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Notes

Heavy-Metal-Containing Polyhedral Metallasiloxane Derived from an Aminosilanetriol: Synthesis and Structural Characterization of $[(PbO)_6(R_2Si_2O_3)_2]$ (R = $(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)$)[†]

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Summary: The reaction of $RSi(OH)_3$ with $Pb[N(SiMe_3)_2]_2$ in a 1:1.5 molar ratio in THF/hexane afforded a hexameric lead(II)siloxane $[(PbO)_6(R_2Si_2O_3)_2]$ [R = $(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)$] ***1****. The molecular structure of* ***1*** *shows a central $(PbO)_6$ motif enclosed by two outer $R_2Si_2O_3$ siloxane ligands.*

Introduction

We have a longstanding interest in polyhedral metallasiloxanes derived from silanetriols.[1] This is due to many reasons. First, utilizing the silanetriols as synthons allows the preparation of soluble metallasiloxanes with a high metal content.[1] Second, many soluble metallasiloxanes can function as structural models for complex metallasilicates and metal-containing zeolites.[2] We have, for example, shown that cubic titanasiloxanes $[RSiO_3TiR^1]_4$ (R = $(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)$, R^1 = Et, *i*Pr), apart from being good models for titanium-containing zeolites such as TS-1 and TS-2,[3] also are themselves good catalysts, particularly for epoxidation reactions.[4] A third and emerging interest in this class of compounds is the possibility of stabilizing molecular inorganic oxide fragments.[5] Thus, we have recently been able to show that molecular $(SnO)_6$ could be trapped in a Sn(II) siloxane.[6] Despite the diverse and varied polyhedral metallasiloxanes that have been synthesized from silanetriols and monosilanols, the number of structurally characterized metallasiloxanes containing heavy main-group metals is very rare.[7] It must be noted, however, that uranium-containing silicon-rich metallasiloxanes have been derived from incompletely condensed silsesquioxanes. However, the metal/silicon ratio in these compounds is very low.[8] We now report the synthesis and structural characterization of the novel hexalead assembly $[(PbO)_6(R_2Si_2O_3)_2]$ (**1**; R = $(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)$). This compound has a Pb/Si ratio of 6/4. Apart from being a unique example of a metallasiloxane containing two fused cages, compound **1** also can be envisaged as possessing an embedded internal $(PbO)_6$ molecular lead(II) oxide enveloped by an external siloxane sheath.

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[†] Dedicated to Professor Nils Wiberg on the occasion of his 70th birthday.

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(1) (a) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W. *Organometallics* **1996**, *15*, 918−922. (b) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−2236. (c) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183−189. (d) Murugavel, R.; Bhattacharjee, M.; Roesky, H. W. *Appl. Organomet. Chem.* **1999**, *13*, 227−243. Roesky, H. W.; Anantharaman, G.; Chandrasekhar, V.; Jancik, V.; Singh, S. *Chem. Eur. J.* **2004**, *10*, 4106−4114.

(2) (a) Liebau, F. *Structural Chemistry of Silicates*; Springer: Berlin, 1985; pp 244−260. (b) Montero, M. L.; Voigt, A.; Teichert, M.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2761−2763; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504−2506. (c) Voigt, A.; Murugavel, R.; Parisini, E.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 823−825; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 748−750. (d) Voigt, A.; Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Parisini, E.; Lubini, P. *Angew. Chem.* **1997**, *109*, 2313−2315; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2203−2205. (e) Voigt, A.; Murugavel, R.; Roesky, H. W. *Organometallics* **1996**, *15*, 5097−5101. (f) Anantharaman, G.; Chandrasekhar, V.; Nehete, U. N.; Roesky, H. W.; Vidovic, D.; Magull, J. *Organometallics* **2004**, *23*, 2251−2256. (g) Nehete, U. N.; Anantharaman, G.; Chandrasekhar, V.; Murugavel, R.; Walawalker, M. G.; Roesky, H. W.; Vidovic, D.; Magull, J.; Samwer, K.; Sass, B. *Angew. Chem.* **2004**, *116*, 3920−3923; *Angew. Chem., Int. Ed.* **2004**, *43*, 3832−3835.

