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Short communication

Unprecedented self-assembled cyclic hexamer of ferrocenyldimethylsilanol, $[FcSiMe_2OH]_6$ (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$)[†‡]

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Ferrocenyldimethylsilanol, $FcSiMe_2OH$, Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, features a self-assembled (through intermolecular hydrogen bonding) cyclohexameric supermolecule with a chair conformation. Copyright © 2005 John Wiley & Sons, Ltd.

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Eaborn and coworkers extensively studied hydrogen bonding in organosilanols[1–7] and, depending upon the nature and number of organic substituents and hydroxyl groups around silicon, many intriguing supramolecular architectures have been discovered.[8–11] To date, however, the number of monosilanols, $R_nR'_{3-n}SiOH$ investigated by single-crystal X-ray diffraction, compared with silanediols ($RR'Si(OH)_2$), silanetriols ($RSi(OH)_3$) and disiloxanediols ($HOR_2SiOSiR_2OH$), is relatively small.[8–11] Thus, only cyclotetrameric monosilanols, $R_3Si(OH)_4$, have been reported, e.g. $[Ph_3Si(OH)]_4$,[12] $[{}^tBu_2SiF(OH)]_4$,[4] and $[{}^tBu_2SiH(OH)]_4$.[13] Similarly, relatively few metalla- and ferrocenyl-silanols have been characterized by single-crystal X-ray diffraction.[14–19]

On the other hand, the structure of water, a subject of considerable current interest with important implications in physics, chemistry and biology, has provided many examples of oligomeric self-association through hydrogen bonds into various supermolecular clusters $(H_2O)_n$. The hexamer $(H_2O)_6$ is one of the most attractive species, especially after the report of its formation in liquid helium, as 'the smallest piece of ice'.[20] Ring, cage, book, bag, prism and other conformations have been suggested,[21,22] and numerous theoretical calculations[23] were performed to model their structures and to estimate their relative energies. Theoretical calculations suggest that the cage form of the $(H_2O)_6$ hexamer has a slightly lower energy than the cyclic hexamer and is relatively more stable.[24–26]

Spectroscopic and other experimental studies have been reported in support of the hexameric $(H_2O)_6$ supermolecules,[27,28] but single-crystal X-ray analysis is limited. The $(H_2O)_6$ hexamers have been found in the crystal structure of the host–guest complex of water with 2,4-dimethyl-5-aminobenzo[*b*]-1,8-naphthyridine (associated in extended tapes).[29] In the crystal structure of $[NH_4]_6[Mo_4Se_4(CN)_{12}]\cdot 6H_2O$, related six-membered cyclic cations $[\{(NH_4)(H_2O)\}_3]^{3+}$ of alternating ammonium ions and water molecules, assembled through $N{-}H\cdots O$ hydrogen bonds, have been discovered.[30]

Alcohols have also been suggested to be associated into hydrogen-bonded cyclic clusters $(ROH)_n$ ($n = 2\text{–}6$).[31,32] Again, the X-ray analysis is limited to the crystal structures of trimeric 2-methyl-1,1-diphenylpropan-1-ol, tetrameric diphenyl(2-thienyl)methanol, or hexameric bis(pentafluorophenyl)methanol.[33] A hexameric cluster in the liquid state of *tert*-butyl alcohol was recently reported using X-ray data.[34]

We now report the single-crystal X-ray structure of ferrocenyldimethylsilanol illustrating a hexacyclomeric assembly, $[FcSiMe_2(OH)]_6$, Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$. The structure contains a 12-membered cyclic core $(OH)_6$, formed through intermolecular hydrogen bonding self-assembly. The ferrocenyldimethylsilanol was obtained from the hydrolysis of $FcSiMe_2Cl$ and was recrystallized from hexanes.[35] The

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[†] Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

[‡] With respect to the work of Colin Eaborn from Keith Pannell, University of Sussex, 1969–1970.

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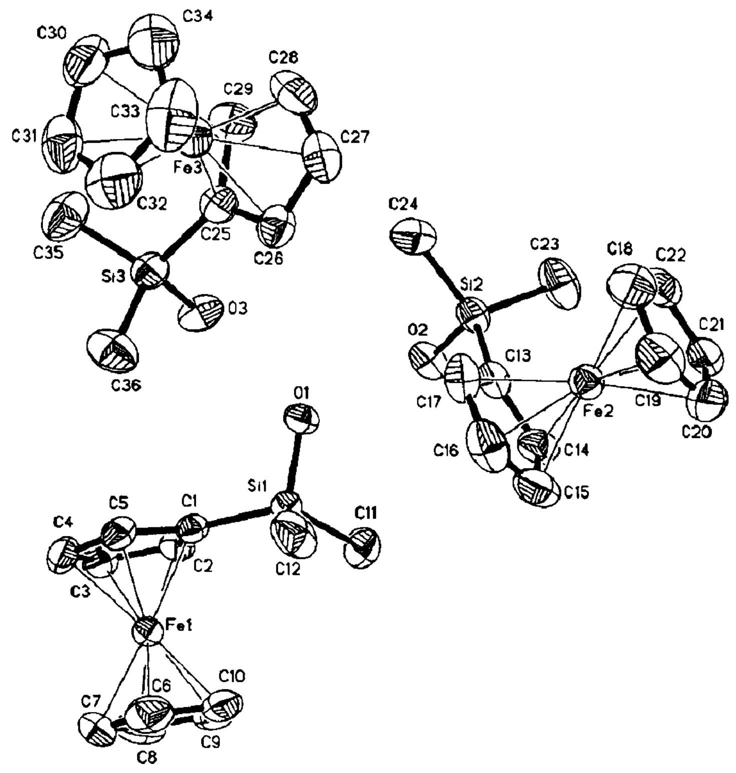

