SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF [Fe(h^5-C$_5$H$_5$)(CO)(μ-SC$_5$H$_9$NCH$_3$)]$_2$

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Summary

The reaction of Fe$_2$(CO)$_4$(h^5-C$_5$H$_5$)$_2$ with 4-N-methylpiperidine-disulphide affords [Fe(h^5-C$_5$H$_5$)(CO)(μ-SC$_5$H$_9$NCH$_3$)]$_2$, the crystal structure of which has been determined. The crystals are monoclinic, space group $C2/c$ with a 18.761(3), b 14.543(2), c 9.556(1) Å, β 103.67(2)°. With $Z = 4$ the calculated density is 1.46 g cm^{-3}; the final weighted R factor was 0.047 for 1645 independent reflections. The two carbonyl groups and the two sulphur-attached piperidine groups in the dimeric structure are both cisoid.

Reaction with CH$_3$I leads to methylation that with aqueous HClO$_4$ to protonation of the nitrogen atoms of the piperidine rings, giving formation of the [Fe(h^5-C$_5$H$_5$)(CO)(μ-SC$_5$H$_9$N(CH$_3$)$_2$]$_2$I$_2$ · 2H$_2$O salt and [Fe(h^5-C$_5$H$_5$)(CO)(μ-SC$_5$H$_9$NHCH$_3$)]$_2^{2+}$ cation, respectively.

Introduction

Considerable attention has been focussed recently on bridging sulphido derivatives of iron in view of their possible relationship to the oligonuclear iron-sulphur chromophores thought to comprise the active sites in the ferredoxines, an important class of non-heme iron electron-transfer proteins having low redox potentials [1]. We recently described the synthesis, properties, and structure of the compound formed in the reaction of N-methyl-4-mercaptopiperidine with Fe$_3$(CO)$_{12}$ [2]. In continuation of our studies on this type of metal complex, we now report on the synthesis, molecular structure, and properties of the dimeric species formed in the reaction of 4-N-methylpiperidinedisulphide with Fe$_2$(CO)$_4$Cp$_2$.

Description of the structure

Information about the data collection and structure refinement is given in Table 1. Table 2 lists the final position and thermal parameters. Table 3 some selected bond lengths and angles, and Table 4 some least-squares planes. A general view of the molecule with the atom numbering scheme is shown in Fig. 1. The structure of $[Fe(h^5-C_5H_5)(CO)(\mu-SC_5H_9NCH_3)]_2$ is comprised of two crystallographically identical $Fe(h^5-C_5H_5)(CO)$ moieties symmetrically linked to each other by two bridging mercapto ligands in such a way that the two carbonyl groups and the two sulphur-attached piperidine groups are both cisoid. The iron atoms are formally in the $+2$ oxidation state, and are six-coordinate if the Cp group is considered as a three-coordinate monoanion. The structure may also be visualized as arising from the intersection of the C–S–S planes of two distorted tetrahedrons formed by these atoms and the centroid of the cyclopentadienyl rings, along the C···S edge. The iron atoms are located at the center of the tetrahedrons. The Fe_2S_2 system is almost exactly planar, as can be seen from Table 4. The S···S distance is 2.993(1) Å shorter than twice the Van der Waals radius for sulphur, suggesting bond interactions [3], and the Fe···Fe distance is 3.438(1) Å. The Fe–S–Fe angles of 98° are characteristic of M–B–M bridging angles in complexes not containing metal–metal interactions [4].

The Fe–S, Fe–C and C–O bond lengths of 2.278(5), 1.745(5), and 1.137(6) Å are in the expected range for iron carbonyl derivatives with Fe_2S_2 core [5]. The Fe–C–O atoms are within 3° of linear.

TABLE 1

CRYSTAL AND DATA COLLECTION PARAMETERS FOR $[Fe(h^5-C_5H_5)(CO)(SC_5H_9NCH_3)]_2$

Formula	$C_{24}H_{34}N_2O_2S_2Fe_2$
Formula weight	558.35
Crystal system	monoclinic
Space group	$C2/c$
a, Å	18.761(3)
b, Å	14.543(2)
c, Å	9.556(1)
β, deg	103.67(2)
V, Å^3	2533(1)
Z	4
d_{calc}, g cm^{-3}	1.46
$F(000)$	1160
Diffractometer	Philips PW-1100
Radiation, λ, Å	Mo-K_α 0.71069
μ, cm^{-1}	13.6
Crystall. dimens. mm	$0.1 \times 0.1 \times 0.2$
Scan type	ω
θ range, deg	2–25
Total number of reflections	1645
Reflections with $I \geqslant 2.5\sigma$	1638
Final R_F [a]	0.045
Final R_{wF}	0.047

