Cage Compounds

Polyhedral Ferrous and Ferric Siloxanes[**]

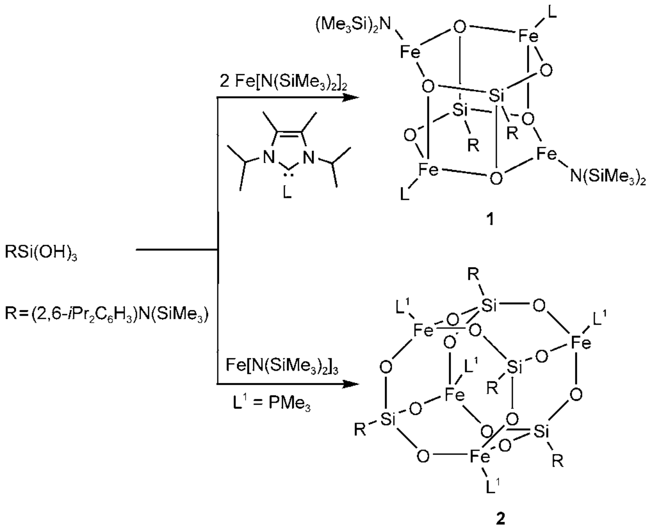
Umesh N. Nehete, Ganapathi Anantharaman, Vadapalli Chandrasekhar, Ramaswamy Murugavel, Mrinalini G. Walawalkar, Herbert W. Roesky, Denis Vidovic, Jörg Magull, Konrad Samwer, and Björn Sass*

Dedicated to Professor Michael Veith
on the occasion of his 60th birthday

Iron is the fourth most abundant element in the earth's crust after oxygen, silicon, and aluminum. Although iron atoms are present in the ore hematite (Fe_2O_3) in the formal oxidation state +III, in magnetite (Fe_3O_4) they exhibit both the +II and +III oxidation states. In the naturally occurring olivine, $MgFeSiO_4$, iron atoms are present in the +II oxidation state while in garnets, $[M^{2+}{}_3 M^{3+}{}_2(SiO_4)_3]$ (M^{2+} = Co, Mg, Fe; M^{3+} = Al, Cr, Fe) they are found in both oxidation states.[1,2] Other examples of iron-containing silicate frameworks include zeolites such as iron-modified ZSM-5, which have been shown to be important as catalysts, as for example in the synthesis of phenol from benzene and N_2O.[3] Moreover the Lewis acidity of the iron centers in iron-modified ZSM-5 enables its use as an acid catalyst in the benzylation reaction of benzene by using benzyl chloride[4] and also in the esterification of *tert*-butanol by acetic anhydride.[5]

We have a long-standing interest in molecular assemblies that contain the {Si-O-M} motif.[6] Firstly, this is in view of the importance of such compounds as models for naturally occurring minerals.[7] Secondly, these compounds are also quite valuable in understanding the mechanism of many catalytic processes particularly those involving silica-supported transition-metal catalysts.[8] A case in point are the molecular cubic titanosiloxanes $[\{Ti(OR^1)O_3SiR\}_4]$ [R^1 = *t*Bu, *t*BuO, *t*BuCH$_2$; R = (2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)], which have not only helped in the elucidation of the Si-O-Ti stretching frequency observed in TS-1 and TS-2 catalysts (TS is titanium silicate) but have also themselves been quite effective in catalytic reactions that involve the epoxidation of 1-hexene and 1-octene.[9,10] In view of this success, it was of interest to build analogous molecular iron siloxane frameworks. Previous work on iron siloxanes centered around the use of R_3SiO[11] or silsesquioxane ligands.[12] However, polyhedral iron siloxanes have remained elusive and the preparation of such compounds is a synthetic challenge in view of the instability of iron alkyls. We have overcome this synthetic hurdle by choosing bis- and trisamido derivatives of iron[13,14] as the starting precursor and have been able to assemble two different iron siloxanes that contain iron atoms in the formal oxidation states of +II and +III, respectively. Accordingly, herein we report the synthesis and single-crystal molecular structures of ferrous $[\{(Me_3Si)_2NFe\}_2\{LFe\}_2\{O_3SiR\}_2]$ (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) **1** and ferric siloxanes $[\{(L^1Fe)(O_3SiR)\}_4]$ [L^1 = PMe$_3$; R = (2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)] **2** (Scheme 1).

