A preorganised doubly tripodal hexathiol: syntheses and crystal structures of complexes with two 3 : 1 subsite-differentiated Fe_4S_4 clusters

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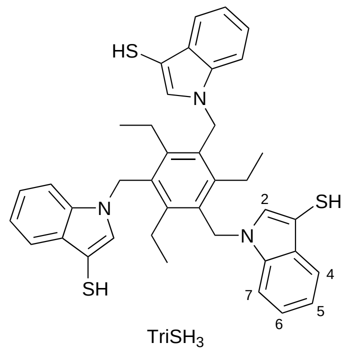
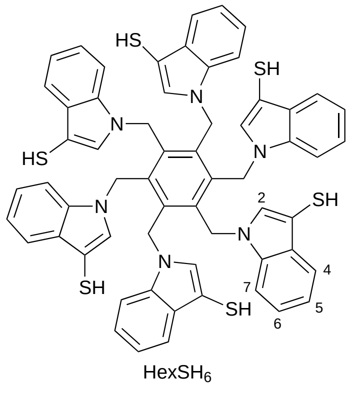
Hexakis(3-sulfanylindolyl[1]methyl)benzene is highly preorganised to embed upon deprotonation two Fe_4S_4 clusters at a rigid separation of 12.8 Å.

We have recently reported the convenient synthesis of 1,3,5-tris(3-sulfanylindolyl[1]methyl)-2,4,6-triethylbenzene ($TriSH_3$) from 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene.[1] This trithiol is highly preorganised to coordinate in the deprotonated form $TriS^{3-}$ to three iron subsites of Fe_4S_4 cluster cores thereby affording 3 : 1 subsite differentiated clusters. A key feature in the preorganisation of the molecular framework is the central hexasubstituted benzene ring that enforces a predominant *ababab*-conformation.† A detailed account of the design, underlying principles, synthesis and coordination properties has been given along with concise bibliographical reference.[1] Replacing 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene[2] with hexakis(bromomethyl)benzene[3] we have adapted the synthesis of $TriSH_3$ to obtain the novel ligand hexakis(3-sulfanylindolyl[1]methyl)benzene ($HexSH_6$), a doubly tripodal hexathiol that is preorganised to provide upon deprotonation two tripodal coordination spheres that are suitable to embed a single cluster core each.‡



$TriSH_3$



$HexSH_6$

Single crystals of $HexSH_6$ for X-ray structure analysis have not been obtained. By analogy with $TriSH_3$ rough S_6 or D_{3d} symmetry should be expected for $HexSH_6$ in that the 3-sulfanylindolyl moieties point alternately above and below the plane of the central arene ring and the bulky annelated benzo groups are directed towards the periphery in order to avoid steric pressure while the HS groups in turn are all directed inward to provide two tripodal coordination spheres. This conformation is reflected in the ^1H NMR spectrum shown in Fig. 1. The indolyl H^2 protons are highfield shifted in the spectra of both $TriSH_3$ and $HexSH_6$ owing to shielding by the central arene ring. A similar shielding of the indolyl H^7 protons in $HexSH_6$ may be expected, since these protons are sandwiched between the neighbouring indolyl groups and should experience a shielding influence from them. Indeed a significant highfield shift is observed with one of the two pseudo-doublets whereas the other one appears in the normal range. This allows the unequivocal assignment of these signals that had remained ambiguous in the spectrum of $TriSH_3$. The sharp lines in the spectrum of $HexSH_6$ (actually dd were resolved instead of mere pseudo-doublets) further illuminate both the predominance and rigidity of the expected conformation.

