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Rearrangement of the siloxane skeleton in Cu–Na-containing phenylsiloxanes

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The conversion of 'sandwich'-like metalophenylsiloxane $[PhSiO_2]_6Cu_4Na_4[PhSiO_2]_6$ to 'horse saddle'-like $[PhSiO_2]_{12}Cu_4Na_4$ was settled; this is the first example of chemical transformation of cage-like metalorganosiloxanes that occurs with rearrangement of Si–O–Si skeleton bonds and with the retaining of the cluster Cu_4Na_4.

The discovery and study[1] of the molecular structure of bimetallic Co–Na-containing cage-like phenylsiloxanes started a new period in the development of metalorganosiloxane chemistry. Later, various types of cage-like metalorganosiloxanes were synthesised, including bimetallic alkaline metallosiloxanes based on transition metals, which also contain alkali metal atoms (sodium or potassium).[2,3] It has been disclosed that, in the case of alkaline copper siloxanes, which contain bimetallic Cu_4M_4 clusters, two types of molecular structures coexist. By now, molecular structures of both 'horse saddle' configuration (type **1**) and a 'sandwich' configuration (type **2**) were detected.[2–5] These structures correspond to various isomeric forms that differ in the siloxane skeleton structure of cage-like molecules. The 'horse saddle' structure (type **1**) contains one curvaceous dodecasiloxane cycle in *tris*-(*cis*)-*trans*-*tris*-(*cis*) configuration, whereas there are two hexasiloxane cycles in the sandwich-like structure (type **2**). Note that both isomeric structures (**1**) and (**2**) are formed simultaneously in the course of the synthesis of alkaline copper organosiloxanes, but in different yields.[5,6] In special cases for some systems, the conditions can be chosen to ensure the selective synthesis of either one or another isomer. The exploration of isomerization, including issues both of co-existence equilibrium and inter-conversion of different isomeric forms are of interest for metalorganosiloxane chemistry. Unfortunately, these general problems are not paid sufficient attention until the present time.

The goal of this work was to study the interconversions of isomeric forms of sodium copper phenylsiloxane, $[PhSiO_2]_{12}Cu_4Na_4$ (isomer **1**, a 'horse saddle' form) and $[PhSiO_2]_6Cu_4Na_4[PhSiO_2]_6$ (isomer **2**, a 'sandwich' form). The isomers were synthesised by an original procedure[7] for obtaining both frame and polymeric metalorganosiloxanes. Using variations of this procedure, we synthesised not only well-known sodium copper phenylsiloxane of the 'horse saddle' structure[4] but also the 'sandwich' form of sodium copper phenylsiloxane $[PhSiO_2]_6Cu_4Na_4[PhSiO_2]_6$. This form (isomer **2**) was isolated in a crystalline form for the first time, and its structure was characterised by X-ray diffraction analysis (Figure 1).†

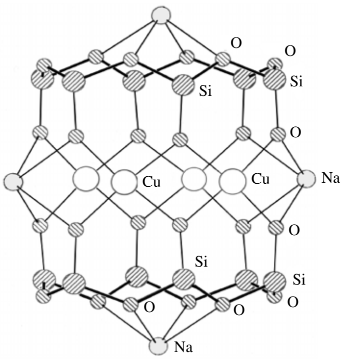

Figure 1 The general view of the copper sodium siloxane framework of a molecule of isomer **2**. Carbon and hydrogen atoms are omitted. The main averaged bond lengths (Å) and bond angles (°): Cu(1)–O(4) 1.880(5), Cu(1)–O(5) 1.896(4), Cu(1)–O(3) 1.937(4), Cu(1)–O(3) 1.955(4), Cu(2)–O(7) 1.873(5), Cu(2)–O(8) 1.888(5), Cu(2)–O(9) 1.950(4), Si–O 1.611(4), Na–O 2.496(6); Cu–O–Cu 96.8(2), Si–O–Cu 132.0 (2).

