

Further Refinement of the Molecular Structure of Triiron Dodecacarbonyl

F. Albert Cotton* and Jan M. Troup

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received December 8, 1973

Abstract: The molecular structure of $\text{Fe}_3(\text{CO})_{12}$ as it occurs in its normal, disordered crystalline form has been determined with much improved accuracy. Precise unit cell dimensions are $a = 8.359$ (2) Å, $b = 11.309$ (2) Å, $c = 8.862$ (2) Å, and $\beta = 97.00$ (2)°. The space group is $P2_1/n$ and $Z = 2$ as previously reported. A total of 1354 reflections, collected on a diffractometer, having $|F_o|^2 > 3\sigma(F_o^2)$ were used. These extended to 2θ values as high as 60° , thus affording theoretical resolution of about 0.4 Å. It was possible to disentangle completely the two disordered "half-molecules" and thus to refine all 12 CO groups. Anisotropic refinement led to final discrepancy indices of $R_1 = 0.046$ and $R_2 = 0.060$ with an essentially featureless final difference electron density map. The disorder scheme of Wei and Dahl is confirmed, as are the general features of the molecular structure proposed by them. The present work shows that, as Wei and Dahl suspected, the two CO bridges are distinctly unsymmetrical. In the improved structure, the terminal CO groups are essentially linear (mean Fe-C-O angle, 173°) with a mean Fe-C distance of 1.82 Å. On the basis of the structure, considerable insight can be gained into the dynamical properties of the molecule in solution.

A complete description of the structural characteristics of triiron dodecacarbonyl, $\text{Fe}_3(\text{CO})_{12}$, has yet to be achieved, in spite of the expenditure of considerable efforts. A very thorough summary of these efforts up to about mid-1968 has been given by Wei and Dahl.¹ The most important accomplishment thus far is the conclusive demonstration by Wei and Dahl that in the crystal the molecule contains an isosceles triangle of metal atoms and that one edge of the triangle is bridged by two CO groups while the remaining ten CO groups are of the terminal type. This was a difficult accomplishment because of disorder in the crystals.

Three major problems still remain to be solved before this molecule can be considered as structurally well characterized. (1) The dimensions of the molecule as it occurs in the crystal need to be determined with precision comparable to that normally attainable with small molecules or, at least, with the highest precision allowed by the confounding effects of the disorder. (2) The structure of the molecule in solution, which seems unlikely to be identical with that in the crystal, needs to be ascertained with certainty. (3) The dynamical behavior of the molecule in solution, *i.e.*, how and at what rate scrambling of the carbonyl groups² occurs, needs to be investigated. This paper is concerned very directly with the first of the three problems just listed but deals also with certain aspects of the third problem.

Wei and Dahl did not provide accurate molecular dimensions in the crystalline state for two reasons. First, their data were recorded by film methods and presumably have precision substantially inferior to what can now be obtained using a diffractometer. Second, and more fundamental, their data set, regardless of its accuracy, was too limited in range to allow resolution of the sets of "overlapping" atoms from the two oppositely oriented structures. Their smallest d spacings were about 1 Å, corresponding to resolution³ of about

0.6 Å. It seemed to us that with a precise data set extending to higher d spacings, there might be a good chance of "prying apart" the two nearly overlapping sets of CO groups or at least many of them. For instance, Mo $K\alpha$ ($\alpha = 0.7107$ Å) data out to a 2θ value of 60° would correspond to d spacings of $\lambda/2 \sin 30^\circ = (0.7107)/(2 \times 0.500) = 0.711$. This would allow resolution of atoms only about 0.4 Å apart. A preliminary study indicated that data could be measured out to such a 2θ value, and thus the present study was undertaken.

Experimental Section

Large crystals of triiron dodecacarbonyl were grown from a mixture of diethyl ether-hexane solution. The solid triiron dodecacarbonyl was purchased from Pressure Chemical Co. A nearly spherical crystal measuring $0.30 \times 0.32 \times 0.33$ mm was mounted in a thin glass capillary. Precise unit cell dimensions and data collection were performed on a Syntex P1 computer-controlled diffractometer equipped with a graphite-crystal monochromator. The operation of the diffractometer and other details of data collection have been described elsewhere,⁴ and only deviations from that procedure are mentioned here.

