

Letters to the Editor

A new type of supramolecular organization in the cage-like metallasiloxanes*

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Combination of single molecules of the cage-like metallasiloxanes (CMS) into supramolecular structures is a rare type of the intermolecular coordinative interaction. The supramolecular structures based on the cyclic sodium and potassium organosilanolates, viz., $[\text{PhSi}(\text{ONa})\text{O}]_4 \cdot 8\text{Bu}^n\text{OH}$,¹ $[\text{PhSi}(\text{ONa})\text{O}]_3 \cdot 8\text{H}_2\text{O}$, $[\text{PhSi}(\text{ONa})\text{O}]_3 \cdot 4\text{H}_2\text{O} \cdot \text{EtOH}$, $\{[\text{PhSi}(\text{OK})\text{O}]_3\}_2 \cdot 7\text{H}_2\text{O} \cdot 3\text{MeOH}$,² have been described. In these compounds, the supramolecular structures are formed by the coordinative interaction between the solvate molecules and alkaline metal ions located in the neighboring molecules: — $\text{PhSiONa} \cdots \text{L}_2 \cdots \text{NaOSiPh}$ — ($\text{L} = \text{H}_2\text{O}$, MeOH , BuOH). Both the one-dimensional supramolecular structures (chain of linked single molecules)¹ and the formations consisting of single molecules interlinked in two dimensions were obtained.²

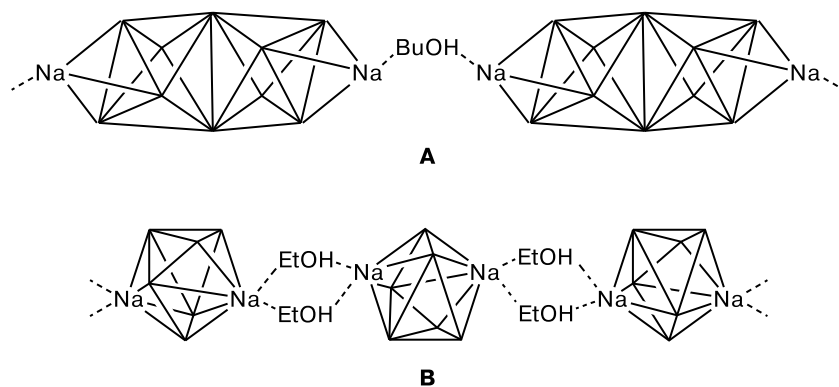
There exist supramolecular assemblies consisting of CMSs containing simultaneously transition and alkaline metals. In the iron-containing CMS $(\text{PhSiO}_{1.5})_{20}(\text{FeO}_{1.5})_6(\text{Na}_2\text{O})_4(\text{BuOH})_9\text{C}_7\text{H}_8$,³ the cages** are combined into one-dimensional chain structures **A** due to coordination of the Na ions located in the neighboring molecules to butanol.

The parameters of coordination site (the Na—O(C) bond length is 2.4 Å and the Na—O—Na angle is 111.8°) virtually coincide with the analogous ones within the cage structure. In the Cu-containing CMSs of the compositions $[\text{PhSiO}_{1.5}]_{10}[\text{CuO}]_2[\text{Na}_2\text{O}][\text{EtOH}]_4$ ⁴ and $[\text{VinSiO}_{1.5}]_{12}[\text{CuO}]_4[\text{Na}_2\text{O}]_2[\text{EtOH}][\text{H}_2\text{O}]_5$,⁵ the one-dimensional chain structure** **B** forms upon coordination of the Na ions to the EtOH molecules.

The parameters of coordination cycle are as follows: the Na—O(C) bond length is 2.2 Å and the Na—O—Na angle is 88.4°. The decrease in the bond angle compared to that in Fe-CMS is explained by the formation of cyclic bonding fragment.

