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Registry No. $RhCl[(C_6H_5)_2PCH_2CH_2CH{=}CH_2]_2$, 56629-85-7.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50395P-12-75.

References and Notes

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(2) R. Jones, *Chem. Rev.*, **68**, 785 (1968).

(3) R. S. Nyholm, *Suom. Kemistil. B*, **42**, 165 (1969).

(4) E. L. Muetterties and R. A. Schunn, *Q. Rev., Chem. Soc.*, **20**, 245 (1966).

(5) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

(6) R. Cramer, J. B. Kline, J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 2519 (1969).

(7) (a) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957); (b) C. W. Burnham, "IUC World List of Crystallographic Computer Programs", 1962, Program 338; (c) A. C. Larson, D. T. Cromer, and R. B. Roof, Jr., Report LA-3043, Los Alamos Scientific Laboratory, Los Alamos, N.M., 1964.

(8) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, in press.

(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(10) G. Del Pino, G. Perego, and M. Cesari, *Cryst. Struct. Commun.*, **3**, 15 (1974).

(11) M. O. Visscher, J. C. Huffman, and W. E. Streib, *Inorg. Chem.*, **13**, 792 (1974).

(12) N. Rösch and R. Hoffmann, *Inorg. Chem.*, **13**, 2656 (1974).

(13) J. H. Enemark and R. D. Feltham, *Coord. Chem. Ref.*, **13**, 339 (1974).

(14) S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, **13**, 770 (1974).

(15) Supplementary material.

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Crystal and Molecular Structure of Iron(II) Bis(diethyldithiocarbamate)

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The molecular structure of $[Fe(S_2CN(C_2H_5)_2)_2]_2$ has been determined from single-crystal X-ray diffraction data obtained by counter methods. The compound crystallizes in space group C_{2h}^5-$P2_1/c$ with four monomers per unit cell of dimensions $a = 10.0540$ (69) Å, $b = 10.6937$ (40) Å, $c = 16.5824$ (42) Å, and $\beta = 112.6$ (1)°. The calculated and observed densities are 1.470 and 1.457 (5) g cm^{-3}, respectively. Full-matrix least-squares refinement using data having $F_o^2 > 3\sigma(F_o^2)$ gave $R_1 = 0.058$ for the 2786 data. The compound is dimeric with distorted trigonal-bipyramidal geometry around each iron atom. Thus it is similar in structure to the isomorphous $[Zn(S_2CN(C_2H_5)_2)_2]_2$. The two dithiocarbamate ligands each bridge one axial and one equatorial position of the trigonal bipyramid. The distorted trigonal bipyramid is achieved by dimerization through sulfur bridges with a resultant Fe–Fe distance of 3.350 Å.

Introduction

Iron(II) dithiocarbamates are a class of chemically reactive compounds with some striking physical properties.[1] We have been studying the chemical reactions of iron(II) dithiocarbamates with NO, CO, and NO$^+$.[2,3] The magnetic susceptibility and Mössbauer[4] spectra of $Fe^{II}(S_2CNEt_2)_2$ indicate that it is dimeric. The magnetic susceptibility shows antiferromagnetic coupling between pairs of iron atoms and a Neel temperature of 110 K.

This class of compounds also has properties which may be related to those of iron–sulfur proteins.[5–7] Recently Holm[8] has prepared iron–sulfur clusters containing the Fe_2S_2 and Fe_4S_4 units. The structures of the Fe_4S_4 cluster and the Fe_2S_2 cluster containing **Fe(III)** have been determined by Holm, Ibers, and their coworkers.[9,10] However, as Lippard indicated in his recent review of this subject,[11] there appear to be no structural studies of Fe_2S_2 complexes in which **Fe(II)** is exclusively coordinated to sulfur ligands. While a preliminary investigation of $Fe^{II}(S_2CNEt_2)_2$ by X-ray powder patterns[12] showed it to be isomorphous with the corresponding dinuclear Zn(II) complex[13] and Cu(II) complex,[14] the Cu(II) and Zn(II) complexes have different coordination geometries. Thus, the coordination geometry around Fe(II) remained unknown. The crystal structure determination described below was undertaken to provide a detailed picture of the coordination geometry around the iron atom in $Fe^{II}(S_2CNEt_2)_2$.

