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Synthesis, Structure and Properties of *syn*-Bis(μ-*N*-methylpiperidine-4-thiolate Tricarbonyl Iron)

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Abstract

The reaction of $Fe_3(CO)_{12}$ with *N*-methyl-4-mercaptopiperidine gives the title compound. Crystals are monoclinic, space group $P2_1/c$ with $a = 12.922(2)$, $b = 14.784(5)$, $c = 13.607(2)$ Å, $\beta = 112.41(1)°$. With $Z = 4$ the calculated density is 1.49 g cm^{-3}. Solution of the structure by direct methods led to a final weighted R factor of 0.029 for 2270 independent reflections. The Fe–Fe bond length is 2.534(1) Å and the S···S distance of 2.940(1) suggests bonding interactions. By heating upon reflux in toluene during 10 h, the IR spectrum of the chromatographed solution indicates the *syn* isomer formation. The reaction with CH_3I and $HClO_4$ produces the methylation and protonation, respectively, of the nitrogen atoms of the piperidine rings giving rise to the formation of the $[Fe(\mu\text{-}(CH_3)_2NC_5H_9S)(CO)_3]_2I_2\cdot 2H_2O$ and $[Fe(\mu\text{-}HCH_3NC_5H_9S)(CO)_3]_2\cdot H_2O\cdot CH_3OH$ compounds.

Introduction

As part of our work on the coordination of γ-mercaptoamines to metal ions we have reported the synthesis, properties and structures of some complexes formed by *N*-methyl-4-mercaptopiperidine [1–6]. The observed molecular structures with the ligand in its zwitterionic form $\overset{+}{N}H(CH_3)C_5H_9S^-$ (hereafter HRS) are discrete molecules [3] in $Hg(HRS)_2(ClO_4)_2$, dimeric molecules [2, 5] in $Zn_2(HRS)_2X_4$ (X = Cl, Br and I) and one-dimensional polymeric chains [1] in $Cd(HRS)_2(ClO_4)_2$. When the ligand is in the anionic form $(H_3C)NC_5H_9S^-$ (RS^-), cyclic tetrameric molecules [4] are formed in $Ni_4(RS)_8$. This tetrameric structure has been rationalized in terms of the steric bulk of the ligand. In all the cases the ligand coordinates only by the sulphur atom, although recently chelates with the piperidine ring in a 'boat' configuration have been prepared [7].

In continuation of our studies on this type of metal complexes, we now report on the synthesis, molecular structure and properties of the compound formed in the reaction of RSH with $Fe_3(CO)_{12}$.

Experimental

IR spectra were recorded on a Beckman IR-20A spectrophotometer using KBr pellets or CaF_2 cells (solutions).

$Fe_3(CO)_{12}$ and *N*-methyl-4-mercaptopiperidine were prepared by known methods [8, 9].

Preparation of $[Fe(\mu\text{-}RS)(CO)_3]_2$

The reaction was carried out under dry N_2 using standard Schlenk techniques. To a 30 ml solution of $Fe_3(CO)_{12}$ (1 mmol) in benzene was added *N*-methyl-4-mercaptopiperidine (1.1 mmol) and the solution was refluxed for 1 h and then allowed to cool at room temperature. The red crystalline precipitate was filtered, washed with hexane and cold acetone, dried *in vacuo* and recrystallized in acetone.

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Anal. Calc. for $C_{18}H_{24}N_2O_6S_2Fe_2$: C, 40.02; H, 4.48; N, 5.19. Found: C, 40.0; H, 4.5; N, 5.2%.

