

# A new preorganized tridentate ligand bearing three indolethiolate groups. Preparation of 3:1 subsite-differentiated Fe<sub>4</sub>S<sub>4</sub> clusters

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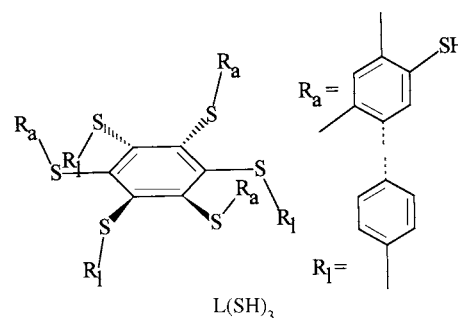
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1,3,5-Triethyl-2,4,6-tris(3-sulfanylidolyl[1]methyl)benzene (TriSH<sub>3</sub>) has been prepared in three steps from 3-sulfanylidole and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene. X-Ray analysis and NMR spectroscopy demonstrated it is highly preorganized for co-ordination to three subsites of a Fe<sub>4</sub>S<sub>4</sub> cluster core. The clusters [PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(TriS)(Br)] and [PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(TriS)(SPh)] were obtained by reaction of [PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(SEt)<sub>4</sub>] with TriSH<sub>3</sub> under dynamic vacuum followed by addition of [(Me<sub>2</sub>N)<sub>2</sub>CSSC(NMe<sub>2</sub>)<sub>2</sub>]Br<sub>2</sub> and substitution of bromide with PhS<sup>-</sup> respectively. The latter was characterized by X-ray structure analysis. No crystallographic symmetry is imposed on the cluster anion and the cluster core exhibits the tetragonal distortion typical of tetrathiolate-substituted Fe<sub>4</sub>S<sub>4</sub> cores. This implies that the trithiolate ligand TriS<sup>3-</sup> is sufficiently rigid to guarantee co-ordination to a single cluster core, while it is still flexible enough to match the preferred core distortions.

The search for trithiolates capable of co-ordination to a single Fe<sub>4</sub>S<sub>4</sub> core has been a challenging topic in bioinorganic chemistry during the last decade. This was stimulated by a desire for model compounds that would mimic structural and functional features of certain biological assemblies, where a 3:1 subsite differentiation of cluster cores is given by the protein environment.<sup>1,2</sup> The basic problem with synthetic potential polydentate ligands for co-ordination to Fe<sub>4</sub>S<sub>4</sub> cores is to keep them with a bite distance that long from bridging of different clusters. This implies that, while the bite distance has to match the geometry of the cluster, the internal conformational freedom of the compound should be low in order to keep the decrease of the entropy within it low when a complex is formed. In practice this requires 'preorganized ligands', where the term refers to compounds that inherently prefer a conformation which differs only slightly from the one that is required for co-ordination.

Stack and Holm<sup>3</sup> were the first to prepare a sufficiently preorganized synthetic trithiol. Based on structural work on hexahosts by the group of MacNicol,<sup>4</sup> they took advantage of the conformational pattern which is common to hexasubstituted benzenes, where the substituents tend to adopt an overall staggered-like so-called<sup>5</sup> ababab conformation thereby forcing each other into a position alternately a(bove) or b(elow) the benzene plane.<sup>3b,6,7</sup> Thus their compound L(SH)<sub>3</sub> had its 1,3,5-substituents which carry the thiol sites pregrouped in one of the hemispheres defined by this plane. Sterically demanding groups are attached to these substituents so as to result in an orientation in which the thiol groups are directed inwardly towards a common space. This compound has been unrivalled as a stepping-stone towards a wide field of investigations concerning subsite-specific reactions of Fe<sub>4</sub>S<sub>4</sub> clusters.<sup>2,8</sup> Especially, it played a crucial role in the synthesis of the first synthetic model of Fe<sub>3</sub>S<sub>4</sub> cuboidal iron-sulfur clusters.<sup>9</sup> However, Holm and co-workers<sup>9b</sup> frankly conceded that the synthesis of L(SH)<sub>3</sub> requires more than casual effort. Three other tridentate thiolates have been introduced for co-ordination to Fe<sub>4</sub>S<sub>4</sub> clusters,<sup>10</sup> but their non-bridging co-ordination to a single cluster core has not been determined crystallographically and the difficulty in distinguishing between bridging and non-bridging co-ordination of polydentate ligands to Fe<sub>4</sub>S<sub>4</sub> clusters has been demonstrated.<sup>11</sup>

Here we report the synthesis of 1,3,5-triethyl-2,4,6-tris(3-sulfanylidolyl[1]methyl)benzene (TriSH<sub>3</sub>) which is easily performed from inexpensive and simple reagents. The trithiolate

