Brief Communications

Cage-like manganesephenylsiloxane with an unusual structure

A. N. Bilyachenko, M. S. Dronova, A. A. Korlyukov, M. M. Levitsky, M. Yu. Antipin, and B. G. Zavin*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation.
E-mail: levitsk@ineos.ac.ru

A polyhedral (manganese,sodium)phenylsiloxane of the composition $(C_6H_5SiO_{1,5})_{20}(MnO)_8(NaO_{0,5})_{12} \cdot 2NaOH \cdot 15C_2H_5OH \cdot 11\,H_2O$ (the molecular formula is $C_{150}H_{214}Mn_8Na_{14}O_{72}Si_{20}$) was synthesized. This compound possesses the earlier undescribed shape of the cage and a rare combination of silanolate anions $Si—O^-$ and metalloxide fragments Mn—O—Mn in one structure. The coordination sphere of Mn ions is filled with silanolate anions, the O atoms in the fragments Mn—O—Si, Mn—O—Mn, and encapsulated molecules of water. The molecules of solvate ethanol are coordinated exclusively with Na^+ cations and are not involved into coordination sphere of Mn^{II} ions.

Key words: cage-like metallasiloxanes, X-ray crystallography.

The cage-like metallasiloxanes (MS) containing a silsesquioxane fragment $[RSiO_{1,5}]$, attract considerable attention as compounds with unique polyhedral structure of the molecules[1—3] and wide catalytic possibilities.[4,5]

We carried out a reaction of sodium phenylsilanolate with anhydrous manganese chloride. The X-ray studies of the structure of the compound obtained showed that the complex contains two cube-like fragments, these cubes are formed by the oxygen-bridged Mn atoms. The vertices of one of these cubic fragments are formed by the Mn(1)—O(24)—Mn(3)—O(21)—Mn(4)—O(22)—Mn(2)—O(23) atoms (Fig. 1). The second cubic fragment is placed centrosymmetrically with respect to the first. These cubic fragments are coordinated with two six-unit siloxane cycles Si(1)—O(7)—Si(2)—O(2)—Si(3)—O(3)—Si(4)—O(4)—Si(5)—O(5)—Si(6)—O(6) and two four-unit siloxane fragments, which are parts of the five-unit cycles Si(7)—O(8)—Si(8)—O(9)—Si(10)—O(11)—Si(9)—O(13)—Mn(4)—O(10) (see Fig. 1). The six-unit cycles form six coordination bonds each, whereas the four-unit fragments form only three each. The shortage of coordinating atoms in the coordination sphere of Mn ions, supplied by the cubic manganese-containing fragments, is compensated by the formation of bonds with 14 Na atoms from the cluster periphery (Fig. 2). The Na atoms coordinate the O atoms of the metallasiloxane cage and the solvate molecules of EtOH and H_2O. It is interesting to note that the shortage of oxygen atoms in the close proximity of the Na(3) atom leads to its interaction with the π-system of the phenyl substituent: the distance between the Na(3) atom and the centroid of the six-membered ring is 2.69 Å (Fig. 3).

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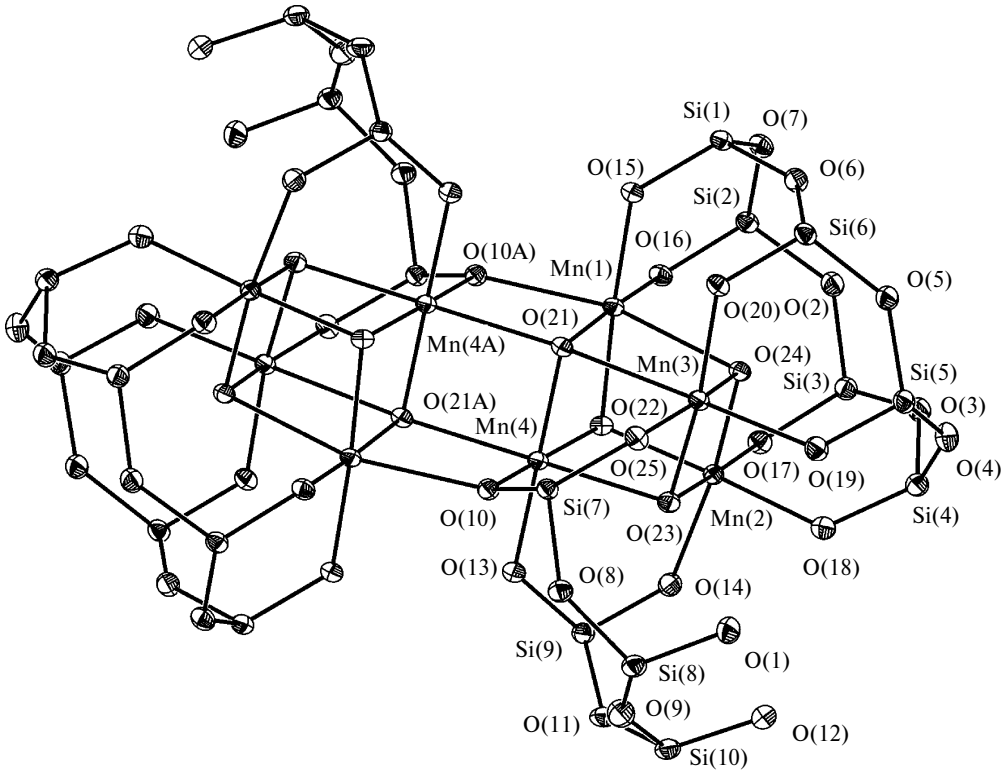