The addition of two equivalents of $Fe[N(SiMe_3)_2]_2\cdot THF$[13] to a suspension of $RSi(OH)_3$ in hexane/toluene mixture at room temperature in the presence of the N-heterocyclic carbene L (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) affords **1** in moderate yield (Scheme 1). The use of the auxiliary coordinating ligand L allowed the isolation of the ferrous siloxane **1** as a crystalline product. Single crystals of **1**, thus obtained, were found to be soluble in many common organic solvents. The IR spectrum of **1** shows characteristic absorptions for the {Fe-O-Si} groups in the range of 900 to 1000 cm^{-1}. However no peak attributable to the molecular ion of **1** can be observed in the EI or other mass spectrometric methods.



Scheme 1. Synthesis of ferrous **1** and ferric siloxanes **2**.

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[*] U. N. Nehete, G. Anantharaman, Prof. Dr. H. W. Roesky, D. Vidovic, J. Magull
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3373
E-mail: hroesky@gwdg.de

Prof. Dr. K. Samwer, B. Sass
I. Physikalisches Institut
Universität Göttingen
Tammannstrasse 1, 37077 Göttingen (Germany)

Prof. Dr. V. Chandrasekhar
Department of Chemistry
IIT-Kanpur
Kanpur-208 016 (India)

Prof. Dr. R. Murugavel, Dr. M. G. Walawalkar
Department of Chemistry
IIT-Bombay
Powai, Mumbai, 400 076 (India)

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The molecular structure of **1** has been determined by single-crystal X-ray diffraction experiments[15a] and it consists of an {$Fe_4O_6Si_2$} core (Figure 1 a). The structure of **1** exhibits two {Fe_2O_3Si} rings that are fused to each other, which results in the formation of a drumlike architecture with a pseudoinversion center. The sides of the drum are defined by two four-membered {FeO_2Si} and two six-membered {Fe_2O_3Si} rings. Two types of iron centers are present in the structure of **1**. While Fe1 and Fe4 have a coordination environment comprising one N and two O atoms with one intact $N(SiMe_3)_2$ ligand, Fe2 and Fe3 have a coordination environment of one C and three O atoms, in which the N-heterocyclic carbene takes up the fourth coordination side. The tricoordinate iron centers (Fe1 and Fe4) are in a trigonal planar geometry while the tetracoordinate iron centers, (Fe2 and Fe3) have an approximate tetrahedral geometry. Another view of the structure of **1** (Figure 1 b) shows that the four iron centers are nearly in one plane and are held together by two essentially bicapping $RSiO_3$ units. This mode of interaction of the $RSiO_3$ ligand is similar to that of the RPO_3 ligand as found in molecular metal phosphonate and phosphate structures.[16–18]

