New cage-like metallasiloxane containing Fe^{III} ions in different coordination spheres

A. N. Bilyachenko, A. A. Korlyukov, M. M. Levitskii,★ 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

The first cage-like ferrophenyl siloxane containing Fe^{III} ions in different coordination spheres (four iron ions have a trigonal-bipyramidal coordination and two iron ions have a distorted octahedral coordination) was synthesized by the exchange reaction of sodium phenylsilanolate with Fe^{III} chloride. An exotic lantern-like structure is formed with the involvement of two metal oxide fragments Fe—O—Fe. The structure of this compound was established by X-ray diffraction.

Key words: cage-like metallasiloxanes, X-ray diffraction study.

Among the known cage-like metallasiloxanes (MS), there are a few compounds, in which metal ions have different coordination environment in the same molecule[1—4] (Ni- and Ti-containing MS). The second unusual structural feature of cage-like MS is the presence of metal oxide fragments M—O—M, and only three such structures, *viz.*, Ni—MS[2], Nb—MS,[5] and Pb—MS, were characterized.[6] A rare combination of the above-mentioned two structural features is observed in the cage-like sodium iron phenyl siloxane described in the present study.

The bimetallic Na,Fe-containing MS was synthesized according to a procedure described earlier[7] involving hydrolysis of phenyltrichlorosilane and alkaline cleavage of polyphenylsiloxane followed by the partial replacement of Na atoms with Fe atoms by the exchange reaction with iron chloride.

The X-ray diffraction study of Na,Fe-MS demonstrated that this compound has the previously unknown lantern-like structure, in which two cylindrical fragments containing the five-membered siloxane rings in the base are linked to each other by the ten-membered metallasiloxane belt (Fig. 1). The latter is open so that its terminal oxygen atoms (O(1), O(2), O(12), and O(23)) are coordinated to the Fe(1), Fe(2), and Fe(5) atoms (Fig. 2).

An interesting structural feature is the presence of one of the Na atoms inside the iron siloxane cage. The Na(1) atom (see Fig. 2) is located inside the cavity formed by the metallasiloxane belt. Other Na atoms are located outside the iron siloxane cage and are additionally coordinated by one or two butyl alcohol molecules. The Na atom, which is located above the five-membered siloxane fragment, is statistically disordered over two positions (Na(8) and Na(9)) in a ratio of 3 : 2.

The distinguishing structural feature of this compound is that it contains six Fe^{III} atoms in different coordination spheres, *viz.*, four iron atoms having a trigonal-bipyramidal environment and two iron atoms (Fe(1) and Fe(3)) in a distorted octahedral environment (see Fig. 2). An additional rather unusual (for cage-like MS)[8] feature is the presence of two metal oxide fragments Fe—O—Fe. The representation of the metallasiloxane as a Lewis structure, in which all coordination bonds are removed, shows that this compound contains two metal—oxygen—metal fragments, *viz.*, Fe(2)—O(39)—Fe(5) and Fe(4)—O(27)—Fe(6).

The axial bonds in the coordination octahedra of the Fe(1) and Fe(3) atoms are 0.3—0.4 Å longer than the equatorial bonds. In turn, the Fe atoms in the trigonal-bipyramidal environment are characterized by a smaller (at most 0.1 Å) elongation of the axial bonds compared to the equatorial bonds (except for the Fe(1)—O(24) bond, for which this value is, on the average, 0.25 Å).

Experimental

Synthesis of sodium ferrasiloxane. A solution of phenyltrichlorosilane (10 g) in toluene (35 mL) was added dropwise with stirring to a mixture of water (45 mL), toluene (15 mL), and Bu^nOH (7 mL). After separation of the aqueous layer, the organic layer was washed with distilled water to pH ~7 and dried over anhydrous Na_2SO_4 for one day. After filtration of the solution and complete removal of the solvent by evacuation, polysiloxane resin $[PhSiO_{1.5}]_n$ was obtained in a yield of 95% (5.80 g). Found (%): C, 56.08; Si, 21.53. Calculated (%): C, 55.78; Si, 21.74.

Sodium hydroxide (1.55 g, 38.8 mmol) was added to a solution of polyphenylsilsesquioxane (5 g, 38.8 mmol) in toluene

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 522—524, March, 2007.

