

Contribution No. 7587 from the Arthur Amos Noyes Laboratory, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Contribution from the Department of Chemistry, McGill University, 801 Sherbrooke Street, West Montreal, Quebec, Canada H3A 2K6

Structure of Tricarbonyl(η^4 -cyclobutadienyl)iron(0) at -45°C

Pierre D. Harvey,^{1,2} William P. Schaefer,^{*1} Harry B. Gray,^{*1} Denis F. R. Gilson,³ and Ian S. Butler³

Received September 1, 1987

The crystal structure of tricarbonyl(η^4 -cyclobutadienyl)iron(0), $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$, has been determined at -45°C . The molecule has a plane of symmetry passing through the iron atom, two ring carbon atoms, and one carbonyl group. The ring is square within experimental error: the two independent C-C distances are 1.420 (3) and 1.430 (3) Å. Crystals are orthorhombic, space group *Pnma*, with $a = 12.494$ (3) Å, $b = 9.503$ (2) Å, $c = 6.113$ (1) Å, and $Z = 4$. The temperature dependence of the ^1H NMR spin-lattice relaxation time has been reinterpreted. For the Cole- Davidson distribution of correlation times, the barrier to ring rotation is 22.6 kJ mol^{-1} in the solid state, in good agreement with the barrier evaluated by nonbonded atom-atom potential energy calculations, 25.6 kJ mol^{-1} . This barrier arises almost entirely from ring-carbonyl interactions.

There have been extensive discussions concerning the structure of the cyclobutadienyl ring in tricarbonyl(η^4 -cyclobutadienyl)iron(0), $\text{CbFe}(\text{CO})_3$. Electron diffraction^{4,5} and microwave spectroscopic studies in the vapor phase⁶ have shown that the cyclobutadienyl ring does not deviate significantly from a square. A review⁷ of the crystal structures of many substituted derivatives of $\text{CbFe}(\text{CO})_3$ reveals that, within experimental error, these compounds also have square geometry. However, several NMR studies of the complex partially oriented in nematic liquid crystal solvents⁸⁻¹¹ have shown that the proton distance ratios do not correspond to a square and that vibrational averaging effects are not responsible for the observed ratios.⁹ Indirect evidence from studies¹² of the vibrational spectrum and proton spin-lattice relaxation times in the solid phase suggested that there might be four molecules per unit cell in two crystallographically different sites. An earlier theoretical calculation¹³ predicted that the ring should be square, but recent theoretical studies of distortions in metal-arene complexes¹⁴ indicate that the bond lengths in the ring should depend upon the conformation, such that bonds eclipsed by carbonyl groups are longer than those that are staggered. In the case of the cyclobutadienyl ring, there are two possible symmetrical structures. If one ring carbon atom is eclipsed by a carbonyl group, then there should be two short and two long bonds in the ring. Alternatively, if one bond is eclipsed, then there would be one long, one short, and two intermediate-length bonds. Chinn and Hall^{14c} favored the first case on the basis of the structure of the tetraphenyl derivative. The crystal structure of the parent compound has not been reported, perhaps because of its low melting point (26°C) and air- and light-sensitivity. In this paper we present the results of an X-ray crystallographic study of $\text{CbFe}(\text{CO})_3$ at -45°C .

Experimental Section

Yellow prismatic crystals were grown by slow sublimation^{15a} and

Table I. Crystal Data for $\text{CbFe}(\text{CO})_3$

$\text{FeC}_7\text{H}_4\text{O}_3$	fw 191.96
$a = 12.494$ (3) Å	space group <i>Pnma</i> (No. 62)
$b = 9.503$ (2) Å	$T = -45$ (5) °C
$c = 6.113$ (1) Å	$\lambda(\text{Mo K}\alpha) = 0.71073$ Å
$V = 725.7$ (4) Å ³	$d_{\text{exptl}} = 1.76\text{ g cm}^{-3}$
$Z = 4$	$\mu = 20.67\text{ cm}^{-1}$
$F(000) = 384$ electrons	

