Letters to the Editor

New heterometallic organosiloxanes

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Among a diversity of bimetallic[1] organometallosiloxanes (OMSO), compounds simultaneously containing transition and main-group metals remained unknown. Combinations of transition and alkaline-earth metals are of particular interest because alkali and alkaline-earth metals are similar in electronegativity. Hence, the characteristics of the structure formation of OMSO would be expected to be similar for such compounds. In addition, it is worthwhile to compare the influence of alkaline-earth and other main-group metals in the OMSO structure.

We synthesized bimetallic OMSO, *viz.*, calcium copper phenylsiloxane (**1**) and cadmium copper phenylsiloxane (**2**), according to a procedure described earlier.[2] This procedure involves the alkaline hydrolysis of phenyltriethoxysilane followed by the exchange reaction of the resulting organosilanolate and polyvalent metal halides.

X-ray diffraction study of OMSO **1** and **2** demonstrated that these compounds are structurally similar and can be described as hexagonal prisms, whose upper and lower bases are formed by the six-membered organosiloxane rings linked to each other by the metal oxide fragments O—M—O (Fig. 1).

In all sandwich-type bimetallic OMSO synthesized earlier, the prismatic cage has a cylindrical shape. By contrast, the cage in complexes **1** and **2** has an ellipsoid shape, the ellipsoid being elongated along the line between two main-group metals, which is due to the fact that the ionic radii of the Ca and Cd atoms (1.00 and 0.87 Å, the coordination numbers are 5 and 6, respectively)[3] substantially differ from that of the Cu atom (0.65 Å, the coordination number is 5).[3] The deviation from the cylindrical shape can be estimated from the distance between the opposite copper atoms. In μ^6-(hexaphenylcyclohexasiloxanolato)hexacopper(II), which has been synthesized earlier,[4] the corresponding distance is 5.5—5.7 Å. In complex **2**, this distance is substantially shorter (4.462(1) Å). The replacement of the Cd atom by Ca leads to a further decrease in this distance (to 4.004(1) Å), and the latter is comparable to the analogous distance (3.958(1) Å) in the "globular" Cu,Na-OMSO complex.[5]

Therefore, the partial replacement of Cu atoms by atoms with larger ionic radii leads to a distortion of the cylindrical shape of the cage, the degree of distortion being more likely determined by the ionic radius rather than by the nature of the introduced metal atom.

X-ray diffraction studies were performed on a Bruker Smart CCD 1000 diffractometer. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms against F^2. The hydrogen atoms of the Ph, CH_2, and Me groups were calculated geometrically and refined using a

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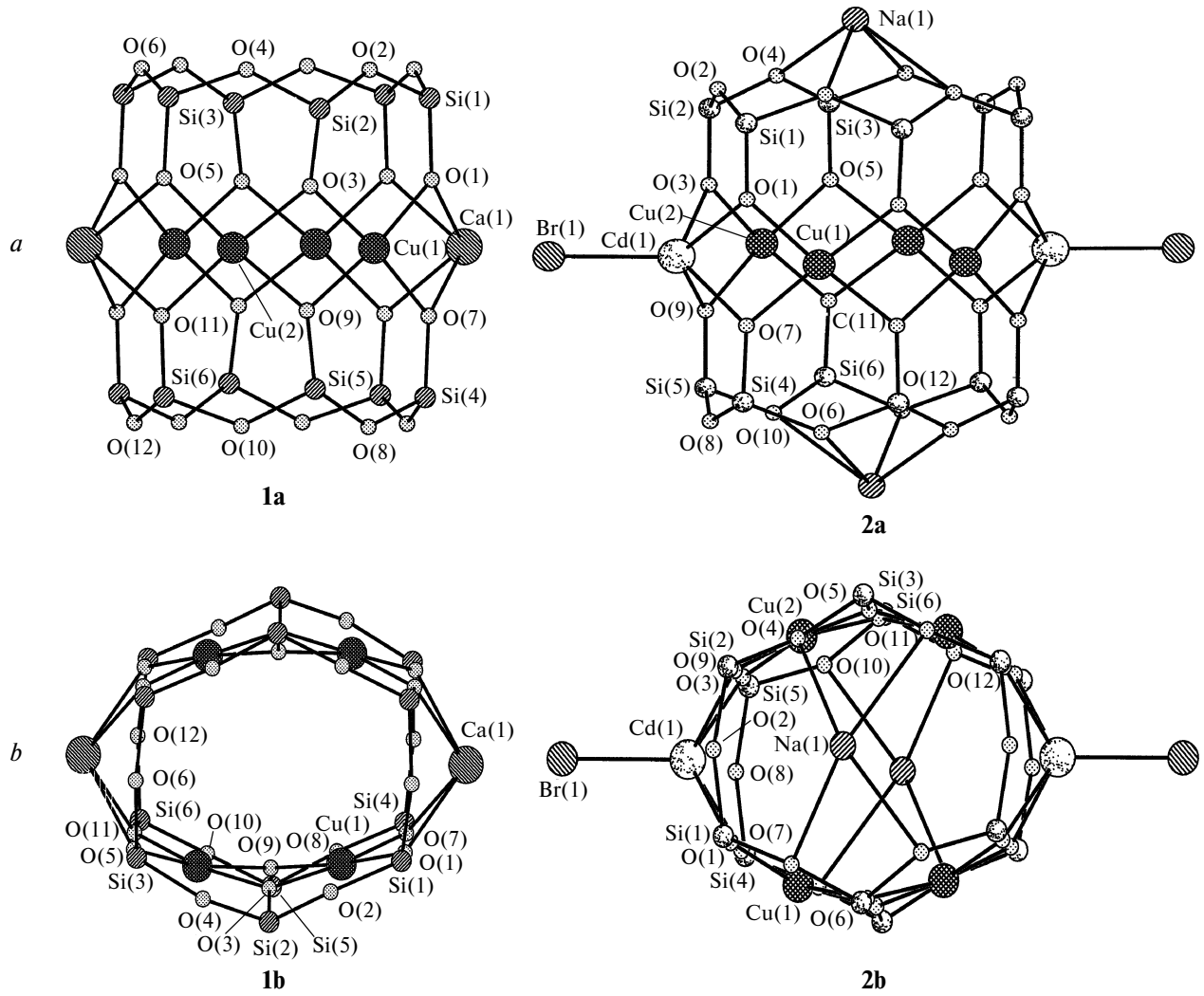

