

*Journal of Organometallic Chemistry*, 145 (1978) 49–55  
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## A CATIONIC DICARBENE COMPLEX OF IRON. THE CRYSTAL STRUCTURE OF $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]\text{PF}_6 \cdot \frac{1}{2}\text{C}_2\text{H}_4\text{Cl}_2$

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(Received August 8th, 1977)

### Summary

The structure of the compound  $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]\text{PF}_6 \cdot \frac{1}{2}\text{C}_2\text{H}_4\text{Cl}_2$  has been determined by X-ray crystallography. The compound crystallizes in space group  $C2/c$  with eight formula units in a unit cell of dimensions  $a$  23.939(18),  $b$  15.771(7),  $c$  12.314(4) Å,  $\beta$  92.01(5)°. Full-matrix least-squares refinement of 2084 counter data yielded  $R = 0.051$ . The complex cation contains an unusual chelating dicarbene ligand, and the structure of this complex is compared with related species. The bonding properties of the dicarbene ligand are discussed.

### Introduction

In an earlier paper we have reported the synthesis of the compounds  $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]\text{X}$  ( $\text{X} = \text{PF}_6^-$ ,  $\text{BPh}_4^-$ ) [1] by the reaction of dimethylthiocarbamoyl chloride,  $\text{ClCSNMe}_2$ , with  $\text{Fe}(\text{CO})_4^{2-}$ . Because of their ambiguous NMR spectra and uncertainty as to their electrolyte type, the full characterization of these compounds required an X-ray crystal structure determination, which revealed the presence of an unusual chelating dicarbene ligand. The details of the structure determination of the hexafluorophosphate salt (as the hemi-(1,2-dichloroethane) solvate) are reported here.

### Experimental

Crystals of  $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]\text{PF}_6 \cdot \frac{1}{2}\text{C}_2\text{H}_4\text{Cl}_2$  were obtained by crystallization from 1,2-dichloroethane/ether as yellow needles. A suitable crystal was mounted on a glass fiber and placed on a Syntex P2<sub>1</sub> automated diffractometer. Centering and refinement of fifteen high-angle reflections yielded

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lattice and orientation parameters, and the observed systematic absences ( $h0l$ ,  $l$  odd;  $hkl$ ,  $h+k$  odd) identified the space group as  $Cc$  or  $C2/c$ . The statistical distribution of intensities indicated a centrosymmetric space group, so  $C2/c$  was chosen, and this choice was confirmed by the successful solution and refinement of the structure. Further crystal data are given in Table 1.

Intensity data were collected using graphite-monochromatized Mo- $K_{\alpha}$  radiation ( $\lambda$  0.71073 Å) for reflections for which  $k \geq 0$ ,  $l \geq 0$ ,  $h+k \neq 2n+1$ ,  $5^{\circ} \geq 2\theta \geq 50^{\circ}$ , in the bisecting mode with stationary background counts at the beginning and end of each scan. The data were corrected for Lorentz and polarization effects. Standard deviations were assigned to the intensities [2] using  $p = 0.05$ . Three test reflections were taken every 100 reflections to monitor crystal and electronic stability; no decay was noted. Of a total of 4495 reflections collected, 2084 were considered observed ( $I > 3\sigma(I)$ ); only observed reflections were used in the structure solution and refinement. No corrections were made for absorption.

The structure was solved by direct methods. Normalized structure factors ( $E$ 's) were calculated using overall scale and temperature factors obtained from a Wilson plot. The 499 reflections with highest  $E$ 's were used as input to the computer program MULTAN. Reflections in the starting set were (25 5 6), (4 12 9), (13 5 6), (10 6 8), with the first two used for origin specification. An electron density map based on the phase set having the highest figure of merit clearly showed the iron and three sulfur atoms. After isotropic least-squares refinement of these four atoms, a Fourier synthesis phased on their locations revealed all nonhydrogen atoms; the presence of the chlorine and carbon atoms of the solvent molecule was confirmed after isotropic refinement of the other atoms.

Refinement of the structure proceeded smoothly. The final model used anisotropic thermal parameters for all nonhydrogen atoms (262 variables; data-to-parameter ratio 7.95/1). The hydrogen atoms were not located. The final discrepancy factors (conventionally defined) were  $R = 0.051$ ,  $R_w = 0.067$ . The error in an observation of unit weight was 1.63. A final difference Fourier synthesis showed a maximum electron density of  $0.23 \text{ e } \text{Å}^{-3}$ .