The unit cell and space group were found to be nearly the same as those reported by Wei and Dahl.¹ The precise unit cell dimensions were determined using Mo $K\alpha$ radiation by least-squares refinement of 15 carefully centered strong reflections as $a = 8.359$ (2) Å, $b = 11.309$ (2) Å, $c = 8.862$ (2) Å, and $\beta = 97.00$ (2)°. The volume of the monoclinic unit cell is 831.5 (3) Å³ and the space group is $P2_1/n$. The crystal was found to be of good quality with an ω scan peak width at half-height of 0.15° for several strong reflections.

Data were collected using Mo $K\alpha$ radiation at 22° employing a θ - 2θ variable scan technique with a scan rate ranging from 2.0 to $24.0^\circ/\text{min}$, depending on the intensity of the reflection. Standard reflections, collected every 100 reflections, showed no evidence for crystal decomposition or crystal movement. Unique data were collected up to a 2θ (Mo $K\alpha$) angle of 60.0° using a scan range of 0.8° before Mo $K\alpha_1$ to 1.0° after Mo $K\alpha_2$. No absorption correction was made in view of the small variation in transmission factors of $41 \pm 2\%$ during data collection. Lorentz and polarization corrections were made. A total of 2726 reflections were collected and 1354 reflections having $|F_o|^2 > 3\sigma(F_o^2)$ were used for the refinement of the structure. No evidence for secondary extinction was observed.

(1) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

(2) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

(3) R. W. James, "The Optical Principles of the Diffraction of X-Rays," Cornell University Press, Ithaca, N. Y., 1965, p 400.

(4) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, **50**, 227 (1973).

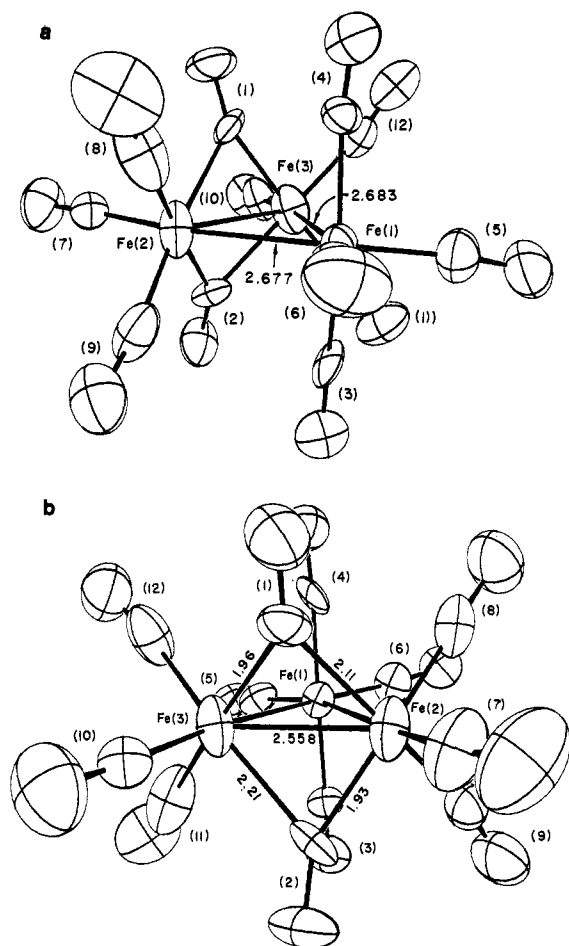


Figure 1. The molecular structure of $\text{Fe}_3(\text{CO})_{12}$: (a) a view from the direction of Fe(1); (b) a view toward the bridged edge showing the degrees of asymmetry of the two bridges.

Solution and Refinement of the Structure. The positions of the three independent half-weight iron atoms were used as reported by Wei and Dahl¹ and were refined by two cycles of full-matrix least squares to give the agreement factors

