Experimental Section

Colorless rodlike crystals of **I** were obtained in ~40% yield, by the hydrothermal reaction in the presence of piperazine (PIP). Typically, a mixture of $Fe(C_2O_4)\cdot 2H_2O$:H_3AsO_4:PIP:HF:water (1:8:4:6:200) was heated at 150°C for 72 h in a PTFE-lined acid digestion bomb (7 mL). The initial pH of the reaction mixture was 2; this did not change significantly after the heat treatment. Mildly pink colored platelike crystals of **II** (50% yield) were obtained by reacting the above mixture at 150°C for 168 h or at 180°C for 24 h, and deep green colored rodlike crystals of **III** (35% yield) resulted when the mixture was heated at 180°C for 60 h. **II** and **III** can also be obtained by heating a mixture of $Fe(acac)_3$:$6H_3AsO_4$:4-PIP:4HF:$200H_2O$ at 180°C for 48 h, or $Fe(C_2O_4)\cdot 2H_2O$:$8.6H_3AsO_4$:1.4-PIP:$285H_2O$ at 150°C for 48 h. When the crystals of **I** (0.5 g) were heated with water (2 mL) at 150°C in an acid digestion bomb, **III** was formed, along with a mixture of condensed iron arsenates. The compounds **I**, **II**, and **III** have been obtained as pure single-phase materials, and were characterized using energy dispersive X-ray analysis (EDAX), IR, and thermogravimetric analysis (TGA). An X-ray photoemission spectroscopy (XPS) investigation clearly indicated the presence of both Fe^{II} and Fe^{III} species in **III**.

Suitable single crystals of **I**, **II**, and **III** were subjected to X-ray diffraction studies on a Siemens SMART-CCD diffractometer at 298 K. Crystal data for **I**: triclinic, space group $P\bar{1}$ (no. 2), $a = 6.5668(3)$, $b = 9.1040(3)$, $c = 10.4715(4)$ Å, $\alpha = 86.35(1)$, $\beta = 85.34(1)$, $\gamma = 83.32(4)°$; $V = 618.8(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.184$ g cm^{-3}, and $\mu(Mo_{K\alpha}) = 3.928$ mm^{-1}. Crystal data for **II**: monoclinic, space group $P2_1/c$ (no. 14), $a = 8.4048(1)$, $b = 22.000(5)$, $c = 10.848(2)$ Å, $\beta = 95.97(1)°$; $V = 1995.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.709$ g cm^{-3}, and $\mu(Mo_{K\alpha}) = 7.201$ mm^{-1}. Crystal data for **III**: monoclinic, space group $C2/c$ (no. 15), $a = 14.6850(3)$, $b = 10.6696(3)$, $c = 10.1699(3)$ Å, $\beta = 90.12(1)°$; $V = 1593.4(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 3.067$ g cm^{-3}, and $\mu(Mo_{K\alpha}) = 9.993$ mm^{-1}. For **I**, a total of 2632 reflections were collected and merged to give 1754 unique reflections ($R_{int} = 0.02$) of which 1488 with $I > 2\sigma(I)$ were observed. For **II**, a total of 8348 reflections were collected and merged to give 2867 unique reflections ($R_{int} = 0.06$) of which 2393 with $I > 2\sigma(I)$ were observed. For **III**, a total of 3255 reflections were collected and merged to give 1145 unique reflections ($R_{int} = 0.04$) of which 993 with $I > 2\sigma(I)$ were observed. The structures were solved and refined using the SHELXTL-PLUS programs to obtain $R_1 = 0.04$, $wR_2 = 0.1$, and $S = 1.06$ for 190 parameters for **I**, $R_1 = 0.04$, $wR_2 = 0.09$, and $S = 1.07$ for 289 parameters for **II**, $R_1 = 0.03$, $wR_2 = 0.08$, and $S = 1.03$ for 121 parameters for **III**. The piperazine molecules within the channels in **III** were difficult to locate, and only a fragment of the molecule was observed. It is likely that the piperazine molecule decomposed during the preparation of the crystal. CCDC-172356 (**I**), -172357 (**II**), and -172358 (**III**) contain the supplementary crystallographic data 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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$[Zn_4(thf)_4(MeZn)_4(O_3SiR)_4]$ ($R = 2,6\text{-}iPr_2C_6H_3N(SiMe_3)$), A Compound Containing Trigonal-Planar, Tetrahedral, and Trigonal-Bipyramidal Metal Atoms: A New Route to Larger Aggregates[**]