Fig. 1. The structure of (manganese,sodium)phenylsiloxane according to the results of X-ray diffraction measurements. The Na atoms, the molecules of solvate solvents, and phenyl groups on the Si atoms are not shown.

Molecules of solvate ethanol are exclusively coordinated with Na^+ cations, which are parts of the silanolate SiONa groups. The molecule of the compound synthesized is given in Fig. 2 as a Lewis structure with the dotted coordination bonds, which allows us to highlight the Mn—O—Mn fragments (shown in bold) arising in the process of synthesis, which are the main object of discussion in this paper, in contrast to the analogous fragments appearing as a result of coordination in the crystal structure.

Among known by now structures of metallasiloxanes based on monoorgano-substituted silicon atoms RSi≡, the following examples of siloxanes contain metalloxide M—O—M fragments: Ni-MS,[6] Fe-MS,[7] Pb-MS,[8] Sn-MS,[9] Nb-MS,[10] Ti-MS.[11—14] All the mentioned MS contain ions of only polyvalent metals and do not contain silanolate anions SiO^- coming into the system from the organosilanolate groups Si—O—M´, where M´ is an alkali metal.

There is described only one example of the cage-like MS (the Fe-MS obtained by us earlier[15]) simultaneously containing metalloxide fragments Fe—O—Fe and silanolate anions SiO^-. Combination of these two structural features is a unique fact. The obtained by us (manganese,sodium)phenylsiloxane (**1**) is the second example of a rare combination of the indicated properties (the cage-like Mn-MSs[16—18] synthesized earlier did not possess such a structural feature).

Experimental

Synthesis of (manganese,sodium)phenylsiloxane 1. Water (0.48 g, 26.7 mmol) was added to a solution of triethoxyphenylsilane (3.24 g, 13.5 mmol) in ethanol (12 mL) with stirring. After 20 min, sodium (0.31 g, 13.5 mmol) was added to the reaction mixture. After sodium was completely reacted, the solution of phenylsilanolate obtained lost its homogeneity. Heating of the reaction mixture to 35—40 °C with stirring resulted in its homogenization, after that, a solution of anhydrous $MnCl_2$ (0.48 g, 3.8 mmol) in ethanol (10 mL) was added to it. The resulting solution was refluxed for 2 h and filtered while hot from the precipitate of NaCl. A brown crystalline precipitate (0.26 g, 12%) was formed during gradual concentration of the filtrate *in vacuo*. A part of the crystalline precipitate that obtained was dried *in vacuo* until the weight was constant and analyzed. Found (%): Si, 15.61; Mn, 12.10; the ratio Si : Mn = 2.5 : 1. $C_{120}H_{102}Mn_8Na_{14}O_{46}Si_{20}$. Calculated (%): Si, 15.14; Mn, 11.84. The structure of crystals of the composition $(C_6H_5SiO_{1.5})_{20}(MnO)_8(NaO_{0.5})_{12} \cdot 2NaOH \cdot 15C_2H_5OH \cdot 11H_2O$ (molecular formula $C_{150}H_{214}Mn_8Na_{14}O_{72}Si_{20}$) was established by X-ray crystallography. The synthesis of this compound is reproducible provided that the ratio of the starting reagents is not changed.

X-ray diffraction studies. Crystals **1**, $C_{150}H_{214}Mn_8Na_{14}O_{72}Si_{20}$, are monoclinic, the space group is $P2_1/n$, $a = 17.7732(7)$, $b = 20.4109(8)$, $c = 26.9435(10)$ Å, $\beta = 90.83°$, $V = 9773.2(7)$ Å^3, $Z = 1$, $M = 8870.54$, $d_{calc} = 1.507$ g cm^{-3}, μ(Mo-Kα) = 0.739 mm^{-1}, $F(000) = 4574$. Intensities of 128937 reflections were measured on a Smart APEX II diffractometer at 100 K (λ(Mo-Kα) = = 0.71073 Å, ω-scanning, $2\theta < 61.12°$), 29966 independent re-