The preorganisation of $HexSH_6$ is mirrored by the smooth reaction with Fe_4S_4 clusters to afford discrete double clusters. This has been established by X-ray structure analysis of the compounds $[PPh_4]_4[(Br)Fe_4S_4(HexS)Fe_4S_4(Br)]$ **1** and $[PPh_4]_4[(PhS)Fe_4S_4(HexS)Fe_4S_4(SPh)]$ **2**.§ Fig. 2 depicts the representative double cluster anion from **2**. Crystal inversion symmetry is imposed on the anion that renders both cluster cores equivalent. Coordination of the cluster cores closely resembles that in $[PPh_4]_2[Fe_4S_4(TriS)(SPh)]$,[1] *e.g.* the ligand deviates from trigonal symmetry, as can be seen from the nonequal thiolate-S···thiolate-S distances, to allow the slight tetragonal distortion that is typical of Fe_4S_4 clusters.[1] The cluster centroids are 12.83 Å apart, similar to the value of *ca.* 12 Å found by protein crystallography of *Peptococcuc aerogenes*,

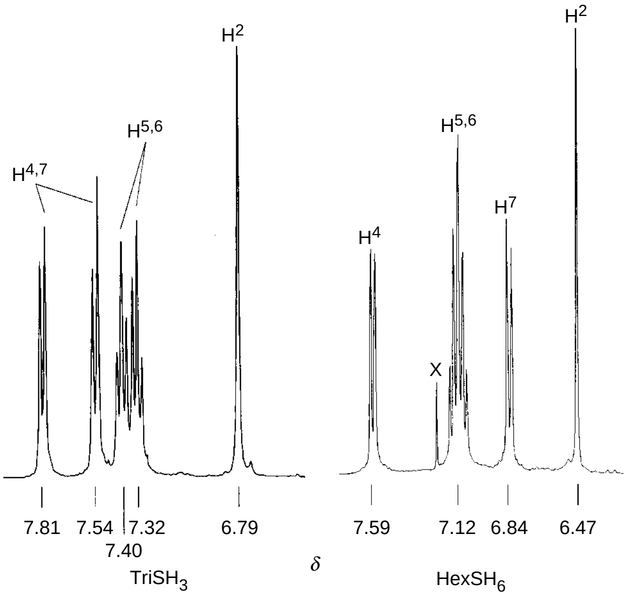


Fig. 1 The range of aromatic protons in the ^1H NMR spectra ($CDCl_3$) of $TriSH_3$ and $HexSH_6$ (X = $CHCl_3$)

