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## THE CRYSTAL STRUCTURE OF DICARBONYL(DIMETHYLTHIOCARBOXAMIDO)DIMETHYLDITHIO- CARBAMATOIRON, $\text{Fe}(\text{CO})_2(\text{CSNMe}_2)(\text{S}_2\text{CNMe}_2)$

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### Summary

The crystal structure of  $\text{Fe}(\text{CO})_2(\text{CSNMe}_2)(\text{S}_2\text{CNMe}_2)$  has been determined by X-ray crystallography. The compound crystallizes with four molecules in a unit cell of space group  $P2_1/c$  and dimensions  $a$  13.448(6),  $b$  7.066(2),  $c$  14.590(4) Å,  $\beta$  98.40(3)°. The molecule contains separate dimethyldithiocarbamate and chelating thiocarboxamido ligands in a highly distorted octahedral complex. The Fe—C distance to the thiocarboxamido ligand is quite short (1.876 Å), indicating a considerable degree of  $\pi$ -interaction between these atoms.

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### Introduction

Recently we have reported the synthesis of the complex  $\text{Fe}(\text{CO})_2(\text{SCNMe}_2)(\text{S}_2\text{CNMe}_2)$  by the reaction of  $\text{Fe}_2(\text{CO})_9$  or  $\text{Fe}_3(\text{CO})_{12}$  with dimethylthiocarbamoyl chloride,  $\text{ClCSNMe}_2$ , and of  $\text{Fe}_2(\text{CO})_9$  with tetramethylthiuram monosulfide,  $(\text{Me}_2\text{NCS})_2\text{S}$  [1]. The problem of characterizing this complex, and particularly of determining whether or not it was in fact a complex of tetramethylthiuram monosulfide, was complicated by the fact that the molecule is fluxional at room temperature. In order to characterize this complex unambiguously, the X-ray crystal structure determination was undertaken, and the details of this study are reported here.

### Experimental

Crystals of  $\text{Fe}(\text{CO})_2(\text{CSNMe}_2)(\text{S}_2\text{CNMe}_2)$  were obtained by recrystallization from heptane in the form of six-sided plates. A crystal was mounted on a glass

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TABLE I  
CRYSTAL DATA

Formula (Mol. wt.)	$C_8H_{12}N_2O_2S_3Fe$ (320.222)
Crystal size (mm)	0.45 X 0.55 X 0.50 X 0.15
<i>a</i> (Å)	13.448(6)
<i>b</i> (Å)	7.066(2)
<i>c</i> (Å)	14.590(4)
$\beta$ (degrees)	98.40(3)
Volume (Å <sup>3</sup> )	1371.6(9)
<i>Z</i>	4
$D_{calc}$ (g cm <sup>-3</sup> )	1.551
$D_{exp}$ (floatation)	1.54
$F(000)$ (electrons)	656
$\mu$ (cm <sup>-1</sup> )	15.50
Estimated range of transmission coefficients	0.64–0.76

fiber with epoxy cement and placed on a Syntex P2<sub>1</sub> automated diffractometer. Centering and refinement of fifteen high-angle reflections yielded lattice and orientation parameters, and the observed systematic absences ( $h0l$ ,  $l$  odd;  $0k0$ ,  $k$  odd) uniquely determined the space group as monoclinic  $P2_1/c$ . 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 which  $k \geq 0$ ,  $l \geq 0$ ,  $5^\circ \geq 2\theta \geq 50^\circ$  and 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 2738 data collected, 1780 were considered observed ( $I > 3\sigma(I)$ ); only observed data were used in the structure solution and refinement. No corrections were made for absorption.

The structure was solved by heavy-atom methods. A three-dimensional Patterson map yielded coordinates for the iron atom and a Fourier synthesis phased on this position showed the three sulfur atoms. After isotropic least-squares refinement of these four atoms, a second Fourier synthesis yielded coordinates for all remaining nonhydrogen atoms.

Refinement of the structure proceeded smoothly. The final model used anisotropic thermal parameters for all atoms (145 variables, data-to-parameter ratio 12.3 : 1). The hydrogen atoms of the methyl groups were not located. The final discrepancy factors (conventionally defined) were  $R$  0.062,  $R_w$  0.084. The error in an observation of unit weight was 2.427. A final difference Fourier synthesis showed peaks near the iron atom of electron densities of 1.00, 0.87, and 0.64 e Å<sup>-3</sup>; otherwise the highest peak was 0.62 e Å<sup>-3</sup>.