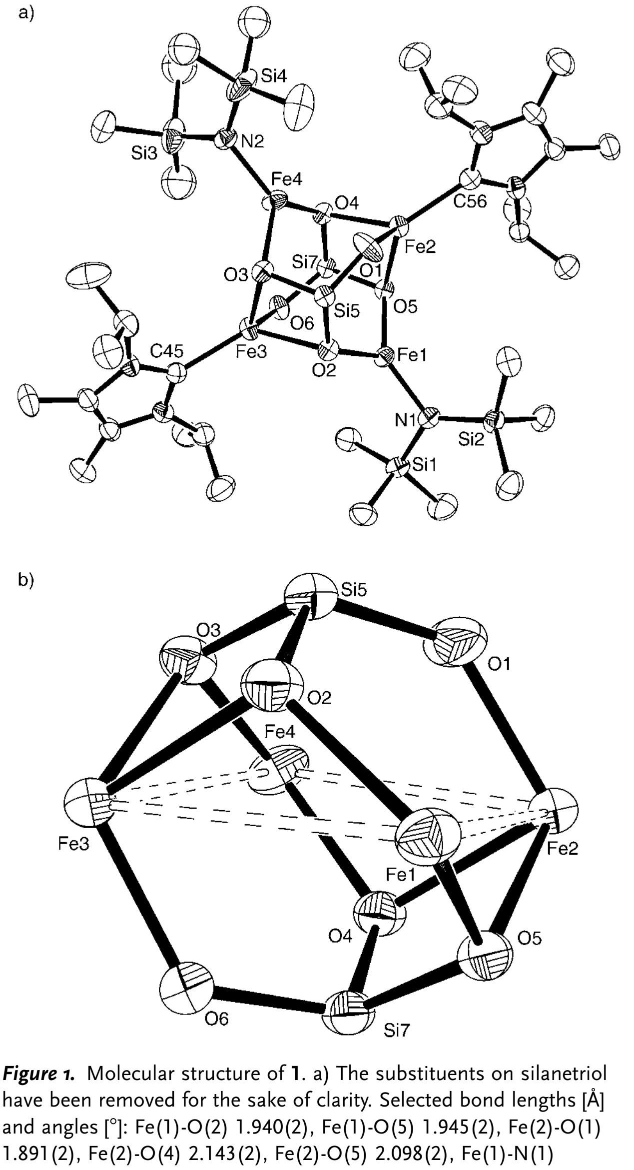

Figure 1. Molecular structure of **1**. a) The substituents on silanetriol have been removed for the sake of clarity. Selected bond lengths [Å] and angles [°]: Fe(1)-O(2) 1.940(2), Fe(1)-O(5) 1.945(2), Fe(2)-O(1) 1.891(2), Fe(2)-O(4) 2.143(2), Fe(2)-O(5) 2.098(2), Fe(1)-N(1) 1.938(3), Fe(2)-C(56) 2.123(4), Si(5)-O(1) 1.605(3), Si(5)-O(2) 1.641(3), Si(5)-O(3) 1.653 (2); O(2)-Fe(1)-O(5) 105.15(10), O(2)-Fe(1)-N(1) 128.58(12), O(5)-Fe(1)-N(1) 126.27(11), O(1)-Fe(2)-O(5) 106.00(10), C(56)-Fe(2)-O(1) 118.92(12), C(56)-Fe(2)-O(5) 124.35(11), O(1)-Si(5)-O(2) 115.01(14), O(1)-Si(5)-O(3) 105.84 (15), O(2)-Si(5)-O(3) 100.78(12), Fe(1)-O(2)-Fe(3) 112.67(10), Fe(3)-O(2)-Si(5) 90.79(11), Fe(1)-O(2)-Si(5) 123.09(14), Fe(2)-O(1)-Si(5) 131.19(15). b) Core structure of **1**. Imaginary lines are drawn between iron atoms to show its planar arrangement.

One of the three oxygen atoms (O1, O6) of each silanetriol in **1** is involved in a μ-bridging mode (Fe-O-Si), while the other two oxygen atoms (O2, O3, O4, O5) are involved in a μ_3-bridging mode that links two iron centers and one silicon. In general, the bond lengths that involve the μ_3-oxygen centers are found to be longer (av. Si–O, 1.651 Å; Fe–O, 2.055 Å) than the corresponding distances that involve the μ-oxygen atom (av. Si–O, 1.605 Å; Fe–O, 1.892 Å).

The reaction of the silanetriol with the ferric amide $[Fe\{N(SiMe_3)_2\}_3]$[14] proceeds with complete elimination of $HN(SiMe_3)_2$ to afford the ferric siloxane **2** which was crystallized in the presence of trimethyl phosphane L^1 (Scheme 1). Compound **2**, like **1** discussed above is highly lipophilic and is soluble in common organic solvents including hexane. The ferric siloxane **2** is thermally stable up to its melting point (242–244 °C). The ESIMS of **2** shows the base peak for $[M^+-PMe_3]$, which suggest a remarkable stability of the core structure of **2** under these conditions. Compound **2** exhibits broad resonances in its NMR spectra, thus indicating that it is paramagnetic.

The molecular structure of **2** (Figure 2) is made up of a {$Fe_4O_{12}Si_4$} cuboid core at which the corners of the cube are alternately occupied by iron and silicon atoms.[15b] Each of the twelve edges of the cube contain the bridging oxygen atoms. Thus, the overall core structure of the ferric siloxane contains six {$Fe_2O_4Si_2$} eight-membered rings as the faces of the cube. Unlike in the ferrous siloxane **1**, in compound **2** all the oxygen atoms are involved in a μ-bridging mode that interconnects a silicon and an iron atom. Each iron is tetracoordinate with a coordination environment of one P and three O atoms. The coordination geometry around both iron and silicon centers is nearly tetrahedral. The average Fe–O distance (1.824 Å) found in the ferric siloxane **2** is much shorter due to the smaller ionic radius of an Fe^{III} center compared to that of an Fe^{II} in **1**. In contrast the Si–O distance in **2** is similar (av. 1.618 Å) to that found in **1** (μ-O).

