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Cubane-like structure of a silanethiol – primary amine assembly – a novel, unusual hydrogen bond pattern†

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A reaction of silanethiol and primary amine leads to a product whose crystals are built of well-defined supermolecules – assemblies of four ammonium silanethiolate units ($RS^{-}H_3N^{+}R'$)$_4$ with a novel, unusual 3D hydrogen bond pattern.

The recognition-controlled self-assembly of complementary molecules most frequently relies on such non-covalent interactions as hydrogen bonding.[1] As an example a recent preparation of a diamond-like network based on N–H···O hydrogen bonds may be given.[2] Sulfur is relatively common in biological systems and the N–H···S hydrogen bond is usually considered as having an influence on the properties of, for example, metal–sulfur proteins (see, for example, ref. 3). A hydrogen bond should also form when a thiol reacts with an amine. However, owing to the proton transfer from a thiol to the organic base, instead of common N–H···S we have N–H$^{(+)}\cdots$S$^{(-)}$ interactions. Since the hydrogen bond is electrostatic in nature, the ionic charge should strengthen the interaction and make the thiol–amine assembly stable enough to be isolated and characterized structurally. Surprisingly, a search of the Cambridge Structural Database[4] did not reveal any compound with a structure characterized by a thiol–amine-based hydrogen bond or anything that may be classified as a thiolate salt $RS^{(-)(+)}NH_nR_{4-n}$. The only comparable case was that of *o*-phenylenediammonium bis(hydrogensulfide).[5] This contrasts with the frequent usage of thiol–amine mixtures as sources of thiolate anions. Dance, for example, used a crystalline product obtained by mixing $(Hex^c)_2NH$ and PhSH in acetonitrile as a source of thiophenolate anion.[6] We prepared monocrystals of this compound and determined its crystal and molecular structure[7] – the two ionic fragments are linked together in long zigzag chains by ···N–H···S··· hydrogen bonds, motif $C_2^1(4)$ according to the graph set nomenclature.[8] To the best of our knowledge these structural data were the first reported for ammonium thiolate. It seems that despite the role of the N–H···S hydrogen bond in biological systems (albeit recently questioned[9]) this research area remains somewhat neglected and almost nothing is known about structures of simple ammonium thiolates.

The main objective of our research is the investigation of silicon–sulfur compounds with particular interest devoted to silanethiols, especially those of a general formula $(RO)_3SiSH$. (See, for example, ref. 10 and papers cited therein.) Unlike thiols, silanethiols easily hydrolyse with elimination of hydrogen sulfide. The only exception is $(Bu^tO)_3SiSH$.[11] Its Brønsted acidity is higher than that of thiols and with a pK_a of *ca.* 5–7, comparable to that of carboxylic acids.[12] Silanethiols react with amines and we were able to isolate crystalline products.[13] We would now like to present the structures of three compounds (**1**–**3**), obtained in a reaction of silanethiols – $(Pr^iO)_3$ [14] and $(Bu^tO)_3SiSH$ [13,15] – with primary amines – *tert*-butylamine[16] and 3-methylbutylamine:

$(Bu^tO)_3SiS^{-}\,{}^{+}H_3NBu^t$ (**1**),
$(Pr^iO)_3SiS^{-}\,{}^{+}H_3NBu^t$ (**2**), and
$[(Bu^tO)_3SiS^{-}\,{}^{+}H_3N(CH_2)_2CH(Me)_2]_4$·toluene (solvate) (**3**).

At room temperature the compounds **1**–**3** exposed to laboratory air are not stable and decompose after a few hours. Therefore their crystal and molecular structures were determined at 200 K.

The structures of all three compounds are similar. The crystals are built of well-defined supermolecules – assemblies of four ammonium silanethiolate units. In any supermolecule, S atoms of silanethiolate anions and N atoms of ammonium cations are arranged in space in a form of mutually interpenetrating, more or less distorted, tetrahedra. Taken together they form a distorted cube where twelve N–H···S hydrogen bonds connecting both tetrahedra may be regarded as the edges of the cube. The geometry of (N–H···S)$_4$ kernels prompted us to name the assembly as 'cubane-like'. Fig. 1 shows one supermolecule of $[(Pr^iO)_3SiSNH_3Bu^t]_4$ (**2**).