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

\* The table of structure factors has been deposited as NAPS Document No. 03159 (11 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017, U.S.A. A copy may be secured by citing the document number, remitting \$5.00 for photocopies or \$3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

where  $w = \sigma(F_o)^{-2}$ . The atomic scattering factors used were from Cromer and Mann [3a] with corrections for anomalous scattering by Fe and S atoms [3b]. Positional and thermal parameters for all atoms are presented in Table 2. Interatomic distances and bond angles 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 Patterson and Fourier's maps; Ibers' NUCLS5 refinement program, the Martin—Busing—Levy ORFFE function and error program, and Johnson's ORTEP plotting program.

TABLE 2  
FINAL ATOMIC PARAMETERS

A. Atomic coordinates

Atom	x	y	z
Fe	0.2784(1)	0.2810(1)	0.6317(1)
S(1)	0.3062(2)	0.2086(1)	0.4777(2)
S(2)	0.1113(1)	0.3602(3)	0.5810(1)
S(3)	0.1852(1)	0.0337(3)	0.6801(1)
O(1)	0.4710(4)	0.1282(10)	0.7146(4)
O(2)	0.2751(5)	0.5522(9)	0.7776(4)
N(1)	0.3597(4)	0.5732(8)	0.5107(5)
N(2)	-0.0116(4)	0.0838(9)	0.6218(4)
C(1)	0.3969(6)	0.1881(11)	0.6818(5)
C(2)	0.2763(5)	0.4434(11)	0.7215(5)
C(3)	0.3267(5)	0.4101(9)	0.5348(4)
C(4)	0.3758(7)	0.7350(10)	0.5739(7)
C(5)	0.3835(7)	0.5994(13)	0.4136(6)
C(6)	0.0807(5)	0.3493(10)	0.1268(4)
C(7)	-0.0322(7)	-0.0994(12)	0.6638(6)
C(8)	-0.0979(6)	0.1906(14)	0.5775(6)

B. Anisotropic thermal parameters<sup>a</sup>

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Fe	3.38(5)	3.16(4)	3.16(4)	-0.32(3)	0.63(3)	0.18(3)
S(1)	5.9(1)	4.55(9)	3.98(9)	-0.69(8)	1.33(7)	-0.74(7)
S(2)	3.78(8)	4.07(8)	4.53(9)	-0.01(7)	0.67(6)	1.01(7)
S(3)	3.93(9)	3.87(8)	4.78(9)	-0.28(7)	0.75(7)	1.21(7)
O(1)	4.0(3)	8.4(4)	7.2(4)	0.8(3)	0.2(2)	2.3(3)
O(2)	8.2(4)	7.0(4)	4.9(3)	-0.5(3)	1.7(3)	-2.3(3)
N(1)	3.7(3)	3.8(3)	4.6(3)	0.5(2)	0.9(2)	1.3(2)
N(2)	3.5(3)	5.3(3)	3.7(3)	-0.9(2)	1.0(2)	0.4(2)
C(1)	3.9(4)	4.5(4)	4.3(3)	-0.4(3)	0.9(3)	0.6(3)
C(2)	4.3(4)	5.1(4)	3.6(3)	-0.3(3)	0.7(3)	-0.9(3)
C(3)	3.0(3)	3.5(3)	3.2(3)	0.3(2)	1.1(2)	0.5(2)
C(4)	6.2(5)	2.7(3)	8.9(6)	-0.4(3)	1.9(4)	-0.3(3)
C(5)	6.0(4)	6.7(5)	5.3(4)	1.3(4)	2.5(3)	3.2(4)
C(6)	4.0(3)	3.8(3)	2.5(3)	0.0(3)	0.8(2)	0.0(2)
C(7)	5.8(4)	5.3(4)	6.6(5)	-1.9(4)	1.9(4)	0.7(4)
C(8)	3.6(4)	7.9(5)	6.1(5)	-0.2(4)	0.5(3)	1.7(4)