Ganapathi Anantharaman, Herbert W. Roesky,[*] and Jörg Magull

Dedicated to Professor Dieter Fenske
on the occasion of his 60th birthday

Metallasiloxanes derived from Si–OH species have received considerable attention in recent years. A number of such compounds obtained starting from monosilanol, silanediol, silanetriol, disilanol, and trisilanol have been discussed in recent reviews.[1] These compounds can be used as precursors for metal silicates and mixed-metal oxide systems[2] as well as for models for heterogeneous silica-supported catalytic systems.[3] Recently, a zinc-containing zeolite (H-ZSM5) system has been reported that catalyzes aromatization reactions, dehydrochlorination and dehydrofluorination, and conversion of methyl iodide to hydrocarbons.[4] Metallasiloxanes are also important because of their ability to act as model compounds for complex zeolite systems.[5] In recent years we have synthesized a variety of metallasiloxane compounds starting from kinetically stable silanetriol ($2,6\text{-}iPr_2C_6H_3N(SiMe_3)Si(OH)_3$) that exhibits novel structural features.[6] We[7] and others[8] have also reported that the framework of aluminosiloxane and gallasiloxane compounds has similar structural features to naturally occurring mineral and zeolite systems.

A polyhedral zinc siloxane compound which was obtained by using dimethylzinc and trimethylsilanol has been reported by Schmidbaur et al.[9] More recently, dimeric, trimeric, and

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[*] H. W. Roesky, G. Anantharaman, J. Magull
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-393373
E-mail: hroesky@gwdg.de