Preparation of $[Fe(\mu\text{-}H_3CRS)(CO)_3]_2I_2 \cdot 2H_2O$

To a 25 ml solution of $[Fe(\mu\text{-}RS)(CO)_3]_2$ (1 mmol) in chloroform, a slight excess of CH_3I (2 mmol) was added slowly and with vigorous stirring. Further stirring for 15 min produced a red precipitate. The water soluble product was filtered, washed with chloroform and diethyl ether and dried *in vacuo* over silicagel. *Anal.* Calc. for $C_{20}H_{34}N_2O_8S_2Fe_2I_2$: C, 27.93; H, 3.98; N, 3.26. Found: C, 27.3; H, 4.0; N, 3.2%.

Preparation of $[Fe(\mu\text{-}HRS)(CO)_3]_2(ClO_4)_2 \cdot H_2O \cdot CH_3OH$

To a 25 ml solution in MeOH of $[Fe(\mu\text{-}SR)(CO)_3]_2$ (1 mmol), a slight excess of conc. $HClO_4$ solution (2 mmol) was added slowly and with stirring. Further stirring for 5 min produced a red–orange precipitate, which was filtered, washed with ethylether and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_{19}H_{32}N_2O_{16}S_2Cl_2Fe_2$: C, 28.85; H, 4.08; N, 3.54. Found: C, 28.9; H, 4.1; N, 3.4%.

X-ray Data Collection and Structure Determination

A prismatic (0.1 × 0.1 × 0.2 mm) crystal was mounted on an ENRAF-NONIUS CAD-4 diffractometer. The unit-cell parameters were measured from the automatic centring of 20 reflections ($4 \leqslant \theta \leqslant 12°$) and refining the orientation matrix and cell-parameters by least-squares. Intensities were measured with graphite monochromatized Mo Kα radiation, using the $\theta/2\theta$ scan technique, 4232 intensities were collected in the range $2 \leqslant \theta \leqslant 25°$; 2270 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured each two hours as orientation and intensity control, significant variations were not observed. The structure was solved by direct methods, using the MULTAN system of computer programs [10]. An E-map computed from the set of phases with the highest combined figure of merit revealed the position of all non-hydrogen atoms. The position of origin was corrected with the TRADIR method of DIRDIF system of computer programs [11]. The structure was isotropically and anisotropically refined by least-squares method, using the SHELX-76 computer program [12]. The function minimized was $w\|F_o| - |F_c\|^2$, where $w = (\sigma^2(F_o) + 0.00119|F_o|^2)^{-1}$, f, f' and f'' were taken from International Tables of X-ray Crystallography [13]. Hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The final R factor was 0.027 ($R_w = 0.029$) for all observed reflections.

TABLE I. Crystal and Data Collection Parameters for $[Fe(\mu\text{-}RS)(CO)_3]_2$

Formula	$C_{18}H_{24}N_2O_6S_2Fe_2$ (*anti* isomer)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	12.922(2)
b (Å)	14.784(5)
c (Å)	13.607(2)
β (deg)	112.41(1)
V (Å^3)	2403(2)
Z	4
F_w	540.18
D_{calc} (g cm^{-3})	1.49
$F(000)$	1144
Diffractometer	Enraf-Nonius CAD-4
Radiation, λ (Å)	Mo Kα, 0.71069
μ (cm^{-1})	14.3
Crystal dimensions (mm)	0.1 × 0.1 × 0.2
Scan type	$\theta/2\theta$
θ range (deg)	2–25
Total no of reflections	4232
Observed reflections[a]	2270
Final R_F[b]	0.027
Final R_{wF}	0.029

[a] Reflections with $I \geqslant 2\ 5(\sigma(I))$. [b] The function minimized was $w(|F_o| - |F_c|)^2$ where $w = (\sigma^2(F_o) + 0.00119|F_o|^2)^{-1}$.