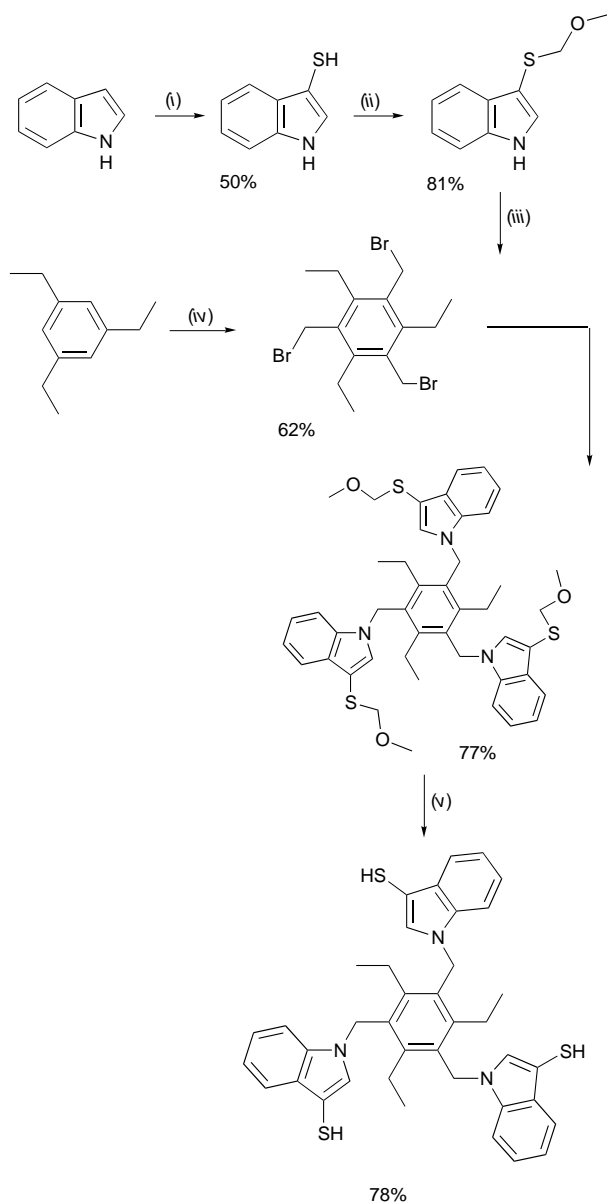


anion smoothly generates 3:1 subsite-differentiated isolated Fe<sub>4</sub>S<sub>4</sub> clusters.

## Results and Discussion

### Ligand design and synthesis

Conceptually the basic topological features of TriSH<sub>3</sub> are derived from the L(SH)<sub>3</sub> of Stack and Holm. Both compounds are based on a hexasubstituted benzene ring. The structural moieties carrying the thiol donor sites are anchored in the 2,4,6-positions, whereas substituents in the 1,3,5-positions merely serve to keep the former groups together by enforcing an overall staggered-like ababab conformation. To picture these two sets of substituents as 'arms' and 'legs' respectively is highly evocative. The 'arms' in both ligands are sterically unbalanced in order to keep the thiol sites turned inward towards a common space, thereby forming a kind of cavity for uptake of a single Fe<sub>4</sub>S<sub>4</sub> core. Nevertheless these features are synthetically realized in entirely independent approaches (Scheme 1). In the case of L(SH)<sub>3</sub> the substituents are linked by thioether groups to the central benzene plane, while 'benzylic' methylene groups are employed in TriSH<sub>3</sub>. Obedience to the ababab pattern seems to be more rigid in hexamethylene-substituted benzenes, at least in the solid state, whereas violation of this pattern is quite common with the hexathio-substituted analogues.<sup>3b,12</sup> Tripodal ligands based on 'benzylic' links are readily accessible by nucleophilic substitution of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene.<sup>7</sup> In the search for a suitable nucleophilic 'arm' the chemistry of indole was found to be ideal. Indole is (unlike pyrrole) liable to electrophilic substitution at the 3 position, thereby providing an easy access to 3-sulfanylidole, which is



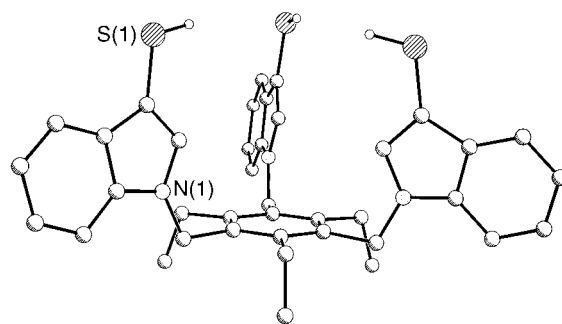
**Scheme 1** Synthesis of  $\text{TriSH}_3$  from commercial starting compounds. (i) (a) Thiourea,  $\text{I}_2$ , (b)  $\text{NaOH}$ , (c)  $\text{HCl}$ ; (ii) (a)  $\text{NaH}$ , (b)  $\text{ClCH}_2\text{OMe}$ ; (iii)  $\text{NaH}$ ; (iv)  $\text{HBr}$ ,  $(\text{CH}_2\text{O})_m$ ,  $\text{MeCO}_2\text{H}$ ; (v) (a)  $\text{Hg}(\text{O}_2\text{CMe})_2$ , (b)  $\text{H}_2\text{S}$

required for an appropriate bite distance. With the 3 position blocked (and the HS group protected, of course), on deprotonation the indolyl anion acts as a nucleophile exclusively at the 1(N) position, otherwise rivalled by the 3 position.<sup>13</sup> Along with this the [4,5]benzo group of indole causes an inherent asymmetry of the 'arms', which is sufficient to have the HS groups of the tripodal ligand  $\text{TriSH}_3$  turned inwards.

