Inorganica Chimica Acta, *120* (1986) 191–195

The Search for a Coordinated Dialkyl Disulphide: the Crystal and Molecular Structure of (μ-Ethanedithiolato)bis(tricarbonyliron)(*Fe–Fe*)

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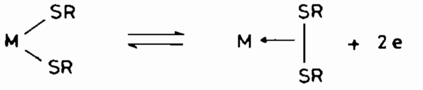
(Received May 20, 1986)

Abstract

Despite considerable effort, no compounds containing an alkyl disulphide linked to a single metal ion have been isolated. The complex $[\{Fe(SCH_2CH_2S)_2\}_2]^{2-}$ is a strong reducing agent. $[Fe_3(CO)_{12}]$ with 1,2,5,6-tetrathiacyclooctane yields $[(SCH_2CH_2S)\{Fe(CO)_3\}_2]$, the structure of which has been determined by X-ray analysis.

Introduction

There have been several suggestions that sulphur ligands in the same metal coordination sphere exhibit sulphur–sulphur interactions which are additional to the formal electron-pair interactions of the sulphurs individually with the central metal ion [1]. The evidence for this is primarily the sulphur–sulphur separations, which are often shorter than expected, and a particularly good example is MoS_2, wherein each molybdenum is coordinated by six sulphurs, and the S–S separations are *ca.* 3.15 Å [2], compared with the expected non-bonding minimum of 3.7 Å [3]. We have observed similar phenomena in $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ and $[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$ [4]. A logical extension of this is that in the limit there might be complete oxidation of two adjacent thiolato-sulphurs to form a formal S–S bond and that such a transformation might be used in biological systems as a reversible source of electrons (eqn. 1) [1]. In fact, it has already been found to occur intermolecularly in the conversion of $[MoS_4]^{2-}$ to $[Mo_2S_8]^{2-}$, which has been shown by X-ray crystallography to be best represented by the formula $[(\mu\text{-}S)_2\{MoS(S_2)\}_2]^{2-}$, where the S–S separations in the coordinated S_2 are *ca.* 2.06 Å [5]. However whereas S_2 is well known as a ligand, there is, to our knowledge, no unequivocal identification of dialkyl or diaryl disulphides as ligands. What lends credence to the suggestion that complexes of dialkyl disulphides might be obtainable is the fact that metal salts in higher oxidation states, and especially iron(III) chloride, are used to convert thiols to disulphides [6]. We therefore decided to start our investigations with iron compounds and selected disulphides.



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Results and Discussion

We approached the synthesis of disulphide complexes by oxidation of iron thiolato-complexes, as well as by the reaction of low-oxidation-state iron compounds with disulphides. To date, neither approach has been successful, though interesting observations have been made.

Some years ago, Holm *et al.* [7] described a dinuclear complex ion $[\{Fe(SCH_2CH_2S)_2\}_2]^{2-}$. Following the procedure and quantities reported in the literature for its preparation resulted in the formation of a completely insoluble, presumably polymeric material. However, the published recipe contains a typographical error such that it prescribes the use of a large excess of iron(III) chloride in reaction with ethanedithiol. Using a strict 1:2 ratio of chloride to dithiol, the dinuclear complex $[\{Fe(SCH_2CH_2S)_2\}_2]^{2-}$ was isolated in good yield.

The insoluble material analysed for $Fe(SCH_2CH_2S)_2$. We have not been able to determine its structure. Holm's dinuclear complex was presumably oxidised by iron(III) in the preparation as described [7], although, containing iron(III) itself, there is no obvious source of electrons. We were able to obtain the insoluble material upon oxidation of Holm's complex by iron(III) chloride, iron(II) perchlorate, iron(II) iodide, dibromobis(triphenylsilyl)cobalt, potassium ferricyanide, tin(II) chloride, vanadium(III) chloride, 1,2-dibromoethane, and various aryldiazonium salts. Clearly Holm's com-

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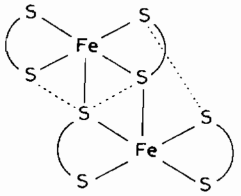
0020-1693/86/$3.50

pound is a very strong reducing agent, and in the oxidations quoted above each dianion gives up two electrons. The oxidation is chemically reversible, and sodium borohydride regenerates the dianion cleanly. The complex, due to the insolubility of the oxidised form, may have synthetic utility, and we have used it to reduce $[MoCl_4(thf)_2]$ to $[MoCl_4(thf)_2]^-$ [8], albeit in low yield.