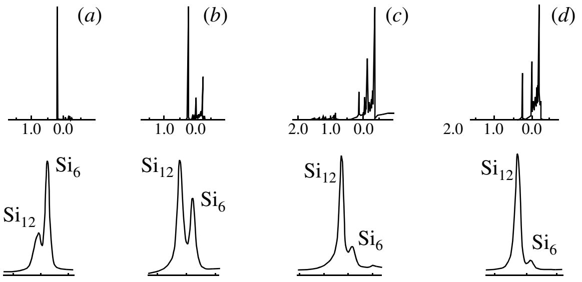

Figure 2 ^1H NMR spectra and chromatograms of trimethylsilylation products: (*a*) copper sodium phenylsiloxane of the sandwich-like structure (isomer **2**); (*b*) isomer **2** after refluxing in butanol for 10 h; (*c*) isomer **2** after refluxing in butanol for 30 h; (*d*) of copper sodium phenylsiloxane of the 'horse saddle' structure (isomer **1**).

The geometry of two independent molecules of isomer **2**, which lie on a crystallographic axis of the second order, is similar to that for the earlier studied[3] complex $[EtSiO_2]_6Cu_4K_4[EtSiO_2]_6$. Six-membered siloxanolate ligands ($[PhSiO_2]_6$) have a *cis*-configuration. The copper atoms possess a square-planar coordination, the deflection of the copper atoms from the plane where the oxygen atoms lie does not exceed 0.04 Å. The interatomic distance between the opposite atoms Cu(1) and Cu(2), located in different halves of the copper siloxane 'sandwich', is 3.958 Å; this actually excludes an additional interaction between them. The Si–O and Cu–O bond lengths are within the range of values that are typical of copper complexes with siloxanolate ligands.[3,4]

Each sodium atom is bound to two oxygen atoms of six-membered siloxanolate ligands and additionally coordinated to one or two butanol molecules.

The appearance of the said 'sandwich'-like isomer among the reaction products could be recorded as previously[5,8] with the use of the 'indirect' signs, for instance, by destructive trimethylsilylation of framework metallosiloxane followed by the analysis of trimethylsilyloxy (TMS) derivatives formed by GPC and NMR

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† The X-ray diffraction studies of a single crystal of isomer **2** ($C_{104}H_{137}Cu_4Na_4O_{32}Si_{12}$, $M = 2582.34$) was carried out on a Smart CCD 1000K diffractometer at 120 K. The crystal is tetragonal, space group $P4_2/n$, $a = b = 30.836(11)$, $c = 25.437(15)$ Å, $V = 24187(18)$ Å^3. Intensities of 71480 reflections were measured, 23461 independent reflections were used in a further refinement. The structure was solved by the full-matrix (least squares) technique against F^2 in the anisotropic–isotropic approximation. The refinement converged to $wR_2 = 0.2499$, GOF = = 1.099 calculated for all independent reflections, $R_1 = 0.0985$ [calculated for 8372 reflections with $I > 2\sigma(I)$].

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 290022. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

methods. We also used this approach in this work to prove the phenomenon of isomerization (rearrangement) in the series of framework copper sodium phenylsiloxanes.

Isomerization was carried out in organic solvents (*n*-butanol, dioxane) under conditions that favoured the formation of the 'minority' form. The course of the process was monitored by a method of destructive trimethylsilylation of the reaction probe[8] followed by analysing the TMS derivative formed by GPC and ^{1}H NMR methods. The results are given in Figure 2. In the ^{1}H NMR spectra of trimethylsilylation derivatives of isomer **2**, treated with boiling *n*-butanol, we observed a decrease in the intensity of the signal assigned to TMS derivatives of the 'sandwich' structure and the appearance of characteristic signals corresponding to the TMS derivatives of the 'horse saddle' isomer **1**.[9] Similarly, the GPC data for trimethylsilylation products show a continuous decrease of the peak assigned to the cyclosiloxane $[PhSiO(OSiMe_3)]_6$, and the corresponding increase in the concentration of the cyclic product $[PhSiO(OSiMe_3)]_{12}$ among the reaction products. The above conversions proceed in high (almost quantitative) yields. The results obtained indicate that conversions of the "sandwich" structure to the 'horse saddle' structure occured. The process is accompanied by a rearrangement of the Si–O–Si bonds of the siloxane skeleton framework molecules. It is of interest that this is the first example of chemical interconversions in the series of framework metalloorganosiloxanes, which occur with a rearrangement of Si–O–Si skeleton bonds and with the cluster structure being retained.

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