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A COMPLEX WITH A BRIDGING THIOCARBOXAMIDO GROUP: THE CRYSTAL STRUCTURE OF $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$

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Summary

The structure of the compound $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ has been determined by X-ray crystallography. The compound crystallizes in space group $P2_1/c$ with four molecules in a unit cell of dimensions a 8.840(2), b 20.174(9), c 16.856(5) Å, β 114.82(3)°. Full-matrix least-squares refinement of 2881 counter data yielded $R = 0.046$. The molecule consists of two $Fe_2(CO)_6$ units bridged by thiocarboxamido and immoniocarbene ligands and by a common bridging sulfur atom. The structure of this compound is compared with those of related molecules and a detailed comparison is made of the bonding properties of the thiocarboxamido ligand in bridging and chelating configurations.

Introduction

Recently we have reported the synthesis of $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ by the reaction of $(NEt_4)_2[Fe_2(CO)_8]$ with dimethylthiocarbamoyl chloride, ClCSNMe [1]. The difficulty of characterizing this compound necessitated a structure determination by X-ray crystallography, the detailed results of which are presented here.

Experimental

Crystals of $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ were obtained by crystallization from dichloromethane/heptane in the form of dark red prisms. A suitable crystal was mounted on a glass fiber with epoxy cement and placed on a Syntex $P2_1$ automated diffractometer. Centering and refinement of fifteen high-angle reflections yielded lattice and orientation parameters, and the observed systematic

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TABLE 1

CRYSTAL DATA

Formula (mol. wt.)	$C_{18}H_{12}N_2O_{12}S_2Fe_4$ (735.81)
Crystal size	0.35 × 0.50 × 0.15 mm
Space group	$P2_{1/c}$
a	8.840(2) Å
b	20.174(9) Å
c	16.856(5) Å
β	114.82(3)°
Volume	2728(2) $Å^3$
Z	4
d_{calc}	1.791 g cm^{-3}
d_{exp} (flotation)	1.76 g cm^{-3}
F_{000}	1464 e
μ	23.60 cm^{-1}
Estimated range of transmission coefficients	0.52—0.68

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-$K_{\bar{\alpha}}$ radiation (λ 0.71073 Å) for reflections for which $k \geqslant 0$, $l \geqslant 0$, $5° \geqslant 2\theta \geqslant 50°$, 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 observed 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 5319 data collected, 2881 were considered observed ($I \geqslant 3\sigma(I)$); only observed data were used in the structure solution and refinement. No corrections were made for absorption.

The structure was solved by direct methods. Normalized structure factors (E's) were calculated using overall scale and isotropic 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 ($\bar{7}$ 9 11), ($\bar{1}$ 5 4), ($\bar{1}$ 0 2), ($\bar{6}$ 1 8), ($\bar{1}$ 11 4), ($\bar{4}$ 0 2), with the first three used for origin specification. An electron density map based on the phase set having the highest figure of merit clearly showed the four iron and two sulfur atoms. After isotropic least-squares refinement of these six atoms, a Fourier synthesis phased on their locations revealed all remaining nonhydrogen atoms.

Refinement of the structure proceeded smoothly. The final model used anisotropic thermal parameters for all nonhydrogen atoms (343 variables; data-to-parameter ratio 8.40/1). The hydrogen atoms of the methyl groups were not located. The final discrepancy factors (conventionally defined) were $R = 0.046$, $R_w = 0.056$. The error in an observation of unit weight was 1.442. A final difference Fourier synthesis showed a maximum electron density of 0.52 e $Å^{-3}$.

All least-squares cycles were based on the minimization of $\Sigma w||F_0| - |F_c||^2$ where $w = \sigma(F_0)^{-2}$. 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 given in Table 2. Interatomic