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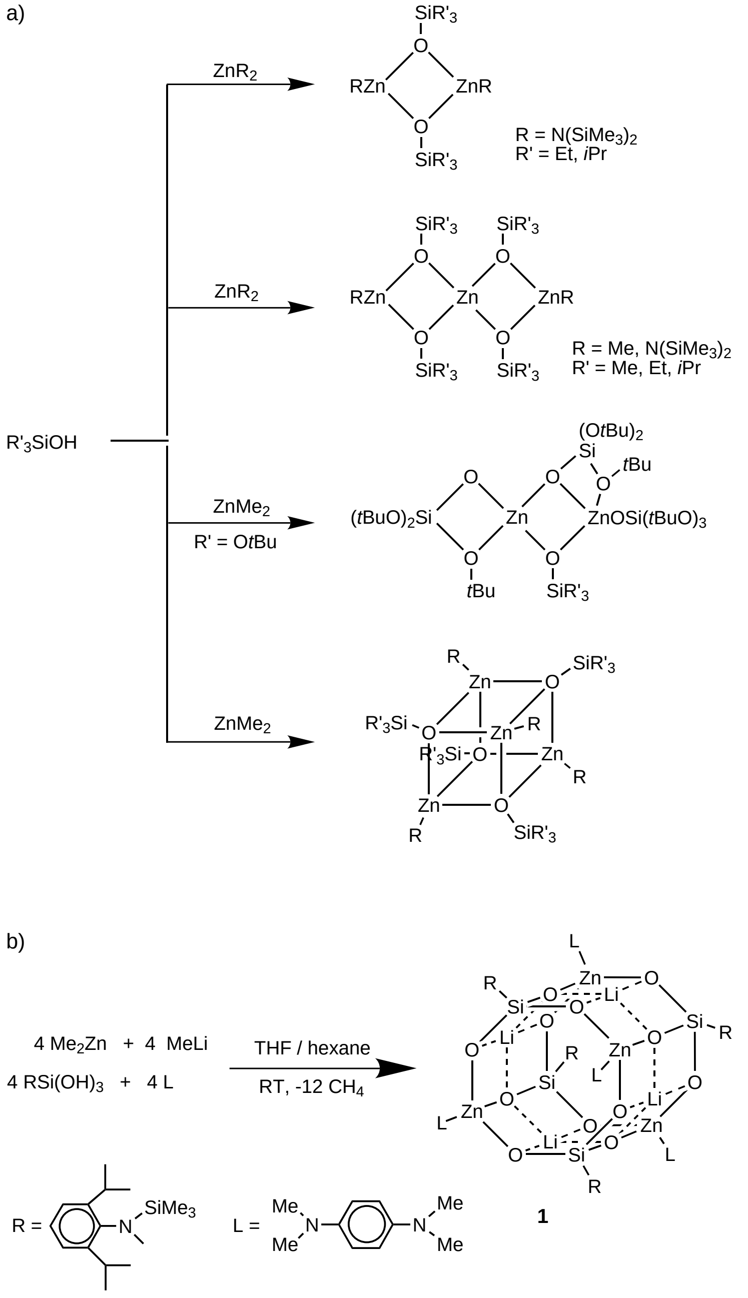
tetranuclear compounds of this kind have been prepared; the nature of the product being dependent on the molar ratio of the monosilanol to the alkylzinc or amidozinc compound (Scheme 1 a).[10] Recently, we have synthesized an oligomeric zinc siloxane **1** using dimethylzinc, methyllithium, and a silanetriol (Scheme 1 b).[11] The structure of the compound is similar to that of Group 13 siloxane compounds.[12]

We were interested in larger aggregates capable of mimicking condensation processes. Therefore we increased the molar ratio of dimethylzinc to the silanetriol with the aim of enhancing the solubility of the resultant product through the presence of more methyl groups on the surface, rather than through changing the substituent on zinc or silicon as has been done before.[9, 10] Indeed, following this procedure we have obtained a larger aggregate of the first octanuclear zinc siloxane compound that contains trigonal-planar, tetrahedral, and trigonal-bipyramidal zinc atoms.



Scheme 1. Synthesis of zinc siloxane using a) monosilanol b) silianetriol (**1**).

The addition of excess of Me$_2$Zn to RSi(OH)$_3$ (R = 2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)) (2:1) in THF/hexane at room temperature resulted in a vigorous exothermic reaction accompanied by methane gas evolution to afford [Zn$_4$(thf)$_4$(MeZn)$_4$(O$_3$SiR)$_4$] (R = 2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)) (**2**). Compound **2** has been characterized based on analytical, spectroscopic, and single-crystal X-ray diffraction studies.[13] The ^{1}H NMR spectrum (in C$_6$D$_6$) shows several multiple resonances due to the dynamic process and skeletal rearrangement of **2** in solution, indicating the absence of a similar structural arrangement in solution.

X-ray diffraction studies of **2** · 3 toluene reveal that its molecular structure is that of an asymmetric compound containing a Zn$_8$Si$_4$O$_{12}$ core (Figure 1). The arrangement of zinc and silicon atoms within the molecule **2** is shown in Figure 2. The imaginary lines drawn between zinc and silicon atoms show that four of the eight zinc atoms and the four silicon atoms in the core occupy the corners of a distorted cube alternatively, while the remaining four zinc atoms are positioned on the faces of the cube. The latter zinc atoms retain a methyl group, while the remaining atoms within the cube lose their alkyl substituents, and complete their coordination by accepting a molecule of THF.