All least-squares cycles were based on the minimization of  $\sum w||F_0| - |F_c||^2$

TABLE 1  
CRYSTAL DATA

Formula (mol. wt.)	$C_{11}H_{18}O_2N_3S_3PF_6Fe \cdot CH_2Cl$ (570.75)
Crystal size	$0.80 \times 0.10 \times 0.10 \text{ mm}$
Space group	$C2/c$
$a$	23.939(18) Å
$b$	15.771(7) Å
$c$	12.314(4) Å
$\beta$	92.01(5) $^{\circ}$
$V$	4646(4) Å <sup>3</sup>
$Z$	8
$d_{\text{calc}}$	1.631 g cm <sup>-3</sup>
$d_{\text{exp}}$ (floatation)	1.62
$F_{000}$	2312
$\mu$	11.71 cm <sup>-1</sup>
Estimated range of transmission coefficients	0.87–0.91

TABLE 2. FINAL ATOMIC PARAMETERS A. ATOMIC COORDINATES

Atom	x	y	z
Fe	0.2240(1)	0.0111(1)	0.0926(1)
S(1)	0.2271(1)	0.0796(1)	0.2300(2)
S(2)	0.3039(1)	0.0611(1)	0.0079(2)
S(3)	0.2071(1)	-0.1152(1)	0.2557(2)
O(1)	0.1781(3)	-0.0840(4)	-0.0934(4)
O(2)	0.1769(3)	0.1773(4)	0.0329(5)
N(1)	0.3740(3)	0.1365(5)	0.1528(6)
N(2)	0.1184(3)	-0.0170(4)	0.2227(5)
N(3)	0.2963(3)	-0.1482(4)	0.1442(5)
C(1)	0.1958(3)	-0.0459(5)	-0.0210(7)
C(2)	0.1936(4)	0.1126(6)	0.0566(6)
C(3)	0.3258(4)	0.0981(5)	0.1335(6)
C(4)	0.4139(4)	0.1482(8)	0.0666(9)
C(5)	0.3901(4)	0.1674(7)	0.2647(8)
C(6)	0.1695(3)	-0.0312(5)	0.1939(5)
C(7)	0.0835(4)	0.0510(6)	0.1720(7)
C(8)	0.0897(3)	-0.0680(6)	0.3065(6)
C(9)	0.2557(3)	-0.0945(5)	0.1549(6)
C(10)	0.3335(4)	-0.1450(7)	0.0478(8)
C(11)	0.3074(4)	-0.2192(6)	0.2231(9)
P	0.0389(1)	0.1853(1)	0.4979(2)
F(1)	0.0676(3)	0.1972(4)	0.3847(4)
F(2)	0.0990(2)	0.1777(3)	0.5565(4)
F(3)	0.0119(3)	0.1777(4)	0.6119(5)
F(4)	-0.0212(2)	0.1949(4)	0.4395(5)
F(5)	0.0408(2)	0.2849(3)	0.5143(4)
F(6)	0.0385(3)	0.0859(3)	0.4808(6)
Cl	0.4279(3)	-0.0511(3)	0.2744(4)
C(12)	0.4787(6)	-0.1311(9)	0.2866(14)