TABLE 2

FINAL ATOMIC PARAMETERS

A. Atomic coordinates

	x	y	z
Fe(1)	0.4472(1)	0.2514(1)	0.1767(1)
Fe(2)	0.1398(1)	0.2317(1)	0.0952(1)
Fe(3)	0.1988(1)	0.4301(1)	0.1261(1)
Fe(4)	0.2251(1)	0.3822(1)	0.2753(1)
S(1)	0.2517(2)	0.3254(1)	0.1671(1)
S(2)	0.4718(3)	0.4490(1)	0.2156(1)
O(1)	0.5289(7)	0.3314(3)	0.0534(4)
O(2)	0.5812(9)	0.1263(3)	0.1489(5)
O(3)	0.7127(8)	0.2894(3)	0.3451(4)
O(4)	0.0445(9)	0.3014(3)	−0.0728(4)
O(5)	0.1465(9)	0.1057(3)	0.0154(5)
O(6)	−0.1860(9)	0.2207(4)	0.0984(6)
O(7)	0.1327(8)	0.5652(3)	0.1687(4)
O(8)	−0.1520(8)	0.3987(3)	0.0229(4)
O(9)	0.2702(9)	0.4506(3)	−0.0261(4)
O(10)	0.1570(8)	0.4992(3)	0.3570(4)
O(11)	−0.1265(9)	0.3466(5)	0.2141(5)
O(12)	0.3355(10)	0.2773(3)	0.4058(4)
N(1)	0.5785(9)	0.4292(3)	0.3836(5)
N(2)	0.3082(9)	0.1547(3)	0.2626(4)
C(1)	0.5002(8)	0.3002(4)	0.1005(5)
C(2)	0.5311(10)	0.1758(4)	0.1586(5)
C(3)	0.6126(10)	0.2749(4)	0.2800(6)
C(4)	0.0807(10)	0.2755(4)	−0.0083(5)
C(5)	0.1427(10)	0.1554(4)	0.0473(5)
C(6)	−0.0592(11)	0.2264(4)	0.0982(7)
C(7)	0.1560(10)	0.5134(5)	0.1512(5)
C(8)	−0.0164(11)	0.4112(4)	0.0636(6)
C(9)	0.2419(10)	0.4416(4)	0.0317(6)
C(10)	0.1866(10)	0.4541(4)	0.3257(5)
C(11)	0.0093(12)	0.3597(5)	0.2357(6)
C(12)	0.2919(11)	0.3189(4)	0.3569(6)
C(13)	0.4513(9)	0.4215(3)	0.3061(5)
C(14)	0.7398(12)	0.4560(6)	0.3902(7)
C(15)	0.5724(14)	0.4092(6)	0.4663(5)
C(16)	0.2992(9)	0.1976(3)	0.2036(5)
C(17)	0.1573(14)	0.1172(5)	0.2584(7)
C(18)	0.4681(12)	0.1377(4)	0.3391(5)

B. Anisotropic thermal parameters[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	2.95(4)	3.76(5)	3.44(5)	0.34(3)	1.66(3)	0.30(4)
Fe(2)	3.25(4)	3.55(5)	4.06(5)	−0.45(4)	1.72(4)	−0.59(4)
Fe(3)	3.62(4)	3.29(5)	3.80(5)	0.23(4)	1.39(4)	0.19(4)
Fe(4)	3.71(4)	3.99(5)	3.37(5)	0.10(4)	1.65(4)	−0.31(4)
S(1)	2.73(7)	3.0(1)	3.1(1)	0.0(1)	1.1(1)	−0.2(1)
S(2)	4.31(9)	4.7(1)	5.0(1)	−0.9(1)	1.6(1)	0.2(1)
O(1)	5.9(3)	7.4(4)	5.4(3)	−0.3(3)	3.4(3)	1.4(3)
O(2)	9.4(4)	5.6(4)	9.0(4)	3.5(3)	5.8(3)	0.6(3)
O(3)	4.9(3)	8.7(4)	4.8(3)	0.3(3)	−0.5(3)	−0.9(3)
O(4)	8.7(4)	6.2(4)	4.4(3)	0.4(3)	1.6(3)	0.7(3)
O(5)	10.5(5)	4.6(4)	8.8(4)	0.0(3)	3.8(4)	−2.1(3)
O(6)	5.6(3)	10.2(5)	18.2(8)	−2.8(3)	7.8(5)	−4.3(5)
O(7)	8.5(4)	4.5(3)	6.8(4)	1.8(3)	2.8(3)	−1.0(3)
O(8)	3.8(3)	7.2(4)	6.9(4)	0.6(3)	0.6(3)	0.4(3)

(Table continued)

TABLE 2 (continued)

