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A Polyhedral Magnesium Silicate with a $Mg_5Si_4O_{10}$ Framework: X-ray Crystal Structure of $[\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3\}_2\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_2(OH)\}_2(Mg\cdot C_4H_8O)_5]$†

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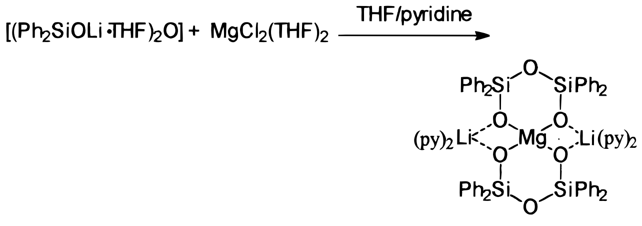
*Summary: The reaction of (2,6-i-$Pr_2C_6H_3$)N($SiMe_3$)Si-(OH)$_3$ (**1**) with Bu_2Mg in THF at room-temperature resulted in the formation of the magnesium silicate **2**. The core of the molecule consists of two four-membered, two six-membered, and three eight-membered rings and can be regarded as a molecular magnesium silicate soluble in conventional organic solvents.*

The estimated relative abundance of magnesium in the earth's crust is 1.94%, and therefore, magnesium belongs to the more frequently occurring elements. The most abundant magnesium-containing minerals are magnesite, dolomite, olivine, enstatite, serpentine, talc, and meerschaum.[1] Due to our experience in the synthesis of soluble silicates containing aluminum, gallium, and indium[2] it was a challenge to synthesize a soluble molecular magnesium silicate. Little is known about the molecular structures of the corresponding cage compounds containing group 2 metals. To the best of our knowledge only one ring system obtained from the reaction of $[(Ph_2SiOLi\cdot THF)_2O]$ with magnesium dichloride (Scheme 1) has been characterized by X-ray structural analysis.[3]

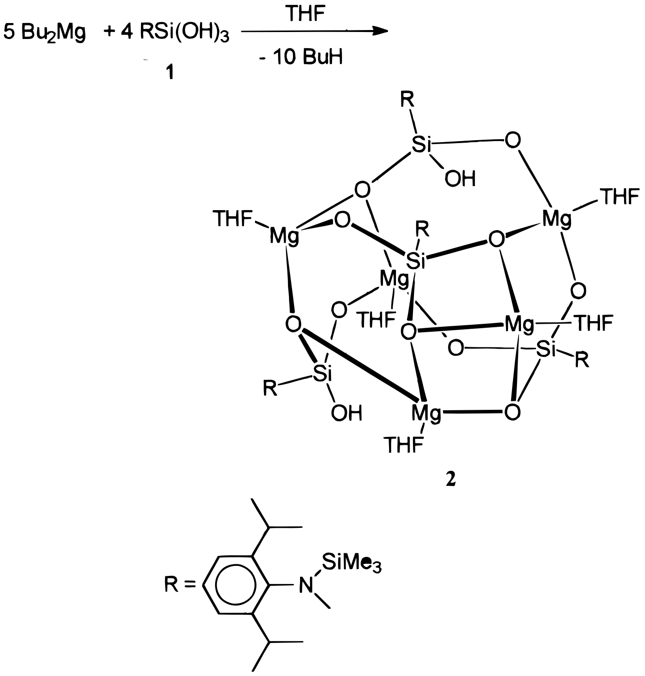
Scheme 1



In this paper we report the synthesis of a new polyhedral magnesium silicate soluble in various organic solvents.

As in previous reactions, we have chosen the kinetically stable silanetriol (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)Si(OH)$_3$ **(1)** to construct three-dimensional structures.[4] Addition of Bu_2Mg to a solution of the silanetriol **1** in THF at room temperature in a 5:4 stoichiometry affords the polyhedral magnesium silicate $[\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3\}_2\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_2(OH)\}_2(Mg\cdot C_4H_8O)_5]$ (**2**) (Scheme 2).[5] Even a variation of the stoichiometry leads in every experiment to compound **2**.

Scheme 2



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Compound **2** shows a good solubility in common organic solvents such as diethyl ether, tetrahydrofuran,

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[†] Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.