Experimental Section

Crystals of the compound $Fe(S_2CNEt_2)_2$ were obtained by the method published elsewhere.[15] Large dark red crystals were obtained by this procedure. The crystals obtained are extremely sensitive toward air and therefore were stored in sealed ampoules under nitrogen. Crystals for X-ray investigation were sealed in glass capillaries under nitrogen. Preliminary precession photographs taken with Mo Kα radiation indicated that the crystals are monoclinic. The systematic absences of $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$ are consistent with the space group C_{2h}^5-$P2_1/c$. At 23 ± 2°C the unit cell parameters are $a = 10.0540$ (69) Å, $b = 10.6937$ (40) Å, $c = 16.5824$ (42) Å, and $\beta = 112.6$ (1)°. These parameters were determined from a least-squares refinement of the setting angles of 12 reflections that were centered on a Picker FACS-I computer-controlled four-circle X-ray diffractometer. The values of 2θ for these reflections were 30–42°. In the refinement the wavelength of Mo K$\bar{\alpha}$ radiation was taken as 0.71069 Å. The crystal density of 1.457 (5) g cm^{-3} determined by flotation in bromobenzene–chlorobenzene is in good agreement with the value of 1.470 g cm^{-3} calculated for four molecules per unit cell.

For data collection a crystal of approximate dimensions 0.4 × 0.4 × 0.3 mm was mounted with its b axis approximately collinear with the ϕ axis of the diffractometer. The mosaicity of the crystal was checked by ω scans at a takeoff angle of 0.7°. All reflections had peak widths of 0.15° or less. An incident beam monochromator equipped with a graphite crystal was used to obtain Mo Kα radiation. The θ–2θ axis of the monochromator is perpendicular to the θ–2θ axis of the diffractometer. Data were collected at a takeoff angle of 2.0° using the θ–2θ scan technique and an asymmetric scan range from $2\theta_{MoK\alpha_1} - 0.85°$ to $2\theta_{MoK\alpha_2} + 0.85°$. The pulse height analyzer was set to admit ~90% of Mo Kα peak and the scintillation counter was 24 cm away from the crystal. Cu foils having attenuation factors of ~1.7 were inserted into the diffracted beam whenever the counting rate exceeded ~10^3 counts/sec. During data collection the intensities of three reflections in diverse regions of reciprocal space were monitored after every 100 reflections. The maximum variation of any standard from its mean value was ~5%. A total of 4893 unique reflections having $2\theta \leq 50°$ were obtained. The data were reduced to F^2 and

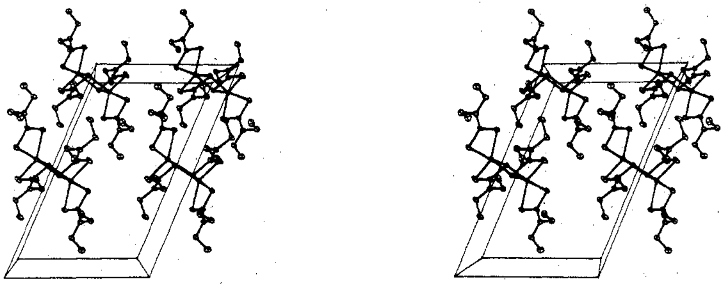

Figure 1. Stereoview of the packing for $[Fe(S_2CN(C_2H_5)_2)_2]_2$. The positive direction of the *b* axis of the unit cell is up out of the plane of the paper; the positive direction of the horizontal *a* axis is to the left. The thermal ellipsoids are drawn at their 50% probability levels.

$\sigma(F^2)$ by procedures similar to those previously described.[16]

The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the reflection being observed. Standard deviations were assigned to the intensities by the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in time t_c, and B_1 and B_2 are the background counts each obtained in time t_b. I is the intensity and p was taken as 0.04. The absorption coefficient for the compound for Mo Kα radiation is 14.53 cm^{-1}. Sample calculations on several representative reflections showed that the magnitude of the absorption correction ranged from 0.591 to 0.634. Therefore no correction was made for absorption.

Solution and Refinement

Positions of the Fe and S atoms were readily located from a Patterson map computed from the corrected intensities. The other heavy atoms were found from a difference electron density map.

Refinement of the structure based upon F was begun,[17] the quantity minimized being $\sum w(|F_o| - |F_c|)^2$ with the weights, w, taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Fe, S, C, N, and O were obtained from Cromer and Waber.[18] The hydrogen scattering factors were from the calculation of Stewart et al.[19] The effects of anomalous dispersion were included[20] in F_c; the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer[21] were used for Fe and S.