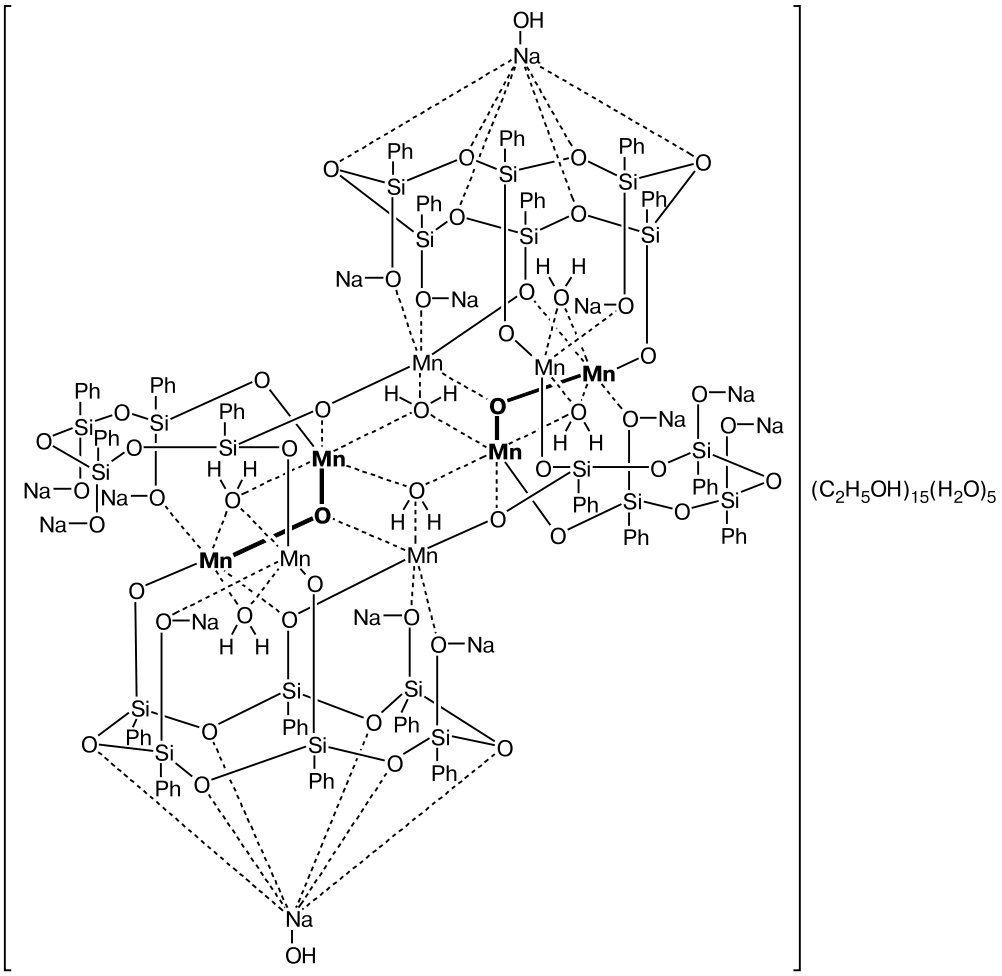

Fig. 2. The structure of (manganese,sodium)phenylsiloxane as a Lewis structure. The Mn—O—Mn fragments are shown in bold.

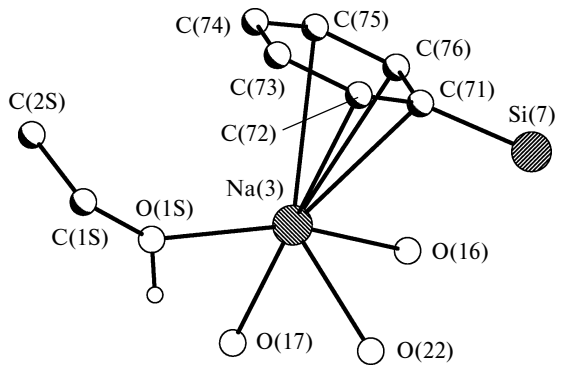

Fig. 3. The interaction of the Na(3) atom with the π-system of phenyl substituent. Only the closest coordination surrounding of the Na atom is shown.

flections (R_{int} = 0.0708) were used for further refinement. The structure was solved by the direct method and refined by the least squares method in the full-matrix anisotropic-isotropic approximation on F^2. The H atoms in the Ph-, CH_3, and CH_2 groups were calculated and refined using the solid body model. Parameters of the refinement: wR_2 = 0.0925, GOOF = 0.995 on all the independent reflections (R_1 = 0.0458 was calculated on 19730 independent reflections with $I > 2\sigma(I)$). The calculations were performed using the SHELXTL PLUS programs.[19]

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