B. Anisotropic thermal parameters [a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(9)	9.8(4)	7.8(4)	6.1(4)	1.4(3)	4.9(3)	1.6(3)
O(10)	8.7(4)	5.7(3)	6.6(4)	1.6(3)	3.5(3)	−1.7(3)
O(11)	5.2(3)	14.1(6)	10.2(5)	−2.7(4)	4.6(4)	−3.7(4)
O(12)	13.2(5)	6.1(4)	6.7(4)	1.5(4)	5.7(4)	2.6(3)
N(1)	4.8(3)	5.3(4)	4.8(4)	−0.3(3)	0.3(3)	−0.4(3)
N(2)	7.4(4)	3.8(3)	4.9(3)	−0.7(3)	4.3(3)	−0.2(3)
C(1)	2.9(3)	4.7(4)	3.8(4)	0.1(3)	1.6(3)	−0.0(3)
C(2)	4.5(4)	5.4(5)	4.6(4)	0.5(3)	2.8(3)	0.5(3)
C(3)	3.5(3)	4.7(4)	5.1(4)	1.2(3)	2.1(3)	0.8(4)
C(4)	4.7(4)	4.4(4)	3.7(4)	0.5(3)	1.1(3)	−1.0(3)
C(5)	4.5(4)	4.3(4)	5.1(4)	−0.0(3)	1.7(3)	−0.2(3)
C(6)	4.7(4)	5.3(5)	8.7(6)	−1.0(4)	3.5(4)	−1.9(4)
C(7)	4.2(4)	5.5(5)	3.7(4)	0.3(3)	1.6(3)	0.4(3)
C(8)	4.6(4)	3.8(4)	5.1(4)	0.7(3)	2.0(4)	0.5(3)
C(9)	5.6(4)	4.7(5)	4.6(4)	0.9(3)	2.6(4)	0.7(3)
C(10)	4.5(4)	5.3(5)	4.0(4)	0.3(3)	1.8(3)	−0.1(3)
C(11)	5.3(4)	7.5(6)	5.3(5)	−0.6(4)	3.2(4)	−1.7(4)
C(12)	6.8(5)	4.6(4)	4.7(4)	0.2(4)	3.6(4)	−0.2(4)
C(13)	4.5(3)	2.9(3)	4.2(4)	0.0(3)	1.6(3)	−0.1(3)
C(14)	4.6(4)	8.5(7)	8.5(7)	−2.7(4)	−0.1(4)	−1.2(5)
C(15)	8.9(6)	10.3(7)	2.3(4)	−0.2(5)	0.0(4)	−0.3(4)
C(16)	4.4(3)	3.2(3)	4.2(4)	−0.4(3)	2.8(3)	−0.5(3)
C(17)	9.1(6)	6.7(5)	8.6(6)	−2.4(5)	6.0(5)	0.8(5)
C(18)	8.0(5)	5.2(5)	3.5(4)	1.3(4)	1.8(4)	1.5(3)

[a] 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.

distances and bond angles are presented 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 $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ molecule is shown in Fig. 1. The structure consists of discrete molecular units, with all atoms in general positions; the packing is determined by Van der Waals forces as shown by the intermolecular distances, the shortest of which are given in Table 3.

The molecule consists of two doubly-bridged $Fe_2(CO)_6$ units. These share a common bridging sulfur atom ligand, with one unit being bridged as well by a thiocarboxamido group (through the C—S linkage) and the other unit being bridged by a dimethylimmoniocarbene ligand. The coordination about the sulfur atom is roughly tetrahedral, so that the two $Fe_2(CO)_6$ units are oriented approximately at right angles to one another. The overall structure is thus similar to

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* The table of structure factors has been deposited as NAPS Document No. 03181 (19 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.

