

The X-ray structure of a protonated hypervalent silanol

Alan R. Bassindale,^{*a} David J. Parker,^a Peter G. Taylor,^{*a} Norbert Auner^{*b} and Bernhard Herrschaft^b

^a The Chemistry Department, The Open University, Walton Hall, Milton Keynes, Buckinghamshire, UK MK7 6AA.
E-mail: P.G.Taylor@open.ac.uk

^b Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, Marie-Curie Str. 11, 60439 Frankfurt am Main, Germany

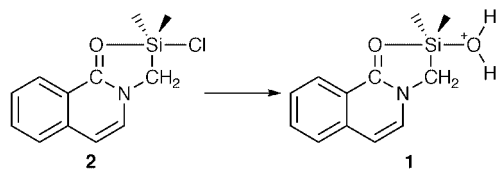
Received (in Basel, Switzerland) 29th November 1999, Accepted 23rd February 2000

Published on the Web 17th March 2000

Careful hydrolysis of a pentacoordinate chlorosilane gives a pentacoordinate protonated silanol that resembles the intermediate in the aqueous hydrolysis of silanes.

One of the key areas of organosilicon chemistry is the study of the mechanism of nucleophilic substitution and in particular the mechanism of hydrolysis of chlorosilanes.¹ Application of crystal structure correlation has shown that formation of the nucleophile–silicon bond is accompanied by lengthening of the silicon-leaving group bond and formation of a trigonal bipyramidal structure with the non-participating groups equatorial.² Many model pentacoordinate silicon species have now been prepared and characterised using X-ray crystallography.^{1c,3} Although a range of ligands have been used to form hypervalent silicon species, we are unaware of any that contain a water molecule as a coordinating ligand. Such elusive species are highly desirable since they mimic the intermediate and/or activated complex for the hydrolysis of silanes.

Here we report the preparation and characterisation of a protonated hypervalent silanol, **1**. Careful hydrolysis of the quinoline derivative **2**⁴ in acetonitrile followed by slow, partial evaporation of the solvent led to colourless, needle-like crystals of **1** (Scheme 1).



Scheme 1

The crystal structure (Fig. 1) shows that there is chloride in the crystal, but it is not bonded directly to the silicon.⁵ The

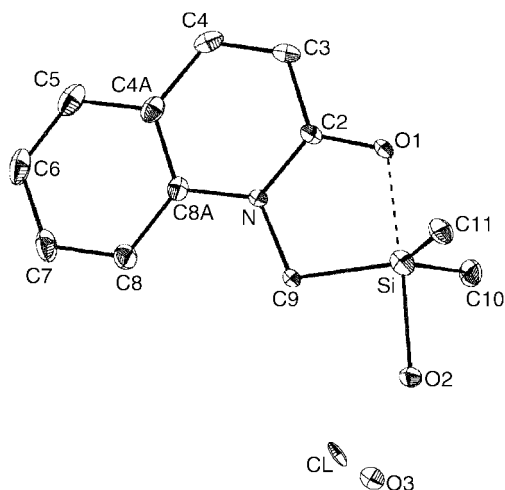
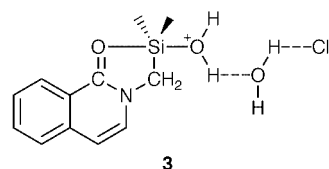


Fig. 1 Structure of **1** in the crystal. Selected bond distances (Å) and bond angles (°): Si–O1 1.9604(14), Si–O2 1.9114(14), Si–C9 1.8726(19), Si–C10 1.856(2), Si–C11 1.867(2), O1–Si–O2 174.62(7), N–C9–Si 106.54(13), O1–Si–C9 86.53(8), O2–Si–C9 88.14(8), C9–Si–C10 118.62(10), C9–Si–C11 119.43(10), C10–Si–C11 121.85(9).

closest contact between the silicon and the chlorine atoms is 4.39 Å. By comparison, a typical Si–Cl bond distance is 2.03 Å and the sum of the van der Waals radii for Si and Cl is 3.85 Å. The Si–O bond length corresponding to the protonated silanol is 1.9114(14) Å. An additional oxygen atom (O3) is also present in the unit cell. The closest silicon atom to O3 is 3.97 Å away while a typical Si–O distance is 1.63 Å⁶ and the sum of the van der Waals radii for Si and O is 3.62 Å.