B. ANISOTROPIC THERMAL PARAMETERS <sup>a</sup>

	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Fe	2.55(6)	3.00(5)	2.55(4)	-0.05(4)	0.09(4)	-0.07(4)
Cl	19.2(5)	14.1(4)	14.6(4)	8.8(3)	1.3(3)	1.2(3)
S(1)	3.2(1)	4.3(1)	2.95(9)	-0.46(8)	0.13(8)	-0.53(8)
S(2)	3.6(1)	5.3(1)	3.17(9)	-1.19(9)	0.66(8)	0.04(8)
S(3)	3.2(1)	3.9(1)	3.65(9)	0.17(8)	0.58(8)	0.85(8)
P	3.5(1)	3.5(1)	4.6(1)	-0.23(9)	0.3(1)	-0.20(9)
F(1)	8.4(4)	10.0(4)	4.7(3)	1.1(3)	1.2(3)	-0.4(3)
F(2)	4.3(3)	7.4(3)	7.0(3)	1.2(2)	-1.5(2)	-0.3(2)
F(3)	7.3(4)	11.6(5)	7.6(4)	-0.4(3)	3.0(3)	2.6(3)
F(4)	4.0(3)	7.3(3)	11.3(4)	-0.1(3)	-3.3(3)	-2.2(3)
F(5)	5.3(3)	3.8(2)	8.0(3)	0.1(2)	-0.7(2)	-1.0(2)
F(6)	9.0(4)	3.8(3)	14.1(5)	-0.4(3)	-2.1(4)	-1.2(3)
O(1)	4.7(4)	5.3(3)	3.2(3)	-1.2(3)	-0.0(2)	-0.8(2)
O(2)	7.8(5)	3.5(3)	6.9(4)	1.1(3)	-0.5(3)	0.1(3)
N(1)	2.9(4)	4.9(4)	5.6(4)	-1.7(3)	-0.2(3)	0.1(3)
N(2)	2.5(4)	4.3(3)	2.8(3)	-0.0(3)	0.2(3)	-0.7(3)
N(3)	3.9(4)	3.3(3)	5.0(4)	0.8(3)	0.3(3)	0.2(3)
C(1)	3.0(4)	2.9(4)	3.4(4)	0.3(3)	0.8(3)	0.6(3)
C(2)	4.2(5)	3.6(5)	3.3(4)	-0.6(4)	0.2(3)	-0.4(3)
C(3)	3.8(5)	2.9(4)	3.9(4)	-0.3(3)	0.1(3)	0.3(3)
C(4)	4.5(6)	9.0(7)	6.8(6)	-2.5(5)	2.5(5)	0.8(5)
C(5)	6.1(7)	6.7(6)	5.5(5)	-2.3(5)	-1.5(5)	-1.8(5)
C(6)	3.2(5)	3.0(4)	2.2(3)	-0.1(3)	-0.4(3)	-0.4(3)
C(7)	3.0(5)	5.0(5)	5.3(5)	1.6(4)	-0.1(4)	0.2(4)
C(8)	3.4(5)	6.4(5)	3.5(4)	-1.0(4)	1.7(3)	0.4(4)
C(9)	2.4(4)	3.1(4)	2.8(3)	-0.0(3)	-0.1(3)	-0.4(3)
C(10)	6.7(7)	6.7(6)	6.7(6)	1.9(5)	4.5(5)	0.1(5)
C(11)	5.6(6)	4.9(5)	8.0(6)	2.3(4)	0.3(5)	2.9(5)
C(12)	11.0(12)	9.3(9)	14.7(14)	3.9(8)	3.6(9)	3.0(8)

<sup>a</sup> Anisotropic temperature factors of the form  $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$  were used for these atoms.

where  $w = \sigma(F_o)^{-2}$ . The atomic scattering factors used were from Cromer and Mann [3a] with corrections for anomalous scattering by Fe, Cl, S, and P atoms [3b]. Positional and thermal parameters for all atoms are presented in Table 2.