TABLE 3

INTERATOMIC DISTANCES AND BOND ANGLES

A. Bonding distances (Å)

Fe(1)—Fe(2)	2.512(2)
Fe(1)—S(1)	2.287(2)
Fe(1)—C(1)	1.856(8)
Fe(1)—C(2)	1.843(9)
Fe(1)—C(3)	1.810(9)
Fe(1)—C(16)	1.927(7)
Fe(2)—S(1)	2.318(2)
Fe(2)—C(4)	1.846(9)
Fe(2)—C(5)	1.812(9)
Fe(2)—C(6)	1.784(9)
Fe(2)—C(16)	1.920(8)
Fe(3)—Fe(4)	2.630(2)
Fe(3)—S(1)	2.312(2)
Fe(3)—S(2)	2.282(2)
Fe(3)—C(7)	1.889(10)
Fe(3)—C(8)	1.791(9)
Fe(3)—C(9)	1.801(9)
Fe(4)—S(1)	2.279(2)
Fe(4)—C(10)	1.844(9)
Fe(4)—C(11)	1.801(10)
Fe(4)—C(12)	1.833(10)
Fe(4)—C(13)	2.023(8)
S(2)—C(13)	1.711(8)
O(1)—C(1)	1.140(8)
O(2)—C(2)	1.176(9)
O(3)—C(3)	1.127(9)
O(4)—C(4)	1.138(9)
O(5)—C(5)	1.189(9)
O(6)—C(6)	1.128(9)
O(7)—C(7)	1.176(9)
O(8)—C(8)	1.134(9)
O(9)—C(9)	1.120(8)
O(10)—C(10)	1.171(9)
O(11)—C(11)	1.133(10)
O(12)—C(12)	1.156(9)
N(1)—C(13)	1.328(9)
N(1)—C(14)	1.495(11)
N(1)—C(15)	1.479(12)
N(2)—C(16)	1.325(9)
N(2)—C(17)	1.528(11)
N(2)—C(18)	1.503(11)

B. Nonbonding distances less than 3.3 Å

O(1)...O(11)	3.130(9)
O(11)...C(1)	3.197(10)
O(6)...C(2)	3.213(10)
O(4)...O(12)	3.210(10)
O(2)...C(15)	3.137(12)
O(6)...C(1)	3.258(10)
O(2)...O(6)	3.229(11)
O(3)...O(4)	3.288(9)
O(1)...O(6)	3.288(10)
O(1)...O(12)	3.292(9)

