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Heteroligand nickel siloxane with 4-vinylbenzyl substituents

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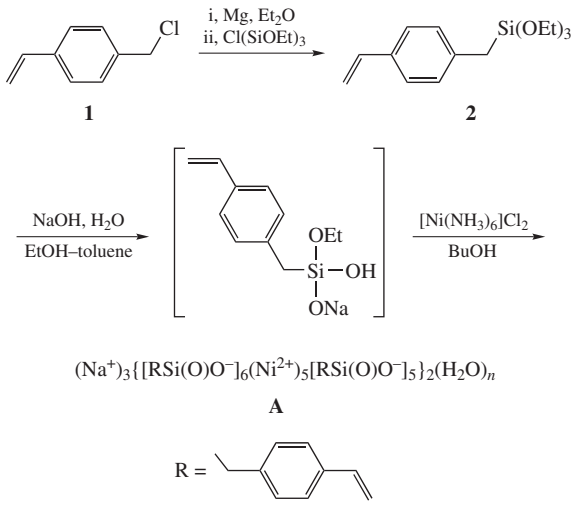
A new polyherdal nickel siloxane was synthesized by the hydrolysis of triethoxy(4-vinylbenzyl)silane in the presence of NaOH and the subsequent interaction with $[Ni(NH_3)_6]Cl_2$. The nickel siloxane has a dimeric structure that consists of two polyhedral sandwiched pentanuclear nickel siloxane units linked by very strong O–H···O bonds into infinite chains in a crystal.

Polyhedral metallasiloxanes were synthesized in 1991[1] and tested as precursors for molecular magnets and catalysts.[2] Such compounds can contain four to six transition metal ions and oligosiloxanolate ligands $[PhSi(O)O^-]_n$ ($n = 6, 8, 12$). Detailed studies have been performed for polyhedral copper-containing organometallasiloxanes;[3] however, there is still not enough data on similar compounds with other transition metals.

Here, we report the synthesis and structure of an unusual dimeric nickel siloxane.

At first, we synthesized triethoxy(4-vinylbenzyl)silane **2** by the interaction of Grignard reagent prepared from 4-vinylbenzyl chloride **1** with chlorotriethoxysilane (Scheme 1).† The structure of product **2** was confirmed by FTIR, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis. Nickel siloxane **A** was obtained *via* the hydrolysis of compound **2** in the presence of sodium and nickel ions.



Scheme 1

Each monomer unit of **A** has a sandwich structure and contains two different siloxane ligands and five nickel atoms. The units are linked by the sodium atom Na(1) coordinated by the oxygen atoms of ten-membered siloxane ligands $[RSi(O)(O)^-]_5$. Compound **A** is the first example of a sandwiched metallasiloxane with an odd number of transition metal atoms.

The structure of ten-membered $[Si(O)(O)^-]_5$ ligands is similar to that in a six-nuclear polyhedral copper siloxane[3(f)] and six-

† All chemicals of high purity grade were purchased from Sigma-Aldrich. Diethyl ether was distilled from sodium/benzophenone. Ethanol, *n*-butanol and toluene were distilled. 1-(Chloromethyl)-4-vinylbenzene **1** was distilled prior to use. IR spectra were recorded on a Bruker Equinox 55/S spectrometer. ^1H NMR spectra were recorded on a Bruker WP 250 SY spectrometer (250.13 MHz). ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker Avance II spectrometer (300 MHz). Chemical shifts are reported relative to chloroform (δ 7.25 ppm for ^1H and δ 77.00 ppm for ^{13}C).

Triethoxy(4-vinylbenzyl)silane **2**. A solution of compound **1** (20 g, 0.13 mol) in diethyl ether (150 ml) was added dropwise to magnesium turning (8 g, 0.2 mol) in diethyl ether (50 ml) under an inert atmosphere within 1 h. Then, the reaction mixture was refluxed for 1 h. The obtained Grignard reagent was dropped from a dropping funnel into a solution of $ClSi(OEt)_3$ (52 g, 0.26 mol) in diethyl ether (50 ml) at –5 to 0 °C. The resulting mixture was refluxed for 4 h; then, it was left overnight with stirring. After that, *n*-hexane (100 ml) was added to the mixture, the magnesium salt was filtered off, the solvents were removed and the residue was distilled *in vacuo* in the presence of butylhydroxytoluene affording the pure product as a colorless liquid. Yield 45%, bp 114–117 °C (1 Torr). ^1H NMR, δ: 1.16 (t, 9H, $SiOCH_2Me$, J 7.0 Hz), 2.19 (s, 2H, CH_2Si), 3.75 (q, 6H, $SiOCH_2Me$, J 7.0 Hz), 5.15 (dd, 1H, $=CH_2^a$, J_{cis} 10.7 and 0.9 Hz), 5.67 (dd, 1H, $=CH_2^b$, J_{trans} 17.7 and 0.9 Hz), 6.61–6.72 (q, 1H, =CH, J_{cis} 11.0 Hz, J_{trans} 17.7 Hz), 7.13 (d, 2H, H_{Ar}, J 8.2 Hz), 7.27 (d, 2H, H_{Ar}, J 8.2 Hz). ^{13}C NMR, δ: 18.15 (CH_2Me), 20.21 (CH_2Si), 58.65 (CH_2Me), 112.24 ($CH=CH_2$), 126.05, 128.93, 133.97, 136.75 (Ar-C), 137.36 ($CH=CH_2$). ^{29}Si NMR, δ: –51.28. IR (CCl_4, ν/cm^{-1}): 1084 (Si–O–C), 1171 (Si–O), 1510 ($C=C_{Ar}$), 1630 ($CH=CH_2$), 2860–3000 (CH). Found (%): C, 64.32; H, 8.43; Si, 9.93. Calc. for $C_{15}H_{24}O_3Si$ (%): C, 64.24; H, 8.63; Si, 10.01.