* Sacred to the memory of M. Yu. Antipin (1951–2013), a charismatic personality of social-character and a scientist grown out of the pleiad of eminent Russian physicochemists, which worthily headed the outstanding Russian school of X-ray diffraction studies.

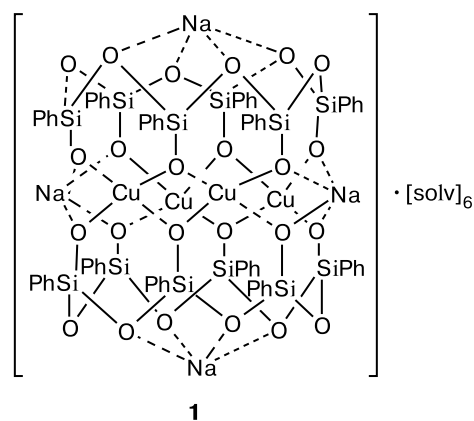
** The cage shapes are shown provisionally.



In all the above-mentioned cases, the formation of supramolecular structures occurs due to the coordinative interaction of the alkaline metal ions with the solvating solvents (ROH , H_2O) acting as bridging ligands.

Earlier, the copper-containing CMS with the cage, whose shape is prismatic and crystal structure consists of single non-interlinked molecules, has been described.⁶ In the present work, we introduced a bridging ligand, *viz.*, dioxane, to the structure of copper-containing CMSs as a bonding unit. As a result, we obtained a prismatic cage-like copper phenylsiloxane (**1**) whose molecules are combined into the two-dimensional network through the dioxane molecules (Fig. 1).

The axis of adjacent cylindric cages are mutually perpendicular, each dioxane molecule coordinates through



$\text{solv} = \text{C}_4\text{H}_8\text{O}_2$

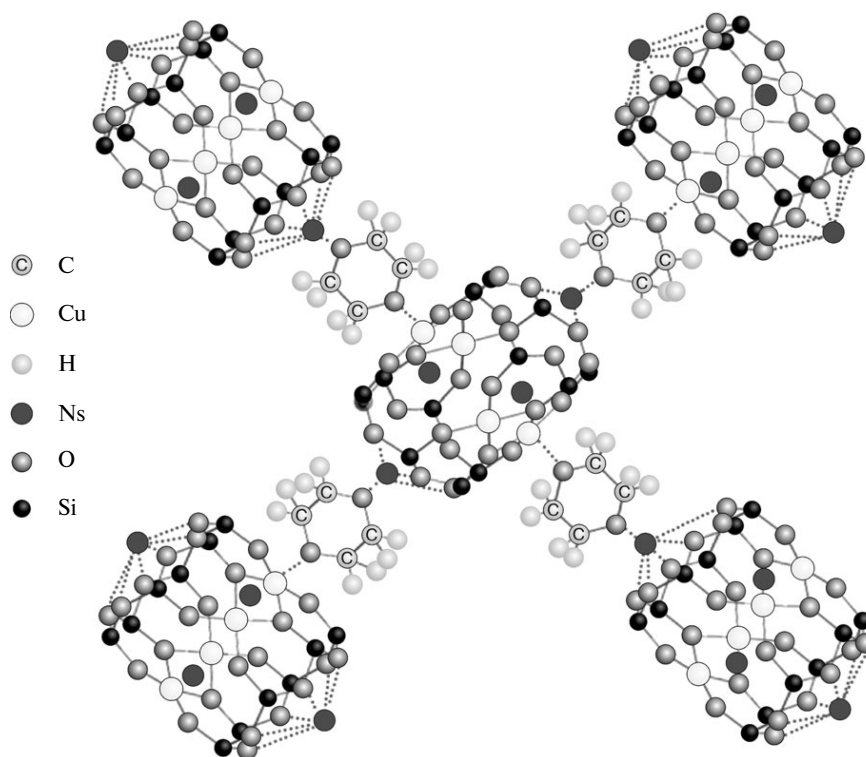


Fig. 1. Supramolecular structure of compound (the phenyl groups and a part of solvating solvents are not shown).