From a chemical point of view the assembly is built of ions primarily held by electrostatic forces. The separation of charges and thus the ionic nature of the both components may be presumed on the basis of the respective Si–S bond lengths – these of compound **3** are among the shortest ever found for silanethiolate derivatives, albeit still longer than 2.013 Å as observed for $Cl_3SiS^{(-)(+)}NEt_4$.[17] Since the ionic interactions are devoid of directionality, the form and shape of the tetrameric supermolecule depends upon the hydrogen bonds. How strong these bonds are is a matter of question. Neutral, bivalent sulfur, as discussed earlier,[9] is a weak acceptor, but the case of the thiolate anion is different. Indeed, the inspection of data presented in the ESI† as Table 1 show that the majority of S···H distances are within *ca.* 2.3–2.5 Å limits, significantly less than 2.7–2.8 Å reported for neutral, divalent sulfur.[9] The same tendency holds for N···S distances: 3.15–3.35 Å *vs.* 3.55–3.60 Å as given in ref. 9. The S···H and N···S distances in **1**–**3** are, however, similar to those found in $PhS^{(-)(+)}NH_2(Hex^c)_2$ [7] and some amine complexes of trimercaptotriazine,[18] and according to the literature data coincide with fairly strong to medium hydrogen bonds.[19] Here we would like to point out the rather exceptional property: in compounds **1**–**3** each sulfur accepts not one or two but three hydrogen bonds.

Compounds **1**–**3** have their 'cubane-like' supermolecules constructed similarly but there are also some differences, schematically depicted in Fig. 2. Those between **1** and **2** are rather subtle – greater

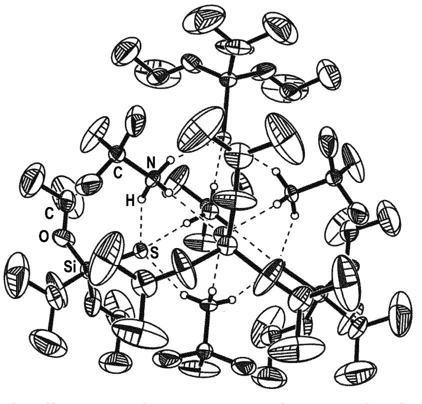

Fig. 1 Ortep plot illustrating the geometry and supramolecular structure of cubic **2**. For clarity, all H atoms, except N–H, have been omitted. Hydrogen bonds are shown as broken lines. Thermal ellipsoids 30%.

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† Electronic supplementary information (ESI) available: experimental details, table with data of hydrogen bonds, Ortep plots in colour of **1**, **2** and **3**. See http://www.rsc.org/suppdata/cc/b3/b313576d/

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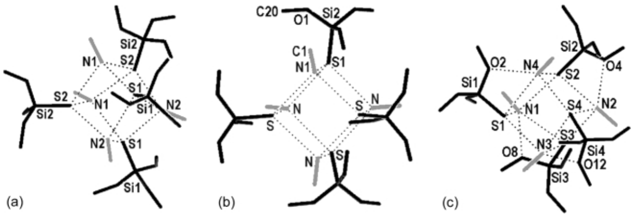

Fig. 2 Tetrameric entities of (a) **1** Si1–S1 2.0617(11), Si2–S2 2.0582(13) Å, (b) **2** Si1–S1 2.062(3) Å, and (c) **3** Si1–S1 2.0368(13), Si2–S2 2.0371(13), Si3–S3 2.0481(14) and Si4–S4 2.0370(15) Å. Hydrogen bonds (broken lines) join the four pairs of ions. For **3** also the additional N–H···O hydrogen bonds are shown. For clarity of the picture all H atoms are omitted, alkyl groups R in $(RO)_3SiS^-$ anions are simplified to O-bonded tertiary or secondary carbon atoms, and instead of ammonium ions only N–C fragments (gray colour) are shown.

steric requirements of Bu^t *versus* Pr^i, which cannot be satisfied without some distortions of the whole assembly, are probably at the origin of the lower symmetry of **1**. Although the same may be assumed also for **3**, the presence of N–H···O hydrogen bonds [Fig. 2(c)] has probably a much more profound effect. The existence of N–H···O hydrogen bonds may be confirmed by comparison of, for example, S–Si–O angles within each $(RO)_3Si$–S group. The angle based on the hydrogen bonded oxygen atom is of *ca.* 8° smaller than the two other S–Si–O angles. Thus, we have O1–Si1–S1 114.88(11)° and O3–Si1–S1 115.67(11)° but O2–Si1–S1 only 107.26(9)°. Also Si–O bonds with O2, O4, O8 and O12 [hydrogen bond acceptors – see Fig. 2(c)] are of *ca.* 0.02 Å longer than the other Si–O bonds within the same molecule. Of course, an additional hydrogen bond may be realized only when we admit bifurcation, *i.e.* acceptance of one hydrogen atom simultaneously by two acceptors. Compound **3** is the only one, which crystallizes as a solvate (one toluene molecule for one supermolecule of **3**). The toluene trapped within the structure does not seem to have any significant effect.

