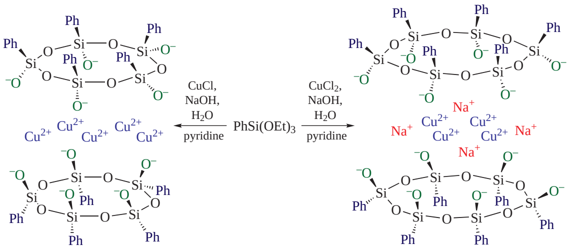
Two new polyherdal copper metallasiloxanes with pyridine ligands were synthesized by the hydrolysis of triethoxyphenylsilane in the presence of NaOH and the subsequent interaction of the alkaline salt thus *in situ* formed with CuCl or $CuCl_2$ in pyridine media. Depending on the salt used, tetra- or pentanuclear sandwich-like Cu-metallasiloxanes were obtained, whose structures were studied by single crystal X-ray diffraction.



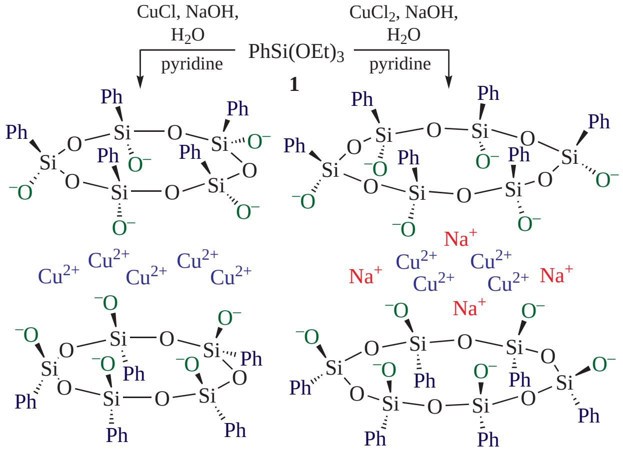
Polyhedral metallasiloxanes represent a unique class of organosilicon compounds and can be used as molecular magnets, catalysts, precursors for ceramics, *etc.*[1–5] These compounds are a unique source of stereoregular siloxane macrocycles that cannot be synthesized using traditional methods of siloxane chemistry. Siloxane macrocycles can easily be obtained by the treatment of metallasiloxanes with triorganylchlorosilanes or with dilute hydrochloric acid.[6–9]

Various approaches to the synthesis of polyhedral metallasiloxanes are underway.[10–18] The main route to obtain metallasiloxanes is based on the variation of reaction conditions such as selection of solvents, metal ions and ligands. The most part of publications report polyhedral metallasiloxanes containing phenyl substituent at the silicon atom. Another approach is based on introducing new organic substituents at the silicon atom of organosilicon precursors.[19–21]

In the continuation of our studies on the synthesis of new metallasiloxanes, we have found that pyridine can also be used as a good medium for their synthesis. Using triethoxyphenylsilane **1** as the organosilicon precursor, copper(I) or (II) chlorides and pyridine as a solvent, tetra- or pentanuclear polyhedral sandwich-like Cu-metallasiloxanes with pyridine ligands can be obtained. The value of this result is the novel access to metallasiloxanes with an odd number of Si–O units in the siloxanolate rings.[21–24]

The synthesis of polyhedral Cu-metallasiloxanes **2a**,**b** containing 10- and 12-membered phenylsiloxanolate cycles with pyridine ligands at metal atoms was carried out similarly to those containing phenyl substituents as shown in Scheme 1.[†]

According to the single crystal X-ray diffraction analysis,[‡] molecular structures of **2a** and **2b** (Figures 1, 2) relate to the sandwich type and contain two pentaphenylcyclopentasiloxanolate or two hexaphenylcyclohexasiloxanolate ligands, respectively. The main metallasiloxane moiety of the molecular structure of **2b** incorporates four copper and four sodium atoms, so its geometry is very similar to that of the previously studied compounds of this type.[17,25] In contrast to the molecular structure of **2b**, metallasiloxane moiety of molecular structure of **2a** contains five copper