Table II. Final Parameters for Tricarbonyl(η -cyclobutadienyl)iron(0) (x, y, z , and $U_{\text{eq}} \times 10^4$)

atom	x	y	z	$U_{\text{eq}}^a \text{ \AA}^2$
Fe	775 (0.2)	2500	457 (0.5)	263 (1)
C1	1444 (1)	1082 (2)	-890 (2)	357 (4)
O1	1866 (1)	164 (1)	-1721 (2)	554 (3)
C2	-423 (2)	2500	-1108 (4)	324 (5)
O2	-1209 (1)	2500	-2069 (3)	513 (5)
C3	-120 (2)	2500	3250 (4)	458 (7)
C4	678 (2)	3561 (2)	3347 (3)	413 (4)
C5	1489 (2)	2500	3440 (4)	379 (6)
H3	-822 (22)	2500	3348 (48)	4.7 (7) ^b
H4	663 (16)	4520 (23)	3535 (32)	4.8 (5) ^b
H5	2217 (22)	2500	3811 (41)	4.0 (6) ^b

^a $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij}(a_i^* a_j^*)(\bar{a}_i \bar{a}_j)$. ^b Isotropic thermal parameters (not $\times 10^4$) for hydrogen atoms.

stored at low temperature. Three equivalent sets of data out to 60° in 2θ (3652 reflections) were collected on a Nicolet P2₁ diffractometer with Mo K α radiation. The data were merged, the structure was solved by Patterson-Fourier techniques and refined by full-matrix least squares using 1119 reflections (1019 with $F_o^2 > 0$) to a final R index of 0.035 and a goodness of fit of 1.56. Crystal data are given in Table I and final parameters in Table II; a complete report of the crystallographic study is in the supplementary material.

Results and Discussion

The molecule has crystallographic mirror symmetry, with the iron atom, one carbonyl group, and two carbon atoms of the cyclobutadienyl group lying in the mirror plane (Figure 1); thus there are two independent carbonyl groups and two independent C-C distances in the cyclobutadienyl ring. Distances and angles are given in Table IIIA; Table IIIB collects results from various studies on this compound. All of the observed distances and angles are normal, including those involving the C-H bonds (average length, 0.91 (3) Å). The interesting feature of this molecule is the symmetry of the cyclobutadienyl ring. The ring is planar (all carbon atoms are within 0.001 Å of the plane), the C-C bond lengths are within 2σ of their average (1.420 (3) and 1.430 (3) Å; average 1.425 (7) Å), and the C-C-C angles have an average deviation of only 0.3° from 90° . The two diagonals in the cyclobutadienyl ring are nearly equal: 2.014 (4) and 2.016 (3) Å. We considered the possibility that this geometry could result from the superposition of two rectangles rotated by 90° with respect to one another, but the thermal ellipsoids do not support such a model (Figure 1). Other arenemetal tricarbonyls have C-C bonds in the arene ring that differ by as much as 0.056 Å.^{15b} The C-C bond lengths in this compound differ only slightly (0.010 Å), but we note that the difference is in the direction that supports the

- (1) California Institute of Technology.
- (2) NSERC-NATO postdoctoral fellow.
- (3) McGill University.
- (4) Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* **1970**, *21*, 401-413.
- (5) Oberhammer, H.; Brune, H. A. *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1969**, *24*, 607-612.
- (6) Lucken, E. A. C.; Pozzi, R.; Ramaprasad, K. R. *J. Mol. Struct.* **1973**, *18*, 377-380.
- (7) Herndon, W. C. *J. Organomet. Chem.* **1982**, *232*, 163-170.
- (8) Bailey, J. W.; Lindon, J. C. *Mol. Phys.* **1973**, *28*, 1373-1375.
- (9) Emsley, J. W.; Lindon, J. C. *Mol. Phys.* **1974**, *28*, 1373-1375.
- (10) Diehl, P.; Moia, F.; Boesiger, H.; Wirz, J. *J. Mol. Struct.* **1983**, *98*, 297-308.
- (11) Gilson, D. F. R. *J. Mol. Struct.* **1985**, *127*, 121-126.
- (12) Harvey, P. D.; Butler, I. S.; Gilson, D. F. R. *Inorg. Chem.* **1986**, *25*, 1009-1013.
- (13) Anderson, A. B.; Fitzgerald, G. *Inorg. Chem.* **1981**, *20*, 3288-3291.
- (14) (a) Chinn, J. W.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930-4941. (b) Chinn, J. W.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 2759-2766. (c) Chinn, J. W.; Hall, M. B. *Organometallics* **1984**, *3*, 284-288.
- (15) (a) The yellow liquid (Strem Chemicals) was vacuum transferred (10^{-6} Torr) to a sublimator equipped with a liquid-nitrogen cold finger. After complete condensation the cold finger was warmed with a flow of air and the sublimator was quickly placed in a refrigerator ($\sim 5^\circ\text{C}$). Large yellow crystals grew onto the walls of the sublimator. (b) Fitzpatrick, P. J.; LePage, V.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852-2861.