(3) (a) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem.* **1994**, *106*, 1414−1416; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352−1354. (b) Voigt, A.; Murugavel, R.; Chandrasekhar, V.; Winkhofer, N.; Roesky, H. W.; Schmidt, H.-G.; Usón, I. *Organometallics* **1996**, *15*, 1610−1613.

(4) (a) Fujiwara, M.; Wessel, H.; Park, H.-S.; Roesky, H. W. *Tetrahedron* **2002**, *58*, 239−243. (b) Fujiwara, M.; Wessel, H.; Park, H.-S.; Roesky, H. W. *Chem. Mater.* **2002**, *14*, 4975−4981.

(5) Roesky, H. W. *Solid State Sci.* **2001**, *3*, 777−782.

(6) Nehete, U. N.; Chandrasekhar, V.; Anantharaman, G.; Roesky, H. W.; Vidovic, D.; Magull, J. *Angew. Chem.* **2004**, *116*, 3930−3932; *Angew. Chem., Int. Ed.* **2004**, *43*, 3842−3844.

(7) (a) Gaffney, C.; Harrison, P. G.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1251−1252. (b) Terry, K. W.; Su, K.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1998**, *17*, 891−897. (c) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1997**, *16*, 5653−5658. (d) Weinert, C. S.; Guzei, I. A.; Rheingold, A. L.; Sita, L. R. *Organometallics* **1998**, *17*, 498−500. (e) du Mont, W. W.; Grenz, M. *Chem. Ber.* **1981**, *114*, 1180−1181. (f) Schmidbaur, H.; Bergfeld, M. Z. *Anorg. Allg. Chem.* **1968**, *363*, 84−88. (g) Patnode, W.; Schmidt, F. C. *J. Am. Chem. Soc.* **1945**, *67*, 2272−2273.

(8) Lorenz, V.; Fischer, A.; Giessmann, S.; Gilje, J. W.; Gun'ko, Y.; Jacob, K.; Edelmann, F. T. *Coord. Chem. Rev.* **2001**, *206*, 321−368.

10.1021/om049417u CCC: $27.50

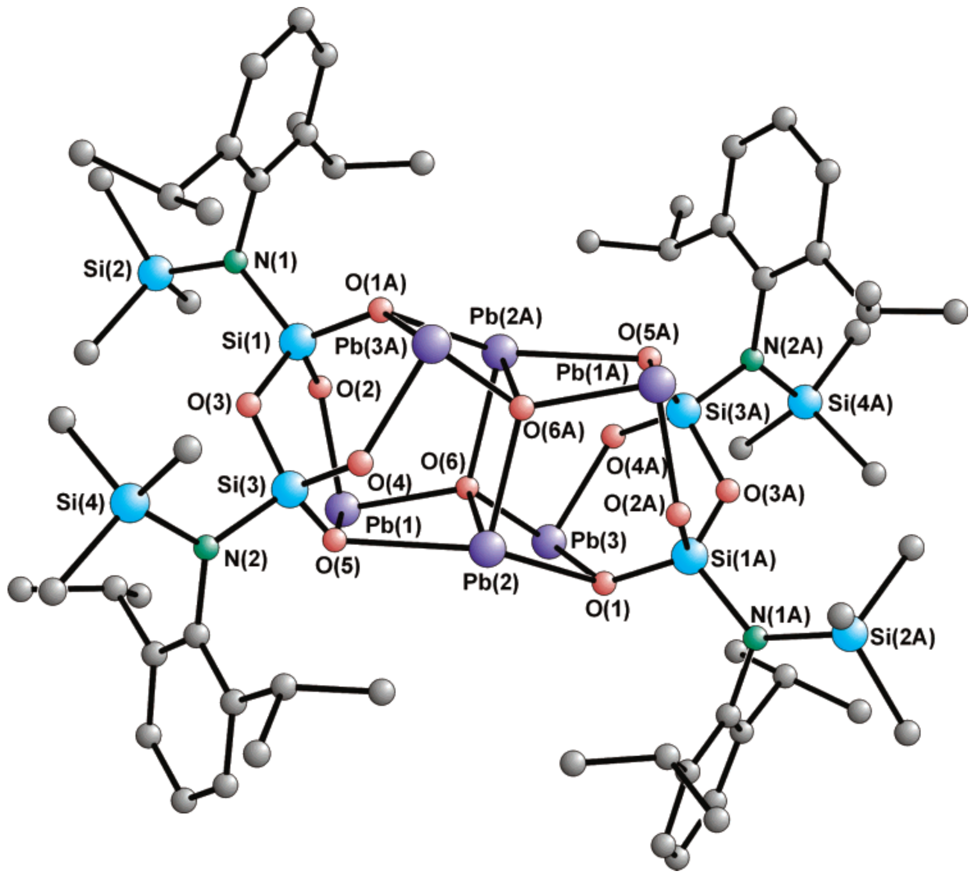
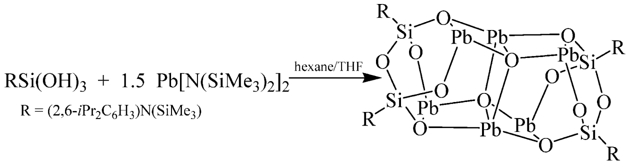