Scheme 1

[†] *Synthesis of* **2a**. A mixture of triethoxyphenylsilane (5 g, 0.021 mol), NaOH (0.83 g, 0.021 mol) and water (0.38 g, 0.021 mol) in dry pyridine (30 ml) was stirred under reflux for 2 h under argon atmosphere. Then solid CuCl (2.08 g, 0.021 mol) was carefully added, and the mixture was refluxed for an additional 1 h. After cooling, the solution was filtered from NaCl. Upon standing at 5 °C for 60 days, yellow crystals (0.67 g) of the product were formed in the solution.

Synthesis of **2b**. The synthesis was performed similarly to that of **2a** using triethoxyphenylsilane (5 g, 0.021 mol), NaOH (0.83 g, 0.021 mol), water (0.38 g, 0.021 mol), $CuCl_2$ (2.82 g, 0.021 mol) and dry pyridine (30 ml). Crystals of **2b** (2.2 g) were formed in several days.

[‡] X-ray studies were carried out with a Bruker APEX II diffractometer at 120 K. The structures were solved using direct method and refined in anisotropic approximation against F^2. All calculations were carried out using SHELX[27] and OLEX 2 software.[28]

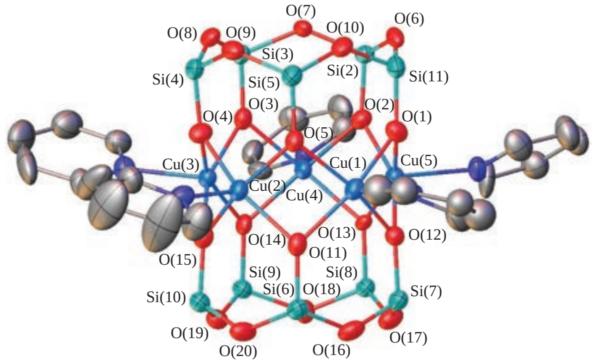


Figure 1 Molecular structure of metallosiloxane fragment of complex **2a** presented in ellipsoids at 50% probability. Phenyl substituents and hydrogen atoms are not shown.

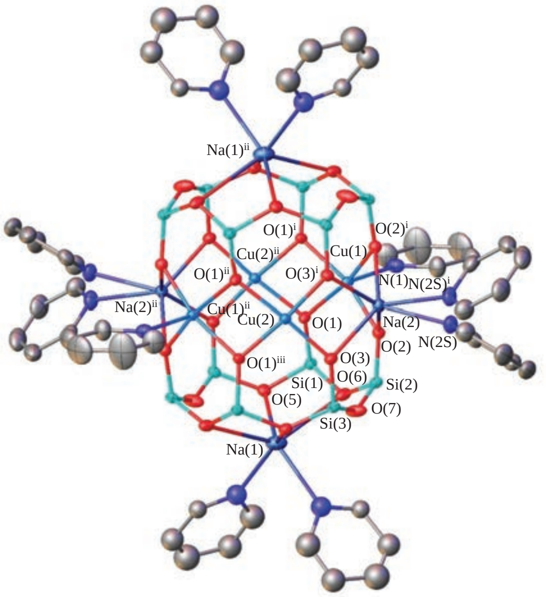


Figure 2 Molecular structure of complex **2b** presented in ellipsoids at 50% probability. Phenyl substituents and hydrogen atoms are not shown. Atoms denoted with i, ii and iii superscripts are generated by $(1-x, 1-y, 1-z)$, $(+x, +y, 1-z)$ and $(1-x, 1-y, +z)$ symmetry operations, respectively.