C. Bond angles (degrees)

Fe(2)—Fe(1)—S(1)	57.5(1)
Fe(2)—Fe(1)—C(1)	104.1(2)
Fe(2)—Fe(1)—C(2)	100.6(3)
Fe(2)—Fe(1)—C(3)	145.4(2)
Fe(2)—Fe(1)—C(16)	49.1(2)
S(1)—Fe(1)—C(1)	88.4(2)
S(1)—Fe(1)—C(2)	158.1(3)
S(1)—Fe(1)—C(3)	99.3(2)
S(1)—Fe(1)—C(16)	81.6(2)
C(1)—Fe(1)—C(2)	97.7(3)
C(1)—Fe(1)—C(3)	100.1(3)
C(1)—Fe(1)—C(16)	152.4(3)
C(2)—Fe(1)—C(3)	100.3(4)
C(2)—Fe(1)—C(16)	83.4(3)
C(3)—Fe(1)—C(16)	106.9(3)
Fe(1)—Fe(2)—S(1)	56.3(1)
Fe(1)—Fe(2)—C(4)	104.2(3)
Fe(1)—Fe(2)—C(5)	100.2(3)
Fe(1)—Fe(2)—C(6)	148.0(3)
Fe(1)—Fe(2)—C(16)	49.4(2)
S(1)—Fe(2)—C(4)	87.4(3)
S(1)—Fe(2)—C(5)	156.0(3)
S(1)—Fe(2)—C(6)	104.4(3)
S(1)—Fe(2)—C(16)	80.9(2)
C(4)—Fe(2)—C(5)	94.5(4)
C(4)—Fe(2)—C(6)	99.7(4)
C(4)—Fe(2)—C(16)	153.1(3)
C(5)—Fe(2)—C(6)	98.9(4)
C(5)—Fe(2)—C(16)	86.9(3)
C(6)—Fe(2)—C(16)	106.7(4)
Fe(4)—Fe(3)—S(1)	54.4(1)
Fe(4)—Fe(3)—S(2)	77.9(1)
Fe(4)—Fe(3)—C(7)	95.2(2)
Fe(4)—Fe(3)—C(8)	97.0(3)
Fe(4)—Fe(3)—C(9)	158.5(3)
S(1)—Fe(3)—S(2)	86.9(1)
S(1)—Fe(3)—C(7)	149.7(2)
S(1)—Fe(3)—C(8)	89.6(3)
S(1)—Fe(3)—C(9)	107.6(3)
S(2)—Fe(3)—C(7)	86.8(2)
S(2)—Fe(3)—C(8)	174.8(3)
S(2)—Fe(3)—C(9)	90.2(3)
C(7)—Fe(3)—C(8)	94.4(4)
C(7)—Fe(3)—C(9)	102.0(4)
C(8)—Fe(3)—C(9)	94.5(4)
Fe(3)—Fe(4)—S(1)	55.6(1)
Fe(3)—Fe(4)—C(10)	99.4(3)
Fe(3)—Fe(4)—C(11)	95.4(3)
Fe(3)—Fe(4)—C(12)	150.6(2)
Fe(3)—Fe(4)—C(13)	76.6(2)
S(1)—Fe(4)—C(10)	155.1(3)
S(1)—Fe(4)—C(11)	90.7(3)
S(1)—Fe(4)—C(12)	96.0(3)
S(1)—Fe(4)—C(13)	90.0(2)
C(10)—Fe(4)—C(11)	91.0(4)
C(10)—Fe(4)—C(12)	108.7(4)
C(10)—Fe(4)—C(13)	84.0(3)
C(11)—Fe(4)—C(12)	92.4(4)
C(11)—Fe(4)—C(13)	169.7(4)
C(12)—Fe(4)—C(13)	97.8(4)
Fe(1)—S(1)—Fe(2)	66.1(1)
Fe(1)—S(1)—Fe(3)	136.9(1)
Fe(1)—S(1)—Fe(4)	129.4(1)
Fe(2)—S(1)—Fe(3)	132.5(1)
Fe(2)—S(1)—Fe(4)	134.9(1)
Fe(3)—S(1)—Fe(4)	69.9(1)
Fe(2)—S(2)—C(13)	93.0(3)
C(13)—N(1)—C(14)	120.4(8)
C(13)—N(1)—C(15)	122.8(7)
C(14)—N(1)—C(15)	116.7(7)
C(16)—N(2)—C(17)	123.1(8)
C(16)—N(2)—C(18)	123.1(7)
C(17)—N(2)—C(18)	113.9(7)
Fe(1)—C(1)—O(1)	178.0(7)
Fe(1)—C(2)—O(2)	177.2(7)
Fe(1)—C(3)—O(3)	178.2(7)
Fe(2)—C(4)—O(4)	178.7(7)
Fe(2)—C(5)—O(5)	178.9(8)
Fe(2)—C(6)—O(6)	177.1(9)
Fe(3)—C(7)—O(7)	178.5(7)
Fe(3)—C(8)—O(8)	178.7(8)
Fe(3)—C(9)—O(9)	177.8(9)
Fe(4)—C(10)—O(10)	177.9(7)
Fe(4)—C(11)—O(11)	176.9(8)
Fe(4)—C(12)—O(12)	176.9(7)
Fe(4)—C(13)—S(2)	112.0(4)
Fe(4)—C(13)—N(1)	129.8(6)
S(2)—C(13)—N(1)	118.2(6)
Fe(1)—C(16)—Fe(2)	81.5(3)
Fe(1)—C(16)—N(2)	138.5(6)
Fe(2)—C(16)—N(2)	139.6(6)

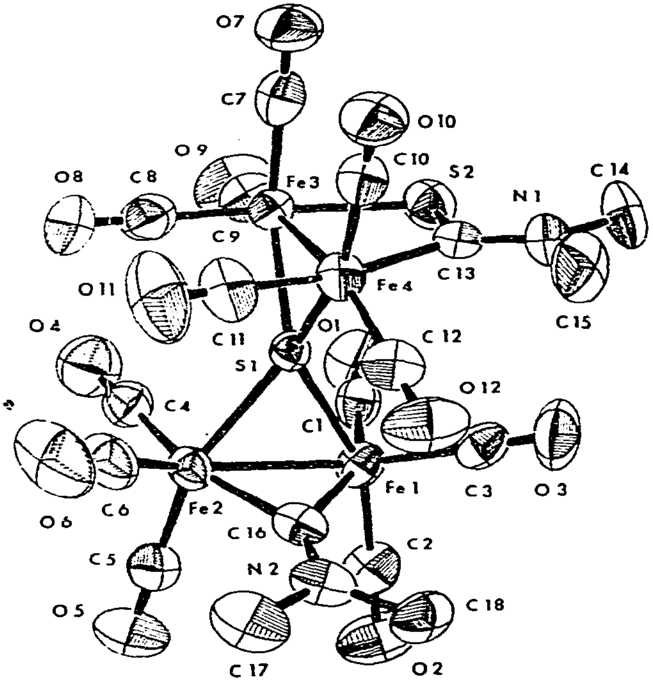

Fig. 1.

that of $Fe_4(CO)_{12}S(SMe)_2$ [4] the main difference being the presence of a two-atom bridge in the present complex.