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

TABLE 3  
INTERATOMIC DISTANCES AND BOND ANGLES

A. Bonding distances (Å)

Fe—S(1)	2.387(2)	S(1)—C(3)	1.653(7)	N(1)—C(3)	1.302(8)
Fe—S(2)	2.330(2)	S(2)—C(6)	1.700(7)	N(1)—C(4)	1.465(10)
Fe—S(3)	2.320(2)	S(3)—C(6)	1.715(7)	N(1)—C(5)	1.509(9)
Fe—C(1)	1.779(8)	O(1)—C(1)	1.123(8)	N(2)—C(6)	1.321(8)
Fe—C(2)	1.745(8)	O(2)—C(2)	1.125(8)	N(2)—C(7)	1.476(10)
Fe—C(3)	1.876(6)			N(2)—C(8)	1.454(10)

B. Non-bonding distances less than 3.6 Å

O(2)···C(5)	3.358(10)	O(1)···O(2)	3.442(9)
O(2)···S(1)	3.425(7)	O(1)···C(5)	3.479(10)

C. Bond angles (degrees)

S(1)—Fe—S(2)	91.6(1)	Fe—S(2)—C(6)	86.7(2)
S(1)—Fe—S(3)	106.9(1)	Fe—S(3)—C(6)	86.7(2)
S(1)—Fe—C(1)	93.0(2)	C(3)—N(1)—C(4)	123.1(6)
S(1)—Fe—C(2)	150.4(3)	C(3)—N(1)—C(5)	119.3(6)
S(1)—Fe—C(3)	43.6(2)	C(4)—N(1)—C(5)	117.6(7)
S(2)—Fe—S(3)	74.8(1)	C(6)—N(2)—C(7)	121.5(6)
S(2)—Fe—C(1)	169.8(2)	C(6)—N(2)—C(8)	121.5(6)
S(2)—Fe—C(2)	87.7(3)	C(7)—N(2)—C(8)	117.0(6)
S(2)—Fe—C(3)	93.9(2)	Fe—C(1)—O(1)	178.8(7)
S(3)—Fe—C(1)	95.1(2)	Fe—C(2)—O(2)	178.0(7)
S(3)—Fe—C(2)	101.4(3)	Fe—C(3)—S(1)	84.9(3)
S(3)—Fe—C(3)	149.0(2)	Fe—C(3)—N(1)	143.4(5)
C(1)—Fe—C(2)	92.7(3)	S(1)—C(3)—N(1)	131.7(5)
C(1)—Fe—C(3)	95.8(3)	S(2)—C(6)—S(3)	111.6(4)
C(2)—Fe—C(3)	106.9(3)	S(2)—C(6)—N(2)	124.7(5)
Fe—S(1)—C(3)	51.5(2)	S(3)—C(6)—N(2)	123.7(5)

## Discussion

The molecular structure of  $\text{Fe}(\text{CO})_2(\text{CSNMe}_2)(\text{S}_2\text{CNMe}_2)$  is shown in Fig. 1. The structure consists of discrete molecular units with all atoms in general positions. It can be seen that this species is not a tetramethylthiuram monosulfide complex, but rather contains two separate sulfur ligands. One of these is a normal dimethyldithiocarbamate group; the other is a chelating thiocarboxamido group such as has been found in several other complexes [4–7].

The overall geometry of the complex is probably best regarded as highly distorted octahedral. However, because of the small angle subtended by the chelating thiocarboxamido group ( $43.6^\circ$ ), the structure may also be regarded as a distorted trigonal bipyramid (the thiocarboxamido group being in this case regarded as a monodentate ligand). The remaining angles about the "equator" are all about halfway between the octahedral angle of  $90^\circ$  and the trigonal angle of  $120^\circ$  (S(1)—Fe—S(3),  $106.9^\circ$ ; S(3)—Fe—C(2),  $101.4^\circ$ ; C(2)—Fe—C(3),  $106.9^\circ$ ). This high degree of distortion undoubtedly contributes substantially to the observed fluxionality of this species [1].