We are aware that the use of mercury acetate for deprotection of  $\text{TriSH}_3$ , where mercury is hardly recovered in an economical way, remains to be replaced by a more sustainable procedure.

### Structure of $\text{TriSH}_3$

Fig. 1 immediately reveals that  $\text{TriSH}_3$  adopts an overall ababab conformation in the solid state. The three thiol sites are thereby pregrouped in one of the two hemispheres that are defined by the central benzene plane. As desired, the thiol sites are directed inward to form a cavity above this plane, which is reasonably explained by the steric demands of the benzo rings of the indolyl moieties. The sulfur atoms are spaced 401.7 pm from each other. The retention of this conformation in solution (chloroform) is demonstrated by the  $^1\text{H}$  NMR spectrum of  $\text{TriSH}_3$ . The protons in the 2 position of the indolyl



**Fig. 1** The structure of  $\text{TriSH}_3$  (only H atoms on S are shown)

moieties exhibit a singlet at  $\delta$  6.79 (Fig. 3). The corresponding resonance of the protected precursor is of the same order and appears at  $\delta$  6.86 and both are remarkably high-field shifted. This is readily explained if the conformational features are preserved in solution. Thereby these protons are firmly placed above the shielding influence due to the arene ring current.<sup>14</sup> 1-Benzyl-3-sulfanylidole was prepared as reference for this signal since it provides a closely similar chemical environment, but otherwise hardly restricts the internal freedom of rotation around the benzylic bonds. For this compound the corresponding signal appears as part of a multiplet well below  $\delta$  7.00, probably at  $\delta$  7.17. A similar effect has been described with  $\text{L}(\text{SH})_3$ ,<sup>3c</sup> and is well known from conformationally fixed cyclophanes.<sup>15</sup>

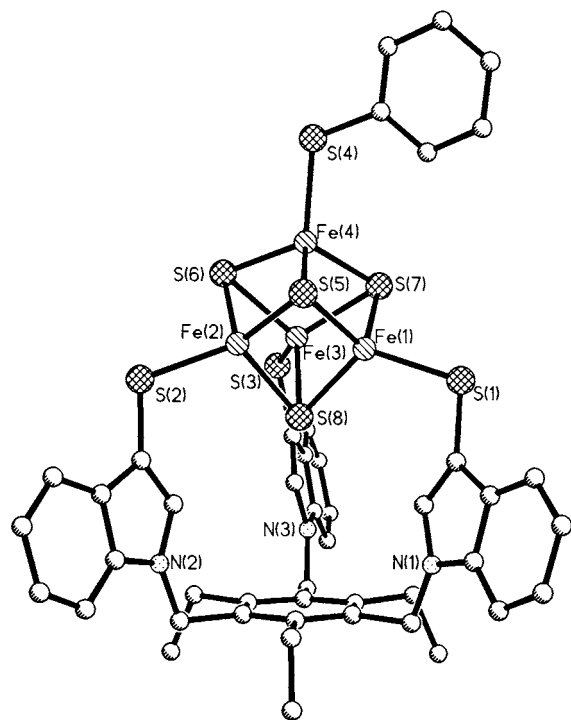
### Formation and reactivity of the $[\text{Fe}_4\text{S}_4(\text{TriS})]$ moiety

When equimolar solutions of  $\text{TriSK}_3$ , prepared *in situ* from  $\text{TriSH}_3$  and  $\text{KSMc}$  under dynamic vacuum in tetrahydrofuran (thf), were added to a stirred suspension of  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4\text{I}_4]$  in acetonitrile the solution immediately turned black and the majority of the cluster dissolved. However some 20% always remained undissolved and no crystalline material could be isolated in this way. We therefore had to take a more circuitous route and prepare  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SEt})]$  from  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{SEt})_4]$  and  $\text{TriSH}_3$  under dynamic vacuum. With  $[(\text{Me}_2\text{N})_2\text{C}(\text{SSC}(\text{NMe}_2)_2)\text{Br}_2]^\dagger$  the remaining  $\text{EtS}^-$  could be replaced oxidatively to yield  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{Br})]$ . Despite the overall subsite-specific substitution the actual mechanism should be more complicated since  $[(\text{Me}_2\text{N})_2\text{C}(\text{SSC}(\text{NMe}_2)_2)]^{2+}$  is a two-electron acceptor. The salt  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{Br})]$  is liable to subsite-specific nucleophilic substitution of bromide and provides a general access to 3:1 subsite-differentiated  $\text{Fe}_4\text{S}_4$  clusters. Accordingly the salt  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]$  was generated by substitution with  $\text{KSPh}$ .