The X-ray analysis revealed the positions of all the hydrogen atoms which show that O2 is part of a water molecule which is bonded to the silicon. This water molecule is hydrogen bonded to a second water molecule containing O3, which in turn is hydrogen bonded to a chloride ion, as shown in **3**. The other



alternative involving a molecule of hydrogen chloride hydrogen bonded to a water molecule which in turn is hydrogen bonded to a hypervalent silanol is ruled out by the bond distances. The covalent O–H bond distances in **3** are between 0.82 and 0.99 Å, and the O···H hydrogen bond distances are between 2.6 and 3.1 Å.

Solid state silanol structures which do not involve any hydrogen bonding are known but are comparatively rare.⁷ Thus, intermolecular hydrogen bonding in silanols has been extensively studied and shown to take many forms.⁸ For example, diisopropylsilanediol,⁹ exists as hydrogen bonded dimers which are linked together in ladder chains by further hydrogen bonds, and tris(trimethylsilyl)silylsilanetriol¹⁰ forms hexameric cages of hydrogen bonds. As expected, there is extensive intermolecular hydrogen bonding throughout the crystal of **1**. Each of the hydrogen atoms associated with the two water molecules are involved in hydrogen bonding and each chlorine is hydrogen bonded to three hydrogens, as shown in Fig. 2. Effectively there are ladders of hydrogen bonding running through the structures.

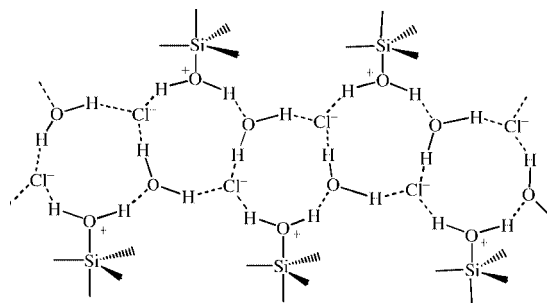


Fig. 2 The arrangement of hydrogen bonding within a crystal of **1**.

These are made of puckered, fused 10-membered rings with hydrogen atoms in alternate positions. The chains extend indefinitely in parallel along the y -axis repeating every 7.22 Å. Along the z axis the chains stack one above the other in an 'AB' fashion, repeating every 21.45 Å. In the x direction the chains stack side by side in a repeating 'AA' manner every 9.13 Å. Hydrogen bonding is confined to within a chain.

The Si–O2 distance observed, [1.9114(14) Å] is, as expected, somewhat longer than that for a traditional Si–O bond. Reed and coworkers have recently reported the crystal structure of a protonated tetracoordinated silanol complex, [Bu^t₃Si(OH₂)]⁺[Br₆CB₁₁H₆]^{−11}. The Si–O distance in this compound is 1.78 Å, which is longer than that of a standard Si–O bond, reflecting the fact that the silanol is protonated. The Si–O2 bond distance in the hypervalent species **1** is greater than that observed for the protonated silanol as a result of the axial bond length distortion that is expected in five-coordinate silicon complexes.²

The Si–O1 bond distance in **1** is 1.9604(14) Å, similar to that for Si–O2. This suggests that the structure resembles a point on the reaction profile where the extent of bond formation is equivalent to that of bond breaking. In the absence of ring strain the structure should be perfectly trigonal bipyramidal. This is confirmed by the fact that the three equatorial substituents and the silicon atom effectively all lie in the same plane. The sum of the three C_{eq}–Si–C_{eq} bond angles, 359.9°, is very close to the 360° expected. The sum of the C–Si–C bond angles in Reed's protonated silanol was 348°, that is, significantly distorted from a trigonal bipyramidal structure and moving towards a tetrahedral species. The larger value observed by Reed and coworkers suggests that the protonated silanol has some characteristics reminiscent of a silyl cation complexed by a water molecule.¹² In this context **1** has some of the features of a silyl cation complexed by two oxygen atoms, but is better described as a covalently bonded trigonal bipyramidal molecule.

