

A Convenient Synthesis of Tetrakis[thiolato- μ_3 -sulphido-iron] (2-) Clusters

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Anaerobic reactions, in methanolic solution, between iron(III) or iron(II) chloride, elemental sulphur, and the lithium or sodium salt of a thiol lead to the formation of the corresponding $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ complex in good yield (R = $\text{CH}_2\text{CH}_2\text{OH}$, Bu^t , or Ph).

RECENT studies of the non-haem iron ('rubredoxins') and iron-sulphur ('ferredoxins and HiPIP's') redox proteins have been greatly assisted, supported and, in certain instances, stimulated by the availability of low-molecular-weight synthetic analogues.¹⁻³ Typically, in these model systems, ligation of the iron centre(s) by simple alkyl- or aryl-thio-groups replaces that of the cysteine residues of the protein polypeptide. The first successful isolation and crystallisation of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ salts was accomplished by Holm and his co-workers⁴ by treatment of a methanolic solution of iron(III) chloride with the sodium salt of the corresponding thiol, followed by the addition of a methanolic solution of sodium hydrogensulphide and sodium methoxide. All manipulations were carried out under strictly anhydrous and anaerobic conditions. A simpler procedure was introduced by Schrauzer *et al.*⁵ who treated FeCl_3 with the lithium salt of the thiol, followed by the addition of lithium sulphide. Although it has been known for some time that preformed $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ complexes are stable in the presence of moderate amounts of water,^{6,7} the preparation of such complexes in partially aqueous media has only recently been documented. Rydon and his co-workers⁸ obtained spectroscopic evidence for the presence of rubredoxin analogues on the addition of cysteinyl peptides to FeCl_3 in dimethyl sulphoxide containing triethylamine. The subsequent addition of aqueous sodium sulphide resulted in the rapid formation of stable $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ species.

Current interest in the chemical reactions and physical properties of synthetic analogues of the four-iron ferredoxin-type centres continues to be considerable.³ We were therefore interested to improve the procedures for the large-scale preparation of such complexes. Prompted by the successful synthesis of $[\text{Fe}_4\text{Se}_4(\text{SPh})_4]^{2-}$, from benzenethiol, FeCl_3 , and elemental selenium,⁹ we have attempted analogous reactions using elemental sulphur. The objective was to evaluate the viability of this procedure for the synthesis of aryl and alkyl four-iron ferredoxin-type centres.

EXPERIMENTAL

All manipulations were carried out under dioxygen-free dinitrogen, previously passed over B.A.S.F. catalyst R3-11 at 140–150 °C, in Schlenk-type apparatus. Solutions were transferred with syringes previously flushed with purified dinitrogen. AnalaR grade acetonitrile, methanol, and ethyl acetate were purged of dioxygen by four cycles

of evacuation followed by admission of purified dinitrogen. Anhydrous iron(III) chloride (B.D.H., Laboratory grade, unsublimed), iron(II) chloride tetrahydrate (B.D.H., AnalaR grade), benzenethiol, 1,1-dimethylethanethiol, 2-hydroxyethanethiol (Koch-Light), and tetra-alkylammonium halides (B.D.H.) were used.

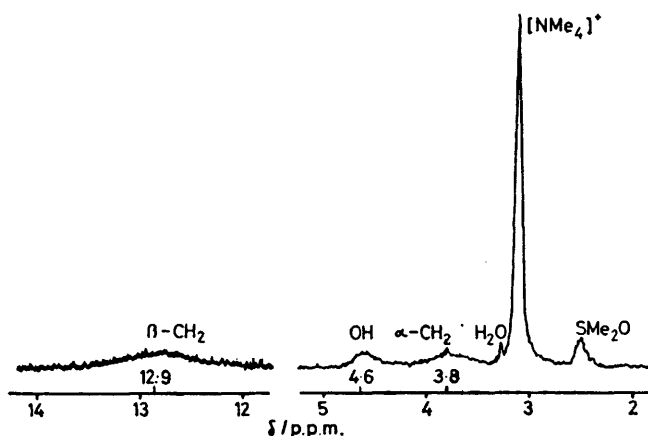
Preparations.—*Bis(tetra-n-butylammonium) tetrakis[benzenethiolato- μ_3 -sulphido-iron]*, $[\text{NBu}_4]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$ (1). Lithium (0.28 g, 40 mmol) was dissolved in methanol (40 cm^3) and the solution treated with benzenethiol (4.1 cm^3 , 40 mmol). Anhydrous iron(III) chloride (1.62 g, 10 mmol) in methanol (25 cm^3) was added to give a deep yellow-black solution. The addition of elemental sulphur (0.32 g, 10 mmol) produced (after *ca.* 5 min) the deep red-brown colour characteristic of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$. The solution was stirred overnight at room temperature and filtered into a solution of tetra-n-butylammonium iodide (2.77 g, 7.5 mmol) in methanol (20 cm^3), whereupon a fine black precipitate was obtained immediately. This was filtered off, washed copiously with methanol, and dried *in vacuo*. The solid was dissolved in warm (45–50 °C) acetonitrile, the solution was filtered, and methanol added at this temperature to incipient crystallisation. Slow cooling to –5 °C gave large black needles which were filtered off, washed with methanol, and dried *in vacuo*. The yield of (1) was 2.43 g (76%), m.p. 190–191 °C (sealed tube under dinitrogen) (lit.,⁴ 190–191 °C) (Found: C, 52.5; H, 7.2; Fe, 17.6; N, 2.1; S, 20.2. Calc. for $\text{C}_{58}\text{H}_{92}\text{Fe}_4\text{N}_2\text{S}_8$: C, 52.8; H, 7.3; Fe, 17.5; N, 2.2; S, 20.1%). The u.v.–visible¹⁰ and ¹H n.m.r.¹¹ spectroscopic properties of the product were fully consistent with its formulation.

