Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 76–77
Mendeleev Communications

Ion exchange in bimetallic cage organosiloxanes incorporating copper and alkali metal atoms

Boris G. Zavin,[a] Natalya V. Sergienko,*[a] Alexander A. Korlyukov,[a] Victor D. Myakushev[b] and Mikhail Yu. Antipin[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: zavin@ineos.ac.ru*
[b] *N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation. Fax: +7 495 335 9000*

DOI: 10.1016/j.mencom.2008.03.006

The globular metallic cage organosiloxanes $[RSiO_2]_{12}[Cu_4M_4]$ (where R = Me, CH_2=CH or Ph and M = Na or K) can be converted to the corresponding alkaline Li derivatives in an ion-exchange reaction with LiCl under mild conditions (in up to 79% yields). The $[RSiO_2]_{12}Cu_4Li_4$ compounds have been synthesised and their structures have been studied by X-ray diffraction analysis.

Metallic cage organosiloxanes are synthesised using the reaction of alkali-metal organosiloxanolates with transition-metal halides.[1] So-called alkali metal cage copper organosiloxanes containing not only copper atoms but also sodium or potassium with a Si:Cu:Na(K) ratio of 3:1:1 have been studied most thoroughly.[2–10] The synthesis of these compounds can be described by the following scheme:

$$12(x+y)/n[RSiO(OM)]_n + 4(x+y)CuCl_2 \rightarrow$$
$$x[RSiO_2]_6Cu_4M_4[RSiO_2]_6 + y[RSiO_2]_{12}Cu_4M_4 + 8(x+y)MCl,$$

where M = Na, K; R = Ph, CH_2=CH, Me; $x + y = 1$.

The bimetallic cage organosiloxanes form two types of molecular structures. In sandwich-shaped isomers, the cage contains two hexasiloxane rings, whereas the cage of saddle-shaped isomers contains just one dodecasiloxane ring.

Copper–lithium siloxanes with similar structures have not been obtained to date. Our attempts to synthesise them using the above scheme also failed. Data are available that it is possible to perform reactions in the outer sphere of bimetallic organosiloxanes. In fact, it was found that sodium atoms in cage copper sodium organosiloxanes are readily replaced by transition-metal atoms.[11] Sodium in the spirocyclic bimetallic complex $[Ti\{O(SiPh_2O)_2\}_3\{Na(py)\}_2]py$ was replaced with lithium using an exchange reaction with lithium iodide.[12]

For bimetallic saddle-shaped complexes as an example, we were the first to synthesise cage copper(II) lithium organosiloxanes using cation exchange with LiCl. Almost immediately after the introduction of LiCl into a suspension of copper sodium organosiloxane in boiling ethanol, a NaCl precipitate was formed. The reaction product, a complex copper lithium organosiloxane, is crystallised as the solvent was evaporated. The reaction can be described by the following general scheme:

$$[RSiO_2]_{12}Cu_4Na_4 + 4LiCl \rightarrow [RSiO_2]_{12}Cu_4Li_4 + 4NaCl.$$

1a–c **2a–c**

a R = Ph
b R = CH_2=CH
c R = Me

According to elemental analysis, the resulting crystalline compounds contain no sodium. Since all metal cage organosiloxanes contain variable amounts of solvating solvents, it is the Si:Cu:Li ratio rather than the absolute contents of the elements that serves as the main characteristic of the products.

Table 1 Yields and compositions of the reaction products **2a–c**.

Compound	R	Yield (%)	Elemental analysis (%)			Si:Cu:Li
			Si	Cu	Li	
2a	Ph	60	15.8	12.2	1.38	3:1.02:1.06
2b	CH_2=CH	58	21.2	15.5	1.58	3:1.02:0.91
2c	Me	79	25.7	18.4	2.22	3:0.95:1.05

The yields and compositions of the reaction products are listed in Table 1.

The structure of reaction products and contents of the residual K (or Na) were determined by known analytical methods,[15,16] for example, spectrophotometry (Si), iodometry (Cu), X-ray spectral fluorescence analysis (K, Cu) and atomic absorption spectrometry (Na, Li).