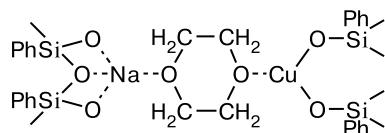


Fig. 2. The structure of coordination site in compound 1.

the O atom to one of the Na ions in the proximate molecule, and the second O atom coordinates to the Cu atom in the neighboring molecule (Fig. 2).

The parameters of coordination site (Na—O(C) 2.27 Å, $\angle(\text{Si})\text{O—Na—O}(\text{C})$ 68.4°) are close to those of the cage ((Na—O(Si) 2.44 Å, $\angle(\text{Si})\text{O—Na—O}(\text{Si})$ 60.5°). Thus, the supramolecular structure that formed can be regarded as a uniform cage assembly. The uniqueness of the structure obtained lies in the fact that, along with the Na ions, the transition metal ions are also involved in the coordinative interaction forming the supramolecular structure (see Fig. 2). It is worthy of note that, in cases when the crystalline structures of bimetallic CMSs is formed solely by the single non-interlinked molecules and there was no formation of supramolecular structures, solvating solvents coordinate only to the alkaline metal ions (not to the transition metal ones).

Table 1. Parameters of X-ray diffraction study and structure refinement for compound 1

Parameter	Value
Molecular formula	$\text{C}_{48}\text{H}_{54}\text{Cu}_2\text{Na}_2\text{O}_{18}\text{Si}_6$
M	1260.51
Space group	$Pbca$
Z	8
$a/\text{\AA}$	19.765(2)
$b/\text{\AA}$	20.851(2)
$c/\text{\AA}$	28.856(3)
α/deg	90.00
β/deg	90.00
γ/deg	90.00
$V/\text{\AA}^3$	11892(2)
$d_{\text{calc}}/\text{g cm}^{-3}$	1.408
μ/cm^{-1}	9.16
$F(000)$	5200
$2\sigma_{\text{max}}/\text{deg}$	61
Number of reflections	
measured	18324
independent	18324
with $I > 2\sigma(I)$	10441
Number of parameters refined	685
R_1	0.0684
wR_2	0.1700
GOOF	1.003
Residual electron density	1.872/−1.649
/e $\text{\AA}^{-3}$ ($d_{\text{max}}/d_{\text{min}}$)	

A rare type of participation of the transition metal in the supramolecular structure formation is defined in this case by a specific shape of the copper-sodium-silicon-containing cluster providing availability of the Cu ions for coordination.

Compound 1 was synthesized according to the procedure described in Ref. 7 (using dioxane as one of the solvents). A solution of polycopperphenyl silsesquioxane⁶ (2.00 g, 0.006 mol) in dioxane (65 mL) and toluene (25 mL) was added to a solution of sodium tetraphenylcyclotetrasiloxanolate¹ (0.95 g, 0.0015 mol) in methanol (10 mL). The crystalline product (1.21 g, 41%) obtained after reduced-pressure drying was analyzed. Found (%): Si, 16.95; Na, 4.60; Cu, 12.72; a ratio of Si : Na : Cu = 3.02 : 0.99 : 1. ($\text{PhSiO}_{1.5}$)₆(CuO)₄(NaO_{0.5})₄($\text{PhSiO}_{1.5}$)₆. Calculated (%): Si, 16.92; Na, 4.62; Cu, 12.76; a ratio of Si : Na : Cu = 3 : 1 : 1. The structure of crystalline product was established by X-ray diffraction study on a Bruker Smart APEX II diffractometer at 100 K. The structure was solved by the direct method and refined by the full-matrix least-squares method over F_2 in the anisotropic approximation for non-hydrogen atoms (Table 1). The hydrogen atoms of the phenyl groups of the metallasiloxane cage and coordinated dioxane molecules were calculated based on the geometric considerations and refined in terms of the riding model.

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