TABLE II. Atomic Coordinates (× 10^4) and Thermal Parameters for *anti*-$[Fe(\mu\text{-}H_3CNC_5H_9S)(CO)_3]_2$

Atom	x	y	z	B (Å^2)
Fe(1)	35094(5)	18433(4)	58257(5)	3.45(2)
Fe(2)	13900(5)	17740(4)	50606(4)	3.39(2)
S(1)	2386(1)	3074(1)	5306(1)	3.55(4)
C(11)	2316(4)	3799(3)	6369(3)	3.52(19)
C(12)	3295(4)	4445(3)	6723(4)	4.57(23)
C(13)	3168(4)	5148(4)	7490(5)	5.39(27)
N(14)	2133(3)	5646(2)	7006(3)	4.65(18)
C(15)	1194(4)	5035(4)	6745(5)	5.01(25)
C(16)	1231(5)	4331(3)	5950(4)	4.78(24)
C(17)	2059(6)	6372(4)	7714(6)	6.98(37)
S(2)	2468(1)	1619(1)	6807(1)	3.30(4)
C(21)	2591(4)	465(3)	7351(3)	3.37(18)
C(22)	3723(4)	371(3)	8256(4)	4.16(22)
C(23)	3798(4)	−553(2)	8781(4)	4.41(22)
N(24)	2912(3)	−658(2)	9182(3)	4.19(18)
C(25)	1830(4)	−613(3)	8315(4)	4.75(24)
C(26)	1663(4)	297(3)	7743(4)	3.96(21)
C(27)	3011(6)	−1489(4)	9803(5)	6.52(30)
C(31)	3833(4)	764(3)	5789(4)	4.34(22)
O(31)	4026(3)	−74(2)	5733(3)	6.30(21)
C(32)	4762(4)	2242(3)	6890(4)	4.151(22)
O(32)	5546(3)	2484(2)	7569(3)	5.71(17)
C(33)	3913(4)	2049(3)	4722(4)	4.39(22)
O(33)	4187(3)	2150(3)	4031(3)	6.88(22)
C(34)	966(4)	1981(3)	3665(4)	4.22(22)
O(34)	670(3)	2122(2)	2778(3)	6.29(19)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C(35)	87(4)	2076(3)	5182(4)	4.62(23)
O(35)	−738(3)	2258(3)	5243(4)	7.30(23)
C(36)	1195(3)	588(3)	4854(3)	4.02(21)
O(36)	1083(3)	−171(2)	4715(3)	5.82(19)

TABLE III. Interatomic Bond Lengths and Bond Angles

(a) Bond lengths (Å)

Fe(1)–Fe(2)	2.534(1)	Fe(2)–C(35)	1.809(5)
Fe(1)–S(1)	2.266(1)	Fe(2)–C(36)	1.778(4)
Fe(1)–S(2)	2.253(1)	C(31)–O(31)	1.142(5)
Fe(2)–S(1)	2.265(1)	C(32)–O(32)	1.137(5)
Fe(2)–S(2)	2.262(1)	C(33)–O(33)	1.134(5)
Fe(1)–C(31)	1.784(5)	C(34)–O(34)	1.137(5)
Fe(1)–C(32)	1.811(5)	C(35)–O(35)	1.133(5)
Fe(1)–C(33)	1.794(4)	C(36)–O(36)	1.138(5)
Fe(2)–C(34)	1.791(5)	S(1)···S(2)	2.940(1)

(b) Bond angles (°)

Fe(1)–S(1)–Fe(2)	68.00(3)	S(1)–Fe(2)–S(2)	81.00(4)
Fe(1)–S(2)–Fe(2)	63.30(3)	S(1)–Fe(1)–S(2)	81.20(4)
S(1)–Fe(2)–Fe(1)	56.00(3)	Fe(1)–S(1)–C(11)	116.2(1)
S(1)–Fe(1)–Fe(2)	56.00(3)	Fe(2)–S(1)–C(11)	114.6(1)
S(2)–Fe(2)–Fe(1)	55.70(3)	Fe(1)–S(2)–C(21)	113.2(1)
S(2)–Fe(1)–Fe(2)	56.00(3)	Fe(2)–S(2)–C(21)	116.1(1)