The crystals suitable for an X-ray diffraction study† were prepared in butanol (**2a**) or THF (**2b**).

† All the diffraction experiments were carried out on a Smart 1000 CCD diffractometer at 120 K. The structures of compounds **2a** and **2b** were solved by the direct method and refined by the least-squares method in the full-matrix approximation with respect to F^2. The majority of phenyl and vinyl groups, as well as butanol (in **2a**) and THF (in **2b**) solvate molecules, are disordered. The positions of the methyl-group hydrogen atoms were calculated geometrically and refined using the rigid body model with $U(H) = 1.2U_{eq}(C)$, where C and H designate carbon and hydrogen atoms, respectively.

Crystallographic data for **2a**: the crystals of $C_{90}H_{101}Cu_4Li_4O_{33}Si_{12}$ are tetragonal, space group $P4_12_12$, $a = 18.972(2)$ and $c = 32.164(6)$ Å, $V = 11577(3)$ Å^3, $Z = 4$, $M = 2329.71$, $d_{calc} = 1.337$ g cm^{-3}, μ(MoKα) = = 0.92 mm^{-1}, $F(000) = 4804$. The intensities of 136661 reflections were measured [λ(MoKα) = 0.71073 Å, ω-scanning, $2\theta < 54°$]; 17260 independent reflections ($R_{int} = 0.0643$) were used for the further refining. The final refinement parameters are: $wR_2 = 0.2143$ (based on all reflections), GOF = 1.056, $R_1 = 0.0740$ [based on 8861 reflections with $I > 2\sigma(I)$].

Crystallographic data for **2b**: the crystals of $C_{56}H_{100}Cu_4Li_4O_{32}Si_{12}$ are tetragonal, space group $P42_1/c$, $a = 14.6359(19)$ and $c = 21.452(4)$ Å, $V = 4595.2(12)$ Å^3, $Z = 2$, $M = 1904.06$, $d_{calc} = 1.376$ g cm^{-3}, μ(MoKα) = = 1.14 mm^{-1}, $F(000) = 1976$. The intensities of 68780 reflections were measured [λ(MoKα) = 0.71073 Å, ω-scanning, $2\theta < 52°$]; 6600 independent reflections ($R_{int} = 0.0456$) were used for the further refining. The final refinement parameters are: $wR_2 = 0.1637$ (based on all reflections), GOF = 0.959, $R_1 = 0.0748$ [based on 3975 reflections with $I > 2\sigma(I)$].

CCDC 680555 and 680556 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

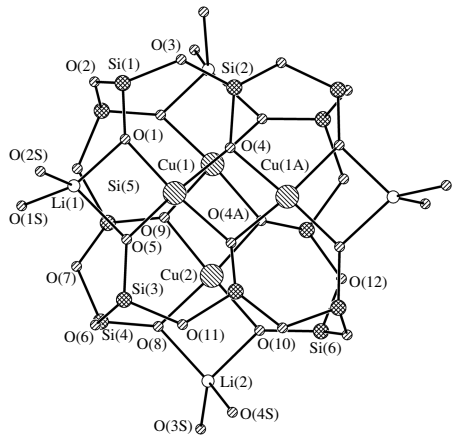

Figure 1 Molecular structure of complex **2a**. Atoms are presented by thermal ellipsoids at 30% probability. Phenyl groups and butanol molecules are not shown. Selected bond lengths in metallasiloxane skeleton (Å): Cu(1)–O(1) 1.911(3), Cu(1)–O(4) 1.954(3), Cu(1)–O(5) 1.921(3), Cu(2)–O(8) 1.933(3), Cu(2)–O(9) 1.957(3), Cu(2)–O(10) 1.906(4), Li(1)–O(1) 1.939(13), Li(1)–O(5) 1.957(12), Li(1)–O(2S) 1.913(14), Li(1)–O(1S) 1.947(13), Li(2)–O(10) 1.895(11), Li(2)–O(8) 1.940(11), Li(2)–O(3S) 1.891(12), Li(2)–O(4R) 1.986(14).

