Synthesis and Structural Characterization of $(Ph_3SiOH)_2$·12-c-4. A Model for Chemistry occurring at the Sediment–Water Interface in Natural Waters

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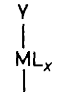
The first hydrogen bonded adduct formed from an organosilanol and a crown ether has been synthesized, structurally characterized, and compared to species found in natural aquatic systems.

The presence of complexing ligands in natural waters radically affects the adsorption of trace metals on hydrous oxides or clay particles.[1] Since the transport and eventual removal of metals are often governed by their association with such mineral particulates, an understanding of the chemistry occurring at the sediment–water interface is important. The work described herein is a model for one possible type of surface interaction and details the first hydrogen bonded adduct formed between a silanol and a donor ligand to be prepared and structurally characterized.

The elegant work by Stumm has led to the postulated existence of two types of complexes for describing the inter-relationships between a surface hydroxy group, a ligand, and a metal.[2] The types of complex differ from one another in whether the metal (Type A) or ligand (Type B) is directly adsorbed on the surface. It is difficult to study these systems directly.[3] We have therefore begun a program to structurally characterize model systems which may be of relevance to the situation found in natural waters.

A hydrogen bonded adduct formed between a surface hydroxy group and an organic donor ligand can be considered a necessary step in forming Type B complexes. If the mineral particle is siliceous in nature, then the active site would be a surface silanol. However, this type of bonding mode for silanols, until now, has not been structurally confirmed. We report the preparation and structure of the 2:1 hydrogen bonded adduct $(Ph_3SiOH)_2$·12-c-4. Triphenylsilanol reacts with 12-c-4 in hot toluene to produce large air stable crystals of the 2:1 adduct. The structure of the molecule is shown in Figure 1.[†] The molecule lies over a centre of symmetry constraining the crown oxygens to be coplanar. The adduct is held together *via* two strong hydrogen bonds. The hydrogen bonding interactions are O(1)–O(2) 2.76 and H(10)–O(2) 1.91 Å. The Si–O and Si–Ph bonds are normal.[4] The crown ether adopts an unusual chair configuration. This geometry is also displayed by the adduct $(AlMe_3)_2$·12-c-4.[5]



Type A

Type B

Crown ethers have been extensively used to complex metal ions but their role as ligands in neutral adducts is less

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[†] *Crystal data* for $(Ph_3SiOH)_2$·12-c-4: $C_{44}H_{48}O_6Si_2$, $M = 728$, triclinic, space group $P\bar{1}$, $a = 8.628(5)$, $b = 10.628(9)$, $c = 11.795(9)$ Å, $\alpha = 82.31(8)$, $\beta = 87.04(9)$, $\gamma = 67.19(7)°$, $U = 988.1$ Å^3, $Z = 1$, $D_c = 1.22$ g cm^{-3}. The structure was solved by direct methods and refined by full matrix least squares using 2469 reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer. Hydrogen atoms were calculated at idealized positions and added to the structure factor calculations but their positions were not refined. The final residuals were $R = 0.044$ and $R_w = 0.056$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

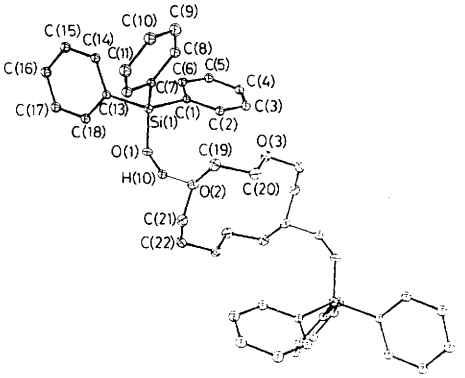

Figure 1. Molecular structure of $(Ph_3SiOH)_2\cdot$12-c-4. Selected bond lengths (Å): Si(1)–C(1) 1.865(3), Si(1)–C(7) 1.855(2), Si(1)–C(13) 1.858(2), Si(1)–O(1) 1.632(2), H(10)–O(2) 1.91(2).

common.[6—10] This is especially true for 12-c-4. $(Ph_3SiOH)_2\cdot$12-c-4 represents only the second such adduct to be structurally characterized. It is also the first example to incorporate silanol hydrogen bonding. The compound is insoluble in water but, when slurried, shows no decomposition at 25 °C and pH 7.

The vast majority of organic material present in natural waters contain either oxygen or nitrogen donor sites. The existence of $(Ph_3SiOH)_2\cdot$12-c-4 is an important contribution to the understanding of how these potential ligands interact with mineral matter.

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