'Cubane-like' supermolecules of ammonium silanethiolates **1**–**3** have another interesting property: although their interior, *i.e.* the 'cube', constitutes the polar part of the supermolecule, owing to the extensive coverage by alkyl groups, the whole assembly appears from the exterior as completely hydrophobic. Indeed, despite salt-like character compound **1** is very well soluble in *n*-hexane. In fact the supermolecules of **1**–**3** may be regarded as 'reverse micelles'.

The structures of a silanethiol–primary amine assemblies found in solid **1**–**3** appear unique.‡ According to our knowledge this novel hydrogen bond pattern has no precedents in the chemical literature. For the moment this poses some nomenclature problems as it seems that graph set notation[8] used to conveniently describe the various hydrogen bonding patterns does not contain definitions easily applicable for the present case. We believe, however, that even without precise naming conventions the new hydrogen bond pattern should be of significant importance in biochemical research and present a new challenge for crystal engineers. The question, whether this 'cubane-like' structure can be realized by other hydrogen bond donor–acceptor systems is still open.

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Notes and references

‡ Crystal data for **1**: $C_{16}H_{39}NO_3SSi$, colourless plates, 0.5 × 0.4 × 0.2 mm, monoclinic, space group *C2/c*, $a = 27.786(6)$, $b = 13.892(3)$, $c = 26.858(5)$ Å, $\beta = 115.74(3)°$, $V = 9339(4)$ Å^3, $\rho_{calc.} = 1.006$ Mg m^{-3}, $2\theta_{max} = 50.16°$, MoKα = 0.71073 Å, $\omega - 2\theta$ scan mode; $T = 200.0(2)$ K, 14 148 measured and 7583 independent reflections, 4598 reflections with $I > 2\sigma(I)$, Lorentzian polarization,[20] absorption correction: none ($\mu = 0.20$ mm^{-1}, $T_{min} = 0.9066$, $T_{max} = 0.9611$ K) SHELX 97,[21] 445 parameters, refinement against $|F^2|$, $R = 0.0488$, $wR = 0.1090$ for $I > 2\sigma(I)$, $R = 0.1072$, $wR = 0.1307$ for all, residual electron density: peak 0.66, hole -0.51 e Å^{-3}. For **2**: $C_{13}H_{33}NO_3SSi$, colourless rods, 0.5 × 0.3 × 0.25 mm, cubic, space group $I\bar{4}3m$, $a = b = c = 15.974(2)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 4076.1(9)$ Å^3, $\rho_{calc.} = 1.015$ Mg m^{-3}, $2\theta_{max} = 55.08°$, MoKα = 0.71073 Å, $\omega - 2\theta$ scan mode; $T = 200.0(2)$ K, 531 measured and 531 independent reflections, 440 reflections with $I > 2\sigma(I)$, Lorentzian polarization,[20] absorption correction: none ($\mu = 0.22$ mm^{-1}, $T_{min} = 0.8973$, $T_{max} = 0.9467$ K), SHELX 97,[21] 41 parameters, refinement against $|F^2|$, $R = 0.0598$, $wR = 0.1673$ for $I > 2\sigma(I)$, $R = 0.0792$, $wR = 0.1791$ for all, residual electron density: peak 0.32, hole -0.20 e A^{-3}. For **3**: $C_{75}H_{172}N_4O_{12}S_4Si_4$, colourless plates, 0.5 × 0.4 × 0.2 mm, monoclinic, space group $P2_1/c$, $a = 21.709(4)$, $b = 15.326(3)$, $c = 30.588(6)$ Å, $\beta = 91.96(3)°$, $V = 10\,171(3)$ Å^3, $\rho_{calc.} = 1.021$ Mg m^{-3}, $2\theta_{max} = 49.99°$, MoKα = 0.71073 Å, $\omega - 2\theta$ scan mode; $T = 200.0(2)$ K, 21 140 measured and 21 140 independent reflections, 9864 reflections with $I > 2\sigma(I)$, Lorentzian polarization,[20] absorption correction: none ($\mu = 0.189$ mm^{-1}, $T_{min} = 0.9114$, $T_{max} = 0.9632$ K), SHELX 97,[21] 943 parameters, refinement against $|F^2|$, $R = 0.0566$, $wR = 0.1566$ for $I > 2\sigma(I)$, $R = 0.1984$, $wR = 0.2041$ for all, residual electron density: peak 0.58, hole -0.43 e A^{-3}.

All non-hydrogen atoms were refined anisotropically. H atoms bonded to C atoms were treated as riding, with isotropic displacement parameters proportional to relevant parameters of carbon atoms. For **1** and **2** nitrogen-bonded H atoms were located from Fourier maps and refined without constrains. In the case of **3**, ammonium H atoms were refined as riding, idealized tetrahedrally. CCDC 215024, 214671 and 215789. See http://www.rsc.org/suppdata/cc/b3/b313576d/ for crystallographic data in .cif or other electronic format.

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