	$n = 1$	$n = 2$
(c) Bond lengths		
S(n)–C(n1)	1.830(4)	1.842(4)
C(n1)–C(n2)	1.510(6)	1.517(6)
C(n2)–C(n3)	1.525(7)	1.527(6)
C(n1)–C(n6)	1.517(6)	1.512(6)
C(n5)–C(n6)	1.516(7)	1.525(6)
C(n3)–N(n4)	1.447(6)	1.453(6)
C(n5)–N(n4)	1.443(6)	1.447(6)
N(n4)–C(n7)	1.469(6)	1.469(6)
(d) Bond angles		
S(n)–C(n1)–C(n2)	109.6(3)	108.6(3)
S(n)–C(n1)–C(n6)	108.9(3)	109.7(3)
C(n2)–C(n1)–C(n6)	109.5(4)	110.2(4)
C(n1)–C(n2)–C(n3)	110.7(4)	109.3(4)
C(n2)–C(n3)–N(n4)	110.9(4)	110.6(4)
C(n3)–N(n4)–C(n7)	110.7(4)	113.4(4)
C(n5)–N(n4)–C(n7)	111.1(4)	110.7(4)
C(n3)–N(n4)–C(n5)	109.8(4)	110.0(4)
N(n4)–C(n5)–C(n6)	110.7(4)	111.1(4)
C(n1)–C(n6)–C(n5)	111.3(4)	110.3(4)
(e) Puckering parameters		
q_2	−0.042	0.029
q_3	−0.575	−0.584
Q	0.577	0.585
ϕ	−177.2	−149.1
θ	−4.1	−2.9

TABLE IV. Distances (Å) of Atoms from Selected Least-squares Planes

Plane I: Plane through S(1) S(2) and the midpoint of Fe(1)–Fe(2).
Equation. $0.926x + 0.040y + 0.376z - 2.995 = 0^{a}$

Fe(1)	1.267	C(34)	−1.751
Fe(2)	−1.267	C(35)	−2.809
C(31)	1.585	C(36)	−1.569
C(32)	2.781	C(11)	−0.049
C(33)	1.771	C(21)	0.074

Plane II: Plane through S(1), S(2), C(31) and C(32)
Equation: $0.567x + 0.386y + 0.727z - 6.879 = 0$

Fe(1)	0.363	C(31)	−0.091
S(1)	−0.081	C(32)	2.169
S(2)	0.081	C(33)	0.091

Plane III: Plane through S(1), S(2), C(34), C(36)
Equation: $-0.938x + 0.322y + 0.125z - 2.058 = 0$

Fe(2)	0.359	C(34)	0.073
S(1)	−0.072	C(35)	2.161
S(2)	0.101	C(36)	−0.103

[a] x,y,z are coordinates in Å in the orthonormal system a,b,c^*.

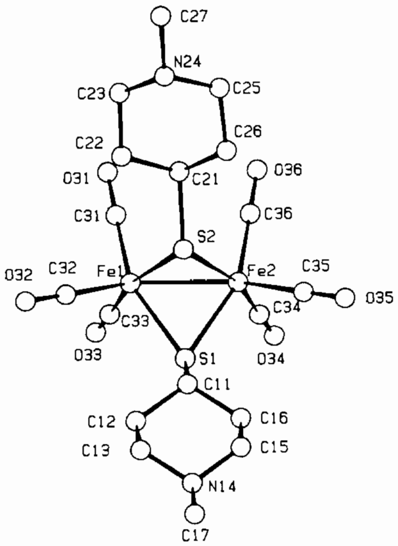

Fig. 1. Perspective view of the *anti* $[Fe(\mu\text{-}SR)(CO)_3]_2$ molecule showing the numbering scheme.