The distances and angles involving the atoms of the carbonyl and dithiocarbamate groups are all of the expected values. The Fe—C bond distance to the

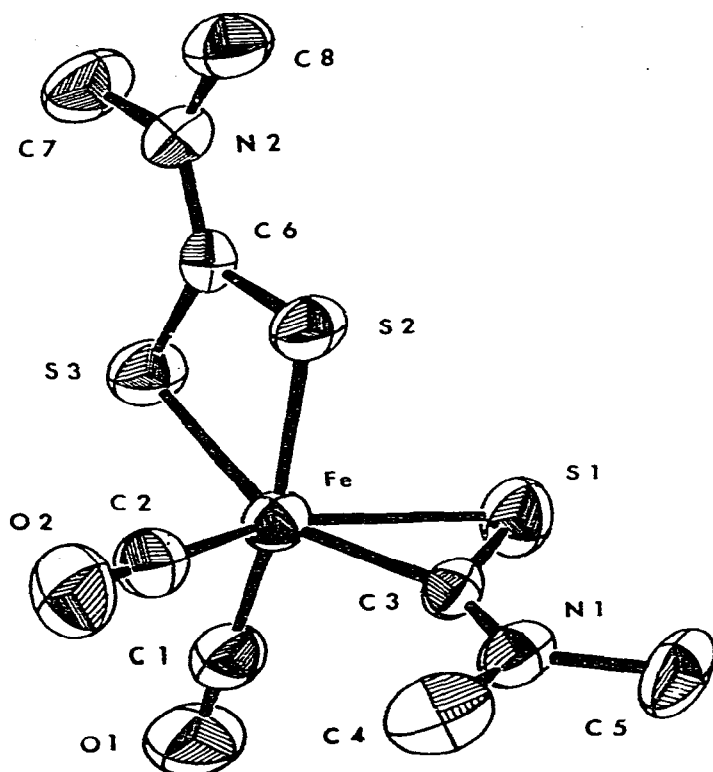


Fig. 1. The structure of  $\text{Fe}(\text{CO})_2(\text{CSNMe}_2)(\text{S}_2\text{CNMe}_2)$  (50% probability ellipsoids).

carbon atom of the thiocarboxamido group is quite short, only 1.876 Å. This is considerably shorter than the range of 1.98–2.03 Å reported for a number of other  $\text{Fe}-\text{C}(sp^2)$  distances [8–15], and even shorter than the  $\text{Fe}-\text{C}(sp)$  distance of 1.920(6) Å reported for  $\text{CpFe}(\text{CO})_2\text{C}\equiv\text{CPh}$  [16]. It would seem that the bonding between iron atom and the thiocarboxamido ligand is very similar to that seen in the closely related complex  $\text{Ph}_3\text{PMn}(\text{CO})_3\text{CSNMe}_2$ , where shortening of the  $\text{Mn}-\text{C}$  bond (with respect to the expected length of a  $\text{Mn}-\text{C}(sp^2)$  bond) is also observed [6], and a comparable degree of metal–carbon  $\pi$ -interaction in both complexes may be inferred. This is in contrast to the situation in the  $\text{Me}_2\text{NSCNiCS}(\text{NMe}_2)\text{CS}(\text{NMe}_2)^+$  ion, where the  $\text{Ni}-\text{C}$  distance to the thiocarboxamido ligand is 1.854 Å, almost exactly equal to the sum of the covalent radii and showing little or no evidence of shortening due to metal–carbon  $\pi$ -interaction [7]. The reason for this difference is not clear, especially in the case of the iron and nickel complexes in both of which the metal is nominally in the +2 oxidation state.

The presence of both a thiocarboxamido and a dithiocarbamate ligand in the same complex affords a good opportunity to make a detailed comparison of the bonding of these ligands. The  $\text{Fe}-\text{S}$  distance to the thiocarboxamido group (2.387 Å) is somewhat longer than the dithiocarbamate  $\text{Fe}-\text{S}$  distances (avg. 2.325 Å), while the thiocarboxamido  $\text{C}-\text{S}$  distance (1.653 Å) is shorter than the dithiocarbamate  $\text{C}-\text{S}$  distances (avg. 1.708 Å) by about the same amount. This may be taken as reflecting the strong  $\pi$ -acidity of the carbon atom of the

chelating thiocarboxamido ligand, which has been noted before [6]; this atom interacts strongly with all adjacent atoms, at the expense, it would seem, of Fe-S bonding the same ligand. The C-N distance in the thiocarboxamido group (1.30 Å) is also slightly shorter than the corresponding distance in the dithiocarbamate ligand (1.321 Å), but this difference is probably not significant.

The crystal packing is determined primarily by van der Waals forces, as shown by the intermolecular distances, the shortest of which are shown in Table 3.

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