We cannot unequivocally identify the source of the electrons involved in these reductions. The Holm complex [7] is of intermediate spin and has a Mössbauer spectrum with isomer shift of 0.20 mm s^{-1} and quadrupole splitting of 3.23 mm s^{-1}, and contains formal iron(III). The spectrum of the oxidised product contains two signals, one, representing about 75% of the intensity, has an isomer shift of 0.34 mm s^{-1} and a quadrupole splitting of 1.90 mm s^{-1}, and the other with shift of 0.44 mm s^{-1} and splitting of 0.85 mm s^{-1}

There are no good model systems with which to evaluate these data. The product is not contaminated by $FeCl_3$ since this has a value at 78 K of $\delta = 0.53$ mm s^{-1} and a considerably smaller splitting than any reported here. It seems likely that since the isomer shifts do not change dramatically upon oxidation, then the oxidation state of the iron has not changed [9]. This can only be surmised in the absence of data on iron(III) and iron(IV) in appropriate sulphur environments, but it is at least of interest that upon oxidation of iron(III) porphyrinato-complexes, the porphyrin is oxidised before iron [9]. If a similar thing happens here, starting with Holm's structure [7], one might envisage several kinds of S–S bond formation upon oxidation, each giving rise to iron in different environments. Some are indicated by the dotted lines for intramolecular S–S bond making



in the diagram, but intermolecular coupling also seems likely in view of the insolubility of the product. Clearly, there is no problem to account for the Mössbauer data. Despite many attempts, we were not able to prepare samples of $\{Fe(SCH_2CH_2S)_2\}^n$ suitable for X-ray structure analysis, but the paper by Hoffmann *et al.* [10] on the extended structures of metal bis(dithiolenes) and tetrathiolates makes it clear that there is ample precedent for intermolecular S–S interactions in such compounds.

We have also attempted to use disulphides directly as ligands. The compound $HNCH_2CH_2NHCH_2$-$CMe_2SSCMe_2CH_2$ does not form isolable adducts with a wide range of iron materials investigated, and only with iron(II) iodide was a characterisable product obtained. This is apparently an organic salt, and not a complex. Model studies show clearly that the heterocyclic disulphide is too small to contain a metal ion bound to both nitrogens and the disulphide moiety.

This is also true of 1,2,5,6-tetrathiacyclooctane, which reacts with a range of iron-containing materials to give no well-defined materials other than $(C_2H_4S_2)_n$. However, from the reaction with $[Fe_3(CO)_{12}]$ we isolated red crystals of a carbonyl complex which analysed for $[C_2H_4S_2\{Fe(CO)_3\}_2]$. Such a material was first isolated by King [11], who reported that his product had IR stretching frequencies in the carbonyl region at 2080(s), 2045(s), and 2000(s) cm^{-1} (presumably in Nujol) and a molecular weight in accordance with the di-iron formulation. This compound was later obtained by Seyferth and Henderson [12] using an alternative route. Our product showed a much more complex IR spectrum (in hexane), with bands at 2084(s), 2044(s), 2012(s), 1997(vs), and 1988(m) cm^{-1}, and less pure samples showed an additional sharp band at 2000 cm^{-1} which may be due to $[Fe_2(CO)_6S_2]$ [13]. We therefore postulated that our product was a larger cluster than King's [11], maybe with four irons, although its melting point (74–75 °C) is similar to that reported by King (74–76 °C) [11]. Only later did we ascertain that the Nujol spectrum presents bands at *ca.* 2080, 2040, and 2000 cm^{-1}, together with a wide envelope free of well-defined maxima down to below 1900 cm^{-1}. This was presumably seen by King [11] and Seyferth [12], but not reported.

The crystal structure analysis of our product (Fig. 1) showed that it is indeed of the structure proposed

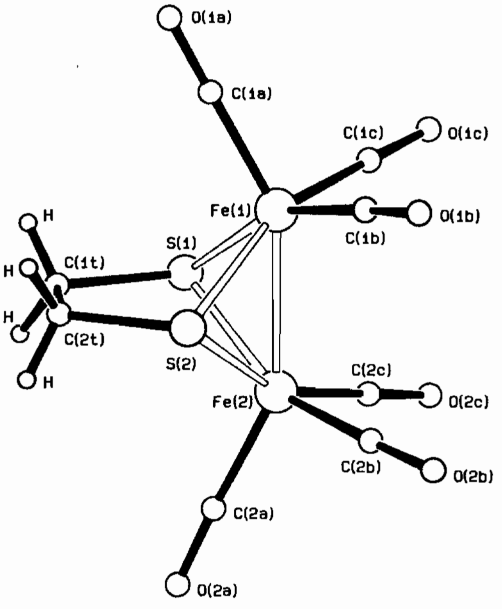


Fig. 1. One of the two virtually identical molecules of $[\{Fe(CO)_3\}_2(SCH_2CH_2S)]$.

