Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 344–346
Mendeleev Communications

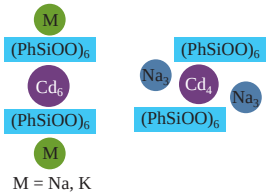
Metallosiloxanes containing period 5 transition metals: synthesis and X-ray studies of three cadmium siloxanes

Natalia V. Sergienko, Alexander A. Korlyukov,* Dmitry E. Arkhipov, Valentin V. Novikov, Marina A. Eskova and Boris G. Zavin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax:+7 499 135 5085; e-mail: alex@xrlab.ineos.ac.ru

DOI: 10.1016/j.mencom.2016.07.026

Hydrolysis of $PhSi(OEt)_3$ in the presence of MOH (M = K, Na) and $CdBr_2$ affords new cadmium siloxanes of sandwich type, whose encapsulated species (Br^-, H_2O, OH) are defined by the solvent used for synthesis and crystallization.



Sandwich metallosiloxanes of period 4 transition metals is the most abundant structural type of the complexes formed by interaction between halides of transition metals (Cr, Mn, Ni, Co, Cu)[1] and sodium organosiloxanolates in polar solvents. Despite the lack of information about the mechanism of the formation of metallosiloxanes, the structural data available in the Cambridge Structural Database[2] can be used as starting point to predict their structural stability. According to this database, the sandwich frameworks containing 4–10 atoms of period 4 transition metal and two cyclic $[R(SiO)_{1.5}]_n$ species (R = Alk, Ar, n = 5–10) were found to be very stable most probably owing to effective combination of various factors (ionic radii of transition metals, oxidation state of metal +2, high negative charge of siloxanolate oxygen atoms and high flexibility of siloxanolate cycles). The change of one or several of these factors can lead to the pronounced distortion of sandwich framework or formation of the frameworks that belong to different types. For instance, the frameworks with four copper atoms and two heavy alkali-earth metals (Sr, Ba) are highly distorted (flattened)[3] as compared to the hexacopper frameworks of cylindrical shape. On the other hand, the inclusion of two cadmium atoms into copper siloxane framework remains the sandwich framework almost undistorted.[4]

Hence, cadmium can be the most convenient element for the synthesis of the first representatives of sandwich metallosiloxanes of period 5. Ionic radius of pentacoordinated cadmium is larger than that for pentacoordinated copper (0.87 and 0.65[5]), so the size of cadmium siloxane framework can be larger in comparison with its copper siloxane analogue.

The synthesis of cadmium siloxane was carried out in a two step route (Scheme 1).†

The single crystal X-ray study of compounds **1**–**3**‡ has shown that they correspond to the sandwich cadmium siloxanes with two hexasiloxanolate ligands $[PhSiO_{1.5}]_6$ (Figures 1–3). The

$$PhSi(OEt)_3 + MOH + H_2O \rightarrow (PhSiOOM)_n + EtOH$$

$$(PhSiOOM)_n + CdBr_2 \rightarrow [(PhSiOO)_6]_2Cd_mM_kBr_2 + MBr$$

M = Na, K

1–**3**: $m = 4$, $k = 6$; $m = 6$, $k = 2$

Scheme 1

shape of the sandwich structure of hexacadmium siloxanes (**1** and **2**) corresponds to the distorted cylinder due to the presence of two covalent Cd–Br bonds. Owing to retention of two Cd–Br

† All chemicals of high purity grade were purchased from Sigma–Aldrich. All solvents were distilled prior to synthesis. IR spectra were recorded on a Bruker Tensor 37 Fourier spectrometer. ^{29}Si NMR spectra were recorded from solution in C_6D_6, EtOH and toluene mixture using a Bruker Avance 600 spectrometer. The ^{29}Si chemical shifts were referenced to external TMS.