$$R_1 = (\sum |F_o| - |F_c|) / \sum |F_o| = 0.385$$

and

$$R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2} = 0.463$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given by $4|F_o|^2/\sigma^2$ where σ is the esd of $|F_o|^2$. Scattering factors were taken from the international tables.⁵ Anomalous dispersion effects were included for the iron atoms using $\Delta f'$ and $\Delta f''$ values by Cromer and Liberman.⁶ A difference Fourier map based on the iron atom positions revealed 12 ellipsoidal peaks at the positions determined for the overlapping carbonyls by Wei and Dahl.¹ Half-weighted carbon(1)-carbon(2) atoms and oxygen(1)-oxygen(2) atoms were placed at each end of the respective carbon or oxygen atom ellipsoidal peaks and these atoms were refined isotropically and the iron atoms anisotropically by three cycles of full-matrix least squares. It was found that the two halves of each carbon(1)-carbon(2) or oxygen(1)-oxygen(2) peak refined independently and that the two overlapping structures related by an inversion center could be resolved. An inspection of the bond distances and angles showed that for each of the 12 pairs of carbonyl groups one was chemically reasonable for one set of three iron atoms and the other carbonyl group was chemically reasonable for the inversion related set of three iron atoms. The agreement factors at this point in the re-

finement were $R_1 = 0.062$ and $R_2 = 0.072$. All atoms were refined anisotropically to convergence after six cycles of full-matrix least squares. The final agreement factors were $R_1 = 0.046$ and $R_2 = 0.060$ with no parameter shift in the final cycle of refinement exceeding the standard deviation of that parameter. The esd in an observation of unit weight is 1.54.

A final difference Fourier map showed no peaks greater than $0.53 \text{ e}\text{\AA}^{-3}$ where the smallest peak for a carbon atom appeared on previous difference Fourier maps at $2.22 \text{ e}\text{\AA}^{-3}$.

A list of observed and calculated structure factor amplitudes is available.⁷ The atomic coordinates and their estimated standard deviations are given in Table I. Anisotropic thermal parameters

Table I. Atomic Positional Parameters^a

Atom	x	y	z
Fe(1)	-0.0544 (1)	-0.0204 (1)	-0.1684 (1)
Fe(2)	0.1735 (1)	-0.0162 (1)	0.0716 (1)
Fe(3)	-0.1123 (1)	0.0476 (1)	0.1100 (1)
O(1)	0.117 (3)	0.245 (2)	0.135 (2)
O(2)	0.007 (3)	-0.190 (1)	0.252 (2)
O(3)	-0.109 (3)	-0.270 (2)	-0.089 (2)
O(4)	0.003 (3)	0.234 (1)	-0.237 (3)
O(5)	-0.373 (4)	-0.029 (3)	-0.344 (5)
O(6)	0.155 (5)	-0.080 (3)	-0.412 (5)
O(7)	0.411 (4)	0.016 (3)	0.332 (5)
O(8)	0.368 (2)	0.120 (2)	-0.131 (2)
O(9)	0.285 (4)	-0.265 (4)	0.008 (5)
O(10)	-0.134 (5)	0.100 (3)	0.425 (5)
O(11)	-0.389 (3)	-0.110 (2)	0.066 (2)
O(12)	-0.307 (3)	0.244 (3)	-0.001 (4)
C(1)	0.078 (4)	0.150 (3)	0.120 (4)
C(2)	0.034 (3)	-0.110 (3)	0.183 (3)
C(3)	-0.081 (4)	-0.177 (3)	-0.103 (3)
C(4)	-0.011 (3)	0.137 (2)	-0.206 (3)
C(5)	-0.257 (2)	-0.020 (1)	-0.274 (2)
C(6)	0.063 (2)	-0.061 (2)	-0.319 (2)
C(7)	0.316 (2)	0.003 (1)	0.240 (2)
C(8)	0.290 (2)	0.066 (2)	-0.051 (2)
C(9)	0.250 (2)	-0.165 (2)	0.023 (2)
C(10)	-0.132 (2)	0.079 (1)	0.303 (2)
C(11)	-0.277 (3)	-0.051 (3)	0.095 (2)
C(12)	-0.226 (2)	0.174 (3)	0.033 (2)

^a Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables.

are given in Table II. A table of root-mean-square amplitudes of thermal vibration is also available.⁷

Results and Discussion

The chemically meaningful results of this work are summarized in Tables III, IV, and V. Figure 1 shows two views of the molecule with several of the most important distances marked.

As indicated in detail in the Experimental Section, with the extensive and accurate data now available it has been possible to refine each of the 12 CO groups of the molecule independently. All 27 atoms have been refined anisotropically, and anomalous dispersion has been taken into account for the iron atoms. The low values of the final residuals ($R_1 = 0.046$, $R_2 = 0.060$) and the satisfactorily flat final difference map attest to the fact that the structure is accurate. This structure is, in fact, appreciably more accurate than those of the isomeric $\text{Fe}_3(\text{CO})_{11}\text{PPh}_3$ molecules⁸ with which comparisons will later be made. The relative accuracies of the structures are best indicated by the comparison of esd's for various types of bonds and angles, as listed in Table VI.

