Bis(tetra-n-butylammonium) Tetrakis[benzenethiolato-μ_3-selenido-iron], an Iron–Selenium Cubic Cluster Compound

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The compound $[Fe_4Se_4(SPh)_4]^{2-}$ has been prepared in good yield from benzenethiol, $FeCl_3$, and elementary selenium. Its spectroscopic and redox properties are very similar to those of the corresponding sulphido-compound $[Fe_4S_4(SPh)_4]^{2-}$, and it is concluded that it too contains a cubane-like nucleus.

SELENIUM is an important trace element in Nature and three enzymes (formate dehydrogenase, glycine reductase, and glutathione peroxidase) have been shown to contain it as an essential constituent.[1] It seems possible, therefore, that there may exist in Nature selenium analogues of iron–sulphur proteins, especially since it has been shown [2] that a fully biologically active selenium analogue of putidaredoxin can be obtained by treatment of the apoprotein with iron and selenide. No such replacement of sulphur by selenium in a four- or eight-iron ferredoxin has been reported and it seemed of interest to make such a replacement in the simple four-iron sulphur cluster compound $[Fe_4S_4(SPh)_4]$ (1) [3] with a view to comparing the properties of the two compounds. This paper reports the synthesis and some properties of the iron–selenium cluster compound $[Fe_4Se_4(SPh)_4]^{2-}$ (2); the isomer $[Fe_4S_4(SePh)_4]^{2-}$ (3), in which the peripheral sulphurs are replaced by selenium, was prepared in 1974 by Holm and his colleagues.[4,*]

RESULTS AND DISCUSSION

We obtained the bis(tetra-n-butylammonium) salt of (2) in good yield (81%) as large, almost black, prisms by the reaction of lithium benzenethiolate with iron(III) chloride and elementary selenium in methanol. Elementary selenium was used in preference to lithium selenide because of the relative instability of alkali-metal selenides; the reaction involves the *in situ* reduction of the selenium by the excess of benzenethiol used in the reaction. The compound is stable in both the solid state and solution, except that, like its sulphur analogue (1), it is very oxygen sensitive and must be prepared, and handled, under strictly anaerobic conditions (*e.g.* in oxygen-free nitrogen).

The principle band in the visible-absorption spectrum of (2) is red-shifted by 13 nm from the corresponding band for (1) and is less intense [$\varepsilon_{max.}$ 0.91 of that for (1)]; the position and intensity of this band are almost identical with those reported [4] for the corresponding band in the spectrum of the isomer (3).

The ^1H n.m.r. spectrum of compound (2) is also very similar to that of the parent sulphur compound (1),[5] the bands for the *o*- and *p*-hydrogens being shifted upfield, and that for the *m*-hydrogens downfield, from their positions in the spectrum of the diamagnetic reference compound benzenethiol (Table 1). This behaviour, observed for (1) by Holm *et al.*,[5] is characteristic of

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[*] Professor Holm has informed us, since the completion of our work, that he and his co-workers have also prepared (2) (M. A. Bobrik, E. J. Laskowski, R. W. Johnson, W. O. Gillum, J. M. Berg, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.*, in the press).

[1] For a review, see T. C. Stedtman, *Science*, 1974, **183**, 915.

[2] J. C. M. Tsibris, M. J. Namtvedt, and I. C. Gunsalus, *Biochem. Biophys. Res. Comm.*, 1968, **30**, 323.

[3] B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3523.

[4] L. Que, M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, 1974, **96**, 4168.

[5] R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle, and T. Herskovitz, *J. Amer. Chem. Soc.*, 1974, **96**, 2109.

contact shifts in benzenoid ligands[6] and indicates that the shifts we have observed are predominantly of this type. This similarity between the two compounds is strongly indicative of a close similarity in structure, a conclusion further supported by the positive (anti-Curie) temperature coefficient, characteristic of antiferromagnetically coupled systems, found for both (1) and (2) (ref. 5 and Table 2). The ^{13}C n.m.r. spectra of (1) and (2) both show four sharp singlets corresponding to the four types of carbon atom in the benzene rings; the isotropic shifts from the corresponding bands in the spectrum of benzenethiol[7] are given in Table 3. It will be seen that the bands for the *o*- and *p*-carbon atoms, like that for C^1, are shifted downfield and that for the *m*-carbon atoms upfield. This behaviour, opposite to that observed for the protons attached to these atoms, is again characteristic of contact shifts in benzenoid ligands.[6,8] The close similarity of their ^{13}C n.m.r. spectra is a further strong indication of similar structures for (1) and (2).