General synthetic route for cadmium siloxanes **1**–**3**. A reactor was charged with MOH [M = K (**1**), Na (**2**, **3**)], H_2O and $PhSi(OEt)_3$ (0.75 g mol^{-1}) in molar ratio 1:1:1 (EtOH was used as solvent). Then the mixture was refluxed for 1 h with subsequent addition of sixfold excess toluene (**1**, **2**) or dioxane (**3**). After that, the solution of $CdBr_2$ in EtOH–MeOH mixture was added dropwise to maintain Si:Cd ratio of 2:1 (**1**, **2**) and 3:1 (**3**) upon stirring to boiling reaction mixture. The mixture then was refluxed on stirring for 4 h and NaBr/KBr was filtered off as white precipitate. The residue after removal of solvent was recrystallized from THF–MeOH–dimethylacetamide (**1**), THF–MeOH–DMF (**2**) and dioxane–MeOH–dimethylacetamide (**3**) giving thus single crystals suitable for X-ray study. One of single crystals was used for X-ray diffraction and the rest were dried *in vacuo* at room temperature.

For **1** (M = K) yield of crystalline product was 59%. IR (Nujol, ν/cm^{-1}): 3616, 3076, 3047, 2920, 1650, 1606, 1505, 1429, 1403, 1262, 1126, 1008, 745, 722, 701, 639, 540, 494, 438. ^{29}Si NMR, δ: –65.38 ppm. Found (%): Si, 10.98; Cd, 22.50; K, 2.80; Br, 5.65. Calc. for $C_{104}H_{132}Br_2Cd_6K_2N_8O_{33}Si_{12}$ (%): Si, 13.17; Cd, 26.36; K, 3.06; Br, 6.25.

For **2** (M = Na) yield of crystalline product was 61%. IR (Nujol, ν/cm^{-1}): 3633, 3076, 3047, 2926, 1651, 1591, 1430, 1385, 1127, 1011, 744, 725, 701, 639, 539, 496, 439. ^{29}Si NMR, δ: –65.96 and –66.92. Found (%): Si, 11.06; Cd, 24.00; Na, 1.65; Br, 4.93. Calc. for $C_{89}H_{114}Br_2Cd_6Na_2O_{33}Si_{12}$ (%): Si, 13.34; Cd, 26.69; Na, 1.82; Br, 6.33.

In the case of **3** only few crystals were collected and their structure was established by X-ray diffraction.

Due to the presence of residual solvent in crystal, the composition was defined only for atoms of metallosiloxane framework. The ratio Si:Cd:M:Br calculated from the experimental X-ray data is in satisfactory agreement with the theoretical one for $[(PhSiOO)_6]_2Cd_6M_2Br_2$, moiety (12 Si, 6 Cd : 2 M and 2 Br).

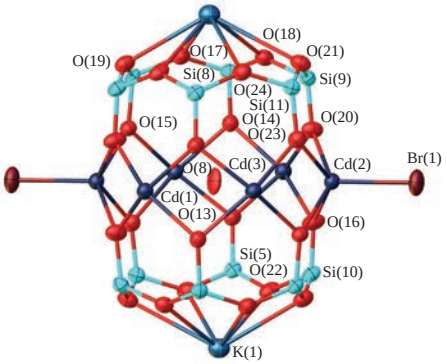


Figure 1 The structure of cadmium siloxane **1**. Pnenyl groups and coordinated molecules of solvents are omitted for clarity.

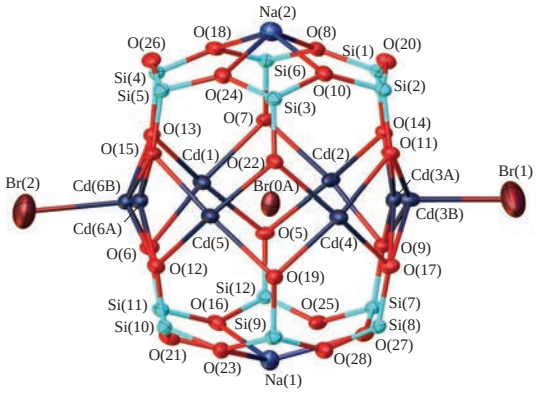


Figure 2 The structure of cadmium siloxane **2**. Phenyl groups and coordinated molecules of solvents are omitted for clarity. Br(1) and Br(2) are the positions of the disordered bromine atom.

bonds, the structures of **1** and **2** contain potassium and sodium atoms, respectively, which 'sealed' the cadmium siloxane 'barrel' bonded to the oxygen atoms of hexasiloxane cycles. At the same time, the geometry of **3** is quite different. In fact, the cylindrical