TABLE 3  
INTERATOMIC DISTANCES AND BOND ANGLES

A. Bonding distances (Å)		C. Bond angles (degrees)	
Fe—S(1)	2.344(3)	S(1)—Fe—S(2)	74.7(1)
Fe—S(1)	2.347(3)	S(1)—Fe—C(1)	169.5(3)
Fe—C(1)	1.777(9)	S(1)—Fe—C(2)	88.4(3)
Fe—C(2)	1.808(10)	S(1)—Fe—C(6)	93.2(2)
Fe—C(6)	1.954(8)	S(1)—Fe—C(9)	85.3(2)
Fe—C(9)	1.974(8)	S(2)—Fe—C(1)	96.5(2)
S(1)—C(3)	1.718(8)	S(2)—Fe—C(2)	85.5(3)
S(2)—C(3)	1.718(9)	S(2)—Fe—C(6)	166.3(2)
S(3)—C(6)	1.760(8)	S(2)—Fe—C(9)	98.5(2)
S(3)—C(9)	1.760(8)	C(1)—Fe—C(2)	96.6(3)
O(1)—C(1)	1.144(9)	C(1)—Fe—C(6)	94.9(3)
O(2)—C(2)	1.130(9)	C(1)—Fe—C(9)	90.5(3)
N(1)—C(3)	1.317(10)	C(2)—Fe—C(6)	100.7(3)
N(1)—C(4)	1.465(11)	C(2)—Fe—C(9)	171.4(3)
N(1)—C(5)	1.498(11)	C(6)—Fe—C(9)	73.7(3)
N(2)—C(6)	1.305(9)	Fe—S(1)—C(3)	86.6(3)
N(2)—C(7)	1.483(10)	Fe—S(2)—C(3)	86.7(3)
N(2)—C(8)	1.495(9)	C(6)—S(3)—C(9)	84.1(4)
N(3)—C(9)	1.300(9)	C(3)—N(1)—C(4)	121.0(8)
N(3)—C(10)	1.500(11)	C(3)—N(1)—C(5)	120.7(8)
N(3)—C(11)	1.508(10)	C(4)—N(1)—C(5)	118.2(8)
P—F(1)	1.587(6)	C(6)—N(2)—C(7)	121.9(6)
P—F(2)	1.593(6)	C(6)—N(2)—C(8)	123.6(7)
P—F(3)	1.569(6)	C(7)—N(2)—C(8)	114.5(6)
P—F(4)	1.592(6)	C(9)—N(3)—C(10)	121.5(7)
P—F(5)	1.584(5)	C(9)—N(3)—C(11)	122.4(7)
P—F(6)	1.582(6)	C(10)—N(3)—C(11)	116.0(7)
Cl—C(12)	1.754(14)	Fe—C(1)—O(1)	178.6(7)
C(12)—C(12)'	1.386(25)	Fe—C(2)—O(2)	176.8(8)
		S(1)—C(3)—S(2)	111.8(5)
		S(1)—C(3)—N(1)	124.3(6)
		S(2)—C(3)—N(1)	123.8(7)
		Fe—C(6)—S(3)	100.9(4)
		Fe—C(6)—N(2)	140.2(6)
		S(3)—C(6)—N(2)	118.9(6)
		Fe—C(9)—S(3)	100.1(4)
		Fe—C(9)—N(3)	142.0(6)
		S(3)—C(9)—N(3)	117.8(6)
		F(1)—P—F(2)	89.7(3)
		F(1)—P—F(3)	177.2(4)
		F(1)—P—F(4)	90.3(4)
		F(1)—P—F(5)	89.0(3)
		F(1)—P—F(6)	90.0(4)
		F(2)—P—F(3)	89.0(3)
		F(2)—P—F(4)	178.9(3)
		F(2)—P—F(5)	89.7(3)
		F(2)—P—F(6)	89.2(3)
		F(3)—P—F(4)	91.1(4)
		F(3)—P—F(5)	88.4(3)
		F(3)—P—F(6)	92.5(4)
		F(4)—P—F(5)	89.2(3)
		F(4)—P—F(6)	91.9(3)
		F(5)—P—F(6)	178.6(4)
		Cl—C(12)—C(12)'	117.9(9)

B. Nonbonding distances less than 3.30 Å

F(4)···C(7)	3.019(10)
F(2)···O(1)	3.069(8)
O(1)···N(2)	3.080(9)
F(3)···C(8)	3.177(10)
O(1)···C(6)	3.189(9)
F(1)···O(1)	3.195(9)
F(5)···C(5)	3.224(10)
S(1)···O(1)	3.274(6)
F(2)···C(2)	3.279(10)
F(2)···N(2)	3.280(8)
F(2)···C(5)	3.293(11)
F(2)···C(6)	3.293(9)

Interatomic distances and bond angles are given in Table 3\*.

Computer programs used in this study included a local program for data reduction as well as modified versions of Zalkin's *FORDAP* for Fourier maps, Ibers' *NUCLS5* refinement program, the Martin—Busing—Levy *ORFFE* function and error program and Johnson's *ORTEP* plotting program.

## Results and discussion

The structure of the  $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]^+$  cation is shown in Fig. 1. The contents of the unit cell consists of eight discrete complex cations and hexafluorophosphate anions with all atoms in general positions, and four dichloroethane solvent molecules, one half of each of which is related to the other half by a twofold rotation axis.

The crystal packing is determined mainly by electrostatic and Van der Waals forces, as shown by the intermolecular distances, the shortest of which are given in Table 3.

The iron atom of the complex cation is octahedrally coordinated, with the major distortions resulting from the small angles subtended by the chelating ligands ( $74.7^\circ$  for the dithiocarbamate ligand and  $73.7^\circ$  for the dicarbene ligand). The bond distances and angles among the atoms of the carbonyl and dithiocarbamate ligands are all of the expected values; the carbonyl groups are essentially linear.