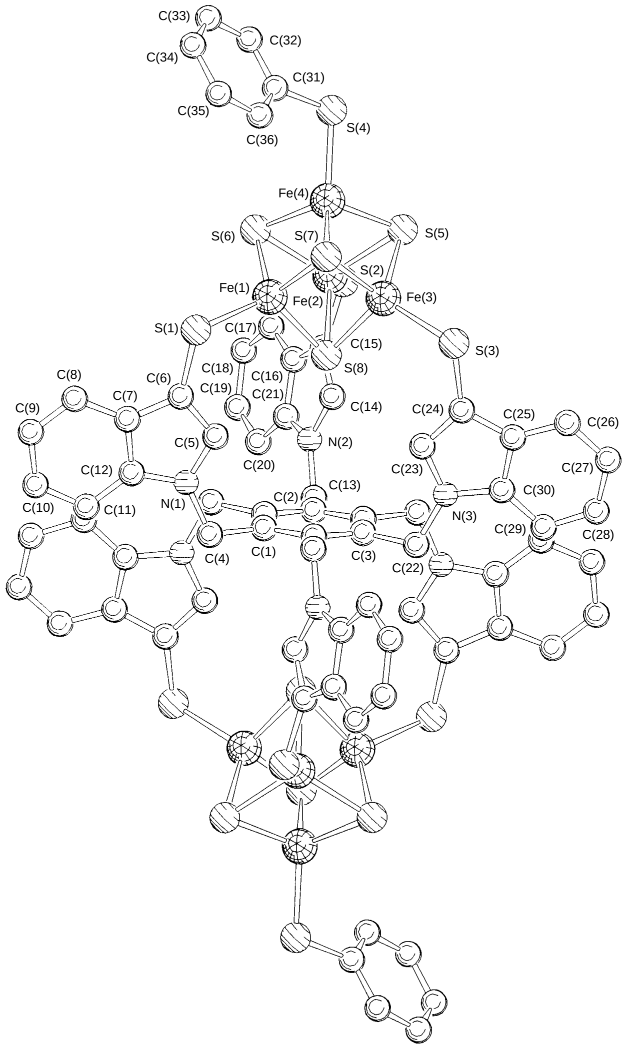


Fig. 2 The double cluster anion from the structure of **2**·4dmf·2Et_2O (H atoms omitted for clarity). Selected interatomic distances (pm): Fe(1)–S(6) 229.7(2), Fe(1)–S(7) 230.1(2), Fe(1)–S(8) 226.9(2), Fe(2)–S(5) 229.8(2), Fe(2)–S(6) 226.9(2), Fe(2)–S(8) 229.1(2), Fe(3)–S(5) 230.2(2), Fe(3)–S(7) 227.3(2), Fe(3)–S(8) 229.7(2), Fe(4)–S(5) 226.3(2), Fe(4)–S(6) 229.6(3), Fe(4)–S(7) 228.4(2), S(1)···S(2) 685.0, S(1)···S(3) 631.4, S(2)···S(3) 650.3. The structure of the anion from **1**·6dmf is very similar. Selected interatomic distances (pm): Fe(1)–S(4) 229.8(3), Fe(1)–S(6) 229.9(3), Fe(1)–S(7) 225.6(3), Fe(2)–S(4) 226.5(3), Fe(2)–S(5) 230.3(3), Fe(2)–S(7) 229.5(2), Fe(3)–S(5) 230.0(3), Fe(3)–S(6) 226.9(3), Fe(3)–S(7) 229.2(3), Fe(4)–S(4) 229.1(3), Fe(4)–S(5) 225.9(3), Fe(4)–S(6) 230.0(3), Fe(4)–Br 236.6(2), S(1)···S(2) 634.8, S(1)···S(3) 666.5, S(2)···S(3) 654.0.

a ferredoxin with two separate Fe_4S_4 clusters.[4] A series of model compounds for such two-cluster enzymes that employ bidentate thiolate ligands to link the cluster cores have been reported.[5] However, separation and relative orientation of the cluster cores are poorly defined in these compounds owing to the flexible bridging. On the contrary the rigid polydentate ligand $HexS^{6-}$ may be reasonably expected to control the relative arrangement of the cluster cores in solution, too. This very property makes us believe that the ligand as a prototype for further ligands of a similiar design deserves considerable interest also in various fields beyond iron–sulfur chemistry.

Footnotes and References

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† The '*ab*' terminology was introduced by MacNicol *et al.*[5] According to force-field calculations for the closely related hexaethylbenzene and hexa(*n*-propyl)benzene the ground-state *ababab* conformation lies some 15–19 kJ mol^{-1} below the conformers that are next higher in energy.[7]

‡ Typical synthetic procedures, purification of solvents and experimental techniques have been described elsewhere.[1] Yields are given for isolated, crystalline and ^1H NMR spectroscopically pure compounds.

Hexakis(3-methoxymethylthioindolyl[1]methyl)benzene: (88%); δ_H ($CDCl_3$, 300 MHz) 3.43 (18 H, s, OCH_3), 4.70 (12 H, s, SCH_2), 5.27 (12 H, s, NCH_2), 6.79 (6 H, s, indolyl H^2), 6.90 (6 H, d, indolyl H^7), 7.21 (12 H, m, indolyl $H^{5,6}$), 7.76 (6 H, d, indolyl H^4); δ_C ($CDCl_3$, 75 MHz) 44.16, 56.06, 79.63, 106.64, 109.63, 120.05, 121.32, 123.36, 129.26, 130.23, 136.62, 138.75.

$HexSH_6 \cdot 0.5Et_2O$: (20%); δ_H ($CDCl_3$, 300 MHz) 2.78 (6 H, d, J 1.3 Hz, SH), 5.25 (12 H, s, NCH_2), 6.47 (6 H, d, J 1.3 Hz, indolyl H^2), 6.84 (6 H, dd, J_{12} 6.6 Hz; J_{13} 1.5 Hz, indolyl H^7), 7.12 (12 H, m, indolyl $H^{5,6}$), 7.59 (6 H, dd, J_{12} 6.8 Hz; J_{13} 1.7 Hz, indolyl H^4); δ_C ($CDCl_3$, 75 MHz) 44.27, 98.49, 109.02, 119.77, 121.02, 123.22, 128.73, 130.44, 136.04, 138.58.