(7) See paragraph at the end of the paper concerning the availability of supplementary material.

(8) D. J. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, **90**, 5106 (1968).

(5) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, in preparation.

(6) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1971).

Table II. Anisotropic Thermal Parameters^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0131 (2)	0.0067 (1)	0.0079 (1)	0.0008 (1)	0.0005 (1)	-0.0007 (1)
Fe(2)	0.0105 (2)	0.0162 (2)	0.0104 (1)	0.0038 (1)	0.0003 (1)	-0.0014 (1)
Fe(3)	0.0099 (2)	0.0140 (2)	0.0103 (1)	0.0015 (1)	0.0011 (1)	-0.0042 (1)
O(1)	0.037 (2)	0.007 (2)	0.015 (2)	-0.006 (2)	0.004 (2)	-0.002 (1)
O(2)	0.030 (2)	0.008 (2)	0.015 (2)	-0.003 (2)	0.005 (1)	0.004 (1)
O(3)	0.027 (2)	0.007 (1)	0.017 (2)	-0.005 (1)	0.004 (2)	0.000 (1)
O(4)	0.028 (2)	0.007 (1)	0.019 (2)	0.000 (2)	0.003 (1)	0.002 (1)
O(5)	0.019 (4)	0.009 (1)	0.021 (2)	0.002 (2)	-0.003 (3)	0.000 (1)
O(6)	0.028 (3)	0.016 (2)	0.018 (2)	0.001 (2)	0.005 (2)	-0.002 (2)
O(7)	0.017 (3)	0.016 (2)	0.022 (3)	0.003 (2)	-0.008 (2)	-0.002 (2)
O(8)	0.015 (2)	0.018 (1)	0.024 (2)	-0.001 (1)	0.005 (2)	0.007 (2)
O(9)	0.025 (4)	0.018 (3)	0.020 (3)	-0.002 (2)	0.006 (2)	0.005 (2)
O(10)	0.028 (4)	0.013 (2)	0.014 (2)	0.001 (2)	0.007 (2)	-0.002 (2)
O(11)	0.020 (2)	0.014 (1)	0.031 (3)	0.000 (1)	-0.005 (2)	-0.001 (2)
O(12)	0.015 (2)	0.011 (1)	0.025 (3)	0.002 (2)	0.004 (2)	-0.001 (2)
C(1)	0.013 (2)	0.007 (3)	0.011 (2)	0.000 (2)	0.001 (1)	0.004 (1)
C(2)	0.011 (2)	0.013 (2)	0.008 (2)	-0.006 (1)	0.004 (1)	0.000 (1)
C(3)	0.018 (2)	0.005 (2)	0.009 (2)	-0.002 (2)	-0.001 (2)	-0.001 (2)
C(4)	0.011 (2)	0.009 (2)	0.010 (2)	-0.003 (2)	0.007 (1)	0.000 (2)
C(5)	0.021 (2)	0.007 (1)	0.011 (2)	0.003 (1)	-0.001 (1)	-0.001 (1)
C(6)	0.021 (3)	0.011 (1)	0.011 (1)	0.002 (1)	0.002 (2)	-0.001 (1)
C(7)	0.024 (3)	0.010 (1)	0.012 (2)	0.005 (1)	0.000 (2)	-0.002 (1)
C(8)	0.010 (2)	0.012 (1)	0.009 (2)	0.001 (1)	-0.002 (1)	-0.005 (1)
C(9)	0.012 (2)	0.014 (2)	0.012 (2)	0.000 (1)	0.003 (2)	0.001 (2)
C(10)	0.023 (3)	0.005 (1)	0.012 (2)	0.001 (1)	0.004 (2)	0.000 (1)
C(11)	0.020 (3)	0.015 (2)	0.012 (2)	0.007 (2)	-0.007 (2)	-0.009 (2)
C(12)	0.012 (2)	0.021 (2)	0.010 (2)	-0.001 (2)	0.002 (2)	0.004 (2)

^a The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Bond Lengths (Å)