The most unusual feature of this complex is the unique chelating dicarbene ligand in which the two carbenoid carbon atoms are linked by a sulfur atom. Structurally, this ligand is related to the dicarbene ligand in the  $[(\text{MeNC})_4\text{Fe}(\text{CNMeH})_2\text{NMe}]^{2+}$  ion [4], where the aminocarbene units are connected by a methylimino group. The Fe—C bonds to the dicarbene ligand in  $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]^+$  (Fe—C(6), 1.954(8) Å; Fe—C(9), 1.974(8) Å; ave. 1.964 Å) are slightly shorter than those found in  $[(\text{MeNC})_4\text{Fe}(\text{CNMeH})_2\text{NMe}]^{2+}$  (ave. 2.04 Å). This is expected since substitution of sulfur for nitrogen as a linking heteroatom in the  $(\text{CNMe}_2)_2\text{X}$  ligand should reduce carbon—heteroatom  $\pi$ -bonding and thus increase the potential for Fe—C  $\pi$ -interaction, resulting in shorter Fe—C bonds. These Fe—C distances in the present complex are also in the range observed for several other iron carbene complexes (1.88–2.01 Å) [5–8] and also may be compared with Fe—CNR<sub>2</sub> distances in several other complexes, viz. 1.902–1.914 Å in  $\text{Fe}_2(\text{CO})_6(\text{CNet}_2)_2$  [9], 1.877–1.898 Å to the bridging CNMe<sub>2</sub> group and 1.935 Å to the bridging thiocarboxamido group in  $\text{Fe}_4(\text{CO})_{12}\text{S}(\text{CSNMe}_2)(\text{CNMe}_2)$  [10], and 1.876 Å to the chelating thiocarboxamido group in  $\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CSNMe}_2)$  [11]. It is worth noting that the Fe—C distances are distinctly shorter when the carbon atom is part of a three-membered ring ( $\text{FeC}(=\text{NR}_2)\text{S}$  and  $\text{FeC}(=\text{NR}_2)\text{Fe}$ , 1.876–1.914 Å) than when it is part of a four-membered ring ( $\text{FeC}(=\text{NR}_2)\text{SFe}$ ,  $\text{FeC}(=\text{NR}_2)\text{SC}(=\text{NR}_2)$ , and  $\text{FeC}(=\text{NR}_2)\text{NRC}(=\text{NR}_2)$ , 1.935–2.04 Å). This seems to indicate a relationship between metal—

\* The table of structure factors has been deposited as NAPS Document No. 03177 (14 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting \$5 for photocopies or \$3 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

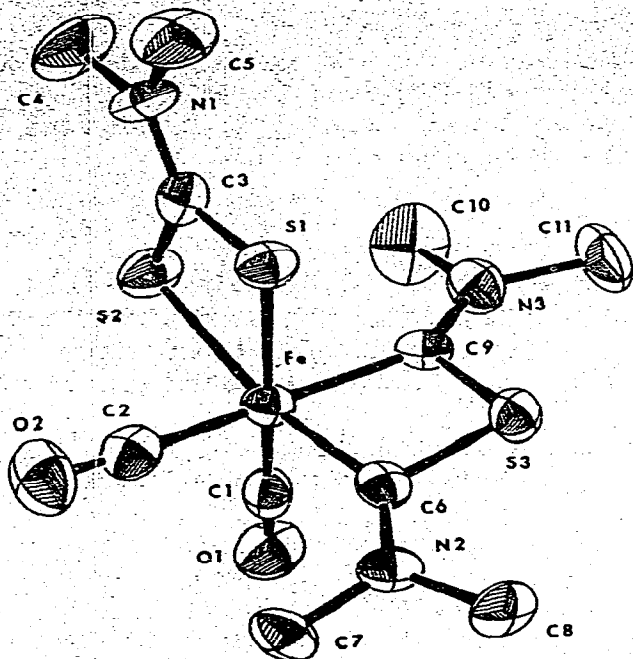


Fig. 1. The structure of the  $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNMe}_2)(\text{CNMe}_2)_2\text{S}]^+$  ion (50% probability ellipsoids).

carbon  $\pi$ -interaction (and resulting bond length) and ring size (and strain) in such systems. We have previously suggested such a relationship in another context [12].

The hexafluorophosphate ion in this structure is remarkably well-behaved for a species so prone to disorder. There is no evidence of disorder; the P—F bonds range over only 1.569–1.593 Å, none of the *cis*-F—P—F angles deviates by more than 1.6° from a right angle, and there is no important excess electron density in the neighborhood of the ion.

The  $\text{C}_2\text{H}_4\text{Cl}_2$  solvent molecule has a *gauche* configuration; the skew dihedral angle between the two C—C—Cl planes is 71.2°. The carbon—carbon bond in this molecule is remarkably short, only 1.386(25) Å.

### Acknowledgment

This work was supported by grants (to W.K.D.) from the Research Corporation and from the Emory University Research Committee, and by the assistance of the Emory University Computing Center. W.K.D. also thanks Dr. J.A. Bertrand of the Georgia Institute of Technology for generously providing access to his facilities.

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