TABLE 1

Isotropic proton shifts in $(CD_3)_2SO$ at 30 °C

Compound	Shift (p.p.m.)[a] *ortho*	*meta*	*para*
(1)[b]	1.37	−1.14	1.95
(2)[b]	1.98	−1.15	2.49
(3)[c]	0.92	−0.82	1.52

[a] Here and in Tables 2 and 3, upfield shifts are positive. [b] Diamagnetic reference PhSH (multiplet at $\delta = -7.15$ p.p.m.). [c] Diamagnetic reference PhSeSePh. Data from ref. 4.

TABLE 2

Isotropic proton shifts for (2) in $(CD_3)_2SO$

θ_c/°C	Shift (p.p.m.) *ortho*	*meta*	*para*
30	1.98	−1.15	2.49
61	1.99	−1.20	2.57
89	2.00	−1.23	2.66
117	2.02	−1.28	2.73

TABLE 3

Isotropic carbon shifts in $(CD_3)_2SO$ at 30 °C

Compound	Shift (p.p.m.) * C^1	*ortho*	*meta*	*para*
(1)	−74.0	−31.5	5.2	−9.4
(2)	−87.5	−38.6	6.2	−12.0

* Diamagnetic reference PhSH (ref. 7).

A characteristic of the cubane-like nucleus in (1) and its analogues is its reversible reduction from the 2− to the 3− state; De Pamphilis *et al.*[9] found $E_{\frac{1}{2}}$ for this process in (1) to be −0.94 V in dimethyl sulphoxide and we found a value of −0.97 V by polarography in the same solvent, confirmed (−0.92 V) by cyclic voltammetry. Compound (2) behaved very similarly, giving a value of $E_{\frac{1}{2}}$ of −0.96 V by polarography and −0.95 V by cyclic voltammetry; the perfect reversibility of the reduction was shown by the separation (60 mV; theoretical, 59 mV) of the two peaks in the cyclic voltammogram.

The properties of (2), especially its ^1H and ^{13}C n.m.r. spectra and redox properties, are so similar to those of the parent sulphur compound (1) as to leave no reasonable doubt that it contains a cubane-like Fe_4Se_4 nucleus similar to the Fe_4S_4 nucleus present in (1) and the four- and eight-iron ferredoxins; this has been established by *X*-ray crystallography (see footnote on p. 1423). It will be seen from Tables 1 and 3 that the isotropic shifts for both the hydrogens and carbons of the benzene rings in (2) are considerably greater than those for the corresponding atoms in (1). That this is not due to the mere presence of selenium is clear, since the proton shifts for (3), with peripheral selenium atoms, are smaller than those for (1). Since the magnitudes of isotropic contact shifts are directly proportional to the magnetic susceptibility of the antiferromagnetic centre which causes them,[5] compound (2) must be more paramagnetic than (1); this has been confirmed by direct measurement (see footnote on p. 1423). This may well be due to the greater size of the selenium atom. If the Fe_4Se_4 'cube' in (2) is larger than the Fe_4S_4 'cube' in (1) the iron atoms will be further apart; this could reduce the antiferromagnetic coupling of the unpaired spins on the iron atoms in (2), so leading to greater paramagnetism in this compound.

EXPERIMENTAL

All the manipulations were carried out in oxygen-free nitrogen, passed over B.A.S.F. Catalyst R3-11 at 145—150 °C, in a Schlenk-type apparatus[10] or a gas-tight glove-box (Mecaplex model GB 3011). Solutions were transferred with syringes flushed with oxygen-free nitrogen. Solvents were freed from oxygen by four cycles of evacuation followed by admission of oxygen-free nitrogen.