Fe(1)-Fe(2)	2.677 (2)	C(1)-O(1)	1.12 (5)
Fe(1)-Fe(3)	2.683 (1)	C(2)-O(2)	1.14 (2)
Fe(2)-Fe(3)	2.558 (1)	C(3)-O(3)	1.09 (5)
Fe(1)-C(3)	1.89 (4)	C(4)-O(4)	1.14 (3)
Fe(1)-C(4)	1.86 (2)	C(5)-O(5)	1.09 (4)
Fe(1)-C(5)	1.83 (1)	C(6)-O(6)	1.21 (5)
Fe(1)-C(6)	1.81 (2)	C(7)-O(7)	1.07 (5)
Fe(2)-C(1)	2.11 (4)	C(8)-O(8)	1.19 (3)
Fe(2)-C(2)	1.93 (2)	C(9)-O(9)	1.18 (4)
Fe(3)-C(1)	1.96 (4)	C(10)-O(10)	1.11 (5)
Fe(3)-C(2)	2.21 (3)	C(11)-O(11)	1.15 (4)
Fe(2)-C(7)	1.81 (2)	C(12)-O(12)	1.07 (3)
Fe(2)-C(8)	1.80 (2)		
Fe(2)-C(9)	1.87 (3)		
Fe(3)-C(10)	1.77 (2)		
Fe(3)-C(11)	1.77 (3)		
Fe(3)-C(12)	1.80 (3)		

There was only one respect in which the refinement process did not proceed as smoothly as it usually does in comparable situations where there are no complications due to disorder. This, not unexpectedly, was in the development of rather large (*ca.* 0.8) correlation coefficients between coordinates and temperature parameters for those pairs of C and O atoms which lie very "close together" in the superimposed half-molecules. In view of the fact that, even with the extensive data available, a number of such atom pairs are separated by distances comparable to or not very much greater than the nominal resolution, this is scarcely surprising. Unfortunately, beyond the 60° sphere there were very few reflections strong enough to measure accurately, and we did not consider it worthwhile to try to improve the resolution any further.

Within the limits of error and allowing for the replacement of terminal CO groups by $(C_6H_5)_3P$ in the $Fe_3(CO)_{11}P(C_6H_5)_3$ molecules, the agreement between this structure and the latter two is generally satisfactory,

Table IV. Selected Bond Angles (deg)

Fe(2)-Fe(1)-Fe(3)	57.00 (4)	C(1)-Fe(3)-C(2)	92.8 (11)
Fe(1)-Fe(2)-Fe(3)	61.63 (4)	C(1)-Fe(3)-C(10)	90.2 (11)
Fe(1)-Fe(3)-Fe(2)	61.37 (4)	C(1)-Fe(3)-C(11)	176.7 (13)
		C(1)-Fe(3)-C(12)	86.3 (12)
C(3)-Fe(1)-C(4)	172.0 (12)	C(2)-Fe(3)-C(10)	89.7 (8)
C(3)-Fe(1)-C(5)	91.2 (11)	C(2)-Fe(3)-C(11)	85.0 (10)
C(3)-Fe(1)-C(6)	94.7 (12)	C(2)-Fe(3)-C(12)	174.5 (8)
C(4)-Fe(1)-C(5)	95.4 (9)	C(10)-Fe(3)-C(11)	92.2 (8)
C(4)-Fe(1)-C(6)	88.5 (9)	C(10)-Fe(3)-C(12)	95.7 (7)
C(5)-Fe(1)-C(6)	99.9 (6)	C(11)-Fe(3)-C(12)	95.7 (12)
C(1)-Fe(2)-C(2)	96.7 (14)	Fe(1)-C(3)-O(3)	168 (3)
C(1)-Fe(2)-C(7)	87.3 (10)	Fe(1)-C(4)-O(4)	174 (3)
C(1)-Fe(2)-C(8)	84.8 (12)	Fe(1)-C(5)-O(5)	174 (2)
C(1)-Fe(2)-C(9)	177.6 (10)	Fe(1)-C(6)-O(6)	173 (2)
C(2)-Fe(2)-C(7)	91.3 (10)	Fe(2)-C(1)-O(1)	140 (3)
C(2)-Fe(2)-C(8)	173.5 (9)	Fe(2)-C(2)-O(2)	152 (3)
C(2)-Fe(2)-C(9)	82.5 (12)	Fe(2)-C(7)-O(7)	174 (2)
C(7)-Fe(2)-C(8)	95.0 (7)	Fe(2)-C(8)-O(8)	179 (2)
C(7)-Fe(2)-C(9)	95.0 (6)	Fe(2)-C(9)-O(9)	170 (2)
C(8)-Fe(2)-C(9)	95.7 (9)	Fe(3)-C(1)-O(1)	143 (3)
		Fe(3)-C(2)-O(2)	132 (2)
		Fe(3)-C(10)-O(10)	176 (2)
		Fe(3)-C(11)-O(11)	171 (2)
		Fe(3)-C(12)-O(12)	171 (3)