Figure 1. Molecular structure of **1** in the crystal form.

Scheme 1. Synthesis of Compound 1



Results and Discussion

The synthesis of compound **1** is accomplished in about 51% yield and involves a 1.5:1 reaction of the lead(II) amide[9] Pb[N$(SiMe_3)_2]_2$ with the aminosilanetriol[3a] RSi$(OH)_3$ (R = (2,6-*i*$Pr_2C_6H_3$)N$(SiMe_3)$) (Scheme 1). A notable feature of the reaction is that the silanetriol undergoes a self-condensation to generate the disiloxanetetrol [$(RSi(OH)_2)_2O$], which further reacts with the lead(II) amide. Such a condensation reaction has been noted by us earlier.[10]

Compound **1** is soluble in a large number of common organic solvents, including hexane. It is thermally stable, as evidenced by its high decomposition point of 259 °C. Further, compound **1** is stable under EI-mass conditions and shows the parent peak at m/z 2541 (100%) [M^+]. The ^{29}Si NMR of **1** exhibits two resonances (4.4 and −74.8 ppm). The latter corresponds to $\delta(SiO_3N)$, while the former is due to $\delta(SiMe_3N)$. In the infrared spectrum $\tilde{\nu}$(Pb−O−Si) is preliminarily assigned to 881.8 cm^{-1}.[7a]