Magnetic-susceptibility measurements[19] were carried out in the temperature range from 300 K to 5 K for compounds **1** and **2**. A plot of $1/\chi$ (Oe emu^{-1}; χ is magnetic susceptibility) versus T (K) is shown in Figure 3. The plots indicate an antiferromagnetic behavior for both compounds.

In conclusion we report the first examples of polyhedral ferrous and ferric siloxanes. The isolation of these compounds suggests that similar synthetic strategies will allow the preparation of other transition-metal siloxane frameworks. These perspectives will lead to interesting new systems.

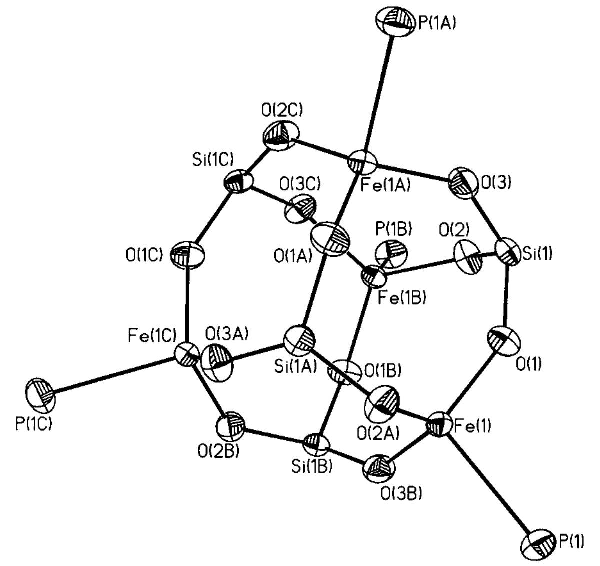

Figure 2. Core structure of **2**. The substituents on silanetriol and the phosphane have been omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Fe(1)-O(1) 1.802(3), Fe(1)-O(3B) 1.829(3), Fe(1)-O(2A) 1.831(3), Fe(1)-P(1) 2.468(1), Si(1)-O(1) 1.628(3), Si(1)-O(2) 1.616(3), Si(1)-O(3) 1.612(3); Si(1)-O(1)-Fe(1) 147.60(19), O(1)-Fe(1)-O(3B) 114.61(14), O(3)-Si(1)-O(2) 111.40(16), O(2)-Si(1)-O(1) 108.73(17).

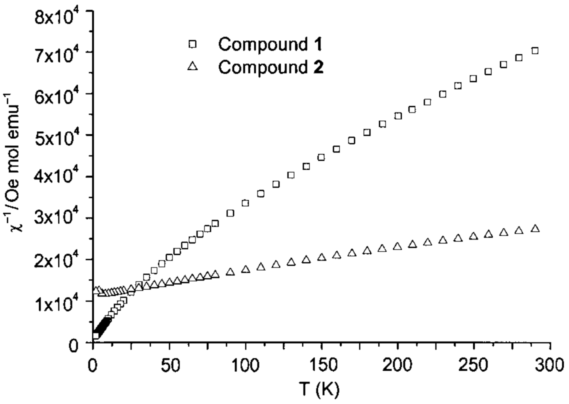

Figure 3. Plot of 1/χ (Oe mol emu^{-1}) versus *T* (K) for compounds **1** and **2**.

Experimental Section

1: [Fe{N(SiMe$_3$)$_2$}$_2$]·THF (3.5 g, 9.17 mmol) was slowly added to a suspension of RSi(OH)$_3$ (**1**) (1.5 g, 4.59 mmol) in THF/hexane (10 mL, 40 mL) at room temperature. The solution turned from green to dark brown. This solution was stirred for further 16 h at room temperature. A solution of N-heterocyclic carbene L (2 g, 11.47 mmol) in toluene (10 mL) was added and the stirring was continued for one more day. The volatile components were removed to obtain a brown solid. To this a mixture of toluene (10 mL) and THF (1 mL) was added. Colorless crystals of **1** were obtained after several days at 0 °C: (0.50 g, 13 % of single crystals); mp > 220 °C; IR (nujol): $\tilde{\nu}$ = 1260, 1245, 1221, 1186, 1100, 1043, 1019, 983, 964, 945, 927, 885, 836, 820, 801, 752, 723, 680, 607, 567, 544, 491 cm^{-1}; elemental analysis (%) calcd (toluene molecules were removed by drying under vacuum) for $C_{64}H_{128}Fe_4N_8O_6Si_8$ (1407.44): C 49.47, H 8.30, N 7.21; found: C 47.7, H 8.0, N 6.2.