### Structure of $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]$

The structure of  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]$  consists of  $\text{Ph}_4\text{P}^+$  cations, discrete cluster anions and two molecules of dimethylformamide per formula unit. The cluster anion is shown in Fig. 2. It is obvious that the main synthetic and structural aims have been achieved. The ligand moiety retains the overall ababab conformation of the substituents at the central benzene ring, and the indolyl thiolate groups establish a framework which keeps a single  $\text{Fe}_4\text{S}_4$  core bound above the plane of the central ring. Atom S(8) of the cluster core is separated 429 pm from this plane, which is somewhat more than the sum of the van der Waals radii. The fourth iron site in the cluster core is coordinated to benzenethiolate. The cluster anion lies on a general position with no crystallographic symmetry imposed. Some important bond lengths of the cluster core are given in Table 1. It exhibits the tetragonal distortion that is typical of  $\text{Fe}_4\text{S}_4$  cores

<sup>†</sup> Used for oxidative removal of thiolate ligands from clusters and complexes.<sup>16</sup>

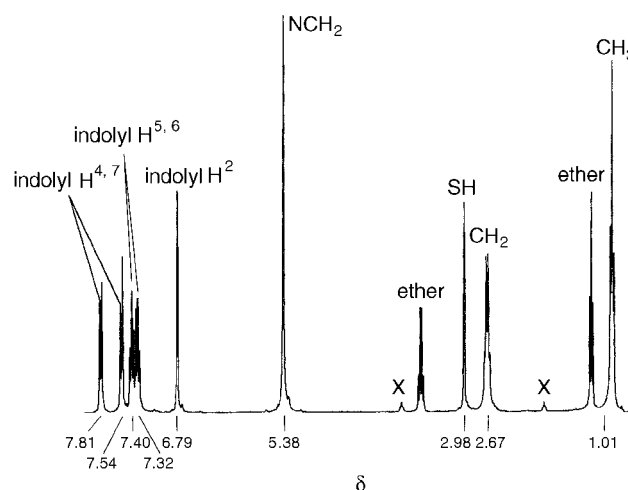


**Fig. 2** Structure of  $[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]^{2-}$  as its  $\text{Ph}_4\text{P}^+$  salt (H atoms omitted for clarity)

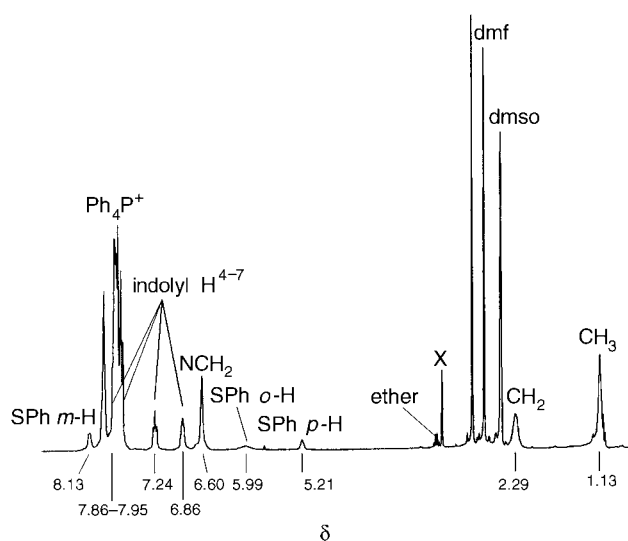
**Table 1** Selected bond distances (pm) for  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})] \cdot 2 \text{ dmf}$

Fe(1)···Fe(2)	277.6(2)	Fe(2)···Fe(3)	271.9(2)
Fe(1)···Fe(3)	276.7(2)	Fe(2)···Fe(4)	274.5(2)
Fe(1)···Fe(4)	272.8(2)	Fe(3)···Fe(4)	277.1(2)
Fe(1)–S(1)	227.2(3)	Fe(1)–S(7)	231.4(3)
Fe(1)–S(5)	232.2(3)	Fe(1)–S(8)	224.0(3)
Fe(2)–S(2)	228.1(3)	Fe(2)–S(6)	231.0(3)
Fe(2)–S(5)	226.9(3)	Fe(2)–S(8)	229.9(3)
Fe(3)–S(3)	228.0(3)	Fe(3)–S(7)	226.0(3)
Fe(3)–S(6)	232.1(3)	Fe(3)–S(8)	230.0(3)
Fe(4)–S(4)	227.6(3)	Fe(4)–S(6)	223.0(3)
Fe(4)–S(5)	231.5(3)	Fe(4)–S(7)	230.4(3)
S(1)–C(15)	176.2(8)	S(3)–C(33)	175.0(10)
S(2)–C(24)	174.7(10)	S(4)–C(40)	176.4(6)