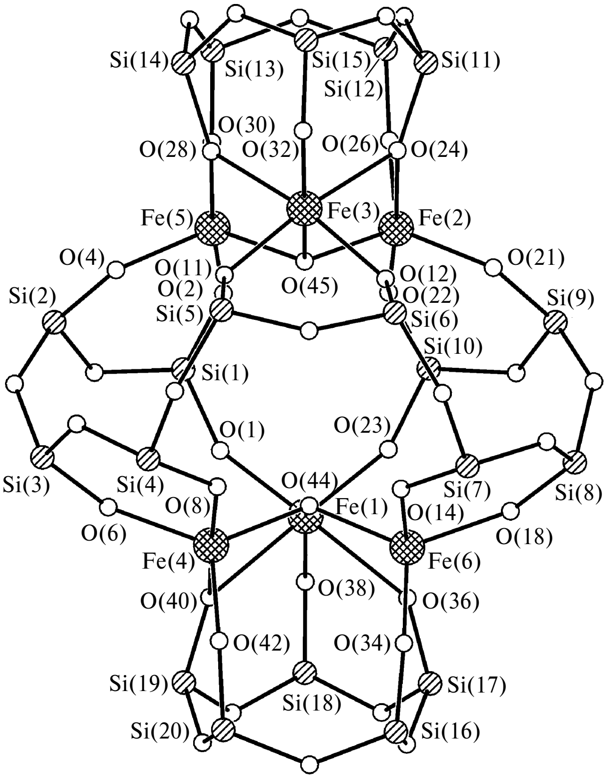

Fig. 1. Overall view of the iron sodium phenyl siloxane cage of the complex (the Na atoms, the Ph groups at the Si atom, and the solvate solvent molecules are omitted). The Fe—O bond lengths (Å): Fe(1)—O(1), 1.898(5); Fe(1)—O(23), 1.892(5); Fe(1)—O(38), 1.936(4); Fe(1)—O(44), 2.020(4); Fe(1)—O(40), 2.319(4); Fe(1)—O(36), 2.376(4); Fe(2)—O(21), 1.901(4); Fe(2)—O(26), 1.905(4); Fe(2)—O(45), 1.909(4); Fe(2)—O(22), 1.915(4); Fe(2)—O(24), 2.188(4); Fe(3)—O(32), 1.916(4); Fe(3)—O(11), 1.977(4); Fe(3)—O(12), 1.995(4); Fe(3)—O(45), 2.024(4); Fe(3)—O(24), 2.140(4); Fe(3)—O(30), 2.154(4); Fe(4)—O(42), 1.916(4); Fe(4)—O(44), 1.931(4); Fe(4)—O(6), 1.932(5); Fe(4)—O(8), 1.993(4); Fe(4)—O(40), 2.044(4); Fe(5)—O(4), 1.900(4); Fe(5)—O(28), 1.916(4); Fe(5)—O(2), 1.922(4); Fe(5)—O(45), 1.925(4); Fe(5)—O(30), 2.160(4); Fe(6)—O(34), 1.904(4); Fe(6)—O(44), 1.923(4); Fe(6)—O(18), 1.929(4); Fe(6)—O(14), 1.982(4); Fe(6)—O(36), 2.039(4).

(20 mL) and Bu^{n}OH (8 mL). After homogenization of the solution (heating to 45 °C and stirring), water was removed by azeotropic distillation using a Dean—Stark trap. The percentage of Na in the resulting solution determined by titration was 2.55%. A solution of anhydrous $FeCl_3$ (1.57 g, 9.7 mmol) in Bu^{n}OH (20 mL) was added dropwise with stirring to a solution of the silanolate. The solution was refluxed for 2 h and filtered in the hot state from the precipitate of NaCl. The reaction solution was gradually concentrated, which led to the formation of a brown crystalline precipitate. The precipitate was separated and dried under vacuum to constant weight. The product was isolated in a yield of 1.16 g (25%). Found (%): Si, 17.05; Fe, 10.23; the Si : Fe ratio was 3.3 : 1. $C_{120}H_{100}Si_{20}O_{43}Fe_6Na_8$. Calculated (%): Si, 16.93; Fe, 10.16. The structure of the crystals of ($C_{120}H_{100}Si_{20}O_{43}Fe_6Na_8 \cdot 9BuOH \cdot C_7H_8$) was established by X-ray diffraction.

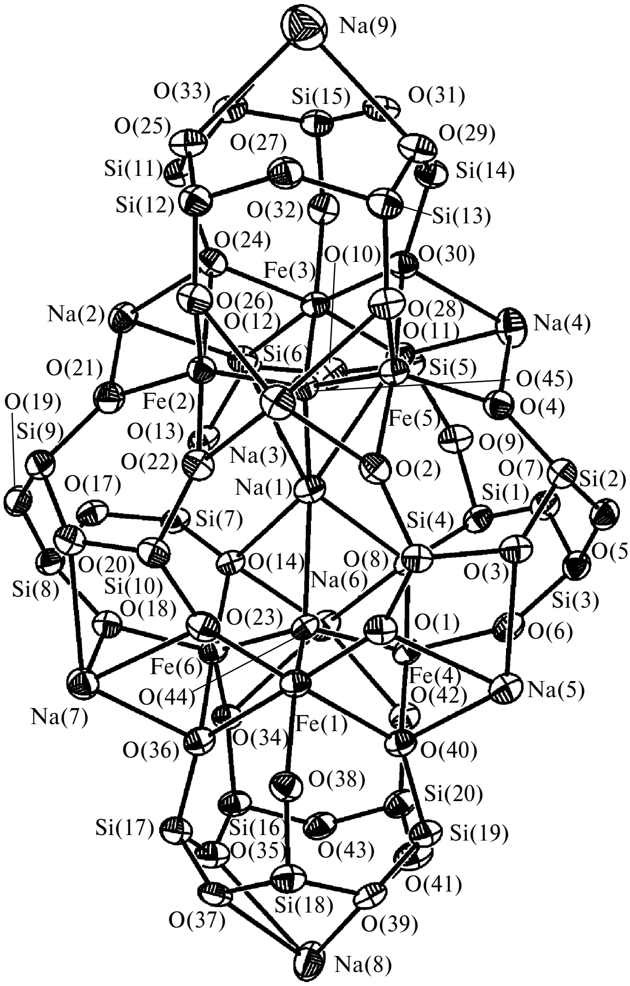

Fig. 2. Structural features of the siloxane fragments and the coordination sphere of the Fe atoms in the MS under study (the Ph groups at the Si atom and the solvate solvent molecules are omitted).