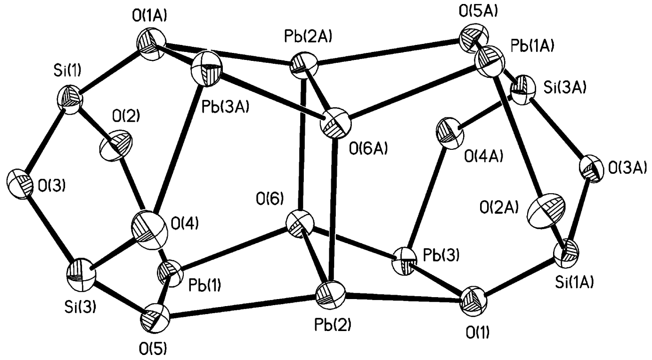


Figure 2. ORTEP core structure of **1**. The substituents on silicon have been omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Pb(1)−O(2) = 2.155(3), Pb(1)−O(5) = 2.267(3), Pb(1)−O(6) = 2.247(3), Pb(2)−O(5) = 2.528(3), Pb(2)−O(6A) = 2.397(3), Pb(2)−O(6) = 2.276(3), Pb(2)−O(1) = 2.546(3), Pb(2A)−O(6) = 2.397(3), Pb(3)−O(1) = 2.245(3), Pb(3)−O(4A) = 2.163(3), Pb(3)−O(6) = 2.242(3); O(2)−Pb(1)−O(6) = 87.81(11), O(2)−Pb(1)−O(5) = 91.87(10), O(6)−Pb(1)−O(5) = 79.09(10), O(6)−Pb(2)−O(6A) = 77.28(10), O(6)−Pb(2)−O(5) = 73.29(9), O(6A)−Pb(2)−O(5) = 101.59(9), O(6)−Pb(2)−O(1) = 72.24(9), O(6A)−Pb(2)−O(1) = 99.31(9), O(5)−Pb(2)−O(1) = 134.16(9), O(4A)−Pb(3)−O(6) = 88.27(11), O(4A)−Pb(3)−O(1) = 93.22(10), O(6)−Pb(3)−O(1) = 78.90(10).

Compound **1** crystallizes in the monoclinic space group $P2_1/n$, along with four molecules of THF per molecule. The molecular structure of **1** is given in Figure 1. The $Pb_6O_{12}Si_4$ core is shown in Figure 2. Selected metric parameters of **1** are summarized in Figure 2.

The molecular structure of **1** can be visualized in the following way. The molecule contains two centrosym-

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[9] Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, *20*, 2004−2009.

[10] Murugavel, R.; Böttcher, P.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W.; Parisini, E.; Teichert, M.; Noltemeyer, M. *Chem. Commun.* **1996**, 2417−2418.

metrically related $Pb_3O_6Si_2$ units that are fused with each other to generate a central diplumboxane motif (Pb_2O_2). Each half of the molecule can be described as possessing a drumlike cage structure. The top and bottom of the drum are comprised of two puckered Pb_2O_3Si six-membered rings, while the sides are made up of three contiguous Pb_2O_2 four-membered rings. In contrast, the recently reported[6] tin(II) siloxane contains two centrosymmetrically related bicyclic $Si_2Sn_2O_5$ rings that are connected to each other by the central four-membered Sn_2O_2 ring, where each tin is three-coordinate. Interestingly, this arrangement leads to an incomplete cage on either side of the distannoxane motif. An alternative way of viewing compound **1** is that it contains a $(PbO)_6$ motif, in the form of fused Pb_2O_2 rings, which are enclosed within two $R_2Si_2O_3$ ligands. While the central lead centers Pb(2) and Pb(2A) are four-coordinate (4O), the others are three-coordinate (3O). Interestingly, in the solid-state structure of PbO the coordination number of lead is 4 (4O), where lead occupies the apex of a square pyramid.[11]

Three types of Pb−O distances are found in **1**. The shortest distances observed are for Pb(1)−O(2) (2.155(3) Å) and Pb(3)−O(4A) bonds (2.163(3) Å). The longest distances found are for Pb(2)−O(5) (2.528(3) Å) and Pb(2)−O(1) bonds (2.546(3) Å). These metric parameters may be compared with those of other lead(II) siloxanes: $[Pb_4(OSiPh_3)_6O]$, 2.25−2.49 Å;[7a] $NaPb[OSi(O\textit{t}Bu)_3]_3$, 2.12−2.15 Å;[7b] $[Pb_7(OSiMe_3)_{10}O_2]$, 2.263(8)−2.660(9) Å.[7d]

There are three different kinds of oxygens in the structure of **1**. Three of these are two-coordinate and bridge either silicon and lead centers (O(2) and O(4)) or two silicon centers (O(3)). There are two three-coordinate oxygens (O(1) and O(5)) that cap two lead centers and one silicon center. The other oxygen (O(6)) is tetra-coordinate and bridges four lead centers. The angles at all of these oxygens are much less than 180°. Thus, the bond angles at oxygens that bridge silicon and lead vary from 128.51(16)° for Si(3)−O(5)−Pb(1) to 109.41(15)° for Si(3)−O(5)−Pb(2). In contrast, the bond angles that bridge two lead centers vary from 114.91(12)° for Pb(1)−O(6)−Pb(2A) to 97.79(10)° for Pb(1)−O(5)−Pb(2).