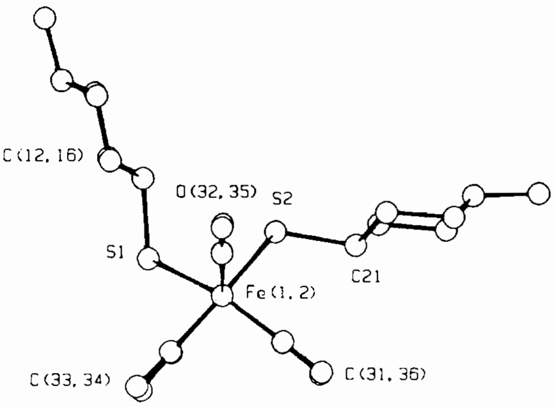

Fig. 2. Projection of the molecule onto the plane passing through the sulphur atoms and the Fe–Fe midpoint.

Description of the Structure

Crystalline $Fe_2(SR)_2(CO)_6$ consists of discrete dimeric molecules of the *anti*-configuration shown in Fig. 1. Although no crystallographic constrains are imposed upon the molecular geometry, the configuration is nearly one of C_s–*m* symmetry, with a pseudo-mirror plane passing through the sulphur atoms and the Fe–Fe midpoint (Fig. 2).

In the $Fe_2(SR)_2(CO)_6$ molecule, each iron atom is coordinated to two sulphur atoms and to the three carbonyl ligands such that the five ligands are located at the corners of a distorted tetragonal pyramid. The degree of distortion of the five ligands about each iron atom from a regular tetragonal pyramid is revealed by a calculation of the least-squares basal plane comprised of the two sulphur atoms and the two equatorial carbonyl ligands, as given in Table III. The iron atoms are displaced by 0.3 Å from their respective basal planes in the direction toward their apical carbonyl ligands C32 and C35.

The molecular geometry can be described, as in the case of similar $Fe_2(SR)_2(CO)_6$ derivatives [14–18] as arising from the intersection of the basal planes of two distorted tetragonal pyramids along the S···S edge at a dihedral angle of 71.5°. The resulting six-coordination about each iron atom can be viewed conceptually as octahedral-like with a bent Fe–Fe bond occupying the sixth coordination site. The two iron atoms are linked by a metal–metal bond of length 2.534(1) Å. The S···S distance is 2.940(1) Å, shorter than the van der Waals radius for sulphur, suggesting bond interactions [19]. The average Fe–S, Fe–C and C–O bond lengths of 2.262(6) 1.795(3) and 1.137(3) Å are in good agreement with corresponding values in similar iron carbonyl derivatives with Fe_2S_2 core (Table V). However the apical Fe–C distances of 1.810(1) Å are slightly larger than the basal Fe–C bond distances averaging 1.787(7) Å.

All six Fe–C–O bond angles are within 2.5° of being linear. The trigonal pyramidal array of CO ligands on the two iron atoms are eclipsed relative to each other. Hydrogen atoms H12 and H16 bonded to C12 and C16 atoms of the piperidine ring number 1 are at 2.98 and 2.89 Å from C32 and C35 atoms, resulting in the displacement of these apical CO groups towards the S2 atom, as can be seen in Fig. 2.

On the other side, hydrogen H21 bonded to C21 atom of piperidine ring number 2 is at 2.73 and 2.70 Å from carbonyl atoms C31 and C35, respectively, thus explaining the angle of 93° between C33, C34, Fe1, Fe2 and C31, C36, Fe1, Fe2 planes.

The *anti* configuration is described by the angles S2···S1–C11 and S1···S2–C21 of 83.05 and 156.65° respectively.

The piperidine rings show the usual 'chair' conformation, slightly distorted as indicated by the 'puckering parameters' [20]. Both sulphur atoms and the CH_3 groups are bonded to the piperidine ring in equatorial positions.