The initial structure factor calculation including all nonhydrogen atoms gave $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.456$ and $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.450$. At this stage all 4893 reflections were used. All atoms were given individual isotropic thermal parameters. Four cycles of refinement with iron and the four sulfur atoms assigned anisotropic thermal parameters gave $R_1 = 0.128$ and $R_2 = 0.102$. At this stage reflections with $F_o^2 \leq 3\sigma(F_o^2)$ were omitted and 2786 reflections were utilized in further refinement. Three additional cycles of refinement were carried out assuming anisotropic thermal motion for all heavy atoms (154 variable parameters). These cycles lowered R_1 and R_2 to 0.066 and 0.081, respectively. The positions of the methylene protons were calculated and the methyl protons were found by running general-plane electron density maps through the methyl groups. The inclusion of all the hydrogen atoms in the final cycle lowered R_1 to 0.058 and R_2 to 0.065.

Discussion

The coordination geometry around the individual iron atoms is best described as distorted trigonal bipyramidal. The coordination sphere is comprised of four sulfur atoms (S(1), S(2), S(3), and S(4')) from two dithiocarbamate ligands and of an additional sulfur atom (S(4)) from an adjacent $Fe^{II}(S_2CNEt_2)_2$ molecule. Sulfur atoms S(2), S(3), and S(4) form an approximately trigonal planar array with nearly equal Fe–S distances of 2.402, 2.408, and 2.437 Å, respectively, and with only small deviations from coplanarity (±0.05 Å) (Table I). The remaining two sulfur atoms S(1) and S(4') occupy the axial positions of the trigonal bipyramid. However, due to the small bite angle of the dithiocarbamate ligands these axial sulfur atoms are strongly distorted from the normal positions in a regular trigonal bipyramid. In addition the two axial Fe–S distances are grossly dissimilar. Thus the iron(II) coordination sphere is very similar to that reported earlier for $Zn^{II}(S_2CNEt_2)_2$ by Bonamico et al.[13] (Figures 1 and 2). The major difference between the iron(II) and zinc(II) structures is the somewhat smaller covalent radius of Zn(II) compared with that of Fe(II). The M–S(4') bond is significantly longer in the zinc complex than in the iron complex (Table II). In contrast, the coordination sphere of Cu(II) in the isomorphous dimeric $Cu^{II}(S_2CNEt_2)_2$ complex is best described as a distorted tetragonal pyramid with the sulfur atom S(4) in the axial position.[14] However, the least-squares plane through S(1), S(2), S(3), and S(4') of $Fe^{II}(S_2CNEt_2)_2$ indicates a large deviation from square-pyramidal geometry in this iron complex (Table III).

Table I. Selected Interatomic Distances (Å) and Angles (deg) in $Fe^{II}(S_2CNEt_2)_2$

	Distances		
Fe–S(1)	2.453 (2)	C(1)–N(1)	1.330 (6)
Fe–S(2)	2.402 (2)	C(2)–N(1)	1.489 (6)
Fe–S(3)	2.408 (2)	C(2)–C(3)	1.500 (8)
Fe–S(4)	2.437 (2)	C(4)–N(1)	1.492 (7)
Fe–S(4')	2.613 (2)	C(4)–C(5)	1.519 (9)
S(1)–C(1)	1.734 (5)	C(6)–N(2)	1.321 (5)
S(2)–C(1)	1.731 (5)	C(9)–N(2)	1.480 (6)
S(3)–C(6)	1.721 (5)	C(7)–C(8)	1.490 (9)
S(4)–C(6)	1.766 (5)	C(9)–C(10)	1.516 (8)
	Angles		
S(1)–Fe–S(4')	159.1 (1)	S(2)–C(1)–S(1)	115.7 (3)
S(1)–Fe–S(2)	74.3 (1)	C(1)–N(1)–C(2)	122.1 (4)
S(1)–Fe–S(3)	102.3 (1)	C(1)–N(1)–C(4)	121.7 (4)
S(3)–Fe–S(4)	107.3 (1)	C(2)–N(1)–C(4)	116.1 (4)
S(2)–Fe–S(4)	109.5 (1)	N(1)–C(2)–C(3)	112.6 (5)
S(2)–Fe–S(4')	98.3 (1)	N(1)–C(4)–C(5)	110.6 (4)
S(4)–Fe–S(4')	97.2 (1)	N(2)–C(6)–S(3)	123.8 (3)
S(2)–Fe–S(3)	142.8 (1)	N(2)–C(6)–S(4)	121.5 (3)
S(4)–Fe–S(1)	103.7 (1)	S(3)–C(6)–S(4)	114.7 (3)
C(1)–S(1)–Fe	84.0 (2)	C(6)–N(2)–C(9)	123.6 (4)
C(1)–S(2)–Fe	85.7 (2)	C(6)–N(2)–C(7)	121.2 (4)
C(6)–S(3)–Fe	90.5 (2)	C(9)–N(2)–C(7)	115.2 (4)
C(6)–S(4)–Fe	101.4 (2)	C(8)–C(7)–N(2)	111.7 (5)
N(1)–C(1)–S(2)	122.4 (4)	N(2)–C(9)–C(10)	111.8 (4)
N(1)–C(1)–S(1)	121.9 (4)	Fe–S(4)–Fe'	82.8 (1)