[a] The function minimized was $w(|F_0| - |F_c|)^2$, where $w = (\sigma^2(F_0) + 0.0036|F_0|^2)^{-1}$

TABLE 2

ATOMIC COORDINATES ($\times 10^4$ Fe and $S \times 10^5$) AND THERMAL PARAMETERS

Atom	x	y	z	B (Å^2)
Fe(1)	42614(3)	31714(5)	10386(7)	2.33(3)
C	4208(3)	1975(4)	915(5)	3.13(24)
O	4151(3)	1200(3)	780(5)	5.58(26)
S	55087(6)	32254(8)	15071(12)	2.40(5)
C(1)	5876(3)	2206(4)	803(5)	2.53(21)
C(2)	5660(3)	2231(4)	−829(5)	3.45(25)
C(3)	5989(4)	1395(5)	1439(6)	3.60(27)
N(4)	6784(2)	1412(3)	−984(5)	3.10(19)
C(5)	7004(3)	1350(5)	599(6)	3.91(27)
C(6)	6704(4)	2159(7)	1282(6)	3.62(27)
C(7)	7102(4)	678(5)	−1639(8)	4.55(35)
C(11)	3506(4)	3323(5)	−944(7)	4.43(30)
C(12)	4082(4)	3928(5)	−882(7)	4.35(30)
C(13)	4100(3)	4530(4)	266(7)	3.96(28)
C(14)	3538(4)	4299(4)	908(7)	3.94(27)
C(15)	3163(3)	3556(5)	189(7)	4.16(29)

The piperidine rings are slightly distorted chairs, as can be seen from Fig. 2 and is also shown by the distances of 0.700 and −0.683 Å of the N(4) and C(1) atoms from the C(2)–C(3)–C(5)–C(6) plane.

TABLE 3

BOND LENGTHS AND BOND ANGLES

(a) Bond lengths (Å)		(b) Bond angles (deg)	
C–Fe(1)	1.745(5)	S–Fe(1)–C	95.1(2)
S–Fe(1)	2.278(1)	Fe(1)–S–Fe(1)*	97.9(1)
C(11)–Fe(1)	2.091(5)	O–C–Fe(1)	177.1(4)
C(12)–Fe(1)	2.098(5)	C(1)–S–Fe(1)	111.0(1)
C(13)–Fe(1)	2.105(5)	S–Fe(1)–S*	82.0(1)
C(14)–Fe(1)	2.114(5)	C(2)–C(1)–S	109.1(3)
C(15)–Fe(1)	2.104(5)	C(6)–C(1)–S	112.0(4)
Fe(1)–Fe(1) *	3.438(1)	C(6)–C(1)–C(2)	108.5(4)
O–C	1.137(6)	C(3)–C(2)–C(1)	109.7(4)
C(1)–S	1.828(5)	N(4)–C(3)–C(2)	110.4(4)
C(2)–C(1)	1.517(6)	C(9)–N(4)–C(3)	109.0(4)
C(6)–C(1)	1.514(8)	C(7)–N(4)–C(3)	111.0(5)
C(3)–C(2)	1.538(8)	C(7)–N(4)–C(5)	110.9(4)
N(4)–C(3)	1.451(7)	C(6)–C(5)–N(4)	110.5(4)
C(5)–N(4)	1.473(6)	C(5)–C(6)–C(1)	111.3(5)
C(7)–N(4)	1.436(7)	C(15)–C(11)–C(12)	107.7(6)
C(6)–C(5)	1.513(10)	C(13)–C(12)–C(11)	107.8(6)
C(12)–C(11)	1.384(8)	C(14)–C(13)–C(12)	108.6(5)
C(15)–C(11)	1.424(9)	C(15)–C(14)–C(13)	108.7(6)
C(13)–C(12)	1.398(8)	C(14)–C(15)–C(11)	107.2(6)
C(14)–C(13)	1.380(8)		
C(15)–C(14)	1.381(8)		
S...S*	2.993(1)		
Fe(1)–Cp(center)	1.736(9)		

TABLE 4

DISTANCES (Å) OF ATOMS FROM SELECTED LEAST-SQUARES PLANES

Plane 1. Plane through Fe(1)–S–Fe(1)*–S*
Equation: $Y = 4.672$ [a]

| Fe(1) | –0.042 | S | 0.042 |
| Fe(1)* | –0.036 | S* | 0.037 |

Plane 2. Plane through C(11)–C(12)–C(13)–C(14)–C(15)
Equation: $-0.482X + 0.624Y - 0.615Z = 0.279$

C(11)	0.001	C(14)	0.001
C(12)	0	C(15)	0.001
C(13)	–0.001	Fe(1)	–1.736

Plane 3. Plane through C(2)–C(3)–C(5)–C(6)
Equation: $0.637X + 0.621Y - 0.456Z = 9.245$

C(2)	0.008	C(6)	–0.008
C(3)	0.008	N(4)	0.700
C(5)	0.008	C(1)	–0.683

[a] The equations of the planes are given in an angstrom orthogonal coordinate system (X, Y, Z) which is related to the monoclinic crystallographic fractional coordinates (x, y, z) by the transformation $X = ax + cz \cos \beta$, $Y = by$ and $Z = cz \sin \beta$. Unit weights were used in the calculations of the planes.

