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Synthesis and X-ray Crystal Structure of a Soluble Zinc Silicate Polyhedron, $[(Me_2NC_6H_4NMe_2)ZnLi\{O_3Si(Me_3Si)N(2,6\text{-}i\text{-}Pr_2C_6H_3)\}]_4$[†]

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*Summary: The reaction between a mixture of Me_2Zn and MeLi with $RSi(OH)_3$ ($R = 2,6\text{-}i\text{-}Pr_2C_6H_3NSiMe_3$) in the presence of N,N,N′,N′-tetramethyl-1,4-phenylenediamine in THF/hexane leads to the formation of compound $(LZnLiO_3SiR)_4$ ($L = Me_2NC_6H_4NMe_2$, $R = 2,6\text{-}i\text{-}Pr_2C_6H_3\text{-}NSiMe_3$), **1**. The molecular structure of compound **1** shows a central planar eight-membered Li_4O_4 ring, which is sandwiched between two puckered eight-membered $Zn_2Si_2O_4$ rings. The periphery of the central $Li_4Zn_4Si_4O_{12}$ polyhedron is surrounded by hydrophobic groups, explaining the high solubility of **1** in common organic solvents. This is the first molecular zinc siloxane compound characterized by single-crystal X-ray diffraction studies.*

Zinc and its compounds are widely used in many organic reactions and biological studies. The deficiency of zinc leads to a severe congenital disorder and a large number of diseases. Excess of zinc is harmful to plants, animals, and human beings. Recently, a study on the toxicity of excess zinc in plants, accumulated as zinc silicate, has been published.[1]

Willemite and hemimorphite are the two naturally occurring zinc silicate minerals.[2] Manganese incorporated zinc silicate (willemite) is an important commercial material, due to its high luminescence property, used in the display industry and for the manufacturing of electroluminescent devices.[3] Zeolites and metal-incorporated zeolites are used as catalysts and ion exchangers and are also widely applied in chemical industries. Zinc-exchanged zeolites (Zn/H-ZSM 5) catalyze aromatization reactions, dehydrofluorination, dehydrochlorination, and conversion of methyl iodide to hydrocarbons.[4]

Recently, our research group has synthesized soluble metallasiloxane compounds which can be precursors for metal silicates and mixed metal oxide systems.[5] Earlier, we have reported on three-dimensional aluminum siloxanes ($Al_4Si_4O_{12}$ and $Al_4Si_2O_6$) having a similar framework to that of a naturally occurring aluminum silicate and aluminum-containing zeolite systems (gismondine).[5b,c] A few zinc siloxanes prepared by the reaction of Me_2Zn and R_3SiOH ($R_2Si(OH)_2$) have been reported in the literature.[6−8] However, to the best of our knowledge there are no reports on a reaction of Me_2Zn, MeLi, and $RSi(OH)_3$. Herein, we report on the synthesis

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[†] Dedicated to Professor Lutz-F. Tietze on the occasion of his 60th birthday.

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(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; John Wiley and Sons: New York, 1988. (b) Oste, L. A.; Dolfing, J.; Ma, W. C.; Lexmond, T. *Environ. Toxicol. Chem.* **2001**, *20*, 1339. (c) Neumann, D.; zur Nieden, U. *Phytochemistry* **2001**, *56*, 685. (d) Lichtenberger, O.; Neumann, D. *Eur. J. Cell Biol.* **1997**, *73*, 378.

(2) Wells, A. F. *Structural Inorganic Chemistry,* 5th ed.; Clarendon Press: Oxford, 1984.

(3) (a) Franz, K. A.; Kher W. G.; Siggel A.; Wieczoreck, J.; Adam, W. In *Ullmann's Encyclopedia of Industrial Chemistry,* 5th ed.; Eivers, B., Hawkins, S., Schulz, G., Eds.; VCH: Weinheim, 1990. (b) Leverenz, H. W. *An Introduction to Luminescence of Solids*; John Wiley and Sons: New York, 1950. (c) Morell, A.; El Khiati, N. *J. Electrochem. Soc.* **1993**, *140*, 2019. (d) Barthou, C.; Benoit, J.; Benalloul, P. *J. Electrochem. Soc.* **1994**, *141*, 524. (e) Misra, K. C.; Johnson, K. H.; DeBoer, B. G.; Berkowitz, J. K.; Olsen, J.; Dale, E. A. *Luminescence* **1991**, *47*, 197. (f) Minami, T.; Miyata, T.; Tarata, S.; Fukuda, I. *Japanese J. Appl. Phys., Part-2 Lett.* **1990**, *30*, L117.