X-ray diffraction study. Preliminary X-ray diffraction data for single crystals of different dimensions demonstrated that the maximum 2θ, at which reflections can be measured, is no larger than 45°. This is, apparently, responsible for a decrease in the convergence of the equivalent reflections with $2\theta > 40°$ and an increase in R_{int}. However, these data were sufficient for the structural analysis of the metallasiloxane cage. The crystals of $C_{120}H_{100}Si_{20}O_{43}Fe_6Na_8 \cdot 9BuOH \cdot C_7H_8$ are monoclinic, space group $P2_1/c$, $a = 30.027(2)$ Å, $b = 20.302(1)$ Å, $c = 32.298(2)$ Å, $\beta = 92.920(1)°$, $V = 19664.1(18)$ Å^3, $Z = 4$, $M = 4121.14$, $d_{calc} = 1.392$ g cm^{-3}, $\mu = 6.47$ cm^{-1}, $F(000) = 8582$. The intensities of 147601 reflections were measured on a Bruker Smart APEX II diffractometer at 100 K (λ(Mo-Ka) = 0.71073 Å, ω-scanning technique, $2\theta < 48°$); 30628 independent reflections ($R_{int} = 0.1094$) were used in the refinement. The absorption correction was applied using the SADABS program of the APEX II software.[9,10] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic and isotropic displacement parameters against F^2. The free refinement (no constraints) involving four coordinated

Bu^{n}OH molecules gave unrealistic C—C and O—C bond lengths. This is indicative of a disorder of these fragments, which could not be taken into account due, apparently, to a small number of reflections at 2θ > 40°. Hence, the coordinated Bu^{n}OH molecules were refined isotropically with the fixed C—C and O—C bond lengths (1.520(6) and 1.420(6) Å, respectively). The H atoms were positioned geometrically and refined using a riding model. The H atoms of the hydroxy groups, which were located in difference Fourier maps, were normalized to the ideal O—H distances (0.85 E). The final refinement parameters were as follows: $wR_2 = 0.2119$ (based on all reflections), GOF = 0.971, $R_1 = 0.0686$ (based on 18901 reflections with $I > 2\sigma(I)$). All calculations were carried out with the use of the SHELXTL program package (version 5.10).[11]

This study was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools and Young Scientists of the Russian Federation, Grant MK-126-2007.3) and the Russian Foundation for Basic Research (Project Nos 05-03-32938, 06-03-32347, and 07-03-00284).

References

1. V. A. Igonin, S. V. Lindeman, K. A. Potekhin, V. E. Shklover, Yu. T. Struchkov, O. I. Shchegolikhina, A. A. Zhdanov, and I. V. Razumovskaya, *Metalloorg. Khim.*, 1991, **4**, 790 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
2. M. M. Levitsky, O. I. Shchegolikhina, A. A. Zhdanov, V. A. Igonin, Yu. E. Ovchinnikov, V. E. Shklover, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1991, **401**, 199.
3. H. M. Lindermann, M. Schneider, B. Neumann, H.-G. Stammler, A. Stammler, and P. Jutzi, *Organometallics*, 2002, 3009.
4. J. O. Nolte, M. Schneider, B. Neumann, H.-G. Stammler, and P. Jutzi, *Organometallics*, 2003, 1010.
5. F. Bottomley and S. Karsioglu, *Ogranometallics*, 1992, **11**, 326.
6. Ch. Gaffney, Ph. Harrison, and T. King. *J. Chem. Soc., Chem. Commum.*, 1980, **24**, 1251.
7. Yu. E. Ovchinnikov, A. A. Zhdanov, M. M. Levitskii, V. E. Shklover, and Yu. T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1206 [*Bull Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35** (Engl. Transl.)].
8. M. M. Levitskii, *Ross. Khim. Zh.*, 2002, **46**, 51 [*Mendeleev Chem. J.*, 2002, No. 3 (Engl. Transl.)].
9. *APEX2*, Bruker AXS Inc., 5465, East Cheryl Parkway, Madison, WI 5317, 2005.
10. G. M. Sheldrick, *SADABS. Version 2.10*, University of Göttingen, Göttingen, Germany, 2003.
11. *SHELXTL*, *Version 5.10*, Bruker-AXS Inc., Madison, WI-53719, USA, 1998.

Received December 7, 2006;
in revised form February 9, 2007