Experimental Section

General Information and Materials. All experimental manipulations were carried out under a dry nitrogen atmosphere, rigorously excluding air and moisture. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Silanetriol and $Pb[N(SiMe_3)_2]_2$ were prepared according to the published procedures. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. NMR spectra were recorded on Bruker Advance 500 MHz spectrometers. Chemical shifts are reported in ppm with reference to TMS. The upfield shifts are negative. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer as Nujol mulls. Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH5 mass spectrometer by EI-MS methods. Melting points were recorded on a HWS-SG 3000 apparatus and are uncorrected.

Synthesis of $[(PbO)_6(R_2Si_2O_3)_2]$ (1; R = (2,6-iPr$_2$C$_6$H$_3$)N(SiMe$_3$)). $Pb[N(SiMe_3)_2]_2$ (2.42 g, 4.59 mmol) was slowly added to a stirred suspension of the silanetriol (1.0 g, 3.06 mmol) in hexane (25 mL) and THF (7 mL). After the addition was complete, the reaction mixture was stirred for 1 h at room temperature. Subsequently, the reaction mixture was refluxed for 1 h. The volatile components were removed to obtain a white solid. To this was added a mixture of hexane (10 mL) and THF (1 mL). The pale yellow crystals of **1** were obtained by slow cooling of its saturated solution after 4 days at room temperature (yield 0.99 g, 51%). Mp: 259 °C dec. ^1H NMR (500 MHz, C_6D_6, TMS): δ 0.28 (s, 36H, Si(CH_3)$_3$), 1.41, 1.43 (d, 48H, CH(CH_3)$_2$), 3.56 (sept, 8H, CH(CH$_3$)$_2$), 7.6 (m, 12H, aromatic). ^{29}Si NMR (99 MHz, C_6D_6, TMS): δ 4.41 (SiMe$_3$), −74.8 (SiO$_3$). IR (Nujol): $\tilde{\nu}$ 1439 (m), 1357 (m), 1322 (m), 1257 (s), 1244 (s), 1185 (m), 1100 (m), 1044 (s), 1019 (m), 936 (s), 909 (s), 881 (m), 835 (s), 800 (s), 757 (w), 721 (w), 684 (w), 600 (w), 556 (w), 546 (w), 512 (m), 465 (m), 439 (m) cm^{-1}. MS (70 eV; m/z (%)): 2541 (100) [M^+]. Anal. Calcd for $C_{60}H_{104}N_4O_{12}Pb_6Si_8$ (2541.4): C, 28.36; H, 4.12; N, 2.20. Found: C, 28.85; H, 4.31; N, 2.14.

Crystal Data for $1\cdot 4C_4H_8O$: $C_{76}H_{136}N_4O_{16}Pb_6Si_8$, M_r = 2829.75, monoclinic, space group $P2_1/n$, a = 18.664(1) Å, b = 12.693(1) Å, c = 20.651(1) Å, $\alpha = \gamma = 90°$, β = 97.19(1)°, V = 4854 (1) Å^3, Z = 2, ρ_{calcd} = 1.936 Mg/m^3, $F(000)$ = 2704, T = 100(2) K, absorption coefficient 21.222 mm^{-1}. The data were collected using the ω-scan mode in the ranges of $-20 \le h \le 20$, $-14 \le k \le 13$, and $-22 \le l \le 22$. Of 21 054 reflections collected, there were 6771 independent reflections (R(int) = 0.0300). Final R1 ($I > 2\sigma(I)$) = 0.0205; wR2 (all data) = 0.0485. Maximum and minimum heights in the final Fourier difference map were 0.723 and −0.774 e Å^{-3}. The pale yellow single crystal suitable for X-ray diffraction studies of the compound $1\cdot 4C_4H_8O$ were obtained from hexane/THF at room temperature. Diffraction data were collected on a IPDS II Stoe image-plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods (SHELX-97)[12] and refined against F^2 on all data by full-matrix least squares with SHELX-97.[13] The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} values of the parent atoms.

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Supporting Information Available: Tables giving single-crystal X-ray structure data of compound **1**; data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 1st ed., Pergamon Press: Oxford, U.K., 1984.

[12] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[13] Sheldrick, G. M. SHELX-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.