(4) (a) Biscardi, J. A.; Meitzner, G. D.; Iglesia, E. *J. Catal.* **1998**, *179*, 192. (b) Circolo, M. F.; Norby, P.; Hanson, J. C.; Corbin, D. R.; Grey, C. P. *J. Phys. Chem. B* **1999**, *103*, 346. (c) Murray, D. K.; Howard, T.; Goguen, P. W.; Krawietz, T. R.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 6354. (d) Murray, D. K.; Chang, J. W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4732. (e) Isao, M.; Czarny, Y. Z.; Oszczudlowski, J. *J. Appl. Chem.* **1991**, *3*, 187.

(5) (a) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem.* **1994**, *106*, 1414; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352. (b) Montero, M. L.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1994**, *106*, 2198; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103. (c) Montero, M. L.; Voigt, A.; Teichert, M.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2761; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504. (d) Voigt, A.; Murugavel, R.; Chandrasekhar, V.; Winkhofer, N.; Roesky, H. W.; Schmidt, H.-G.; Usón, I. *Organometallics* **1995**, *15*, 1610. (e) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Noltemeyer, M.; Schmidt, H.-G.; Roesky, H. W. *Organometallics* **1995**, *14*, 5298. (f) Ritter, U.; Winkhofer, N.; Schmidt, H.-G.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 591; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 524. (g) Ritter, U.; Winkhofer, N.; Murugavel, R.; Voigt, A.; Stalke, D.; Roesky, H. W. *J. Am. Chem. Soc.* **1996**, *118*, 8580. (h) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Noltemeyer, M.; Schmidt, H.-G.; Roesky, H. W. *Chem. Ber.* **1996**, *129*, 591. (i) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Noltemeyer, M.; Schmidt, H.-G.; Roesky, H. W. *Organometallics* **1996**, *15*, 918. (j) Voigt, A.; Murugavel, R.; Parisini, E.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 823; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 748. (k) Voigt, A.; Murugavel, R.; Roesky, H. W. *Organometallics* **1996**, *15*, 5097. (l) Voigt, A.; Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Parisini, E.; Lubini, P. *Angew. Chem.* **1997**, *109*, 2313; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2203. (m) Voigt, A.; Murugavel, R.; Montero, M. L.; Wessel, H.; Liu, F. Q.; Roesky, H. W.; Usón, I.; Albers, T.; Parisini, E. *Angew. Chem.* **1997**, *109*, 1020; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1001. (n) Gouzyr, A. I.; Wessel, H.; Barnes C. E.; Roesky, H. W.; Teichert, M.; Usón, I. *Inorg. Chem.* **1997**, *36*, 3392. (o) Wessel, H.; Rennekamp, C.; Waezsada, S. D.; Roesky, H. W.; Montero M. L.; Usón, I. *Organometallics* **1997**, *16*, 2323. (p) Siefken, R.; Teichert, M.; Chakraborty, D.; Roesky, H. W. *Organometallics* **1999**, *18*, 2321.

(6) (a) Schindler, F.; Schmidbaur, H.; Krüger, U. *Angew. Chem.* **1965**, *77*, 865; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 876. (b) Schindler, F.; Schmidbaur, H. *Angew. Chem.* **1967**, *79*, 697; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 683.

(7) Driess, M.; Merz, K.; Rell, S. *Eur. J. Inorg. Chem.* **2000**, 2517.

(8) Su, K.; Tilley, T. D.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3459.