The bonds Fe–C(11) and Fe–C(12), 2.091(5) and 2.098(5) Å are short. The Fe–C(13) and Fe–C(15) distances are intermediate at 2.105(5) and 2.104(5) Å, and the Fe–C(14) bond is the longest, at 2.114(5) Å.

Hoffman [7] has suggested that a degree of tilting of the Cp ring observable in some $CpML_4$ compounds can be accounted for in terms of interactions involving δ orbitals of the metal and Cp ligand. In projection, the eclipsing of a M–C(Cp) bond
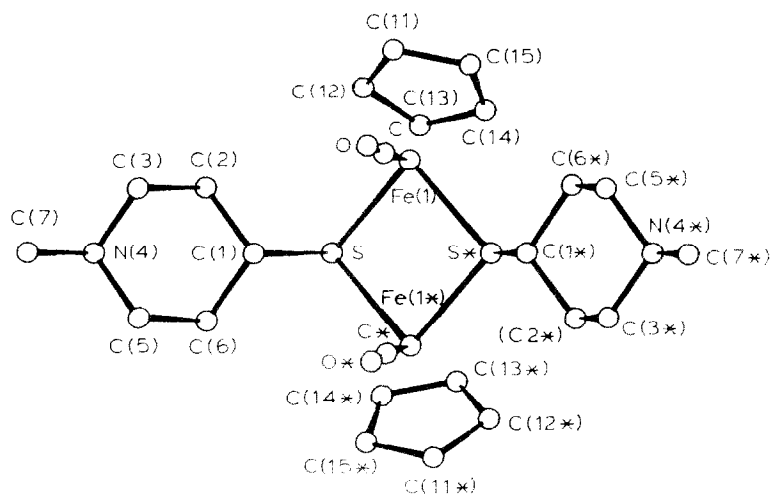

Fig. 1. Perspective view of the molecule showing the numbering scheme. Atoms are represented by circles of arbitrary size [6].
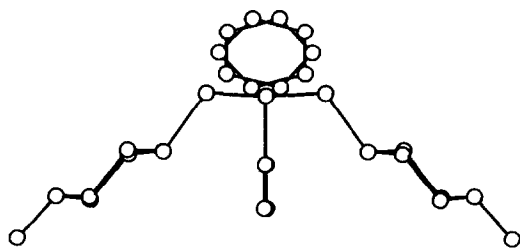
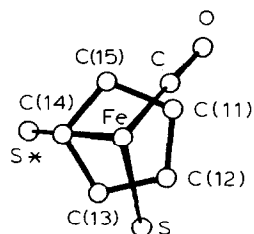Fig. 2. Projection of the molecule on to the C(11)–S–S*–C(11)*.

Fig. 3. Projections on to the planes of the Cp rings.

with a M–L bond results in a slightly long M–C(Cp) bond length, whereas when a M–C(Cp) bond is staggered between the M–L bond, it is short.

The C–C ring dimensions in the Cp ligand are normal, and the carbon atoms form a well-defined plane.

Discussion

The compound $[Fe(Cp)(CO)(\mu\text{-}SR)]_2$, where $Cp = h^5\text{-}C_5H_5$ and $RSH = N$-methyl-4-mercaptopiperidine, was prepared from the redox reaction $RSSR + Fe_2(CO)_4Cp_2$ in boiling toluene. The compound shows two infrared bands in the CO stretching region (1930vs, 1900s) and strong bands at 2810 and 2780 cm^{-1}, characteristic of the CH stretching vibrations of the methyl groups bonded to a nitrogen atom which retains its lone pair of electrons [8], indicating that the nitrogen atoms of the piperidine rings are deprotonated. The reaction of the diiron complex with CH_3I affords the $[Fe(Cp)(CO)(SRCH_3)]_2I_2 \cdot H_2O$ salt. In the IR spectrum of this compound, the absence of the bands at 2810 and 2780 cm^{-1} and the sharp band observed at 3000 cm^{-1} are indicative of the $N(CH_3)_3$ group [9], indicating that the methylation of the nitrogen atoms has taken place.

The reaction of the neutral complex with $HClO_4$ results in the formation of the $[Fe(Cp)(CO)(SRH)]_2^{2+}$ cation. The IR spectrum of its BPh_4^- salt shows a very broad absorption centered at about 2600 cm^{-1}, assigned to the $\nu(N–H)$ vibrations, indicating that protonation of the nitrogen atoms of the piperidine rings has taken place and that the resulting N–H bonds participate in hydrogen-bond formation.