with four thiolate ligands.<sup>17</sup> Under a tetragonal distortion the twelve equal Fe–S bonds of an ideal heterocubus split into two sets of 8 + 4, while the six Fe–Fe and S–S distances are split into sets of 4 + 2 respectively. The core is compressed along Fe(1)–S(8), Fe(2)–S(5), Fe(3)–S(7) and Fe(4)–S(6). Consequently, the former trigonal symmetry of the ligand is not retained in the cluster anion. The distances of the thiolate sulfur atoms from each other are widened, 581.1, 653.3 and 691.5 pm respectively, corresponding to slight turns around the N–CH<sub>2</sub> bonds. The crystal structures of only two other Fe<sub>4</sub>X<sub>4</sub> (X = S or Se) cluster cores with tripodal ligands,  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{LS}_3)(\text{Cl})]^{3b}$  and  $[\text{PPh}_4]_2[\text{Fe}_4\text{Se}_4(\text{LS}_3)(\text{Cl})]^{3c}$  have been reported. No tetragonal distortion was found in either of them. While the structure of the first is somewhat irregular, a trigonal distortion is imposed on the latter by crystallographic symmetry. This may be due to the chemical non-equivalence of the halide ligand at the fourth subsite. Tetragonal distortions are sometimes less pronounced with halide-substituted clusters.<sup>18,19a</sup> A more detailed discussion will have to wait for further structural data. However, the crystal structure of  $[\text{PPh}_4]_2$ -



**Fig. 3** Proton NMR spectrum of  $\text{TriSH}_3$ . X = Trace of thf



**Fig. 4** Proton NMR spectrum of  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})] \cdot 2.5 \text{ dmf} \cdot 0.5 \text{ OEt}_2$  (X = residual water)

$[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]$  clearly reveals that the trithiolate ligand (TriS) is sufficiently rigid to guarantee a firm co-ordination to a single cluster core, while it is still flexible enough to match the preferred core distortions smoothly.

The <sup>1</sup>H NMR spectrum of  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]$  is reproduced in Fig. 4. The signals of the ligand protons were assigned from linewidth and integral considerations. This failed for the protons of the benzo group, where the assignments remain ambiguous. The signal of the indolyl H<sup>2</sup> proton should be the most shifted one and broadened; it could not be detected unequivocally. Isotropic shifts of cluster-bound PhS<sup>-</sup> had been reported.<sup>20,21</sup> No deviation from trigonal symmetry in the ligand framework is revealed in solution within the NMR time-scale.

## Experimental

All air-sensitive compounds were handled under an atmosphere of pure dinitrogen or argon using either Schlenk techniques or glove-boxes equipped with a slurry of MgEtBr–diethyl ether for purification of the atmosphere. The compound (CD<sub>3</sub>)<sub>2</sub>SO was dried over molecular sieves and degassed. Dichloromethane was distilled from CaH<sub>2</sub>, dimethylformamide (dmf) from CaH<sub>2</sub> under reduced pressure, acetonitrile from P<sub>2</sub>O<sub>5</sub> followed by FeI<sub>2</sub><sup>22</sup> and all other solvents from sodium–potassium alloy under an atmosphere of dinitrogen.

## Preparation

**3-Methoxymethylsulfanylindole.** 3-Sulfanylindole †<sup>23</sup> (6.500 g, 43.56 mmol) was dissolved in thf (100 cm<sup>3</sup>), and NaH (95%; 1.100 g, 43.56 mmol) was added to the stirred solution in small portions. After stirring had been continued for 12 h the evolution of hydrogen had ceased. The suspension was chilled in an external ice-bath and vigorously stirred while chloromethyl methyl ether (technical grade ≈90%; 4.6 cm<sup>3</sup>, 54 mmol) was added. **CAUTION:** care should be taken since the ether of technical quality is classified as carcinogenic due to contamination with bis(chloromethyl) ether.<sup>24</sup> The suspension immediately turned clear and then became milky. After stirring had been continued for 10 min the mixture was poured into water and extracted thrice with ether. The combined organic phases were washed with Na<sub>2</sub>CO<sub>3</sub> and NaCl solutions, dried over CaCl<sub>2</sub> and evaporated to afford an oil that crystallized within minutes. Needles were obtained from *tert*-butyl methyl ether–hexane (6.78 g, 81%), m.p. 65 °C (Found: C, 62.15; H, 5.7; N, 7.2. Calc. for C<sub>10</sub>H<sub>11</sub>NOS: C, 62.2; H, 5.7; N, 7.25%; δ<sub>H</sub>(CDCl<sub>3</sub>, 300 MHz) 3.57 (3 H, s, CH<sub>3</sub>), 4.83 (2 H, s, SCH<sub>2</sub>), 7.12 (1 H, s, indolyl H<sup>2</sup>), 7.30 (3 H, m, indolyl H), 7.88 (1 H, m, indolyl H) and 8.40 (1 H, br, NH); δ<sub>C</sub>(CDCl<sub>3</sub>, 75 MHz) 55.89, 79.42, 104.16, 111.49, 118.94, 120.30, 122.43, 128.95, 129.54 and 135.99.