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and *n*-hexane and can be handled in air for about 2 h without any appreciable decomposition. The magnesium silicate was fully characterized by IR, electronic impact mass spectroscopy (EI), multinuclear NMR[6] and a single-crystal X-ray crystal structure determination.[7]

In the IR spectrum of **2** a strong absorption at 3638 cm^{-1} indicates the presence of OH groups. In addition to the expected resonances of aryl, $SiMe_3$, and *i*-Pr protons the OH signals are observed as a singlet (δ 7.85) in the ^1H NMR spectrum. This signifies a shift to lower field compared to the chemical shift of the silanetriol **1** (δ 5.18).[2a] A similar shift of the OH signals to lower field is observed on the titanium silicate $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)]_6Si_6O_{16}(OH)_4Ti_4{\cdot}2THF$.[4c] Compound **2** shows two ^{29}Si NMR resonances due to the SiO_3 silicon centers (δ_{Si} −64.3) and the $SiMe_3$ groups (δ_{Si} 2.2). Due to this observation we assume that in solution a more symmetric species is formed. The temperature-dependent ^1H NMR spectrum gives no further information. Moreover, no peak attributable to the molecular ion of **2** can be observed in the EI mass spectrum. Only smaller fragment ions are found.

X-ray Crystal Structure of 2. The molecular structure of the $Mg_5Si_4O_{10}$ core of **2** is shown in Figures 1 and 2. Details of the data collection, structure solution, and refinement are given in Table 1. The compound crystallizes in the monoclinic space group *Cc* with one molecule in the asymmetric unit. Due to this arrangement no symmetry exists in the molecule. For comparison reasons parts of the structure of the layered silicates serpentine ($Mg_3(OH)_4Si_2O_5$) and talc ($Mg_3(OH)_2Si_4O_{10}$),[8] respectively, can be used because they contain hydroxylic groups such as compound **2**. Additionally, six-membered rings are found in **2** comparable to those in the magnesium silicates quoted above.

The central unit of the molecule consists of a $Mg_5Si_4(\mu\text{-}O)_5(\mu_3\text{-}O)_5(OH)_2$ core and is based on two four-membered, two six-membered, and three eight-membered rings. The Mg−O bond distances (1.878−2.097

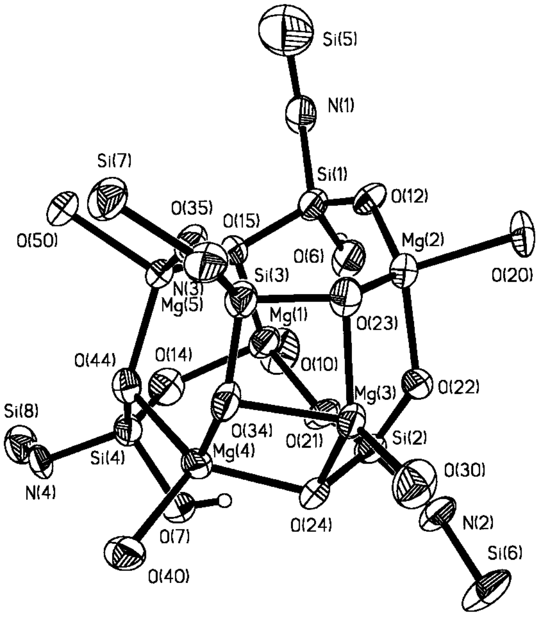

Figure 1. Core structure of **2** showing the polyhedron. Selected bond distances (Å) and angles (deg): Mg−O, 1.788(9)−2.081(9), Si−O, 1.570(11)−1.696(8); O−Mg−O, 76.5(4)−138.9(3); Si−O−Mg, 91.4−156.3(6).

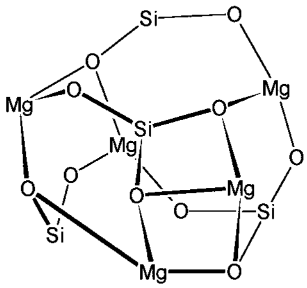

Figure 2.

Table 1. Crystallographic Data for 2

empirical formula	$C_{80}H_{146}Mg_5N_4O_{17}Si_8$
fw	1782.28
temp (K)	150(2)
cryst size (mm)	0.8 × 0.8 × 0.4
cryst syst	monoclinic
space group	Cc
a (Å)	25.853(5)
b (Å)	15.303(3)
c (Å)	27.868(6)
α (deg)	90
β (deg)	106.16(3)
γ (deg)	90
cell volume *V* ($Å^3$)	10 590(4)
Z	4
ρ_c ($g\ mm^{-3}$)	1.118
μ (mm^{-1})	0.187
F(000)	3848
2θ range (deg)	3.51−22.58
no. of data: measd, unique	9741, 9433 (R_{int} = 0.0895)
$R,^a$ $wR2^b(I > 2\sigma(I))$	0.0980, 0.2452
R, wR2 (all data)	0.1243, 0.2777
goodness of fit, S^c	1.033
no. of refined params	1053
no. of restraints	695
largest diff peak, hole (e $Å^{-3}$)	+1.026/−0.558

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/\sum(n - p)]^{1/2}$.