The distances and angles in the Fe—CO linkages are all of the expected lengths. The Fe—S distances to the central sulfur atom (2.279—2.318 Å, avg. 2.299 Å) are about the same as those found in $Fe_4(CO)_{12}S(SMe)_2$ (2.239—2.254 Å, avg. 2.248 Å) [4]. The two Fe—Fe bond distances (Fe(1)—Fe(2), 2.512 Å, Fe(3)—Fe(4), 2.630 Å) are significantly different; the former is the bond bridged only by single-atom bridges and is of about average length. The latter distance might be considered to be longer because of the presence of one two-atom bridge; however it is longer than that of 2.568 Å found in $Fe_2(CO)_6(PhCO)_2$ (which has two two-atom bridges) [5], and is well within the range observed for similar complexes with only one-atom bridges, which range up to 2.821 Å in $Fe_2(CO)_6[P(CF_3)_2]_2$ [6].

The bridging dimethylimmoniocarbene ligand compares closely in its structural parameters with the similar diethylimmoniocarbene ligands found in $Fe_2(CO)_6(CNEt_2)_2$ [9]. The Fe—C distances to this ligand in the present complex (avg. 1.924 Å) are about the same as those in $Fe_2(CO)_6(CNEt_2)_2$ (avg. 1.907 Å) but, curiously, the C—N distance is longer (1.325 Å vs. 1.282 Å average in $Fe_2(CO)_6(CNEt_2)_2$).

This molecule is unusual in that it contains a bridging thiocarboxamido group. Only one other complex is known in which a thiocarboxamido group bridges two metals [7], and little is known about the properties of this group in a bridging role. However, the availability of this structure and that of another iron complex $[Fe(CO)_2(CSNMe_2)(S_2CNMe_2)]$ [8] containing a chelating thiocarboxamido

TABLE 4

COMPARISON OF BOND LENGTHS AND ANGLES IN BRIDGING AND CHELATING THIOCARBOXAMIDO LIGANDS

	Bridging[a]	Chelating[b]
Fe—S (Å)	2.282(2)	2.387(2)
Fe—C (Å)	2.023(8)	1.876(6)
C—S (Å)	1.711(8)	1.653(7)
C—N (Å)	1.328(9)	1.302(8)
Fe—S—C (deg)	93.0(3)	51.5(2)
Fe—C—S (deg)	111.0(4)	84.9(3)
Fe—C—N (deg)	129.8(6)	143.4(5)
S—C—N (deg)	118.2(6)	131.7(5)

[a] $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$, this study. [b] $Fe(CO)_2(CSNMe_2)(S_2CNMe_2)$, ref. 8.

ligand makes possible a detailed comparison of the bonding of this ligand in the two situations. The relevant structural parameters for both complexes are shown in Table 4.

It appears that the carbon atom in the chelating thiocarboxamido ligand acts more strongly as a π-acceptor than its counterpart in the bridging ligand. The C—N distances are experimentally equivalent (indicating a near double bond in both cases, as expected), but the Fe—C and C—S distances are both distinctly longer in the bridging ligand. In addition the Fe—S distance to the bridging ligand is over 0.1 Å shorter than that to the chelating ligand, and about the same as the average Fe—S distance (2.290 Å) to the central sulfur atom. This may indicate some enhancement of Fe—S π-interaction in the bridged complex, but the fact that the Fe—S distance to the chelating ligand is longer than the Fe—S bonds to the central sulfur suggests the probability that this difference results at least partially from the much higher degree of ring strain in the chelated complex (as shown by the bond angles, especially the Fe—S—C angles) or, put another way, from the different hybridization at the thiocarboxamido sulfur atom in the two complexes.

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