**1,3,5-Triethyl-2,4,6-tris(3-methoxymethylsulfanylindolyl[1]-methyl)benzene.** 3-Methoxymethylsulfanylindole (5.770 g, 29.86 mmol) was dissolved in thf (90 cm<sup>3</sup>) and NaH (95%; 0.755 g, 29.86 mmol) was added to the stirred solution in small portions. After stirring for 24 h the clear solution was cooled in an external ice-bath. 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene<sup>7</sup> (4.389 g, 9.95 mmol) was added to the stirred solution and NaBr precipitated. The suspension was stirred for a further hour and then poured into water. It was twice extracted with ether and the organic phases were washed with saturated NaCl solution, dried over CaCl<sub>2</sub> and evaporated to dryness to afford a sticky solid. On treatment with ether small needles formed which were washed with ether and dried *in vacuo* (5.99 g, 77%) (Found: C, 69.5; H, 6.45; N, 5.45. Calc. for C<sub>45</sub>H<sub>51</sub>N<sub>3</sub>O<sub>3</sub>S<sub>3</sub>: C, 69.5; H, 6.55; N, 5.4%; δ<sub>H</sub>(CDCl<sub>3</sub>, 300 MHz) 1.01 (9 H, t, *J* = 7.4, CH<sub>2</sub>CH<sub>3</sub>), 2.70 (6 H, q, *J* = 7.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 3.44 (9 H, s, OCH<sub>3</sub>), 4.72 (6 H, s, SCH<sub>2</sub>), 5.40 (6 H, s, NCH<sub>2</sub>), 6.86 (3 H, s, indolyl H<sup>2</sup>), 7.30 and 7.39 (3 H, 3 H, m, m, indolyl H<sup>5,6</sup>), 7.54 and 7.85 (3 H, 3 H, m, m, indolyl H<sup>4,7</sup>); δ<sub>C</sub>(CDCl<sub>3</sub>, 75 MHz) 15.10, 23.34, 43.62, 55.98, 79.88, 103.99, 109.29, 119.75, 120.58, 122.47, 130.27, 130.47, 136.70 and 146.06. The signal of one non-equivalent carbon nucleus could not be resolved.

**1,3,5-Triethyl-2,4,6-tris(3-sulfanylindolyl[1]methyl)benzene.** 1,3,5-Triethyl-2,4,6-tris(3-methoxymethylsulfanylindolyl[1]-methyl)benzene (3.25 g, 4.18 mmol) was dissolved in dry degassed acetonitrile (150 cm<sup>3</sup>). To the stirred solution was added ethanol (50 cm<sup>3</sup>) and mercury acetate (6.10 g, 19.1 mmol). A yellow suspension formed within minutes, which was stirred for 12 h and then evaporated to dryness under reduced pressure. The residue was dissolved in chloroform–glacial acetic acid (160:40 cm<sup>3</sup>). Hydrogen sulfide was bubbled through this solution for 3 h and a black suspension formed. It was filtered over a plug of Celite and the residue washed with chloroform–glacial acetic acid. On removal of solvents under reduced pressure a white solid was obtained. This was redissolved in thf and evaporated again under reduced pressure. The remainder was treated with ether and a microcrystalline solid separated which was washed with ether and dried *in vacuo*. The NMR spectra suggest the formation of a solvate with half a molecule of ether per formula unit with the latter substituted to a small degree by thf (2.23 g, 78%) (Found: C, 71.65; H, 6.45; N, 6.05; S, 14.15.

† The thiol had been recrystallized from *tert*-butyl methyl ether–hexane.

Calc. for C<sub>41</sub>H<sub>44</sub>N<sub>3</sub>O<sub>0.5</sub>S<sub>3</sub>: C, 72.15; H, 6.45; N, 6.15; S, 14.1%; ν<sub>max</sub>/cm<sup>-1</sup> 2523 (SH); δ<sub>H</sub>(CDCl<sub>3</sub>, 300 MHz) 1.01 (9 H, t, *J* = 7.4, CH<sub>2</sub>CH<sub>3</sub>), 1.28 (3 H, t, CH<sub>3</sub>/ether), 2.67 (6 H, q, *J* = 7.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.98 (3 H, s, SH), 3.55 (2 H, q, CH<sub>2</sub>/ether), 5.38 (6 H, s, NCH<sub>2</sub>), 6.79 (3 H, s, indolyl H<sup>2</sup>), 7.32 and 7.40 (3 H, 3 H, m, m, indolyl H<sup>5,6</sup>), 7.54 and 7.81 (3 H, 3 H, d, d, indolyl H<sup>4,7</sup>); δ<sub>C</sub>(CDCl<sub>3</sub>, 75 MHz) 15.23 (ether), 23.40, 43.61, 65.73 (ether), 96.14, 109.23, 119.66, 120.50, 122.57, 129.74, 130.57, 130.84, 136.65 and 146.01.