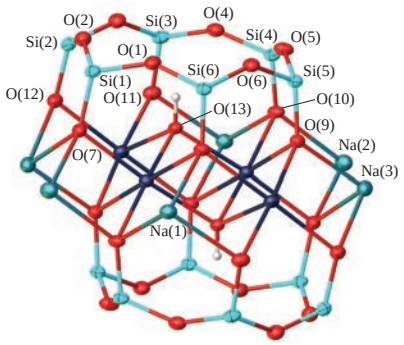


Figure 3 The structure of cadmium siloxane **3**. Phenyl groups and coordinated molecules of solvents are omitted for clarity.

structure was not realized, the structure of **3** is asymmetric and it can be described as 'skewed sandwich'. Regardless of the structure of sandwich framework the geometry of hexasiloxanolate ligands $[PhSiO_{1.5}]_6$ remains the same as in the case of hexacopper siloxanes. The crystal structure of **1**–**3** contains sodium atoms and coordinated molecules of polar solvents [DMF (**1**), MeOH/EtOH (**2**), dimethylacetamide/MeOH/dioxane (**3**)]. Hence, the structure of cadmium siloxanes was defined most likely by the nature of solvents used during synthesis and crystallization.

The most prominent difference of the hexacadmium siloxane framework from the hexacopper siloxane one is the size of inner void. Indeed, mean distances between opposite atoms of cadmium (*i.e.*, diameter of inner void) in **1** and **2** are 6.78 and 6.53 Å that is noticeably larger than analogous values for hexacopper siloxanes (5.47–5.82 Å, see for instance ref. 6). The Cd–O bonds (2.21–2.25 Å) in **1** and **2** are longer than the Cu–O bonds in hexacopper siloxanes (1.96–2.01 Å) that is favorable for the increase of inner void. In the case of **1** the center of cadmium siloxane framework is occupied with a water molecule. Inside the cadmium siloxane framework of **2** a bromine atom was revealed. The presence of bromine atom inside the inner cavity of metallosiloxane is the first example of such an inclusion. To date, only OH^- and Cl^- anions were found inside the metallosiloxane cage.[7–10] The exocyclic Br atom is disordered over two positions [Br(1) and Br(2), Figure 2]. As a consequence, Cd(3) and Cd(6) atoms are also disordered.

The skewed sandwich structure of **3** is characterized by the absence of halogen atoms, while it contains six sodium atoms due to the presence of two μ^3 hydroxyl groups inside the cadmium siloxane framework. In literature, this type of metallosiloxane framework was initially described for nickel siloxane synthesized and crystallized from BuOH.[9]

In summary, the cadmium siloxanes can be synthesized by the route similar to previously described for the period 4 transition metals. The structure of cadmium siloxanes is defined by the nature of polar solvents used for synthesis and crystallization. As a result, framework isostructural to sandwich hexacopper siloxanes and tetranickel siloxanes can be prepared. In addition, hexacadmium siloxane framework can serve as an anion trap for heavy halogen atoms (Br and possibly I) that is most likely impossible in the case of sandwich metallosiloxanes of period 4.

This study was supported by the Russian Science Foundation (grant no. 14-23-00231).

‡ *Crystal data.* All measurements 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[11] and OLEX 2 software.[12]

For **1**: $C_{104}H_{132}Br_2Cd_6K_2N_8O_{33}Si_{12}$, calc. formula moiety $[Ph_6Si_6O_{12}]_2$-$Cd_6Br_2K_2(C_4H_9NO)_8(H_2O)$, M = 3271.68 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 15.1527(5), b = 24.6143(9) and c = 18.6154(7) Å, β = 106.6190(10)°, V = 6653.0(4) Å^3, Z = 2, T = 100 K, μ(MoKα) = = 1.786 mm^{-1}, d_{calc} = 1.633 g cm^{-3}. 26566 reflections were measured (2.82° ⩽ 2θ ⩽ 52.04°), 12919 unique (R_{int} = 0.0225, R_σ = 0.0346) which were used in all calculations. The final R_1 was 0.0579 [$I > 2\sigma(I)$] and wR_2 was 0.1779 (all data).