Comparison of the $\nu(C–O)$ stretching region of the IR spectra of these compounds with that of the neutral complex reveals no significant difference suggesting that the dimeric structure with terminal CO groups is maintained.

Experimental

IR spectra were recorded on a Beckman IR-20 A spectrophotometer using KBr pellets or CaF_2 cells (solutions). $Fe_2(CO)_4Cp_2$ and the 4-N-methylpiperidine disulphide were prepared by known methods [10,11].

Preparation of $[Fe(h^5-C_5H_5)(CO)(\mu-SC_5H_9NCH_3)]_2$

The reaction was carried out under dry N_2 using standard Schlenk techniques. To a 30 ml solution of $Fe_2(CO)_4Cp_2$ (1 mmol) in toluene was added 4-N-methylpiperidine disulphide (1 mmol) and the solution was refluxed overnight and then allowed to cool at room temperature. After filtration the solvent was removed in vacuo and a solution of the residue, in methanol was chromatographed on a SiO_2 column. The last fraction was evaporated to dryness and the residue was crystallized on a CH_2Cl_2/hexane mixture. Anal. Found: C, 51.7; H, 6.1; N, 4.9. $C_{24}H_{34}N_2O_2S_2Fe_2$ calcd.: C, 51.6; H, 6.1; N, 5.0; O, 5.7; S, 11.5; Fe, 20.0%.

Preparation of $[Fe(h^5-C_5H_5)(CO)(\mu-SC_5H_9N(CH_3)_2]_2I_2 \cdot 2H_2O$

A slight excess of CH_3I (2 mmol) was added slowly with vigorous stirring to a 25 ml solution of $[Fe(h^5-C_5H_5)(CO)(\mu-SC_5H_9N(CH_3)_2]_2$ (1 mmol) in chloroform. Further stirring for 15 min produced a green precipitate. The precipitate (which was water soluble) was filtered off, washed with chloroform and diethyl ether, and dried in vacuo over silica gel. Anal. Found: C, 35.7; H, 4.9; N, 3.0. $C_{26}H_{44}N_2O_4S_2Fe_2I_2$ calcd.: C, 35.6; H, 5.1; N, 3.2; S, 6.3; O, 7.3; Fe, 12.7; I, 28.9.

Preparation of $[Fe(h^5-C_5H_5)(CO)(\mu-SC_5H_9NHCH_3)]_2(BPh_4)_2 \cdot 2H_2O$

A slight excess of concentrate aqueous $HClO_4$ (2 mmol) was added slowly with stirring to a 25 ml solution in chloroform of $[Fe(h^5-C_5H_5)(CO)(\mu-SC_5H_9NCH_3)]_2$ (1 mmol). Further stirring produced a green colour in the aqueous phase. Addition of a $NaBPh_4$ solution to the aqueous phase gave a green solid which was filtered off, washed with chloroform and diethyl ether, and dried in vacuo over silica gel. Anal. Found: C, 69.6; H, 6.2; N, 2.4. $C_{72}H_{80}N_2O_4S_2B_2Fe_2$ calcd.: C, 70.0; H, 6.5; N, 2.3; O, 5.2; S, 5.2; B, 1.8; Fe, 9.0%.

X-ray data collection and structure determination

A crystal ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 < \theta \leqslant 9°$) and the cell-parameters and orientation matrix refined by least-squares. Intensities were collected with Mo-K_α radiation, using the ω-scan technique. The scan width and scan speed were $1°$ and $0.03°$ s^{-1}, respectively. Three intensities were measured every 2 h and no significant variations were observed. 1645 independent reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 1638 of which were taken as observed by applying the condition $I \geqslant 2.5\sigma(I)$. Corrections were made for Lorentz-polarization but not absorption effects.

The Fe atoms were located from a Patterson synthesis, the S atoms from a subsequent weighted Fourier synthesis, and the remaining non-hydrogen atoms from direct methods, using the DIRDIF system of computer programs [12]. The structure was refined isotropically and anisotropically by full-matrix least-squares. The function minimized was $w[|F_o| - |F_c|]^2$, where $w = (\sigma^2(F_o) +$

$0.0036 | F_0 |^2)^{-1}$, f, f' and f'' were taken from International Tables of X-ray Crystallography [2]. 29 hydrogen atoms were located by a difference synthesis and refined with an overall isotropic temperature factor. The final R factor was 0.045 ($R_w = 0.047$) for all observed reflections *.

Acknowledgements

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* The structure was initially refined in the Cc space group. In view of very unusual bond lengths this gave for the cyclopentadienyl rings, a referee suggested the space group $C2/c$, which was found to be correct.