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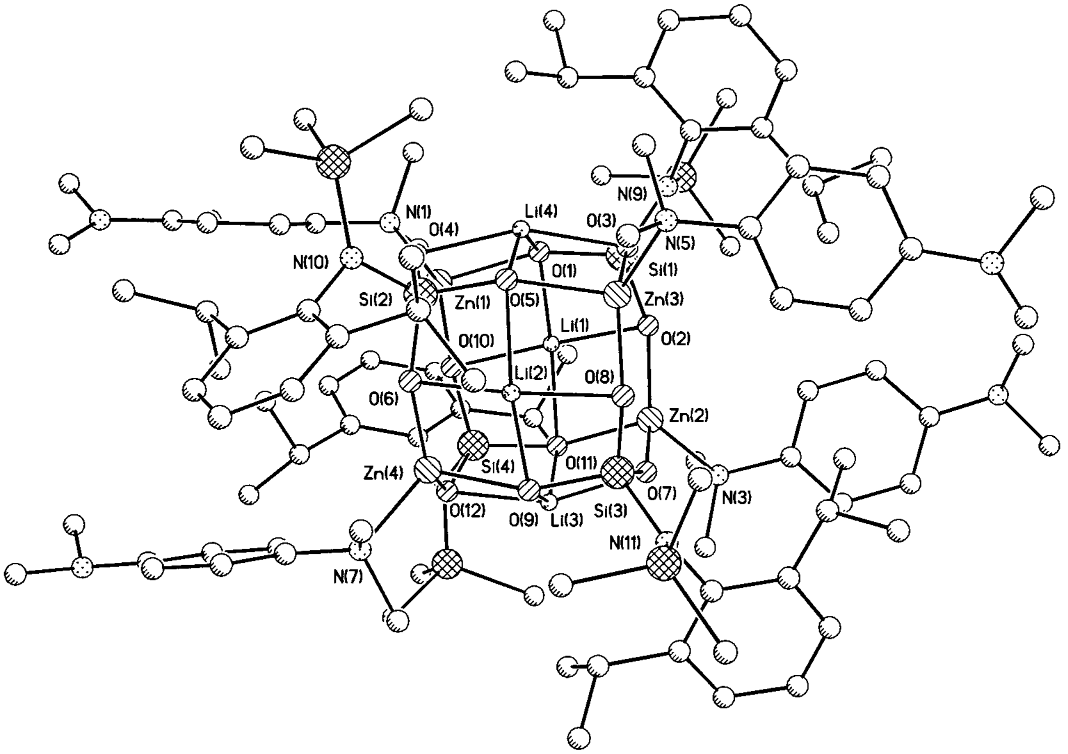
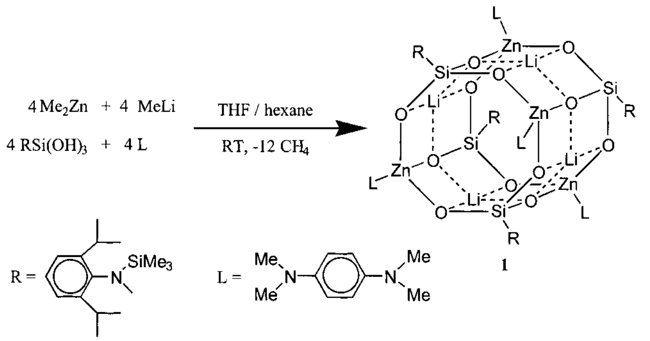


Figure 1. Molecular structure of **1**. Hydrogen atoms have been omitted for clarity.

Scheme 1. Synthesis of Ionic Zinc Siloxane (1)



and single-crystal X-ray structure analysis of a soluble ionic zinc siloxane polyhedron, **1**.

Compound (LZnLiO$_3$SiR)$_4$ (L = Me$_2$NC$_6$H$_4$NMe$_2$, R = 2,6-*i*-Pr$_2$C$_6$H$_3$NSiMe$_3$) (**1**) is prepared by the addition of a mixture of THF solution of Me$_2$Zn and MeLi, in 1:1 ratio, to a suspension of RSi(OH)$_3$ in hexane at room temperature (Scheme 1).[9] The reaction proceeds with the evolution of methane gas. Our attempt to crystallize the resultant compound from the solvent mixture has not been successful. Addition of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (L) is necessary to obtain single crystals of **1** suitable for X-ray structural analysis. Compound **1** is soluble in common organic solvents such as hexane, diethyl ether, and THF.