Polyherdal nickel siloxane **A**. A three-neck flask was charged with NaOH (0.166 g, 4.16 mmol), toluene (3.5 g) and EtOH (95%, 1.28 g) containing 0.064 g (3.57 mmol) of H_2O. After the dissolution of NaOH, compound **2** (1 g, 3.57 mmol) was added dropwise with vigorous stirring at room temperature. The mixture was stirred at room temperature for 1.5 h, and a solution of $[Ni(NH_3)_6]Cl_2$ (0.42 g, 1.78 mmol) in 5 ml of BuOH was added dropwise. The mixture was stirred at room temperature for 30 min and then refluxed for 1 h. The precipitate was filtered off. Upon standing at 5 °C for 30 days, the crystals of polyhedral nickel siloxane **A** were formed in the solution. A single crystal was selected for X-ray analysis. The other crystals were filtered off and dried *in vacuo* (10 Torr) at room temperature. Green-yellow crystalline product was obtained, $(Na^+)_3\{[C_9H_9Si(O)O^-]_6(Ni^{2+})_5[C_9H_9Si(O)O^-]_5\}_2(C_7H_8)_7(H_2O)_{33}$, yield 0.086 g (6.4%). Molecular weight, 5794.91. Found (%): C, 50.54; H, 5.22; Si, 10.49; Ni, 10.00; Na, 1.17. Calc. for $C_{247}H_{320}O_{77}Si_{22}Ni_{10}Na_3$ (%): C, 51.19; H, 5.56; Si, 10.66; Ni, 10.12; Na, 1.19.

nuclear iron siloxanes.[4] The geometry of a twelve-membered siloxanolate ligand is, however, quite different from that of the siloxanolate ligand in previously studied sandwiched phenylmetallasiloxanes with six transition metals.[1(*b*),(*c*)] The conformation of the twelve-membered siloxanolate ligand is corona-like, and six metal atoms are sufficient to coordinate six oxygen atoms of each siloxanolate ligand. In the metallo-oxygen layer of **A**, there are only five nickel atoms, so the lack of coordination vacancies causes conformational changes in the structure of the siloxanolate ligand. The conformation of the twelve-membered siloxanolate ligands in **A** can be described as a distorted sofa. Indeed, one of the six oxygen atoms in each siloxanolate ligand coordinates the terminal sodium atoms Na(2) and Na(3).

In the center of an inner cavity of the nickel siloxane unit, the oxygen atom is located to form coordination bonds with each of the nickel atoms; mean Ni···O(1A) and Ni···O(1B) distances [2.332(4) and 2.336(4) Å] are only 0.3 Å longer than the coordination bonds between the nickel and oxygen atoms of the siloxane ligands [2.0447(4) Å]. As a result, the inner oxygen atoms can be considered as the pathway for an exchange interaction between the opposite nickel atoms. The mean Ni···Ni distance is 2.739(1) Å, which is considerably lower than in complexes with four, six and eight atoms (2.88, 2.85 and 3.12 Å, respectively) and six-membered siloxanolate ligands (Figure 1).‡

In a crystal of **A**, the molecules are assembled into infinite chains *via* hydrogen bonds between coordinated ethanol moieties. Moreover, the O(1) and O(43) atoms form a very close intermolecular contact; the O(1)···O(43) distance [2.426(5) Å] is typical of very strong hydrogen bonds as in a Zundel cation[5] ($H_2O···H_3O^+$). Unfortunately, the positions of hydrogen atoms were not identified from difference Fourier maps; however, the analysis of Si(1)–O(1) and Si(20)···O(43) bond lengths [1.603(4) and 1.615(4) Å] has shown that a hydrogen atom can be localized

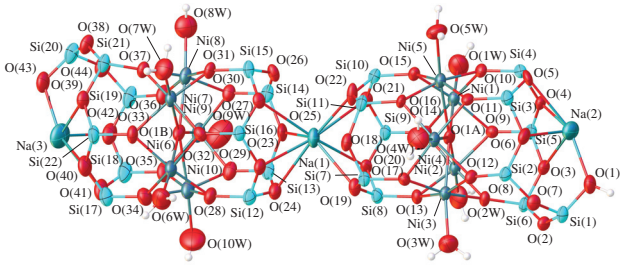


Figure 1 Metallasiloxane fragments of **A** given as thermal ellipsoids at a 50% probability. Substituents at the silicon atoms are omitted for clarity.