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(5) Synthesis of the magnesium silicate **2**: To a solution of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)Si(OH)_3$ (3.00 g, 9.16 mmol) in THF (40 mL) was added Bu_2Mg (11.45 mL of a 1.0 M solution in *n*-heptane). The evolution of butane ceased within 30 min, and the reaction mixture was stirred for another 48 h at room temperature. Subsequently, the solvent was removed under reduced pressure at room temperature and the white residue was washed with *n*-pentane, affording **2** (3.24 g, 1.82 mmol) as a white solid (79% yield).

(6) Characterization data for **2**. Mp: 165 °C dec. IR (Nujol): 3638 (OH), 1914, 1859, 1701, 1597, 1578, 1439, 1320, 1246, 1186, 1105, 1073, 1034, 963, 881, 801, 756, 724, 683 cm^{-1}. ^1H NMR (200.13 MHz, THF-d_8, 25 °C, TMS): δ 0.05 (s, 36 H, $Si(CH_3)_3$), 1.12 (d, ^3J(H, H) = 6.9 Hz, 24 H, $CH(CH_3)_2$), 1.23 (d, ^3J(H, H) = 6.9 Hz, 24 H, $CH(CH_3)_2$), 3.80 (m, 8 H, $CH(CH_3)_2$), 6.95 (m, 12 H, Ar H), 7.85 (s, 2 H, OH). ^{29}Si NMR (49.63 MHz, THF-d_8, 25 °C, TMS): δ −64.3 (SiO_3), 2.2 ($Si(CH_3)_3$). MS (EI, 70 eV): *m*/*e* (%) 162 ($[2,6\text{-}i\text{-}Pr_2C_6H_4]$, 100%), 177 ($[2,6\text{-}i\text{-}Pr_2C_6H_3]NH_2$, 38%). Anal. Calcd for $C_{80}H_{146}Mg_5N_4O_{17}Si_8$ (1782.28): C, 53.9; H, 8.3; N, 3.1. Found: C, 53.8; H, 8.3; N, 3.0.

(7) X-ray Structure Determination of **2**: Colorless crystals suitable for X-ray diffraction studies were grown from 2:1 v/v THF/*n*-hexane mixtures at room temperature. A suitable crystal of compound **2** was mounted on a glass fiber and coated with paraffin oil.[10] Diffraction data were collected on a Siemens-Stoe AED diffractometer (−120 °C) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods[11] and refined against F^2 on all data by full-matrix least squares with SHELXL-93.[12] All non-hydrogen atoms were refined anisotropically. A total of 695 similarity restraints were applied to eventually disordered isopropyl groups. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model (in the case of methyl and hydroxyl groups with torsion angles). Other details of the data collection, structure solution, and refinement are listed in Table 1.

(8) *Römpp-Chemie-Lexikon*; Falbe, J., Regitz, M., Eds.; Thieme: Stuttgart, New York, 1992; p 4447.

Å) are consistent with Mg−O bond lengths compiled by Holloway and Melnik for compounds of magnesium of coordination number 4 (1.819−2.219 Å).[9] The Si−O bond distances (average 1.633 Å) are in the range with those found in the aluminosilicates [(2,6-$Me_2C_6H_3$)N-($SiMe_3$)SiO_3Al·$C_4H_8O_2$]$_4$ (average 1.62 Å) and [(2,4,6-$Me_3C_6H_2$)NSi(OAl(*i*-Bu))(OAl(*i*-Bu)$_2$)O]$_2$ (average 1.68 Å), respectively.[2e] The environment of the magnesium atoms as well as that of the silicon atoms is tetrahedrally distorted. Depending on the ring size, the O−Mg−O angles are in the range 76.5(4)−86.7(3)° in the four-membered rings, 90.8(4)−138.9(3)° in the six-membered rings, and 103.9(4)−132.7(3)° in the eight-membered rings, respectively. The behavior of the Si−O−Mg angles is analogous (four-membered rings, 91.8(4)−92.3(4)°; six-membered rings, 94.3(4)−136.9(5)°; eight-membered rings, 120.3(5)−156.3(6)°).

Conclusions

In addition to the known metal ions containing silicates we were able to synthesize the molecular, three-dimensional magnesium silicate **2**. This indicates that the method of preparing soluble model compounds of silicates can be extended to group 2 metals. Furthermore, the synthesis involves only the elimination of butane during the reaction, thereby making the workup procedure very facile. We are currently investigating the synthesis of silicates containing the heavier alkaline earth metals.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **2** (17 pages). Ordering information is given on any current masthead page.

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