even with respect to the bridging CO groups, to be discussed presently. Similarly, the present structure seems to be in satisfactory accord with the $Fe_3(CO)_{11}H$ -structure,⁹ although a detailed comparison is not possible since details of the latter have not been published; there is, however, marked disagreement in the bridging region, since the single CO bridge in this anion is essentially symmetrical.

The asymmetry of the bridging system in $Fe_3(CO)_{12}$ is clearly shown in Figure 1b. Contrary to prediction⁸ the "asymmetry of the bridges of $Fe_3(CO)_{12}$ " is *not* "hopelessly hidden in the disorder which superposes

(9) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373(1965).

Table V. Weighted Least-Squares Planes and Dihedral Angles

Plane	Atoms defining plane	Equation of mean plane ^a
I	Fe(1), Fe(2), Fe(3)	$-2.092x - 10.669y + 2.170z = -0.0345$
II	Fe(2), Fe(3), C(1)	$0.673x - 2.080y + 8.465z = 0.7563$
III	Fe(2), Fe(3), C(2)	$2.135x + 5.272y + 7.119z = 0.7943$

Displacement of Atoms from Mean Plane (Å)					
	Plane I		Plane II		Plane III
C(1)	-1.47	C(7) -0.14	O(1)	-0.04	O(2) 0.01
C(2)	1.53	C(8) -1.38			
C(3)	1.87	C(9) 1.32			
C(4)	-1.85	C(10) 0.12			
C(5)	0.19	C(11) 1.36			
C(6)	-0.14	C(12) -1.27			

Dihedral Angles between Planes (deg)			
Planes			
I-II	68.5	I-III	71.1
		II-III	139.6

^a Equations have the form $Ax + By + Cz = D$ where x , y , and z are fractional monoclinic coordinates.

Table VI. Comparison of Estimated Standard Deviations in $\text{Fe}_3(\text{CO})_{12}$ and the Isomeric $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{C}_6\text{H}_5)_3$ Molecules

Parameter	Range of esd's, Å × 10 ² or deg		Mean esd, Å × 10 ² or deg	
	$\text{Fe}_3(\text{CO})_{12}$	$\text{Fe}_3(\text{CO})_{11}\text{-PPh}_3$	$\text{Fe}_3(\text{CO})_{12}$	$\text{Fe}_3(\text{CO})_{11}\text{-PPh}_3$
Fe-Fe	0.1-0.2	0.8-0.9	0.13	0.86
Fe-C	2-4	4-6	2.6	4.8
C-O	2-5	4-5	4.0	4.3
∠Fe-C-O	2-3	3-5	2.8	3.9

terminal and bridging carbonyls." The present work unequivocally shows that the bridging system is highly asymmetric as Wei and Dahl strongly suspected but could not actually prove. Unfortunately, the esd's of 0.02-0.04 Å are such as to leave this feature still a little less clearly defined than one would like. For the C(2)-O(2) bridge, the asymmetry is well outside the experimental error, the difference in the lengths of the Fe(2)-C(2) and Fe(3)-C(2) bonds, 0.28 Å, being nearly six times the sum of the esd's. For the C(1)-O(1) bridge, the difference in the two Fe-C distances, 0.15 Å, is only about twice the sum of the esd's.

The two short Fe-C distances differ by less than the sum of their esd's while the difference in the two long ones is only 1.4 times the sum of their esd's. Thus, it is possible that the two unsymmetrical bridges are essentially equivalent (thereby giving the molecule essentially C_2 symmetry) with mean long and short distances of 2.16 ± 0.05 and 1.94 ± 0.02 Å and a mean difference of about 0.22 Å.