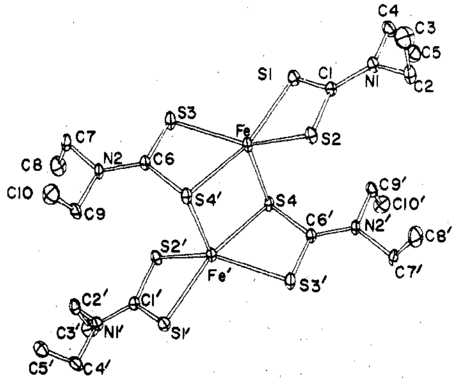

Figure 2. Projection of the $[Fe(S_2CN(C_2H_5)_2)_2]_2$ molecule. The hydrogen atoms have been omitted for clarity.

The dimer can best be viewed as one formed from two bridging monodentate dithiocarbamate ligands as originally

Table II. Least-Squares Planes

Equation in the Form $Ax + By + Cz - D = 0$ by the Hamilton Method

Plane	A	B	C	D	Atoms defining the plane
1	0.3709	0.9747	−0.5154	0.1355	S(1), S(2), S(3), S(4)
2	0.7079	−0.5605	0.2850	0.1576	S(1), S(2), S(3), S(4′)
3	0.5590	0.8880	−0.2960	0.1245	Fe, S(2), S(3), S(4)
4	0.8008	−0.4426	0.1674	0.1338	Fe, S(2), S(3), S(4′)
5	0.4093	0.9525	−0.5700	0.1163	Fe, S(1), S(2), S(3), S(4)
6	0.7480	−0.5290	0.2138	0.1293	Fe, S(1), S(2), S(3), S(4′)
7	0.4232	0.6161	−0.1341	0.7529	Fe, S(1), S(3), S(4)
8	0.5240	−0.4938	0.7669	0.1119	Fe, S(1), S(3), S(4′)

Deviations from the Planes, Å

Atoms	1	2	3	4	5	6	7	8
Fe			0.041	−0.207	−0.235	−0.275	−0.432	−0.139
S(1)	1.569	−0.169			1.778	0.241	0.586	0.366
S(2)	−0.955	0.118	−0.051	0.390	−0.812	0.359		
S(3)	−0.548	0.206	−0.058	0.686	−0.228	0.610	0.718	−0.047
S(4)	0.183		−0.028		0.328	0.119	0.370	
S(4′)		−0.117		−0.049				0.240

Dihedral Angles between the Planes, Deg

Plane	Angle	Plane	Angle
(Fe, S(1), S(2))–(Fe, S(3), S(4))	97.3	(Fe, S(1), S(2))–(Fe, S(3), S(4′))	141.3