Figure 1. Molecular structure of the three independent molecules of $FcSiMe_2OH$; hydrogen atoms omitted for clarity. Selected geometric parameters: Si1–O1 1.639(2), Si2–O2 1.652(2), Si3–O3 1.639(2) Å; O1–Si1–C1 109.5(1), O1–Si1–C11 104.1(2), O1–Si1–C12 109.2(2), C11–Si1–C12 112.6(2), O2–Si2–C13 106.9(1), O2–Si2–C23 104.9(2), O2–Si2–C24 110.4(2), C23–Si2–C24 112.2(2), O3–Si3–C25 109.4(1), O(3)–Si3–C35 109.4(2), O3–Si3–C36 105.6(2), C35–Si3–C36 111.7(2)°.

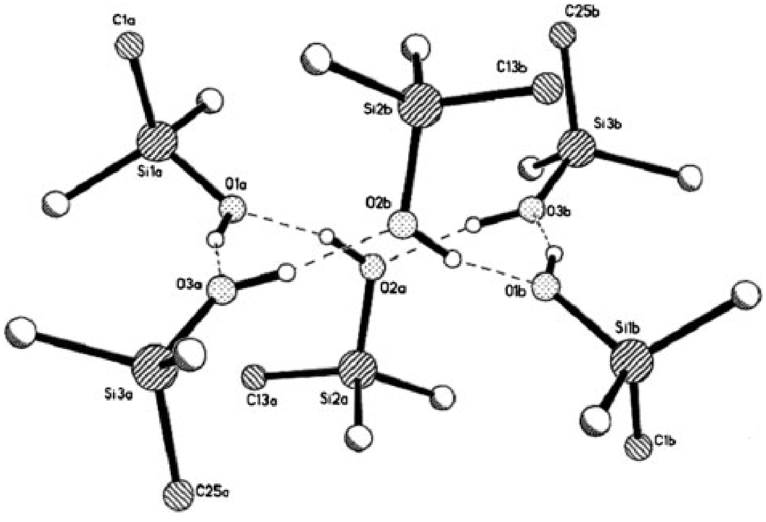

Figure 2. Self-assembled hexameric structure of $FcSiMe_2OH$; hydrogen-bonded arrangement with CH and Fe atoms omitted. Hydrogen bond interactions: O1–H1···O3 1.81 Å; O1···O3 2.709(4) Å and angle at hydrogen 160°; O2–H···O1 1.76 Å, O2···O1 2.718(4) Å, angle at hydrogen 164°; and O3–H···$O2^i$ 1.73 Å, O3···$O2^i$ 2.666(4) Å and angle at hydrogen 165° for $i = 1 - x, 1 - y, 1 - z$.

hexacyclomer contains three independent molecules in the asymmetric unit, illustrated in Fig. 1. The geometric parameters of each molecule are unremarkable, but some distortions at silicon are evident; see caption to Fig. 1. The independent molecules associate about a centre of inversion to form a cyclohexameric ring mediated by hydrogen bonds.

Crystallographic data: $C_{12}H_{16}FeOSi$, $M = 260.2$, triclinic, $P\bar{1}$, $a = 12.712(4)$, $b = 12.784(5)$, $c = 14.256(6)$ Å, $\alpha = 74.83(3)$, $\beta = 67.49(3)$, $\gamma = 62.97(2)^\circ$, $Z = 6$; $V = 1895.6(12)$ Å^3, Nicolet R3m/V diffractometer, 4873 independent reflections ($\theta_{max} = 22.5^\circ$), $R = 0.032$ (4228 reflections with $I > 2\sigma(I)$), $wR = 0.091$ (all data). Programs used: SHELXTL PLUS, ORTEP. CCDC deposition number: 249300.

The conformation of the $(OH)_6$ core is illustrated in Fig. 2. A chair conformation of the ring is determined by the positions of the six oxygen atoms, which occupy the corners of a non-planar six-membered ring and are connected through hydrogen bonds; see Fig. 2 caption for parameters. These O$\cdots$O contact distances are in the range calculated by *ab initio* methods for cyclic $(H_2O)_{4-6}$ clusters, i.e. 2.74–2.71 Å[23] and the O–H$\cdots$O distances are also comparable to the values found in $(H_2O)_6$ (2.71–2.83 Å).[27,28]

The conformation of the $(OH)_6$ cyclic core in $[FcSiMe_2OH]_6$ is similar to that found in other $(ROH)_6$ hexamers (R = H or organic group) cited above. In all crystallographically characterized hexamers, the $(ROH)_6$ supermolecules formed through hydrogen bonds have chair conformations, regardless of the nature of R.

The data reported herein suggest that a range of cyclic structures with different conformations of the self-assembled aggregates is possible for the monosilanols, $R_nR'_{3-n}SiOH$. Further studies should give insight into the factors that control the preference for dimeric, tetrameric or hexameric self-assembly, as the organic substituents at silicon are varied.

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APPENDIX

The synthesis and structure of an unusual hexameric alcohol, $[2,4,6\text{-}(CF_3)_3C_6H_2CH_2OH]_6$ has been reported since completion of this study: Edelamn FT, Poremba P, Bohnen FM, Herbst-Irmer R. *Z. Anorg. Allg. Chem.* 2004; **630**: 1671.