These results may be compared with the distances in the $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{C}_6\text{H}_5)_3$ isomer in which the $\text{P}(\text{C}_6\text{H}_5)_3$ substituent is on the iron atom not involved in the bridge system. (The situation in the other isomer is ambiguous since the two relevant iron atoms do not have equivalent sets of ligands.) In the relevant $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{C}_6\text{H}_5)_3$ isomer, the short Fe-C distances are 1.85 (5) and 1.86 (4) Å and the long ones are 2.04 (5) and 2.07 (4) Å. Here then, averaging the two bridges as if they are equivalent, we have a mean long distance of 2.06 ± 0.03 Å and a mean short distance of 1.86 ± 0.03 Å, with a mean difference of 0.20 Å. In view of

the large uncertainties, the results in the two cases can be considered essentially similar.

The dimensions of the $\text{Fe}_3(\text{CO})_{12}$ structure compare satisfactorily with those in the recently determined accurate structure¹⁰ of $\text{Fe}_2(\text{CO})_9$. Thus, the mean Fe-C distance for the six terminal CO groups on Fe(2) and Fe(3) is 1.80 ± 0.02 Å in $\text{Fe}_3(\text{CO})_{12}$ compared to 1.835 Å (without correction for thermal motion) in $\text{Fe}_2(\text{CO})_9$. The bridged Fe-Fe distance here is 2.558 Å compared to 2.523 Å in $\text{Fe}_2(\text{CO})_9$. The greater length of the Fe-Fe bond here is reasonable since the two highly unsymmetrical CO bridges might be expected to exercise a less compressive effect on the bond than do the three symmetrical bridges in $\text{Fe}_2(\text{CO})_9$.

The three principal results of this work are as follows. (1) The overall structure of the $\text{Fe}_3(\text{CO})_{12}$ molecule in the crystal, as described by Wei and Dahl, is confirmed in all its main features. (2) The detailed dimensions are presented more precisely, although the standard deviations are still larger than would be expected for an ordinary, ordered structure. (3) The asymmetry of the bridging groups has been confirmed and made more precise.

The molecular structure which occurs in the crystalline compound gives some very distinct indications about the probable dynamical behavior of the molecule in solution. First, the occurrence of two carbonyl ligands which are both, to different degrees, intermediate between strictly terminal and fully symmetrical bridging ones indicates that the potential energy surface as a function of all configurations between the one extreme of a completely unbridged structure (the $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ structure) and the other extreme in which there are two perfectly symmetrical bridges on one edge of the Fe_3 triangle is nearly flat. In other words, there is only a low activation energy hindering bridge-terminal rearrangements *via* the type of pairwise opening and closing of bridges that we have previously proposed and verified¹¹ for binuclear species. Bridge-terminal exchange is therefore predicted to be very facile.² We venture to predict that the coalescence temperature may be below -160° ,¹² which is about the practical lower limit of observation.

Second, when the molecular structure is examined carefully, it can be seen that it suggests a straightforward pathway for complete scrambling of all CO groups in

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(12) Assuming bridge and terminal ¹³C resonances to be separated by ca. 60 ppm and assuming $\log A = 13$, this would connote an Arrhenius activation energy of ca. 5 kcal mol⁻¹, and what we are suggesting then is that the activation energy may be ≤ 5 kcal mol⁻¹. Actually, if the molecule in solution is large'y in the form with the $\text{Ru}_3(\text{CO})_{12}$ type structure, where the different CO groups are all terminal and differ only in being axial or equatorial with respect to the Fe_3 triangle, the resonances to be averaged may be separated by less than 10 ppm. In that case the activation energy would have to be as high as 6 kcal mol⁻¹ for the coalescence temperature to be -160° . Since -160° is about the lowest practical temperature for line shape studies, there appears to be little if any likelihood of establishing the predominant solution structure by recording a ¹³C nmr spectrum in the slow exchange limit.