Bis(tetramethylammonium) tetrakis[1,1-dimethylethanethiolato- μ_3 -sulphido-iron], $[\text{NMe}_4]_2[\text{Fe}_4\text{S}_4(\text{SBU}^t)_4]$ (2). A procedure analogous to that described above was carried out using sodium (1.38 g, 60 mmol) or lithium (0.42 g, 60 mmol), 1,1-dimethylethanethiol (5.41 g, 60 mmol), anhydrous FeCl_3 (2.43 g, 15 mmol), elemental sulphur (0.48 g, 15 mmol), and tetramethylammonium bromide (1.54 g, 10 mmol). The crude material crystallised from warm (*ca.* 50 °C) acetonitrile–ethyl acetate as well formed black needles of the monoacetonitrile adduct, yield 1.44 g (45%), m.p. 152–154 °C (decomp.) (sealed tube under dinitrogen) [lit.,¹¹ 153 °C (decomp.)] (Found: C, 34.8; H, 7.0; Fe, 25.0; N, 4.6; S, 28.1. Calc. for $\text{C}_{26}\text{H}_{63}\text{Fe}_4\text{N}_2\text{S}_8$: C, 34.8; H, 7.1; Fe, 24.9; N, 4.7; S, 28.6%). The u.v.–visible and ¹H n.m.r. spectroscopic properties of the product were essentially the same as those reported earlier.^{6,11}

Bis(tetramethylammonium) tetrakis[2-hydroxyethanethiolato- μ_3 -sulphido-iron], $[\text{NMe}_4]_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_4]$ (3). The previous preparation was followed up to the dissolution of the crude material in warm (*ca.* 50 °C) acetonitrile. The solution was then filtered, 2-hydroxyethanethiol (1 cm^3 , 14 mmol) was added, and the liberated 1,1-dimethylethanethiol and the solvent were removed *in vacuo*. The residue was

dissolved in the minimum volume (*ca.* 50 cm³) of acetonitrile at *ca.* 50 °C, the solution was filtered, and ethyl acetate (*ca.* 40 cm³) added to incipient crystallisation. This solution, when allowed to cool slowly to 5 °C, yielded large plate-like crystals of the product in >40% yield, m.p. 144–145 °C (decomp.) (sealed tube under dinitrogen) [lit.,⁷ *ca.* 145 °C (decomp.)] (Found: C, 24.1; H, 5.5; Fe, 27.9; N, 3.7; S, 31.5. Calc. for C₁₆H₄₄Fe₄N₂O₄S₈: C, 23.8; H, 5.5; Fe, 27.6; N, 3.5; S, 31.7%). The u.v.–visible spectroscopic properties of (3) were fully consistent⁷ with its formulation; the ¹H n.m.r. spectrum, recorded in S(CD₃)₂O at 34 °C, is shown in the Figure.

Alternative Preparation of (1).—A procedure analogous to that described above was followed using lithium (0.21 g,



60-MHz ¹H n.m.r. spectrum of [NMe₄]₂[Fe₄S₄(SCH₂CH₂OH)₄] in S(CD₃)₂O at 34 °C

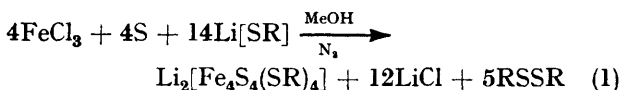
30 mmol) or sodium (0.69 g, 30 mmol) dissolved in methanol (30 cm³), benzenethiol (3.31 g, 30 mmol), iron(II) chloride tetrahydrate (1.99 g, 10 mmol) dissolved in methanol (30 cm³), elemental sulphur (0.32 g, 10 mmol), and [NBu₄]⁺I⁻ (2.77 g, 7.5 mmol) dissolved in methanol (20 cm³). The product was obtained in 66% yield (2.11 g) and characterised as before.

DISCUSSION

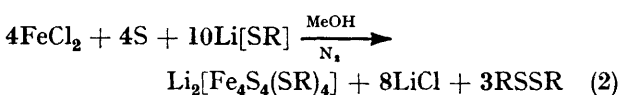
The synthesis of the [Fe₄S₄(SR)₄]²⁻ complexes by the route described here is much more convenient than the routes reported^{4,5} earlier. As already noted,⁸ the formation of these complexes is not particularly sensitive to the presence of water, thus solvent distillations and other time-consuming purification steps are unnecessary. Also, anhydrous FeCl₃ may be replaced by FeCl₂·4H₂O

with relatively little change in the overall yield. Furthermore, the use of elemental sulphur, in place of either sodium hydrogensulphide,^{3,4} lithium⁵ or sodium sulphide,⁸ is considerably more convenient and/or less expensive.

The success of the synthetic route involving FeCl₃ would appear to depend upon the reduction, by the thiolate anion, of half of the iron(III) to iron(II) and all of the elemental sulphur to sulphide [equation (1)].



Accordingly, the preparation requires a larger amount of the thiol than the other synthetic routes. The amount of thiol is, however, significantly (29%) reduced if Fe^{II} is used instead of Fe^{III} [equation (2)].



The convenient synthesis of the [Fe₄S₄(SR)₄]²⁻ species described here from iron(III) [or iron(II)], thiolate anions, and elemental sulphur supports a general view that such units represent the stable arrangement of these components, irrespective of their initial oxidation states.

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