Synthesis and Structural Characterization of $[Ph_2Si(OH)OSi(OH)Ph_2]_3\cdot(C_4H_4N_2)_2$. The First Crystallographic Evidence for Silanol–Amine Hydrogen Bonding and Its Implications for Organic–Sediment Interactions in Natural Waters

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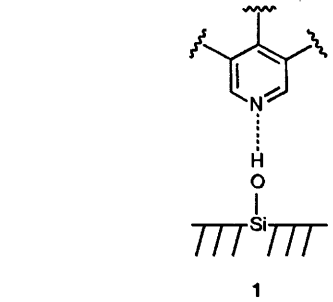
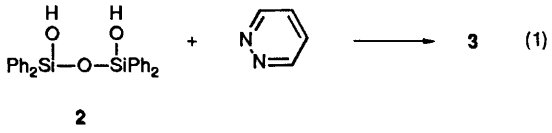
The novel 3 : 2 adduct, $[Ph_2Si(OH)OSi(OH)Ph_2]_3\cdot(C_4H_4N_2)_2$, is bonded *via* silanol–amine hydrogen bonds which have been structurally characterized for the first time; it also contains two distinct geometries for the disiloxane molecules.

There is currently considerable interest in the fate of nitrogen-containing organic bases in natural aquifers.[1-2] Recent sorption and IR spectroscopic studies have identified three types of surface species that form, one of which is the hydrogen-bonded adduct **1**.[2-5] As part of our continued interest in the use of organosilanols as models for surface silanols found in siliceous sediments, we present here the first crystallographic evidence for such hydrogen bonding between a silanol and an amine, namely that in the crystalline 3 : 2 adduct, **3**, formed from the 1,3-diol, $Ph_2Si(OH)$–O–$Si(OH)PH_2$, **2** (chosen as a model of adjacent surface sites) and pyridazine (see eqn. 1). The structure of **3**, as determined by single crystal X-ray diffraction, is shown in Fig. 1.† The phenyl rings have been omitted for clarity. The centrosymmetric adduct consists of three separate disiloxane molecules held together by a combination of intermolecular silanol–silanol and silanol–amine hydrogen bonds. The pertinent interactions are O(1)–O(3), 2.71(1), O(1)–N(1), 2.75(1), and O(5)–N(2), 2.75(2) Å. These are very similar to silanol–oxygen hydrogen bonds found in the $Ph_3SiOH\cdot$12-crown-4 complex, 2.76 Å and in the crystalline diols, *e.g.* $Ph_2Si(OH)OSi(OH)Ph_2$, or $(C_5Me_5)_2Si(OH)_2$.[6-8] The other bond lengths and angles are normal. An interesting feature in the structure of **3** is the different Si–O–Si angles in the disiloxane units. This angle varies greatly in disiloxanes, ranging from 147.6° in one of the three unique molecules in crystalline $Ph_2Si(OH)OSi(OH)Ph_2$ (the others being 156.8° and 161.9°), to 164.1° in $Pr^i_2Si(OH)$-$OSi(OH)Pr^i_2$, to 180.0° in $Ph_3SiOSiPh_3$ and $(PhCH_2)_3SiOSi$-$(CH_2Ph)_3$.[7,9-11] In **3** the central disiloxane angle is constrained by symmetry to be 180°. The remaining disiloxanes have an Si–O–Si angle of 144.5°. To our knowledge, this is the first example of a complex containing the same disiloxane moieties in such radically dissimilar geometries.

Though prepared in an aprotic solvent, **3** can be isolated unchanged after prolonged refluxing in a water–tetrahydrofuran (5 : 1) mixture. There was no evidence for proton transfer which would have resulted in the formation of an ammonium silanolate. The silanol–amine hydrogen bond is quite robust and should be considered a major factor in the immobilization of nitrogen heterocyclic species on siliceous sediment surfaces.



1



2 **3** (1)

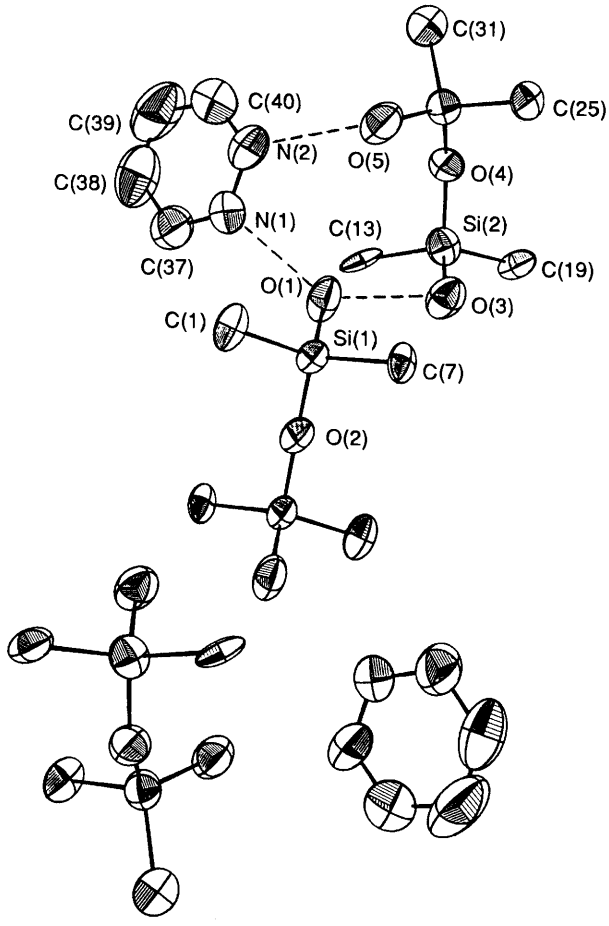


Fig. 1 Molecular structure of $[Ph_2Si(OH)OSi(OH)Ph_2]_3\cdot(C_4H_4N_2)_2$. The phenyl carbons have been omitted for clarity. Selected bond lengths (Å): Si(1)–O(1) 1.632(9); Si(1)–O(2) 1.601(4); Si(2)–O(3) 1.623(9); Si(2)–O(4) 1.647(8); Si(3)–O(4) 1.62(1); Si(3)–O(5) 1.62(1); Si(1)–C(1) 1.88(1); Si(1)–C(7) 1.86(1); Si(2)–C(13) 1.92(2); Si(2)–C(19) 1.83(1); Si(3)–C(25) 1.83(2); Si(3)–C(31) 1.83(1).

† *Crystal data* for $[Ph_2Si(OH)OSi(OH)Ph_2]_3\cdot(C_4H_4N_2)_2$: $C_{80}H_{74}O_9N_4Si_6$, M = 1402, triclinic, space group $P\bar{1}$, a = 9.740(7), b = 11.840(5), c = 17.387(9) Å, α = 93.73(2), β = 93.45(6), γ = 107.94(3)°, V = 1897.0 Å^3, Z = 1, D_c = 1.21 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares using 1378 reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer. Phenyl hydrogen atoms were calculated at idealized positions and added to the structure factor calculation but not refined owing to the paucity of observed data (N_{obs}/N_{var} = 3.05). The final residuals were R = 0.060 and R_w = 0.066. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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