The electrochemical reduction of **2** was investigated by cyclic voltammetry (dmf, Pt electrodes *vs.* SCE, 100 mV s^{-1}, 0.1 M $[NBu_4]ClO_4$) in the range −460 to −1660 mV. The reduction is chemically reversible (no loss of current in successive cycles), but the reduction wave is broadened (E_{pc} = −1000; E_{pa} = −1210) owing to disproportionation equlibria in the two-electron process. Nevertheless no splitting into two separate potentials is observed, that might be caused by a strong electrochemical interdependence of the two cluster cores. However such a splitting should not be expected with two Fe_4S_4 clusters that far apart.[5]

§ Single crystals were grown by vapour diffusion of diethyl ether into the reaction solution (dmf). Suitable specimens were sealed in glass capilaries under an atmosphere of dinitrogen and mounted on a Siemens-Stoe AED 2 four-circle diffractometer. Intensity data collections were performed 296(2) K using Mo-Kα radiation (λ = 71.073 pm), a graphite monochromator and ω scan techniques. Both structures were solved (direct methods) and refined on F^2 using the SHELXTL package.[8] The anion of **2** has been drawn with the program SCHAKAL 92.[9]

Crystal data: **1**·6dmf, $C_{174}H_{164}Br_2Fe_8N_{12}O_6P_4S_{14}$, black plates, crystal size 0.49 × 0.34 × 0.15 mm, M = 3698.51, triclinic, space group $P\bar{1}$, a = 1679.8(2), b = 1686.0(2), c = 1712.6(2) pm, α = 68.82(1), β = 73.54(1), γ = 88.53(2)°, U = 4.3213(9) pm^3, Z = 1, D_c = 1.421 Mg m^{-3}, μ = 1.378 mm^{-1}. 9241 independent reflections (θ_{max} = 20.98°) of which 6686 were observed [$I > 2\sigma(I)$]. A semi-empirical absorption correction from ψ scans was applied. H atoms were refined on fixed positions. The phenyl groups of the cations and the dmf molecules were refined with idealized geometry. The dmf molecules and one cation phenyl group were disordered and refined on split positions with occupancy factors of 0.5 : 0.5. All other atoms were refined anisotropically. Refinement converged with GOF = 1.199 for 838 parameters, R_1 = 0.0652 and wR_2 = 0.1400 [$I > 2\sigma(I)$], R_1 = 0.1037 and wR_2 = 0.1820 (all data), e_{max}, e_{min} = 762, = −687 e nm^{-3}.

2·4dmf·2Et_2O, $C_{188}H_{180}Fe_8N_{10}O_6P_4S_{16}$, black needles, crystal size 2.58 × 0.27 × 0.08 mm, M = 3759.06, triclinic, space group $P\bar{1}$, a = 1513.9(2), b = 1752.1(3), c = 1939.1(2) pm, α = 100.67(1), β = 101.73(2), γ = 110.94(1)°, U = 4.5127(11) nm^3, Z = 1, D_c = 1.383 Mg m^{-3}, μ = 0.903 mm^{-1}. 11 043 independent reflections (θ_{max} = 22.02°) of which 8183 were observed [$I > 2\sigma(I)$]. A volume correction for a long needle was applied. H-atoms were refined on fixed positions. The phenyl groups of the cations and the solvent molecules were refined with idealized geometry. The solvent molecules were disordered and refined on split positions with occupancy factors of 0.5 : 0.5 but one dmf molecule (0.65 : 0.35). All other atoms were refined anisotropically. Refinement converged with GOF = 1.159 for 895 parameters, R_1 = 0.0659 and wR_2 = 0.1509 [$I > 2\sigma(I)$], R_1 = 0.0994 and wR_2 = 0.1936 (all data), e_{max}, e_{min} = 831, = −680 e nm^{-3}. CCDC 182/574.

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