Table III. Final Atomic Parameters for $Fe(S_2CNEt_2)_2$

Atom[a]	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Fe	0.1631 (1)	0.0605 (1)	0.0553 (1)	13.4 (1)	4.9 (1)	2.85 (3)	0.5 (1)	3.28 (4)	0.83 (4)
S(1)	0.3367 (1)	0.2314 (1)	0.1127 (1)	15.6 (2)	7.8 (1)	3.7 (1)	−2.8 (1)	4.4 (1)	−0.8 (1)
S(2)	0.2114 (1)	0.0709 (1)	0.2087 (1)	15.5 (2)	5.6 (1)	3.0 (1)	−1.9 (1)	3.3 (1)	−0.26 (6)
S(3)	−0.2432 (2)	0.0359 (1)	0.0494 (1)	22.6 (2)	5.8 (1)	5.8 (1)	−3.9 (1)	8.7 (1)	−2.2 (1)
S(4)	−0.0627 (1)	0.1676 (1)	−0.0265 (1)	14.3 (2)	4.8 (1)	2.6 (1)	0.07 (10)	3.5 (1)	0.16 (6)
C(1)	0.3181 (5)	0.1986 (4)	0.2102 (3)	10.6 (6)	5.7 (4)	3.2 (2)	0.3 (4)	2.4 (3)	−0.2 (2)
N(1)	0.3817 (4)	0.2677 (4)	0.2815 (3)	13.8 (6)	6.6 (4)	3.3 (2)	−1.9 (4)	2.9 (3)	−1.1 (2)
C(2)	0.3651 (6)	0.2405 (5)	0.3651 (3)	18.3 (8)	8.5 (5)	3.4 (2)	−1.5 (6)	4.2 (4)	1.4 (3)
C(4)	0.4681 (6)	0.3809 (6)	0.2807 (4)	15.9 (8)	9.9 (6)	4.9 (3)	−5.5 (6)	3.8 (4)	−2.5 (4)
C(6)	−0.1454 (5)	0.1682 (4)	0.0501 (3)	13.0 (6)	4.8 (4)	3.0 (2)	−0.3 (4)	3.4 (3)	−0.2 (2)
N(2)	−0.1356 (4)	0.2657 (3)	0.1010 (2)	14.2 (5)	4.5 (3)	3.3 (2)	−0.4 (4)	4.0 (3)	−1.1 (2)
C(7)	−0.2123 (6)	0.2684 (5)	0.1622 (4)	18.3 (8)	7.2 (5)	4.6 (3)	0.3 (5)	6.3 (4)	−1.6 (3)
C(8)	−0.1158 (8)	0.2316 (7)	0.2524 (4)	26.4 (12)	16.0 (9)	4.1 (3)	−1.8 (9)	6.5 (5)	−0.9 (4)
C(9)	−0.0460 (6)	0.3769 (4)	0.1043 (4)	16.4 (8)	5.0 (4)	4.5 (3)	−2.5 (5)	4.2 (4)	−1.2 (3)
C(10)	−0.1348 (7)	0.4831 (6)	0.0492 (5)	21.6 (10)	6.7 (5)	9.3 (5)	0.6 (6)	8.0 (6)	1.1 (4)
C(3)	0.4849 (7)	0.1612 (7)	0.4256 (4)	21.5 (11)	15.2 (9)	4.9 (3)	0.7 (8)	3.3 (5)	1.3 (5)
C(5)	0.3711 (7)	0.4945 (5)	0.2499 (5)	19.3 (10)	7.1 (5)	8.0 (4)	−3.7 (6)	6.1 (5)	−1.7 (4)

Atom[a]	x	y	z	Atom[a]	x	y	z
H(1)[b]	0.2615	0.1919	0.3514	H(11)	−0.3063	0.2051	0.1382
H(2)	0.3615	0.3285	0.3984	H(12)	−0.2532	0.3631	0.1645
H(3)	0.5720	0.1783	0.4269	H(13)	−0.0242	0.2769	0.2853
H(4)	0.5059	0.0935	0.4012	H(14)	−0.1516	0.2024	0.2880
H(5)	0.4572	0.1204	0.4792	H(15)	−0.0667	0.1575	0.2569
H(6)	0.5250	0.3662	0.2363	H(16)	0.0381	0.3511	0.0806
H(7)	0.5492	0.3986	0.3460	H(17)	0.0064	0.4082	0.1721
H(8)	0.2816	0.4737	0.1804	H(18)	−0.0698	0.5640	0.0544
H(9)	0.4342	0.5805	0.2579	H(19)	−0.1814	0.4539	−0.0197
H(10)	0.2892	0.4901	0.2579	H(20)	−0.2261	0.4940	0.0582

[a] x, y, and z are in fractional coordinates. Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviation of the last significant figure is given in parentheses. [b] An isotropic thermal parameter, B, of 8.0 Å^2 was assigned to each of the hydrogen atoms.