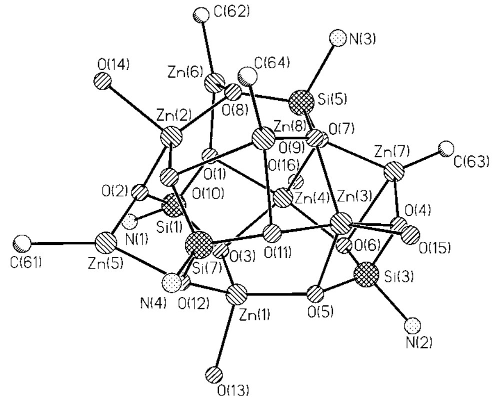


Figure 1. Structure of the central core of **2**. Selected bond lengths [Å]: Zn(8)-O(9) 1.979(2), Zn(8)-O(11) 2.091(3), Zn(8)-O(10) 2.352(3), Si(1)-O(1) 1.622(2), Si(1)-O(2) 1.630(1), Si(1)-O(3) 1.646(3), Zn(2)-Zn(5) 2.881(1), Zn(3)-Zn(8) 2.977(1), Zn(4)-Zn(7) 2.950(1), Zn(3)-Si(3) 2.723(1), Zn(4)-Si(1) 2.751(1), Zn(5)-Si(7) 2.825(1), Zn(7)-Si(3) 2.698(1), Zn(8)-Si(7) 2.746(1).

Interestingly, the zinc atoms in **2** reside in three different geometries in chemically diverse coordination environments.[10a, 14] Out of eight zinc atoms, two of them adopt trigonal-planar geometries (Zn(5) and Zn(6)), two are in trigonal-bipyramidal (Zn(3) and Zn(4)) environments, and the rest adopt tetrahedral geometries (Zn(1), Zn(2), Zn(7), and Zn(8)). Thus, four-, eight-, and ten-membered (Zn$_2$O$_2$, Zn$_4$O$_4$, and Zn$_5$O$_5$) Zn–O rings are formed.

Selected bond lengths and bond angles of **2** are given in the legend of Figure 1. The Zn ··· Zn distance (Zn(2)-Zn(5) 2.881(1), Zn(3)-Zn(8) 2.977(1), Zn(4)-

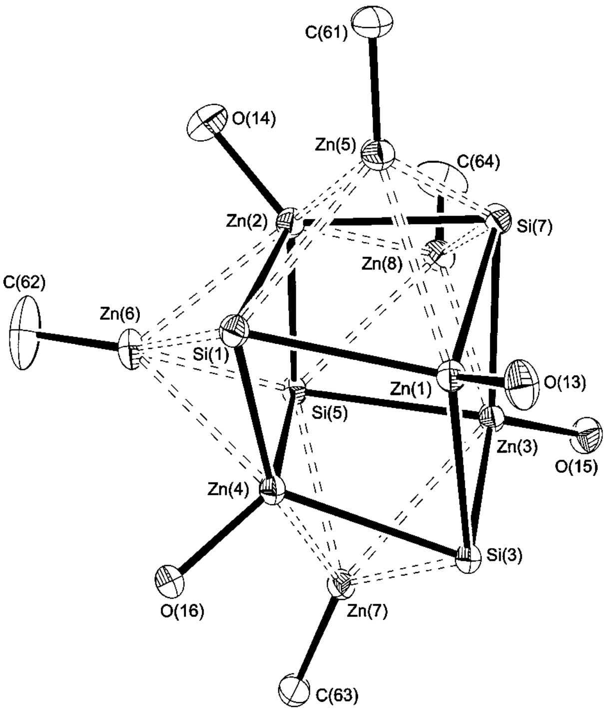


Figure 2. The arrangement of zinc and silicon atoms in the molecular structure of **2**. Imaginary lines are drawn between zinc and silicon atoms. Carbon, hydrogen, nitrogen, and oxygen atoms have been omitted for clarity (except for a few carbon and oxygen atoms around zinc).