Compound **1** has been fully characterized by means of analytical, spectroscopic,[10] and single-crystal X-ray diffraction studies.[11] The absence of a broad band between 3000 and 4000 cm^{-1} in the IR spectrum indicates the involvement of three −OH groups of the silanetriol in the reaction. The ^{1}H NMR spectrum of compound **1** (in C$_6$D$_6$ or THF-d_8) shows broad resonances; hence it is difficult to deduce the structure of the siloxane **1** in solution. The variable-temperature ^{1}H NMR spectrum gives no further information. We assume that the broadening of the resonances in the ^{1}H NMR is due to the dynamic process and skeletal rearrangement of **1** in solution. Moreover, no peak

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[9] Synthesis of **1**: A mixture of solutions of MeLi (2.4 mL of a 1 M solution in diethyl ether, 3.87 mmol) and Me$_2$Zn (1.9 mL of a 2 M solution in toluene, 3.87 mmol) in tetrahydrofuran (5 mL) was slowly added at room temperature to a suspension of RSi(OH)$_3$ (1.27 g, 3.87 mmol) in hexane (40 mL). The reaction mixture was stirred for 10 min and refluxed for 1.5 h. After cooling the solution to room temperature *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (L) (0.64 g, 3.87 mmol) was added and stirred for another 1 h. The solution was filtered and concentrated to one-third of its volume. Colorless crystals were obtained at 0 °C from the concentrated solution (0.92 g, 42%).

[10] Characterization Data for Compound **1**: Mp: 148 °C dec. IR ($\bar{\nu}$, cm^{-1}): 1617, 1521, 1321, 1260, 1250, 1209, 1182, 1093, 1054, 1027, 967, 952, 913, 882, 836, 805, 736, 773, 682, 659, 599, 545, 466. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 0.36 (br, 36H, Si(CH$_3$)$_3$), 1.19 (br, 48H, CH(C*H*$_3$)$_2$), 2.81 (s, 48H, NCH$_3$), 3.80 (br, 8H, C*H*(CH$_3$)$_2$), 6.70 (s, 16H, LArH), 6.90 (br, 12H, ArH). ^{29}Si NMR (99.36 MHz, C$_6$D$_6$, 25 °C, TMS): δ 2.13 (br, Si(CH$_3$)$_3$), −64.8 (br, SiO$_3$). MS (EI, 70 eV): *m*/*e* (%) 162 (2, 6-*i*-Pr$_2$C$_6$H$_3$, 100%), 177 (2, 6-*i*-Pr$_2$C$_6$H$_3$NH$_2$, 38%). Anal. Calcd for C$_{100}$H$_{168}$Li$_4$N$_{12}$O$_{12}$Si$_8$Zn$_4$: C, 53.46; H, 7.48; N, 7.48. Found: C, 53.98; H, 7.78; N, 7.77. A single ^{1}H resonance of the NMe$_2$ groups indicates a rapid exchange of the ligand at Zn.

[11] Crystal Data for Compound **1**·C$_6$H$_{14}$: The single crystals suitable for X-ray diffraction studies of compound **1**·C$_6$H$_{14}$ were obtained from the reaction mixture at 0 °C. Diffraction data were collected on a IPDS II Stoe image-plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELX-97)[13] and refined against F^2 on all data by full-matrix least squares with SHELX-97.[14] The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with $U_{\rm iso}$ tied to $U_{\rm iso}$ of the parent atoms. Other details of the data collection, structure solution, and refinement are given as follows. Crystal data: C$_{106}$H$_{182}$Li$_4$N$_{12}$O$_{12}$Si$_8$Zn$_4$, M_r = 2330.60, monoclinic, space group $P2_1/n$, a = 24.7513(5) Å, b = 19.9986(4) Å, c = 25.2954(5) Å, V = 12339.8(4) Å^3, $\alpha = \gamma = 90°$, β = 99.7590(10)°, Z = 4, $\rho_{\rm calcd}$ = 1.254 mg/m^3, F(000) = 4968, T = 133(2) K, μ(Mo Kα) = 0.904 mm^{-1}. Crystal size (mm) = 0.4 × 0.4 × 0.4. The data were collected using the ω-scan mode in the range $1.31 \le \theta \le 24.84$, $-29 \le h \le 29$, $-23 \le k \le 23$, $-29 \le l \le 29$. Of 202 689 reflections collected, 21 207 were unique. Final R1 ($I > 2\sigma(I)$) = 0.0299; wR2 (all data) = 0.0813. Maximum and minimum heights in the final Fourier difference map were 0.650 and −0.453 e·A^{-3}.