described by Bonamico et al.[13] There appear to be no major structural effects attributable to the antiferromagnetic interaction between the two high-spin iron atoms. The planarity of the Fe_2S_2 unit is crystallographically imposed. The two sulfur atoms S(4) and S(4′) form asymmetric bridges between two iron atoms of the dimer with two distinctively different FeS distances of 2.613 and 2.437 Å, respectively. The geometry of this $Fe^{II}{}_2S_2$ unit is distinctively different from that observed for the $Fe^{III}{}_2S_2$ unit reported earlier by Snow and Ibers[22] and by Mayerle et al.[23] These changes cannot be directly attributed to changes in the electronic structures of these Fe_2S_2 units caused by oxidation from Fe(II) to Fe(III). It is also interesting to note that the Fe_2S_2 unit in $Fe^{II}(S_2CNEt_2)_2$ has geometry very similar to that of $Fe_2[(CH_2N(CH_3)CH_2CH_2S_2]_2$ reported by Lippard, the Fe⋯Fe distances being 3.350 and 3.206 Å, respectively.[24] In addition, in the complex reported by Lippard the iron(II) atoms also have distorted trigonal-bipyramidal coordination with the two trigonal axes of the monomer units parallel. The structure[22] of the dimeric unit in $(Et_4N)Fe(S_2C_2H_4)_2$ also has similar geometry and an Fe–Fe distance of 3.41 Å. The Fe–Fe distances (~3.4 Å) found for these five-coordinate Fe(II) dimers are significantly longer than those found for the four-coordinate Fe(III) dimers (~2.7 Å). This large Fe⋯Fe distance along with the rather weak antiferromagnetic coupling of the two iron atoms would seem to preclude a strong iron–iron bond. The question of iron–iron bonds in dinuclear iron complexes has been extensively discussed by Dahl, Sinclair, and Teo[25] in their recent review of this subject. While these authors pointed out that the Fe–Fe distance does not necessarily provide a valid estimate of the Fe–Fe bond order, they also concluded that Fe–Fe distances greater than ca. 3.1 Å are essentially nonbonded distances.

Larkworthy et al.[1] and de Vries et al.[4] have investigated the magnetic susceptibility, Mössbauer spectrum, and near-infrared–visible spectrum of $Fe_2(S_2CNEt_2)_4$. The magnetic susceptibility indicates that there is an antiferromagnetic interaction between the iron atoms in this dimer. The near-infrared, visible, and Mössbauer spectra were interpreted assuming that each iron atom had approximately square-pyramidal geometry. The large quadrupole splitting (4.16 mm sec^{-1}) is unusual and could not easily be explained on the basis of the simple crystal field model for square-pyramidal geometry. These data should be reexamined in view of the fact that the iron atom actually has distorted trigonal-bipyramidal geometry.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50406E-12-75.

References and Notes

(1) L. F. Larkworthy, B. W. Fitzsimmons, and R. R. Patel, *J. Chem. Soc., Chem. Commun.*, 902 (1973).

(2) H. Büttner and R. D. Feltham, *Inorg. Chem.*, **11**, 97 (1972).

(3) O. A. Ileperuma and R. D. Feltham, unpublished results.

(4) J. L. K. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **12**, 2730 (1973).

(5) For reviews of this subject, see (a) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967); (b) T. Kimura, *Struct. Bonding (Berlin)*, **5**, 1 (1968); (c) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, **5**, 417 (1970).

(6) J. R. Postgate, Ed., "The Chemistry and Biochemistry of Nitrogen Fixation", Plenum Press, New York, N.Y., 1971.

(7) R. C. Bray and J. C. Swan, *Struct. Bonding (Berlin)*, **11**, 107 (1972).

(8) R. H. Holm, *Endeavour*, **34**, 38 (1975).

(9) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3521 (1973).

(10) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2437 (1972).

(11) S. J. Lippard, *Acc. Chem. Res.*, **6**, 282 (1973).

(12) J. P. Fackler and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, **2**, 251 (1966).

(13) M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 898 (1965).

(14) M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 885 (1965).

(15) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Am. Chem. Soc.*, **93**, 360 (1971).

(16) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(17) The program used for data reduction was Raymond's UCFACS, itself a modification of Doedens and Ibers' PIKOUT. Other computer programs used included local versions of Zalkin's FORDAP Fourier summation programs, Ibers' NUCLS group least-squares refinement program based upon Busing and Levy's ORFLS, Busing and Levy's ORFFE, Johnson's ORTEP plotting program, R. J. Dellaca's DANFIG program which itself is a modification of C. K. Johnson's ORTEP, and Raymond and Ibers' FINDH program. All computations were performed on a CDC 6400 computer.

(18) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(19) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(20) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(21) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(22) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973).

(23) J. J. Mayerle, S. E. Denmark, B. V. De Pamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 1032 (1975).

(24) W. Hu and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 2366 (1974).

(25) L. F. Dahl, J. D. Sinclair, and B. K. Teo in "The Organic Chemistry of Iron", E. A. Koerner von Gustorf, Ed., 1975.