Zn(7) 2.950(1) Å) indicates a weak M–M interaction.[15] Similarly, the average Zn ⋯ Si distance is 2.748(1) Å, and we suggest that there may be an interaction between these atoms given that the Zn–Si single bond length in $[Zn\{Si(SiMe_3)_3\}_2]$ is 2.342 Å.[16] The average Zn–C and Si–O bond lengths (1.948(4) and 1.635(3) Å, respectively) lie in the expected range.[9, 10] In addition, there are two unusually long Zn–O bond lengths observed for the two tetrahedral zinc atoms (Zn(7)–O(6) 2.317(3), Zn(8)–O(10) 2.352(3) Å) and the remaining Zn–O bond lengths fall in the range of 1.911(3)–2.203(3) Å.

In summary, by changing the reaction conditions we were able to obtain a larger aggregate of oligonuclear zinc siloxane **2**, which exhibits a novel structural feature namely, zinc atoms in a variety of geometries and coordination environments and a chelating and bridging mode of the siloxane moiety. Furthermore, the hydrolyzable functionalities in compound **2** make it a potential precursor for the preparation of new synthetic Zn-containing zeolites under mild conditions or by sol–gel procedures.

Experimental Section

2: A solution of Me_2Zn (4 mL of a 2 M solution in toluene, 8.00 mmol) was slowly added to a suspension of $RSi(OH)_3$ (1.07 g, 3.87 mmol) in THF/hexane (5 mL, 40 mL) at room temperature. After the evolution of methane gas ceased, the resulting solution was further stirred for 16 h at room temperature. The volatile components were removed and the residue was dried for 6 h under vacuum. The remaining solid was washed with THF/hexane (1/1) and finally recrystallized from toluene (5 mL) to yield colorless crystals of **2** at 0 °C (1.2 g, 64%). M.p. > 200 °C; ^1H NMR (500 MHz, C_6D_6): $\delta = -0.1$, 0.018, 0.037, 0.060, 0.093 (s, 12H; ZnMe), 0.39 (m, 36H; $SiMe_3$), 0.37 (m, 48H; $CH(CH_3)_2$), 1.55 (m, 16H; OCH_2CH_2), 3.70 (m, 16H; OCH_2), 3.81 (br, 8H; $CH(CH_3)_2$), 7.01 (m, 12H; aromat.); ^{29}Si NMR (99.36 MHz, C_6D_6): $\delta = 3.58$, 4.10 (s; $Si(CH_3)_3$), −60.87, −61.34(br; SiO_3).

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[13] Crystal data for compound $\mathbf{2}\cdot 3\,C_7H_8$: $C_{101}H_{172}N_4O_{16}Si_8Zn_8$, $M_r = 2446.11$, triclinic, space group $P\bar{1}$, $a = 14.5274(7)$, $b = 16.0523(10)$, $c = 27.4893(14)$ Å, $\alpha = 99.197(4)$, $\beta = 91.338(4)$, $\gamma = 112.005(4)^\circ$, $V = 5842.7(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.390\ mg\,m^{-3}$, $F(000) = 2572$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.904\ mm^{-1}$. Crystal size $0.2 \times 0.3 \times 0.3$ mm. The data were collected by using the ω scan mode in the range of $1.52 \le \theta \le 24.82$, $-17 \le h \le 17$, $-18 \le k \le 18$, $-32 \le l \le 32$. Of 39805 reflections collected, 17747 were unique. Final $R1$ ($I > 2\sigma(I)$) = 0.0393; $wR2$ (all data) = 0.0961. Maximum and minimum heights in the final Fourier difference map were 0.877 and −0.653 e Å^{-3}. The single crystals suitable for X-ray diffraction studies