TABLE V. Comparison of the Main Molecular Parameters of some $[Fe(\mu\text{-}SR)(CO)_3]_2$ Compounds[a]

	R = C_2H_5 [14]	R = C_6H_5C [15]	R = CH_3 [16]	This work
Fe–Fe	2.537(10)	2.507(5)	2.518(1)	2.534(1)
Fe–S	2.259(7)	2.259(3)	2.273(1)	2.262(6)
S···S	2.932(4)	2.876(7)	2.790(3)	2.940(1)
Fe–S–Fe	68.3(3)	67.4(1)	67.3(1)	65.65(3)
S–Fe–S	81.0(3)	78.7(1)	75.7(1)	81.10(4)
Dihedral Angle				
(Fe1–S1–S2)–(Fe2–S1–S2)	95.2(5)	91.8(5)	90.9	95.0
Fe–C	1.81(2)	1.778(9)	1.745(4)	1.795(3)
C–O	1.15(2)	1.152(12)	1.147(5)	1.137(3)

[a] Distances are in Å and bond angles in degrees. The values given are mean ones. Estimated standard deviation values shown in parentheses are the mean of the individual values divided by the square root of the number of observations.

Discussion

The compound $[Fe(\mu\text{-}RS)(CO)_3]_2$ was prepared from the reaction of RSH with $Fe_3(CO)_{12}$ in boiling benzene. Crystallization in acetone gave air-stable red crystals. The compound shows three infrared bands in the $\nu(CO)$ stretching region (2070(s), 2044(vs) and 2000(vs,br) in CH_2Cl_2 solution, as expected for CO terminal groups in dinuclear $[Fe(RS)(CO)_3]_2$ compounds [21]. The solid state IR spectrum shows strong bands at 2810 and 2780 cm^{-1}, characteristic of the $\nu(C-H)$ vibrations of the methyl groups bonded to a nitrogen atom which retains its lone pair of electrons [22], indicating that the nitrogen atoms of the piperidine rings are not protonated.

For the majority of alkyl thiolato irontricarbonyl compounds $Fe_2(SR)_2(CO)_6$, two isomeric forms are formed [18]. These are the *syn* and *anti* isomers. It has been supposed that for sterically demanding substituents only the *anti* isomer can be observed [23, 24]. In order to investigate whether *anti* $\rightleftarrows$ *syn* isomerization of this sterically demanding substituent occurs, a solution in toluene was refluxed during 10 h. The solution was then chromatographed on alumina using hexane as eluent. The IR spectrum of the last eluted solution showed bands at 2074(s), 2040(vs), 1997(vs) and 1986(vs) cm^{-1}, characteristic of the *syn* isomer [25] showing that in spite of the bulky of the ligand both isomers exist.

The reaction of the diiron complex with CH_3I results in the methylation of the nitrogen atom of the piperidine ring giving rise to the compound: $[Fe(\mu\text{-}H_3CRS)(CO)_3]_2I_2\cdot 2H_2O$. Furthermore, the reaction with $HClO_4$ produces the protonation of the nitrogen atom, affording the compound: $[Fe(\mu\text{-}HRS)(CO)_3]_2(ClO_4)_2\cdot H_2O\cdot CH_3OH$.

On comparing the $\nu(CO)$ stretching region of the IR spectra of these compounds with that of the diiron complex, no significant difference can be observed, indicating that the dimeric structure with terminal CO groups is maintained.

In the IR spectrum of the $Fe_2(H_3CRS)_2(CO)_6I_2\cdot 2H_2O$ compound, the absence of the bands at 2810 and 2780 cm^{-1} and the sharp band observed at 3000 cm^{-1} are characteristic of the $-\overset{+}{N}(CH_3)_3$ group [26], indicating the methylation of the nitrogen atoms of the piperidine rings.

Finally, the IR spectrum of $Fe_2(HRS)_2(CO)_6(ClO_4)_2\cdot H_2O\cdot CH_3OH$ shows a very broad absorption centered at about 2600 cm^{-1}, assigned to $\nu(N-H)$ vibrations, indicating the protonation of the nitrogen atoms, and its participation in strong hydrogen bonds.

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