Visible-absorption spectra were recorded on a Pye-Unicam SP 800B recording spectrophotometer, ^1H n.m.r. spectra on a Jeol MH-100 100 MHz spectrometer, and ^{13}C n.m.r. spectra on a Jeol PFT-100 spectrometer. The polarographic measurements were made at 25 °C with a Tinsley type 19/4 polarograph, using a stationary vitreous carbon electrode and a standard calomel reference electrode; the solvent was dimethyl sulphoxide containing tetra-n-propylammonium perchlorate (5×10^{-2} mol dm^{-3}) as supporting electrolyte.

Preparation of the Cluster Compounds.—Lithium (0.28 g, 40 mmol) was dissolved in anhydrous methanol (40 cm^3). After cooling to room temperature, benzenethiol (4.1 cm^3, 40 mmol) was added, followed by a solution of iron(III) chloride (1.62 g, 10 mmol) in methanol (20 cm^3). After 10 min, selenium powder (0.79 g, 10 mmol) was added rapidly, against a rapid outward flow of nitrogen, and the mixture stirred vigorously overnight; a red-brown colour appeared

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[6] W. D. Horrocks in 'NMR of Paramagnetic Molecules: Principles and Applications,' eds. G. N. LaMar, W. D. Horrocks, and R. H. Holm, Academic Press, New York, 1973, ch. 4.

[7] C. V. Senoff and J. E. H. Ward, *Inorg. Chem.*, 1975, **14**, 278.

[8] I. Morishima, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, 1970, **92**, 6651.

[9] B. V. De Pamphilis, B. A. Averill, T. Herskovitz, L. Que, and R. H. Holm, *J. Amer. Chem. Soc.*, 1974, **96**, 4159.

[10] D. F. Shriver, 'The Manipulation of Air-Sensitive Compounds,' McGraw-Hill, New York and London, 1969, ch. 7, p. 145.

after a few minutes. The mixture was filtered into a solution of tetra-n-butylammonium iodide (2.77 g, 7.5 mmol) in methanol (20 cm^3). The black precipitate was collected by filtration, washed copiously with methanol, and dried *in vacuo*. The solid was dissolved on the sinter with the minimum of acetonitrile at 45 °C; methanol was added to the filtered solution to incipient crystallisation at 45 °C after which it was allowed to cool slowly to room temperature and then kept overnight at −10 °C. The large, almost black, prisms were collected by filtration and dried *in vacuo*. *Bis(tetra-n-butylammonium) tetrakis[benzenethiolato-μ_3-selenido-iron]* (2) so obtained (2.95 g, 81%) had m.p. 220—221 °C (decomp.): $\lambda_{max.}$ 471 nm (ε 16 100 dm^{-3} mol^{-1} cm^{-1}) in $(CD_3)_2SO$; δ (p.p.m. from $SiMe_4$) in $(CD_3)_2SO$, 4.66 (*p*-H), 5.17 (*o*-H), 8.30 (*m*-H), 122.5 (*m*-C), 137.2 (*p*-C), 167.7 (*o*-C), and 218.0 (C^1) (Found: C, 46.25; H, 6.20; Fe, 15.5; N, 2.05; S, 8.80; Se, 21.5. $C_{56}H_{92}Fe_4N_2S_4Se_4$ requires C, 46.05; H, 6.35; Fe, 15.3; N, 1.90; S, 8.80; Se, 21.6%).

Bis(tetra-n-butylammonium) tetrakis[benzenethiolato-μ_3-sulphido-iron] (1) prepared by published procedures,[3,11] had $\lambda_{max.}$ 458 nm (ε 17 600 dm^3 mol^{-1} cm^{-1}) in $(CD_3)_2SO$ and δ (p.p.m. from $SiMe_4$) in $(CD_3)_2SO$ 5.20 (*p*-H), 5.78 (*o*-H), 8.29 (*m*-H), 123.5 (*m*-C), 134.6 (*p*-C), 160.6 (*o*-C), and 204.5 (C^1).

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[11] G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Amer. Chem. Soc.*, 1974, **96**, 641.