§ *Crystal data*. Monoclinic crystals of **A** were obtained from a mixture of toluene and ethanol, composition $C_{212}H_{248}Na_3Ni_{10}O_{59.5}Si_{22}$, space group $P2_1/c$, a = 22.9507(12), b = 29.7214(16) and c = 38.220(2) Å, β = 103.2120(10)°, V = 25381(2) Å^3, Z = 4, M = 5022.14, ρ = 1.314 g cm^{-3}, μ(MoKα) = 9.05 cm^{-1}, F(000) = 10468. The intensities of 318032 reflections were measured on a Smart APEX II diffractometer at 120 K [λ(MoKα) = 0.71073 Å, ω-scanning, $2\theta_{max}$ = 52.0°]; 49876 independent reflections (R_{int} = 0.139) were used for solving and refining the structure. The structure was solved by a direct method and refined by a full-matrix technique against F^2 in the anisotropic approximation. The positions of hydrogen atoms in methyl and methylene groups were calculated geometrically and refined in a rigid body approximation. Final R-factors: R_1 = 0.1029 [21311 reflections with $I > 2\sigma(I)$], wR_2 = 0.1883 (all reflections), GOF = 0.951. All calculations were carried out with SHELX-2013 program complex,[7] molecular graphics were drawn using the OLEX2 program.[8] The contribution of undefined electron density peaks localized in solvent accessible voids was treated as diffusion scattering, and it was excluded using the SQUEEZE routine in the implemented PLATON program.[9]

CCDC 1035262 contains 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.

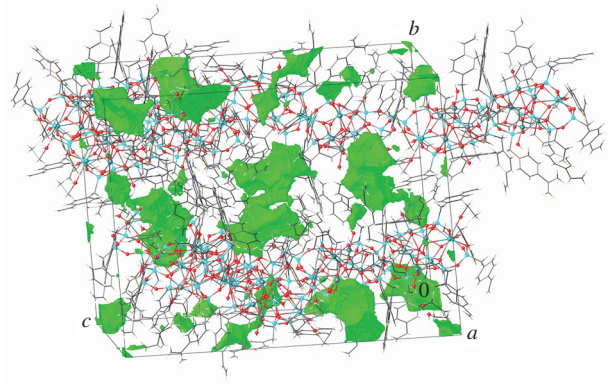


Figure 2 Crystal packing of **A** with voids shown as isosurface built from R_{vdw} + 0.2 Å values. Carbon and hydrogen atoms are shown in a wireframe representation.

at the O(1) atom. Hence, the position of this atom was calculated taking into account the Si(1)–O(1) and Na(2)–O(1) bonds formed by the O(1) atom and refined in riding model with the constrained O–H distance.

The formation of the O(1)–H(1)···O(43) hydrogen bond allowed us to reveal the nature of oxygen atoms in the inner cavity of the nickel siloxane fragments. Given the formal oxidation state of nickel (2+), charges of siloxanolate ligands (5– and 6–) and the presence of three sodium atoms and the O(1)–H(1)···O(43) bond, the formal charges of O(1A) and O(1B) atoms can be derived as 1–, which corresponds to the hydroxyl group. Previously, a hydroxyl group was found in the inner cavity of a hexanuclear sandwiched cobalt siloxane.[6]

The hydrogen-bonded chains in **A** form weak van der Waals contacts between 4-vinylbenzyl moieties. The analysis of intermolecular contacts and residual electron density showed the presence of voids filled by disordered solvent molecules. The positions of one toluene and one ethanol molecules were found in difference Fourier maps. The volume of these voids was calculated as R_{vdw} + 0.2 Å, where R_{vdw} is the van der Waals radius of carbon and hydrogen atoms. The resulted volume of the voids is 7941.12 Å^3, *i.e.*, approximately 30% of the unit cell volume (Figure 2). Such a loose crystal packing is indicative of the ability to hold nonpolar low-molecular compounds in voids of **A**.

Nickel siloxane **A** is of fundamental and applied interest. It combines new features that have never been observed in sandwiched metallasiloxanes, including an odd number of metal atoms and the presence of different siloxanolate ligands and very strong intermolecular hydrogen bonds as in a supramolecular synthone. The lower Ni···Ni distance suggests the possibility to use compound **A** as a molecular magnet, while its loose crystal packing is favorable for applications as microporous materials.

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