of compound $\mathbf{2}\cdot 3\,C_7H_8$ were obtained from toluene at 0°C. Diffraction data were collected on a IPDS II Stoe image-plate diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELX-97)[17] and refined against F^2 on all data by full-matrix least-squares with SHELX-97.[18] 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-173318 contains the supplementary crystallographic data 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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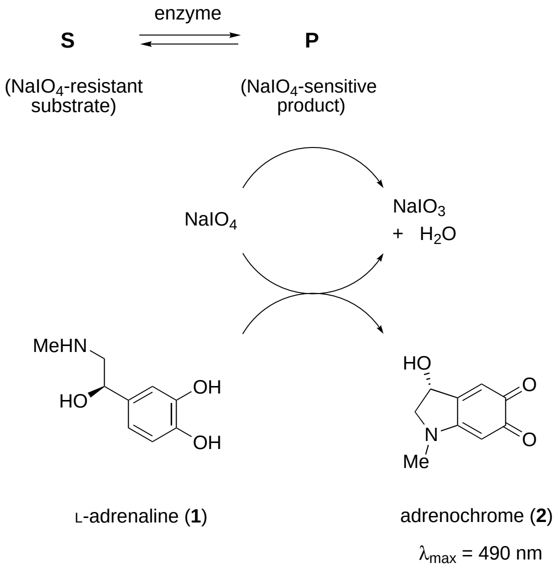
The Adrenaline Test for Enzymes**

Denis Wahler and Jean-Louis Reymond*

Enzyme assays[1] play a key role in the search for novel enzymes,[2] which are in great demand as components of consumer products, industrial processes, diagnostics, and analytical reagents.[3] While many enzyme assays are based on chromogenic or fluorogenic substrates, it is often desirable to have assays that produce a recordable signal indirectly and thus avoid the incorporation of a chromophore into the substrate itself. Such indirect assays are possible with sensors that either record changes in physicochemical parameters such as temperature,[4] pH,[5] or pM[6] upon reaction progress, or that respond by selective recognition of product over substrate through noncovalent interactions.[7, 8] The classical enzyme-coupled enzyme assays achieve the same goal through selective degradation of the reaction product by one or more secondary enzymes, most often by means of a redox chain that leads to the formation of NADH, which is analyzed spectrophotometrically at 340 nm.[9] Enzyme-coupled assays are, however, expensive and incompatible with varying technically important parameters such as cosolvents, pH, and temperature. Herein we report a colorimetric enzyme assay based on the quantification of periodate-sensitive reaction products by back-titration of the oxidant with adrenaline. The assay uses inexpensive, commercially available reagents, and offers a simple solution for assaying a variety of industrially important enzymes with their natural substrates.

We recently reported a series of enzyme substrates that released a colored or fluorescent product by oxidation of the primary enzyme reaction product by alcohol dehydrogenase[10] or sodium periodate.[11] Considering that sodium periodate reacts rapidly with any 1,2-diol or related periodate-sensitive functional groups independent of the presence of a chromophore in the molecule, we reasoned that this oxidant should also be applicable to nonchromogenic and nonfluorogenic substrates if used in a back-titration mode. Thus, any periodate-sensitive reaction product formed from a periodate-resistant substrate should be detectable by adding first a measured amount of sodium periodate, and second a chromogenic or fluorogenic reagent to quantitate the unreacted sodium periodate by optical density (OD) measurements (Scheme 1).



Scheme 1. Principle of the adrenaline test for enzymes.

Adrenaline (**1**) reacts within seconds with sodium periodate to form the red dye adrenochrome (**2**).[12] We have found that this reaction can be used to quantitate sodium periodate independent of the presence of proteins or cosolvents at any pH between 2 and 10 in aqueous buffers.[13] The reaction enabled us to measure various periodate-sensitive functional groups such as 1,2-diols, 1,2-aminoalcohols, 1,2-diamines and α-hydroxyketones by back-titration of sodium periodate (Figure 1).

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[*] Prof. Dr. J.-L. Reymond, Dr. D. Wahler
Department of Chemistry & Biochemistry
University of Bern
Freiestrasse 3, 3012 Bern (Switzerland)
Fax: (+41) 31-631-8057
E-mail: jean-louis.reymond@ioc.unibe.ch

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