atoms. Thus, the molecule **2a** is the first example of organometallasiloxanes with an odd number of copper atoms in a molecule. The metallasiloxane molecules containing odd number of transition metal atoms were found only in the case of cobalt and nickel phenylsiloxanes.[16,23,24,26] The average Cu···Cu distance in **2a** is shorter than in **2b** [2.829 and 2.9868(7) Å, respectively]. Similar tendency was observed on comparison between five and six nuclear cobalt and nickel siloxanes. The coordination polyhedron of copper atoms in **2a** corresponds to distorted square pyramid (4+1) with four oxygen atoms of siloxanolate ligands forming square base and nitrogen atom of pyridine moiety as apex. In **2b**, Cu(1) and Cu(2) atoms are characterized by different coordination environment. Similarly to **2a**, the Cu(1) atom adopts distorted square pyramid. At the same time, Cu(2) is not bonded to pyridinium moiety, so its coordination polyhedron can be described as distorted square planar.

In conclusion, a new synthesis of polyhedral metallasiloxanes on using pyridine as a medium has been developed. The use of copper chloride in different oxidation state leads to two different metallasiloxanes. In the case of CuCl, rare among metallasiloxanes ligand with an odd number of silicon atoms was formed. The presence of pyridine in the metallasiloxane molecule as a ligand allows one to dramatically reduce excess of organochlorosilane reactant.

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Crystal data for **2a**: $C_{96.25}H_{86.25}Cu_5N_{7.25}O_{20}Si_{10}$ [calculated formula moiety $C_{85}H_{75}Cu_5N_5O_{20}Si_{10}$, $2.25(C_5H_5N)$], $M = 2263.07$, space group $P\bar{1}$, $a = 18.8938(12)$, $b = 22.4438(13)$ and $c = 28.3594(18)$ Å, $\alpha = 97.719(4)°$, $\beta = 90.829(4)°$, $\gamma = 90.411(4)°$, $V = 11915.0(13)$ Å^3, $Z = 4$, $T = 120$ K, $\mu(\mathrm{CuK}\alpha) = 2.454$ mm^{-1}, $d_{\mathrm{calc}} = 1.262$ g cm^{-3}. Total of 37843 reflections were measured ($1.572° \leqslant \theta \leqslant 67.679°$), 12919 unique ($R_{\mathrm{int}} = 0.0$, $R_\sigma = 0.1260$) reflections were used in all calculations. The final R_1 was 0.1386 [$I > 2\sigma(I)$] and wR_2 was 0.3317 (all data).

Crystal data for **2b**: $C_{122}H_{108}Cu_4N_{10}Na_4O_{24}Si_{12}$ [calculated formula moiety $C_{112}H_{100}Cu_4N_8Na_4O_{24}Si_{12}$, $2(C_5H_5N)$], $M = 2783.39$, space group *Pnnm*, $a = 16.0716(9)$, $b = 17.7505(10)$ and $c = 23.8195(13)$ Å, $V = 6795.2(7)$ Å^3, $Z = 2$, $T = 120$ K, $\mu(\mathrm{MoK}\alpha) = 0.805$ mm^{-1}, $d_{\mathrm{calc}} = 1.360$ g cm^{-3}. Total of 90761 reflections were measured ($1.911° \leqslant \theta \leqslant 30.614°$), 10692 unique ($R_{\mathrm{int}} = 0.0575$, $R_\sigma = 0.0294$) reflections were used in all calculations. The final R_1 was 0.0551 [$I > 2\sigma(I)$] and wR_2 was 0.1657 (all data).

Both in **2a** and **2b**, the most of pyridinium moieties are disordered, which could be the reason of very weak diffraction at high values of 2θ angle. In the case of **2a** it was almost impossible to measure the reflection with $d_{hkl} < 1$ Å. That was the reason of rather high value of *R*-values. In addition, all crystals of **2a** were twins. To decrease *R*-values, we used SQUEEZE and TWINROTMAT procedures implemented in PLATON software.[29]

CCDC 1519268 and 1519269 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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