2: [Fe{N(SiMe$_3$)$_2$}$_3$] (2.3 g, 4.28 mmol) in hexane (25 mL) was slowly added to a suspension of silanetriol (1.4 g, 4.28 mmol) in the same solvent (40 mL). After the addition was complete, the reaction mixture was stirred for 72 h at room temperature. The green solution slowly turned to greenish brown. The solvents and hexamethyldisilazane were removed in vacuo to give a brownish-green product. This was recrystallized from a mixture of toluene and THF (1:0.05) in the presence of PMe$_3$ as the auxiliary coordinating ligand at room temperature over a period of two weeks (0.29 g, 14 %; it was observed that the yield of compound **2** was improved to about 25 % of single crystals by the use of a mixture of hexane and THF (1:0.25) along with PMe$_3$ for crystallization); mp 242–244 °C; ESIMS (CH$_3$CN): *m*/*z* (%) 1750 (100) [M^+−PMe$_3$]; IR (nujol): $\tilde{\nu}$ = 1585, 1576, 1440, 1420, 1321, 1308, 1290, 1245, 1190, 1107, 1096, 1054, 1033, 967, 956, 923, 836, 800, 757, 749, 726, 682, 642, 613, 599, 549, 534, 489, 462, 434 cm^{-1}; elemental analysis (%) calcd (toluene molecules were removed by drying under vacuum) $C_{72}H_{140}Fe_4N_4O_{12}P_4Si_8$ (1825.89): C 47.36, H 7.73, N 3.07; found: C 46.68, H 7.17, N 3.24.

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[15] Crystal data for compounds: a) The single crystals suitable for X-ray diffraction studies of compound **1**·1.5 C_7H_8 were obtained from toluene at 0 °C. $C_{74.50}H_{140}Fe_4N_8O_6Si_8$, $M_r = 1692.06$, triclinic, space group $P\bar{1}$, $a = 12.6202(5)$ Å, $b = 14.7837(6)$ Å, $c = 27.2205(12)$ Å, $\alpha = 93.949(4)^o$, $\beta = 97.850(3)^o$, $\gamma = 109.689(3)^o$, $V = 4700.8(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.195$ mg m^{-3}, $F(000) = 1814$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.755$ mm^{-1}. The data were collected using the ω scan mode in the range of $1.47 \leq \theta \leq 24.84$, $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-32 \leq l \leq 27$. Of 45117 reflections collected, 16133 were unique. Final $R1$ ($I > 2\sigma(I)$) = 0.0497; $wR2$ (all data) = 0.1452. Maximum and minimum heights in the final Fourier-difference map were 1.031 and −1.016 e·A^{-3}; b) **2**·2 C_7H_8: $C_{86}H_{156}Fe_4N_4O_{12}P_4Si_8$, $M_r = 2010.15$, tetragonal, space group $P42_1c$, $a = b = 19.7056(11)$ Å, $c = 15.1916(11)$ Å, $\alpha = \beta = \gamma = 90^o$, $V = 5899.1(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.132$ mg m^{-3}, $F(000) = 2144$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.666$ mm^{-1}. The data were collected by using the ω scan mode in the range of $1.69 \leq \theta \leq 24.81$, $-23 \leq h \leq 20$, $-23 \leq k \leq 19$, $-17 \leq l \leq 11$. Of 12247 reflections collected, 4732 were unique. Final $R1$ ($I > 2\sigma(I)$) = 0.0431; $wR2$ (all data) = 0.1309. Maximum and minimum heights in the final Fourier difference map were 0.752 and −0.249 e·A^{-3}. The single crystals suitable for X-ray diffraction studies of compound **2**·2 C_7H_8 were obtained from a mixture of toluene and THF in the presence of PMe_3 at room temperature. Diffraction data were collected on a IPDS II Stoe image-plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELX-97)[20] and refined against F^2 on all data by full-matrix least squares with SHELX-97.[21] The heavy atoms were refined anisotropically. Hydrogen atoms were included by using the riding model with U_{iso} tied to U_{iso} of the parent atoms. CCDC-225526 (**1**) and CCDC-225525 (**2**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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