Macharashvili and coworkers have used a series of penta-coordinate silicon species involving amide ligands to map nucleophilic substitution at silicon.^{2b} The maximum extent of pentacoordination was observed for the chloride derivative where the carbonyl oxygen–silicon bond distance was ca. 1.95 Å. This is very close to the Si–O1 bond distance in **1**, confirming that maximum pentacoordination is achieved with two equivalent axial Si–O bond distances.

We thank the EPSRC for financial support for D. J. P.

Notes and references

- (a) A. R. Bassindale, S. J. Glynn and P. G. Taylor, in *The Chemistry of Organosilicon compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, ch 9, pp. 495–511; (b) R. R. Holmes, *Chem. Rev.*, 1990, **90**, 17; (c) C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371.
- (a) M. J. Barrow, E. A. V. Ebsworth and M. M. Harding, *J. Chem. Soc., Dalton Trans.*, 1980, 1838; (b) A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, G. I. Oleneva, E. P. Kramarova, A. G. Shipov and Yu. I. Baukov, *J. Chem. Soc., Chem. Commun.*, 1988, 683; (c) V. F. Sidorkin, V. V. Vladimirov, M. G. Voronkov and V. A. Pestunovich, *J. Mol. Struct. (Theochem)*, 1991, **228**, 1; (d) Yu. E. Ovchinnikov, A. A. Macharashvili, Yu. T. Struchkov, A. G. Shipov and Yu. I. Baukov, *J. Struct. Chem.*, 1994, **35**, 91.
- (a) D. Kost and I. Kalikhman, in *The Chemistry of Organosilicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, ch. 23, pp. 1339–1446; (b) R. R. Holmes, *Chem. Rev.*, 1996, **96**, 927.
- A. R. Bassindale, M. Borbaruah, S. J. Glynn, D. J. Parker and P. G. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2099.
- Crystallographic data* for **1**·H₂O·HCl: colourless, dimensions 0.154 × 0.154 × 0.924 mm, monoclinic, space group, *P*2₁/*c* (no 14), *Z* = 4, *a* = 9.126(2), *b* = 7.223(1), *c* = 21.450(4) Å, *V* = 1413.4(5) Å³, *d* = 1.353 g cm^{−3}; Mo–Kα radiation (*λ* = 0.71073 Å); 9552 total data, 2763 [*F* > 4σ(*F*)] observed independent reflections with 2.2 < *θ* < 26.8° collected: *R* = 0.0763, *wR*₂ = 0.2336. CCDC 182/1555. See <http://www.rsc.org/suppdata/cc/a9/a909504g/> for crystallographic files in .cif format.
- B. Csakvari, Z. Wagner, P. Gomory, I. Hargitta, B. Rozsonda and F. C. Mulhoff, *Acta. Chim. Acad. Sci. Hung.*, 1976, **90**, 149.
- R. D. Brost, G. C. Bruce and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1986, 1580.
- P. D. Lickiss, *Adv. Inorg. Chem.*, 1995, **42**, 147.
- A. H. Buttrus, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1986, **302**, 159.
- S. S. Al-Juaid, A. H. Buttrus, R. I. Damja, Y. Derouiche, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1989, **371**, 287.
- Z. Xie, R. Bau and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, 1994, 2519.
- L. Olsson, C.-H. Otosson and D. Cremer, *J. Am. Chem. Soc.*, 1995, **117**, 7460; M. Arshadi, D. Johnd, U. Edlund, C.-H. Otosson and D. Cremer, *J. Am. Chem. Soc.*, 1996, **118**, 512.

Communication a909504g