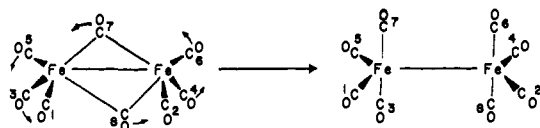


Figure 2. A diagram showing how the CO ligands associated with the bridged edge of the Fe_3 triangle would shift as the bridges are opened in a concerted manner.

the molecule. This can be appreciated easily with the aid of Figure 2, which shows only one edge of the Fe_3 triangle and omits, for clarity, the other $\text{Fe}(\text{CO})_4$ group which actually lies below the plane of the paper. We begin with a bridged structure on this edge and move the bridging CO groups out of bridging positions in a counterclockwise sense, as indicated by the arrows. This leads to a $\text{Ru}_3(\text{CO})_{12}$ type structure, in which the carbonyls numbered 3, 6, 7, and 8 are axial and 1, 2, 4, and 5 are equatorial. However, if the bridges had been rotated out in the opposite sense, the axial groups would have been 4, 5, 7, and 8 and the equatorial ones 1, 2, 3, and 6. If these processes are now repeated successively

on the other two edges of the Fe_3 triangle, all CO groups will be scrambled (1) over the metal atoms, (2) over both axial and equatorial positions of the $\text{Ru}_3(\text{CO})_{12}$ structure, and (3) over both of the bridging and all of the terminal positions of the bridged structure.

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Supplementary Material Available. Tables of observed and calculated structure factor amplitudes and root-mean-square amplitudes of thermal vibration 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 Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4155.

Synthetic Analogs of the Active Sites of Iron-Sulfur Proteins. VI.¹ Spectral and Redox Characteristics of the Tetranuclear Clusters $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$

B. V. DePamphilis, B. A. Averill,² T. Herskovitz, L. Que, Jr., and R. H. Holm*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received January 30, 1974

Abstract: The electronic spectra (250–700 nm) and redox properties of a series of tetrameric complexes $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ (R = alkyl, aryl, Ac-Cys-NHMe) have been examined in nonaqueous and aqueous DMSO solutions. $[\text{Fe}_4\text{S}_4(\text{S-Cys}(\text{Ac})\text{NHMe})_4]^{2-}$ and $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{NMe}_2)_4]^{2+}$ were generated in solution by ligand substitution reactions of the free thiols and $[\text{Fe}_4\text{S}_4(\text{S-}i\text{-Bu})_4]^{2-}$. Alkyl-substituted tetramers possess two principal absorption bands whose positions (297–308, 417–421 nm) and intensities reveal a relationship with the two prominent absorptions in the spectra of the reduced “high-potential” (HP_{red}) and oxidized ferredoxin (Fd_{ox}) proteins. Aryl-substituted tetramers have maxima at 455–510 nm. Polarographic results reveal the electron transfer series $[\text{Fe}_4\text{S}_4(\text{SR})_4]^z$ with $z = 4-, 3-, 2-,$ and $1-$; the $2-/3-$ process is reversible or nearly reversible in all cases. Half-wave potentials for this process involving tetramers with $\text{R} =$ alkyl and $p\text{-C}_6\text{H}_4\text{X}$ [$\text{X} = \text{H}, \text{Me}, ^+\text{NMe}_3(2+/1+ \text{ couple})$] are linearly correlated with the σ^* and σ_p substituent constants, respectively. The relationship between the total oxidation levels, z , of the synthetic analogs and those of the proteins is summarized. Spectra and $2-/3-$ potentials of $[\text{Fe}_4\text{S}_4(\text{S-Cys}(\text{Ac})\text{NHMe})_4]^{2-}$ in DMF, DMSO, and DMSO- H_2O are somewhat solvent dependent, and most closely resemble the corresponding properties of HP_{red} and Fd_{ox} in aqueous DMSO or water solution. Half-wave potentials in DMSO- H_2O after correction for apparent liquid junction potentials are near the values estimated for reduction of HP_{red} to $\text{HP}_{\text{s-red}}$ in this solvent but are estimated to be ca. 0.2–0.6 V more negative than E_0' values for $\text{Fd}_{\text{ox}}/\text{Fd}_{\text{red}}$ in aqueous solution. These and other results indicate that the protein structure and environment make a significant contribution to the redox potentials of the iron-sulfur clusters.

Ferredoxins and other iron-sulfur proteins^{3,4} form a comprehensive class of nonheme iron proteins which are implicated as electron carriers in diverse pro-

cesses of cell metabolism.⁵ The electron-carrying properties of these proteins are related to the ability of their iron-sulfur active sites to exist in several different oxidation levels interrelated by one-electron transfer reactions. In order to provide further clarification of the nature of these active sites, we are engaged in a program directed toward the synthesis and structural and electronic characterization of low molecular weight iron-sulfur complexes which serve as close representa-

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