Fig. 1. Overall view (*a*) and the top view (*b*) of the metallosiloxane cage in complexes **1** and **2** (Ph groups at the silicon atoms and the solvate dioxane and methanol molecules are omitted).

riding model. The hydrogen atoms of the hydroxy groups were not found.

Analysis of difference Fourier maps revealed disorder of the solvate dioxane molecules and a number of Ph groups. These fragments were refined using a rigid-body model.

All calculations were carried out with the use of the SHELXTL PLUS program package (version 5.10).[6] Details of X-ray data collection and structure refinement parameters for compounds **1** and **2** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Table 1. Principal crystallographic data and structure refinement parameters for complexes **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{93}H_{97.5}Ca_2Cu_4O_{37.5}Si_{12}$	$C_{90.5}H_{107}Br_2Cd_2Cu_4Na_2O_{36.5}Si_{12}$
Molecular weight	2486.61	2800.60
T/K	120	120
Scanning mode	ω	ω
Space group	$P\bar{1}$	*Pbca*
a/Å	17.378(4)	18.201(4)
b/Å	18.504(4)	25.599(5)
c/Å	19.034(4)	26.319(5)

(*to be continued*)

Table 1 (*continued*)

Parameter	**1**	**2**
α/deg	83.283(5)	90
β/deg	84.136(5)	90
γ/deg	67.117(5)	90
V/Å^3	5589(2)	12263(4)
d_{calc}/g cm^{-3}	1.478	1.517
Z	2	4
μ/cm^{-1}	10.51	18.7
$F(000)$	2559	5656
$2\theta_{max}$/deg	52	52
Number of measured reflections	36316	104701
Number of independent reflections	22027	11991
Number of reflections with $I > 2(I)$	11607	8761
R_1	0.0630	0.0732
wR_2	0.1983	0.2182
Number of parameters in refinement	1141	530

Table 2. Selected bond lengths (d) and bond angles (ω) in complexes **1** (M = Ca) and **2** (M = Cd)

Parameter	**1**	**2**
Bond	d/Å	
Cu—O	1.936(4)	1.921(5)
Si—O	1.631(4)	1.635(5)
M—O	2.356(5)	2.259(5)
Si—C	1.841(8)	1.841(8)
Cd(1)—Br(1)	—	2.5187(10)
Angle	ω/deg	
O—Si—C	110.1(3)	110.6(3)
Si—O—Cu	132.8(2)	131.7(3)
Cu—O—Cu	99.8(2)	94.1(1)
Cu—O—M	93.9(2)	97.4(2)
O—Si—O	108.7(2)	110.4(2)

Synthesis of calcium copper phenylsiloxane (1) was performed according to a procedure described earlier[2] by the metathesis reaction of $CuCl_2$ (4.43 g, 0.033 mol) and $CaCl_2$ (1.83 g, 0.017 mol) with sodium phenylsilanolate, which was prepared from $PhSi(OEt)_3$ (24.0 g, 0.1 mol), H_2O (3.6 g, 0.2 mol), and Na (2.3 g, 0.1 mol). After hot filtration, the reaction mixture was concentrated, and a blue crystalline precipitate was obtained. The precipitate was separated and dried *in vacuo* to constant weight. Compound **1** was isolated in a yield of 3.56 g (22%). Found (%): Ca 3.92; Cu, 12.55; Si, 16.89. The Si : Cu : Ca: ratio is 12 : 3.9 : 1.95. $C_{72}H_{60}Si_{12}O_{24}Cu_4Ca_2$. Calculated (%): Ca, 4.05; Cu, 12.83; Si, 17.02. The structure was confirmed by X-ray diffraction study.

Synthesis of cadmium copper phenylsiloxane (2) was performed by the metathesis reaction of copper sodium phenylsiloxane (5.3 g, 0.0027 mol), which was prepared according to a procedure described earlier,[2] and $CdBr_2$ (1.47 g, 0.0054 mol). After hot filtration, the reaction mixture was concentrated. Compound **2** was obtained in a yield of 3.76 g (59%) as blue crystals. Found (%): C, 39.13; H, 3.46; Br, 6.53; Cd, 8.36; Cu, 9.77; Na, 1.36; Si, 12.50. The Si : Cu : Cd : Na : Br ratio is 12 : 4.13 : 2.0 : 1.6 : 2.2. $C_{72}H_{60}O_{24}Si_{12}Cu_4Cd_2Na_2Br_2$. Calculated (%): C, 37.1; H, 2.6; Br, 6.9; Cd, 9.6; Cu, 10.9; Na, 2.0; Si, 14.4. The structure was confirmed by X-ray diffraction study.

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