Crystalline complexes **2a** and **2b** are characterised by a saddle configuration. The coordination polyhedron of Cu atoms is a distorted planar square; the deviation of the metal atom from the plane of the oxygen atoms bound to it is within 0.11–0.15 Å. The mean distances between the copper atoms and the opposite siloxane O atoms in complexes **2a** and **2b** are 2.56 and 2.58 Å, respectively; they are shorter than the corresponding values for complexes of this type containing other alkali metals (~3.4 Å).[4,6,7] The distance between the metallasiloxane fragments is shorter, probably, due to the replacement of Na or K atoms with Li that has a small atomic radius. The coordination polyhedron of the Li atoms is a distorted tetrahedron formed due to bonding with two oxygen atoms of the siloxane fragment and with two solvate molecules of THF or butanol. Unfortunately, the THF and butanol molecules are completely disordered. One may propose that the disorder of solvate molecules is caused by a loose packing of metallasiloxane moieties. The Li atoms are bound with two siloxane O atoms in such a way that, together with the copper atoms, they form two metal-containing 'belts' (Figures 1 and 2). The coordination of Li atoms differs considerably from that of Na and K. The latter are most often characterised by coordination with four O atoms belonging to both copper siloxane fragments, which probably prevents the latter from approaching each other.

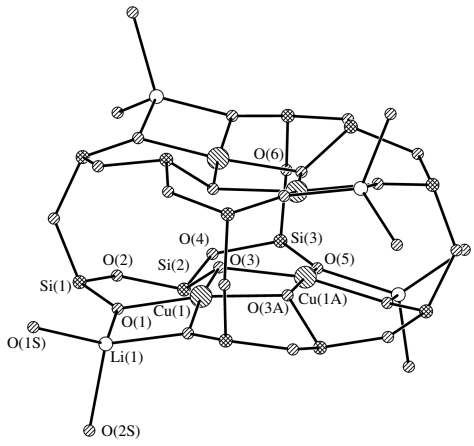

Figure 2 Molecular structure of complex **2b**. Atoms are presented by thermal ellipsoids at 30% probability. Vinyl groups and THF molecules are not shown. Selected bond lengths in metallasiloxane skeleton (Å): Cu(1)–O(1) 1.974(5), Cu(1)–O(3) 1.965(4), Li(1)–O(1) 1.797(15), Li(1)–O(5) 1.967(15), Li(1)–O(2S) 2.020(15), Li(1)–O(1S) 2.272(19), Li(1)–O(1S′) 1.928(9).

According to elemental analysis data, the atomic ratios Si:Cu:Li in **2c** are equal to 3:1:1, which corresponds to the general formula $[RSiO_2]_{12}Cu_4Li_4$ **2a–c**. Unfortunately, we failed to grow a crystal of **2c** suitable for X-ray diffraction studies. Thus, for the elucidation of the structure of **2c**, it was investigated by a technique described previously.[10] The procedure includes the full silylation by the interaction with trimethylchlorosilane (TMS):

$$[RSiO_2]_{12}Cu_4Li_4 + 12Me_3SiCl \rightarrow [RSiO(OSiMe_3)]_{12} + 4CuCl_2 + 4LiCl.$$

The obtained reaction products were analysed by GPC and ^{29}Si NMR spectroscopy.[13,14] According to GPC and NMR data, the silyl derivatives obtained from **1c** and **2c**, are identical to the cyclosiloxane $[RSiO(OSiMe_3)]_{12}$ (where R = Me). It is the sufficient proof for retention of the globular structure in Li complex **2c**, and it allows us to conclude that its structure is analogous to those of complexes **2a** and **2b**.

This work was supported by the Russian Foundation for Basic Research (grant nos. 05-03-32938 and 06-03-32347).