**1-Benzyl-3-sulfanylindole (1-benzylindole-3-thiol).** This thiol was prepared by the method of Harris<sup>23</sup> from 1-benzylindole.<sup>25</sup> M.p. 72 °C (MeOBu<sup>t</sup>); ν<sub>max</sub>/cm<sup>-1</sup> (KBr) 2529 (SH); δ<sub>H</sub>(CDCl<sub>3</sub>, 300 MHz) 2.86 (1 H, s, SH), 5.19 (2 H, s, NCH<sub>2</sub>), 7.00–7.24 (9 H, m, aryl H) and 7.72 (1 H, m, aryl H); δ<sub>C</sub>(CDCl<sub>3</sub>, 75 MHz) 50.14, 96.23, 109.90, 119.46, 120.18, 122.48, 126.88, 127.78, 128.79, 130.66, 132.23, 136.62 and 136.81.

**[PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(SEt)<sub>4</sub>].** This compound was prepared from KSET and [PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub>].<sup>19</sup>

**[Me<sub>2</sub>N]<sub>2</sub>CSSC(NMe<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>.** This compound was prepared by oxidation of tetramethylthiourea with a stoichiometric amount of bromine in ethanol, otherwise similarly to the chloro compound.<sup>16b</sup> The crystals obtained had to be dried over P<sub>2</sub>O<sub>5</sub> in vacuum to remove some tightly bound water and a yellow powder was obtained. ν<sub>max</sub>/cm<sup>-1</sup> (KBr) 1618 (CN).

**[PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(TriS)(Br)].** The salt [PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(SEt)<sub>4</sub>] (0.800 g, 0.628 mmol) was dissolved in dmf (20 cm<sup>3</sup>) and a solution of TriSH<sub>3</sub>·0.5OEt<sub>2</sub> (0.428 g, 0.628 mmol) in thf (20 cm<sup>3</sup>) was added. After dynamic vacuum had been applied to the stirred solution for 4 h, [(Me<sub>2</sub>N)<sub>2</sub>CSSC(NMe<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>] (0.133 g, 0.314 mmol) was added and stirring was continued for 10 min. The purple-black solution was routinely filtered but practically no residue was observed. Ether was allowed to diffuse into the solution at room temperature (r.t.) and an ill-formed solid separated within 3 d. This was collected and washed with ether. The <sup>1</sup>H NMR spectrum revealed the formation of a solvate with two molecules of dmf per formula unit (1.010 g, 85%) (Found: C, 56.9; H, 5.05; Fe, 11.9; N, 3.6; S, 12.95. Calc. for C<sub>93</sub>H<sub>99</sub>BrFe<sub>4</sub>N<sub>5</sub>O<sub>2</sub>P<sub>2</sub>S<sub>7</sub>: C, 58.8; H, 4.8; Fe, 11.75; N, 3.7; S, 11.8%; δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>SO, 300 MHz] 1.10 (9 H, CH<sub>2</sub>CH<sub>3</sub>), 2.26 (6 H, CH<sub>2</sub>CH<sub>3</sub>), 2.70 (6 H, dmf), 2.87 (6 H, dmf), 6.70 (6 H, NCH<sub>2</sub>), 6.83 (3 H, indolyl H), 7.22 (3 H, indolyl H) and 7.70–7.92 (46 H, indolyl H and Ph<sub>4</sub>P).

**[PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(TriS)(SPh)].** Potassium benzenethiolate (0.034 g, 0.229 mmol) was added to a solution of [PPh<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(TriS)]·2 dmf (0.400 g, 0.211 mmol) in dmf (20 cm<sup>3</sup>). The solution was stirred for 10 min, and ether was allowed to diffuse slowly into it. Within 3 d at r.t. black rhombic crystals were obtained. They were filtered off, quickly washed with ether and dried under vacuum for 1 min. Both NMR and elemental analysis suggested the formation of a solvate with 2.5 molecules of dmf and half a molecule of ether per formula unit. However we could not refine this stoichiometry crystallographically, which is probably due to the extended disorder of the solvent molecules in the solid state (0.314 g, 75%) (Found: C, 61.1; H, 5.65; Fe, 11.05; N, 4.0; S, 12.85. Calc. for C<sub>102.5</sub>H<sub>103.5</sub>Fe<sub>4</sub>N<sub>5.5</sub>O<sub>3</sub>P<sub>2</sub>S<sub>8</sub>: C, 61.5; H, 5.2; Fe, 11.15; N, 3.85; S, 12.8%; ν<sub>max</sub>/cm<sup>-1</sup> (KBr) 1670s [ν(C=O), dmf], 1586vw, 1576w, 1483w, 1472w, 1451m, 1435s [ν(P–Ph)], 1385w, 1335w, 1296w, 1244vw, 1204w, 1169vw, 1150vw, 1107s, 1067vw, 1040vw, 1024vw, 1009vw, 997w, 953vw, 791vw, 752 (sh) m, 743m (CH out of plane/indolyl), 723vs and 689s (CH out of plane/Ph<sub>4</sub>P), 527vs, 428vw and 349w (cluster core); δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>SO, 300 MHz] 1.13 (9 H, CH<sub>3</sub>), 2.29 (6 H, CH<sub>2</sub>CH<sub>3</sub>), 5.21 (1 H, SPh *p*-H), 5.99 (2 H, br, SPh *o*-H), 6.60 (6 H, NCH<sub>2</sub>), 6.86 (3 H, indolyl H), 7.24 (3 H, indolyl H), 7.68–7.95 (46 H, m, indolyl H, Ph<sub>4</sub>P) and 8.13 (2 H, SPh *m*-H); λ<sub>max</sub>/nm (dmf) 498 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 8900); E<sub>2</sub>(ΔE<sub>p</sub>) (CH<sub>2</sub>Cl<sub>2</sub>) –1140 mV (60 mV) [2/–3-, vs. saturated calomel electrode (SCE)].