TABLE I. Selected Bond Distances and Angles in Complexes $[YS_2\{Fe(CO)_3\}_2]$

Y	Fe–Fe (A)	Fe–S (mean) (A)	S–S (A)	Fe–S–Fe (mean) (°)	S–Fe–S (mean) (°)	Reference
–	2.552(2)	2.228(4)	2.007(5)	69.9(1)	53.5(1)	17
Et_2	2.537(10)	2.259(7)	2.932(14)	68.3(3)	81.0(3)	18
Ph_2	2.516(2)	2.270(2)	2.910(3)	67.3(1)	79.8(1)	19
=C	2.486(2)	2.292(2)	2.742(2)	65.7(1)	73.5(1)	20
CH_2	2.485(1)	2.262(1)	2.673(2)	66.64(4)	72.45(4)	15
$(CH_2)_2{}^a$	2.497(4)	2.245(2)	2.893(2)	67.6(2)	80.2(1)	this work
$(CH_2)_2$ (at −80 °C)^a	2.502(1)	2.239(1)	2.887(1)	67.92(3)	80.34(4)	14
Ph_2C_2	2.508(4)	2.259(6)	2.866(7)	68.1(2)	78.8(2)	21

^{a}Values are means from two independent molecules.

by King [11] and later by Seyferth [12], so that our synthesis represents yet another route to a well-known complex, not hitherto characterised structurally [14]*. The beautifully symmetric structure should exhibit four strong bands in the CO stretching region, as does $[CH_2S_2\{Fe(CO)_3\}_2]$ [15], which is what we observe, though the medium band at 1988 and a further weak one at 1960 cm^{-1} may suggest a more complex situation in solution. The structure is one of a number (Table I) which possess two $Fe(CO)_3$ residues linked by two sulphurs carrying various substituents, and there are also analogues containing, for example, two phosphoruses [16].

There are two independent molecules in the crystal, each of which has almost ideal C_{2v} (*mm*2) symmetry. The carbonyls are eclipsed, and so, surprisingly, are the hydrogens of the bridging methylenes, which take up ideal axial–axial (*aa*) positions on the Fe_2S_2 base. King [22] has suggested that the complex $[Me_2S_2\{Fe(CO)_3\}_2]$ exists in solution and the solid state in two (*ae* and *ee*) of three possible isomeric forms (*aa*, *ae*, and *ee*; *e* = equatorial) on the basis of ^1H NMR data as was confirmed by Seyferth [23]. The lone singlet resonance we observe at $\delta = 2.38$ ($CDCl_3$) ppm in the ^1H NMR spectrum suggests that in our case the *aa* conformation persists in solution.

The Fe–Fe separation in the crystals is 2.497(4) Å. This is consistent with the comparable distances in all the other complexes (Table I), which lie in the range 2.485(1) to 2.552(2) Å considered to be a normal iron–iron bond. It is considerably shorter than the value of 2.740(1) Å observed in $[Bu^t{}_2P_2\{Fe(CO)_3\}_2]$ [16]. Similarly, the Fe–S separations throughout the series of compounds are relatively invariant (2.228–2.292 Å) and consequently the Fe–S–Fe angles cluster around the same value (range 65.7–69.9°). Thus, the FeSFe triangles are relatively rigid.

However, the S···S separations vary over a range of almost 1 Å, being 2.007(5) Å in the shortest case where there is a clear S–S bond, and 2.932(14) Å in the longest. The S···S contact is obviously the most easily deformed part of the central molecule, but there is an optimum S···S distance of *ca.* 2.9 Å. Since the non-bonding minimum separation is 3.7 Å, there is strong evidence here for some degree of S–S bonding interaction, and there is some justification for regarding the whole class of compounds as complexes of disulphides. In our sample, the S···S contacts have a mean value of 2.893(3) Å, which is achieved by the eclipsing of the C–S (and C–H) bonds with the slight strain showing in the S–C–C angles of 112.5(2)°.

Experimental

All manipulations were carried out under pure dry dinitrogen using Schlenk or dry-box techniques, as appropriate. Most iron compounds were commercial samples, though iron(II) iodide was made by reaction of iron filings and iodine in dichloromethane following the prescription of Hathaway [24], and the Holm complex was synthesised according to ref. 7 using 20 mmol $FeCl_3$ rather than the 50 mmol specified. Tetrathiacyclooctane was prepared by the method of Musker *et al.* [25], and 1,1,8,8-tetramethyl-3,6-diaza-9,10-dithiacyclodecane was prepared by a modification of the method of Corbin and Work [26] in which the cyclic diene precursor was reduced using $NaBH_4$ rather than with $LiAlH_4$ which would give rise to an open-chain linear dithiol.

$$Me_2CHCHO \xrightarrow[CHCl_3]{S_2Cl_2} OHCCMe_2SSCMe_2CHO$$

$$\xrightarrow{H_2NCH_2CH_2NH_2} \overline{SSCMe_2CHNCH_2CH_2NCHCMe_2}$$

$$\xrightarrow{NaBH_4} \overline{SSCMe_2CH_2NHCH_2CH_2NHCH_2CMe_2}$$

This material will be fully described elsewhere.