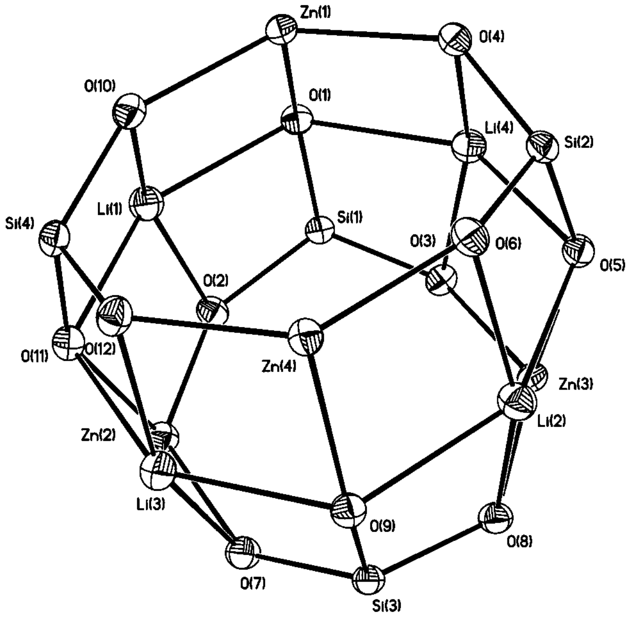

Figure 2. Structure of the central core of **1**. Selected bond lengths (Å) and bond angles (deg): Zn(1)−O(1) = 2.023(1), Zn(1)−O(4) = 1.905(1), Zn(1)−O(10) = 1.890(1), Si(1)−O(1) = 1.640(1), Si(1)−O(2) = 1.620(1), Si(1)−O(3) = 1.609(1), Li(1)−O(1) = 2.029(3), Li(1)−O(2) = 2.016(3), Li(1)−O(10) = 2.009(3), Li(1)−O(11) = 2.053(3); O(3)−Zn(3)−O(8) = 1.383(5), O(3)−Zn(3)−O(5) = 97.63(5), O(8)−Zn(3)−O(5) = 98.98(5), O(1)−Zn(1)−N(1) = 103.97(6), O(1)−Si(1)−N(9) = 112.16(7).

attributable to the molecular ion of **1** can be observed in the EI mass spectrum. Only smaller fragment ion peaks are found.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with one molecule of hexane in the asymmetric unit. The molecular structure of compound **1** shows a planar central eight-membered Li_4O_4 ring, which is sandwiched between two puckered eight-membered $Zn_2Si_2O_4$ rings. Each of the four lithium atoms is coordinated to four oxygen atoms. There are no solvent molecules coordinated to lithium. The oxygen atoms in the two eight-membered $Zn_2Si_2O_4$ rings are bridged to zinc, silicon, and lithium atoms in a μ_3-O fashion, whereas oxygen atoms in eight-membered Li_4O_4 cycles are bridged in a μ_4-O fashion. Each zinc atom is coordinated to one of the N atoms of the amine (Figure 1). The periphery of the central $Li_4Zn_4Si_4O_{12}$ polyhedron is surrounded by hydrophobic groups, explaining the high solubility of **1** in common organic solvents.

Selected bond lengths and bond angles of compound **1** are given in the legend of Figure 2. The average Si−O bond length in compound **1** is 1.624 Å. This is slightly longer than those reported for group 13 metallasiloxane compounds. The average Zn−N (2.120 Å) bond length is comparable to that in similar compounds reported in the literature.[12] The shortest Zn−O bond distance is observed for the Zn−μ_3-O bond (~1.899 Å), and the longest is observed for the Zn−μ_4-O (~2.023 Å). Similarly, the two different short and long bond distances for Li−O were also noticed (Li−μ_3-O = 1.998(3), 2.016(3) Å, Li−μ_4-O = 2.029(3), 2.089(3) Å). A similar Li−O bond length for group 13 metallosiloxanes has also been reported.

In this note, we have given a facile method for the preparation of a highly organic soluble zinc siloxane **1**. Compound **1** can be a potential starting material for the preparation of zinc-containing silicates and mixed metal oxide systems.

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Supporting Information Available: Text giving details of the X-ray crystal structure studies and tables of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and bond angles for compound $1\cdot C_6H_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Malik, M. A.; Brien, P. O.; Motevalli, M.; Jones, A. C. *Inorg. Chem.* **1997**, *36*, 5076.

(13) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(14) Sheldrick, G. M. *SHELX-97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.