References

1 S. N. Borisov, M. G. Voronkov and E. Ya. Lukevits, *Organosilicon Heteropolymers and Heterocompounds*, Plenum Press, New York, 1970.
2 V. A. Igonin, S. V. Lindeman, Yu. T. Struchkov, O. I. Shchegolikhina, Yu. A. Molodtsova, Yu. A. Pozdnyakova and A. A. Zhdanov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 184 (*Russ. Chem. Bull.*, 1993, **42**, 168).
3 O. I. Shchegolikhina, Yu. A. Pozdnyakova, S. V. Lindeman, A. A. Zhdanov, R. Ugo, G. Gavioli, R. Battistuzzi, M. Borsari, T. Ruffer, C. Zucchi and G. Palyi, *J. Organomet. Chem*., 1996, **514**, 29.
4 V. A. Igonin, S. V. Lindeman, Yu. T. Struchkov, O. I. Shchegolikhina, A. A. Zhdanov, Yu. A. Molodtsova and I. V. Razumovskaya, *Metalloorg. Khim.*, 1991, **4**, 1355 (*Organomet. Chem. USSR*, 1991, **4**, 672).
5 A. A. Zhdanov, N. V. Sergienko and E. S. Trankina, *Izv. Akad. Nauk, Ser. Khim*., 1998, 2530 (*Russ. Chem. Bull.*, 1998, **47**, 2448).
6 Yu. A. Molodtsova, Yu. A. Pozdniakova, K. A. Lyssenko, I. V. Blagodatskikh, D. E. Katsoulis and O. I. Shchegolikhina, *J. Organomet. Chem*., 1998, **571**, 31.
7 C. Zucchi, M. Mattioli, G. Gavioli, M. Moret, A. Sironi, R. Ugo, M. Pizzotti, O. I. Shchegolikhina and G. Palyi, *Eur. J. Inorg. Chem*., 2000, 1327.
8 A. A. Zhdanov, N. V. Sergienko and E. S. Trankina, *Ross. Khim. Zh.*, 2001, **XLV** (4), 44 (in Russian).
9 Yu. A. Molodtsova, Yu. A. Pozdnyakova, I. V. Blagodatskikh, A. S. Peregudov and O. I. Shchegolikhina, *Izv. Akad. Nauk, Ser. Khim*., 2003, 2577 (*Russ. Chem. Bull., Int. Ed*., 2003, **52**, 2722).
10 B. G. Zavin, N. V. Sergienko, E. V. Gorodnichev, V. D. Myakushev, A. A. Korlyukov and M. Yu. Antipin, *Mendeleev Commun*., 2005, 245.
11 N. V. Sergienko, E. S. Trankina, V. I. Pavlov, A. A. Zhdanov, K. A. Lyssenko, M. Yu. Antipin and E. I. Akhmet'eva, *Izv. Akad. Nauk, Ser. Khim*., 2004, 337 (*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 351).
12 M. Lazell, M. Motevalli, S. A. A. Shah, C. K. S. Simon and A. C. Sullivan, *J. Chem. Soc., Dalton Trans*., 1996, 1449.
13 O. I. Shchegolikhina, Yu. A. Molodtsova, Yu. A. Pozdnyakova, T. V. Strelkova and A. A. Zhdanov, *Dokl. Akad. Nauk*, 1992, **325**, 1186 [*Dokl. Chem.* (*Engl. Transl.*), 1992, **325**, 168].
14 I. V. Blagodatskikh, O. I. Shchegolikhina, Yu. A. Pozdnyakova, Yu. A. Molodtsova and A. A. Zhdanov, *Izv. Akad. Nauk, Ser. Khim*., 1994, 1057 (*Russ. Chem. Bull*., 1994, **43**, 993).
15 *Metody kolichestvennogo mikroanaliza* (*Methods of Quantitative Microanalysis*), ed. N. E. Gel'man, Khimiya, Moscow, 1987, p. 165 (in Russian).
16 V. N. Alekseev, *Kolichestvennyi analiz* (*Quantitative Analysis*), Khimiya, Moscow, 1972, p. 408 (in Russian).

Received: 3rd July 2007; Com. 07/2973