**Table 2** Crystallographic data for  $\text{TriSH}_3 \cdot 0.5\text{C}_6\text{H}_{14}$  and  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})] \cdot 2\text{dmf}$ 

Formula	$\text{C}_{42}\text{H}_{46}\text{N}_3\text{S}_3$	$\text{C}_{95}\text{H}_{95}\text{Fe}_4\text{N}_5\text{O}_2\text{P}_2\text{S}_8$
<i>M</i>	689.00	1928.62
Crystal system	Hexagonal	Monoclinic
Space group	$R\bar{3}$	$P2_1/c$
<i>a</i> /pm	1754.6(1)	2462.5(3)
<i>b</i> /pm		1416.0(2)
<i>c</i> /pm	2034.7(1)	2789.5(3)
$\beta/^\circ$		108.06(1)
<i>U</i> /nm <sup>3</sup>	5.4248(5)	9.248(2)
<i>Z</i>	6	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.265	1.385
$\mu/\text{mm}^{-1}$	0.240	0.822
Crystal dimensions/mm	0.50 × 0.45 × 0.45	0.65 × 0.47 × 0.29
Data collected	2295	11 625
Unique data	2118	11 309
Observed data [ <i>I</i> > 2σ( <i>I</i> )]	1430	8731
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0767	0.0901
<i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.2145	0.1829

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

### X-Ray crystallography

Suitable crystals for X-ray diffraction were grown by layering hexane on a solution of  $\text{TriSH}_3 \cdot 0.5\text{OEt}_2$  in  $\text{CH}_2\text{Cl}_2$  or obtained as described above  $\{[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]\}$ . Single crystals were sealed in a glass capillary under a dinitrogen atmosphere and mounted on a Siemens-Stoe AED 2 four-circle diffractometer. Intensity-data collections were performed at 296(2) K by using Mo-K $\alpha$  radiation ( $\lambda$  71.073 pm), a graphite monochromator and  $\omega$ -2 $\theta$  scan techniques. No absorption corrections were applied. Both structures were solved (direct methods) and refined on  $F^2$  using the SHELXTL<sup>26</sup> package. Crystal and data collection parameters are summarized in Table 2 together with refinement parameters.

The compound  $\text{TriSH}_3$  crystallized as a solvate with half a molecule of hexane per formula unit; it exhibits crystallographic  $C_3$  symmetry. Hydrogen atoms were included in refinement at calculated positions with isotropic displacement parameters normally 1.2 times greater than those of the corresponding carbon atoms. The hexane is disordered about the three-fold inversion axis and was refined isotropically with fixed C-C distances and no constraints on the torsion angles (occupancy factors: 0.167).

The compound  $[\text{PPh}_4]_2[\text{Fe}_4\text{S}_4(\text{TriS})(\text{SPh})]$  crystallized as a solvate with two molecules of dmf per formula unit. However these solvent molecules are strongly disordered (refinement proceeded isotropically with occupancy factors of 0.6 and 0.4 and 0.65 and 0.35 respectively for the difference positions) and replacement of dmf by ether to a certain extent as well as some solvent loss seems likely. Indications for such a substitution come also from the elemental analysis and NMR spectra. Phenyl groups of the cations were refined with idealized geometry and H atoms as above.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/484.

### Other physical measurements

The NMR spectra were determined with a Bruker AM 300 spectrometer and referenced to solvent signals as internal standard, IR and UV/VIS spectra with a Bio-Rad FTS-7 and a Shimadzu UV-260 spectrometer respectively. A cyclic voltammogram was recorded using platinum electrodes, a SCE for reference and 0.1 mol dm<sup>-3</sup>  $\text{NBu}_4\text{ClO}_4$  in  $\text{CH}_2\text{Cl}_2$  as supporting electrolyte. Elemental analyses were carried out by Beller Mikroanalytisches Labor (Göttingen). Samples were obtained as described and not further purified.

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Received 9th December 1996; Paper 6/08284J