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*The compound has been synthesised by yet another route and characterised structurally by Lorenz *et al.* [14], whose work was published after our research had been completed.

IR spectra were obtained in solution in hexane and in Nujol mulls using a Pye-Unicam SP2000 spectrometer. NMR spectra were obtained using a JEOL FX-90Q spectrometer and reactions were followed where appropriate in the UV using an Unicam SP1800 instrument.

The Mössbauer spectra were obtained by Dr. J. Silver (University of Essex) using a Harwell spectrometer (waveform generator MWG200, servoamplifier MSA200, proportional counter MPC200, vibrator MV200) and a Canberra multichannel analyser, series 30, with an HV power supply 3105, amplifier 2012, and pre-amplifier 200BE. The source was ^{57}Co, 5 mCi in Rh (Amersham International). The spectrometer was operated in a 'saw-tooth' mode and the spectra were computer-fitted. The spectrometer was calibrated with a 25 μm thick natural iron reference and the samples were held at 80 K. We gratefully acknowledge Dr. Silver's help in obtaining and interpreting these spectra.

Analyses were by Mr. C. J. Macdonald, AFRC UNF. Assistance with the X-ray analysis from Mr. A. Hills is gratefully acknowledged.

Ironbis(ethanedithiolate)

This compound can be obtained by the action of a whole range of oxidising agents on the anion $[\{Fe(SCH_2CH_2S)_2\}_2]^{2-}$. A typical preparation is given below.

To $(Bu^n_4N)_2[\{Fe(SCH_2CH_2S)_2\}_2]$ (0.11 g, 0.11 mmol) in MeCN (25 cm^3) was added 1.8 cm^3 aliquots of a solution of $FeCl_3$ (0.10 g, 0.6 mmol) in MeCN (10 cm^3). After the first addition the mixture consisted of an insoluble black solid under a clear supernatant liquid. After the addition of three aliquots the mixture was filtered and the solid washed with acetonitrile and dried *in vacuo*. Yield 0.04 g. *Anal.* Found: C, 20.5; H, 3.46. Calc. for $C_4H_8FeS_4$: C, 20.0; H, 3.33%. The product is insoluble in all common solvents.

μ-Ethanedithiolato(S–S)bis(tricarbonyliron)(Fe–Fe)

A mixture of 1,2,5,6-tetrathiocyclooctane (0.21 g, 1.41 mmol) and triiron dodecacarbonyl (0.76 g, 1.51 mmol) in toluene (50 cm^3) was heated at 90 °C for 1 h. The red–brown solution was stirred overnight at 20 °C, filtered, and reduced to 5 cm^3. It was again filtered, and reduced to dryness. The solid was extracted several times with hexane (10 cm^3) and the extracts combined, and cooled to −20 °C. The crystals obtained were recrystallized from hexane. The material, which is very air-sensitive in solution, can be sublimed at 10^{-3} mmHg without change. Yield 0.07 g. *Anal.* Found: C, 26.0; H, 1.18. Calc. for $C_{16}H_8Fe_4O_{12}S_4$: C, 25.8; H, 1.08%. ^{13}C NMR spectrum: 2 singlets at δ = 37.0 and 28.9 ppm ($CDCl_3$).

X-ray Crystal Structure Analysis of $[\{Fe(CO)_3\}_2(SCH_2CH_2S)]$

We report here only the crystal data for our analysis since this complex has also recently been analysed (at −80 °C) by Lorenz *et al.* [14]. Our crystal and molecular results are in close agreement with those of Lorenz *et al.* [14]; some molecular dimensions are in Table I.

Crystal data

$C_8H_4Fe_2O_6S_2$. M_r = 371.9. Triclinic. Space group $P\bar{1}$ (no. 2). $a = 8.961(3)$, $b = 9.277(3)$, $c = 16.023(6)$ Å. $\alpha = 86.15(3)$, $\beta = 85.18(3)$, $\gamma = 88.49(3)°$, U = 1324.1 Å^3, $Z = 4$, $D_c = 1.87$, μ(Mo Kα) = 25.1 cm^{-1}, $F(000) = 736$. 4645 unique intensity data ($1.2 < \theta <$ 25°) were collected at 20 °C on an Enraf-Nonius CAD4 diffractometer, with monochromated Mo-radiation. Final F_r and R_w values [27] were 0.033 and 0.035 for all but 4 low-θ high-intensity reflections, weighted $w = (\sigma_F{}^2 + 0.000726F^2)^{-1}$.

Supplementary Material

Full Tables of crystallographic data (structure amplitudes, atomic parameters and molecular dimensions) are available from the authors on request.

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