For **2**: $C_{89}H_{114}Br_2Cd_6Na_2O_{35}Si_{12}$, calc. formula moiety $[Ph_6Si_6O_{12}]_2$-$Cd_6Br_2Na_2(EtOH)_6(MeOH)_5$, M = 2961.08 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 14.6032(9), b = 15.4342(10) and c = 26.3839(17) Å, α = = 87.5970(10)°, β = 80.7430(10)°, γ = 77.0090(10)°, V = 5718.9(6) Å^3, Z = 2, T = 120 K, μ(MoKα) = 2.003 mm^{-1}, d_{calc} = 1.72 g cm^{-3}. 77749 reflections were measured (2.7° ⩽ 2θ ⩽ 62.14°), 36188 unique (R_{int} = = 0.0513, R_σ = 0.0859) which were used in all calculations. The final R_1 was 0.0691 [$I > 2\sigma(I)$] and wR_2 was 0.2109 (all data).

For **3**: $C_{103}H_{130}Cd_4N_6Na_6O_{40}Si_{12}$, calc. formula moiety $[Ph_6Si_6O_{12}]_2$-$(OH)_2Cd_4Na_6(C_4H_8O_2)_2(DMF)_6(MeOH)_4$, M = 3016.75 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 16.8010(6), b = 22.8582(8) and c = = 17.8785(7) Å, β = 111.6260(10)°, V = 6382.8(4) Å^3, Z = 2, T = 100 K, μ(MoKα) = 0.872 mm^{-1}, d_{calc} = 1.570 g cm^{-3}. 80137 reflections were measured (3.02° ⩽ 2θ ⩽ 52.04°), 12561 unique (R_{int} = 0.0302, R_σ = = 0.0178) which were used in all calculations. The final R_1 was 0.0416 [$I > 2\sigma(I)$] and wR_2 was 0.1273 (all data).

CCDC 1436720–1436722 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.

References

1 M. M. Levitsky and A. N. Bilyachenko, *Coord. Chem. Rev.*, 2016, **306**, 235.

2 F. H. Allen, *Acta Crystallogr.*, 2002, **B58**, 380.

3 N. V. Sergienko, N. V. Cherkun, A. A. Korlyukov, A. A. Sochikhin, V. D. Myakushev, T. V. Strelkova and B. G. Zavin, *Russ. Chem. Bull., Int. Ed*., 2013, **62**, 1999 (*Izv. Akad. Nauk, Ser. Khim.*, 2013, 1999).
4 A. N. Bilyachenko, N. V. Sergienko, A. A. Korlyukov, M. Yu. Antipin, B. G. Zavin and M. M. Levitskii, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 943 (*Izv. Akad. Nauk, Ser. Khim.*, 2006, 909).
5 R. D. Shannon, *Acta Crystallogr*., 1976, **A32**, 751.
6 A. N. Bilyachenko, M. S. Dronova, A. I. Yalymov, F. Lamaty, X. Bantreil, J. Martinez, C. Bizet, L. S. Shul'pina, A. A. Korlyukov, D. E. Arkhipov, M. M. Levitsky, E. S. Shubina, A. M. Kirillov and G. B. Shul'pin, *Chem. Eur. J*., 2015, **21**, 8758.
7 V. A. Igonin, O. I. Shchegolikhina, S. V. Lindeman, M. M. Levitsky, Yu. T. Struchkov and A. A. Zhdanov, *J. Organomet. Chem.*, 1992, **423**, 351.
8 C. Zucchi, M. Mattioli, A. Cornia, A. C. Fabretti, G. Gavioli, M. Pizzotti, R. Ugo, Y. A. Pozdniakova, O. I. Shchegolikhina, A. A. Zhdanov and G. Pályi, *Inorg. Chim. Acta*, 1998, **280**, 282.
9 V. A. Igonin, S. V. Lindeman, K. A. Potekhin, V. E. Shklover, Y. T. Struchkov, O. I. Shchegolikhina, A. A. Zhdanov and I. V. Razumovskaya, *Organomet. Chem. USSR*, 1991, **4**, 383.
10 A. A. Korlyukov, M. A. Eskova, I. M. Tkachenko, Yu. N. Kononevich, O. I. Shchegolikhina and A. M. Muzafarov, *Mendeleev Commun*., 2015, **25**, 226.
11 G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.
12 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339.

Received: 16th November 2015; Com. 15/4777