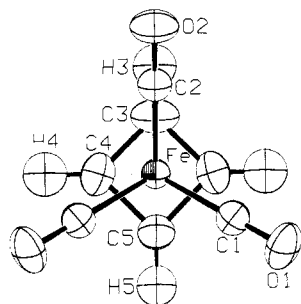


Figure 1. ORTEP drawing of the molecule projected perpendicular to the cyclobutadienyl ring plane. Thermal ellipsoids are shown at the 50% probability level.

Table III

(A) Distances (Å) and Angles (deg) in the Molecule				
Fe-C1	1.787 (2)	Fe-C1-O1	178.9 (1)	
Fe-C2	1.777 (2)	Fe-C2-O2	178.3 (2)	
C1-O1	1.138 (2)	C3-C4-C5	90.0 (2)	
C2-O2	1.144 (3)	C4-C3-C4	90.5 (2)	
Fe-C3	2.042 (3)	C4-C5-C4	89.6 (2)	
Fe-C4	2.038 (2)	C4-C3-H3	134 (2)	
Fe-C5	2.030 (3)	C3-C5-H4	134 (1)	
C3-C4	1.420 (3)	C5-C4-H4	135 (1)	
C4-C5	1.430 (3)	C4-C5-H5	134 (2)	
C3-H3	0.88 (3)	C1-Fe-C2	98.4 (1)	
C4-H4	0.92 (2)	C1-Fe-C1	97.9 (1)	
C5-H5	0.94 (3)			

(B) Comparison of Structural Data for CbFe(CO) ₃ , Obtained by Various Methods				
	electron diffr		X-ray (-45 °C) ^a	calculations ¹³
	ref 4	ref 5		
C-C, Å	1.456 (16)	1.439 (6)	1.426 (7)	1.60
C-H, Å	1.08	1.085	0.91 (3)	1.15
Fe-C(ring), Å	(assumed)	(assumed)	2.037 (7)	2.13
Fe-C(carbonyl), Å	2.063 (10)	2.051 (4)	1.783 (5)	1.78
C-O, Å	1.131 (10)	1.148 (3)	1.140 (4)	1.13
OC-Fe-CO, deg	95.5 (2.5)	98.1 (8)	98.2 (3)	95.5
confign of the H atoms	planar	toward the carbonyls	away from the carbonyls	assumed planar

^a This work.

Chinn-Hall model; i.e., the bonds eclipsed by carbonyl groups are longer.

The hydrogen atoms on the ring are bent away from the carbonyl groups; they all lie about 0.1 Å out of the C3-C4-C5-C4 plane (Figure 2). Such deviation was also observed in the crystal structure of tricarbonyl(η^4 -tetraphenylcyclobutadienyl)iron(0).¹⁶

Prior to this structural determination, the temperature dependence of the proton spin-lattice relaxation times was interpreted in terms of two relaxation processes arising from two crystallographically inequivalent lattice sites.¹² In view of the present results, the earlier interpretation must be revised. For a single relaxation process, the spin-lattice relaxation time, T_1 , is given by eq 1, where $\tau = \tau_0 \exp(E_a/RT)$, E_a is the activation energy,

$$\frac{1}{T_1} = \frac{2}{3}c\tau \left[\frac{1}{1 + \omega^2\tau^2} + \frac{4}{1 + 4\omega^2\tau^2} \right] \quad (1)$$

ω is the resonance frequency (in rad s⁻¹), and c is a constant. The difficulty in assigning a single relaxation process to the observed results lies in the fact that the slopes of the $\ln T_1$ versus reciprocal temperature plots are not equal on either side of the T_1 minimum. To account for the difference in slope, we now assume that an asymmetric distribution of correlation times exists, such as the

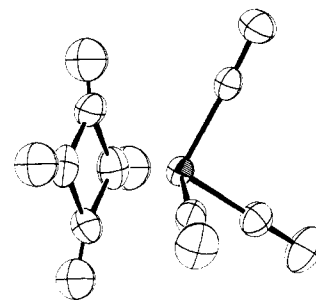


Figure 2. ORTEP view of the molecule showing the displacement of the hydrogen atoms from the cyclobutadienyl plane.

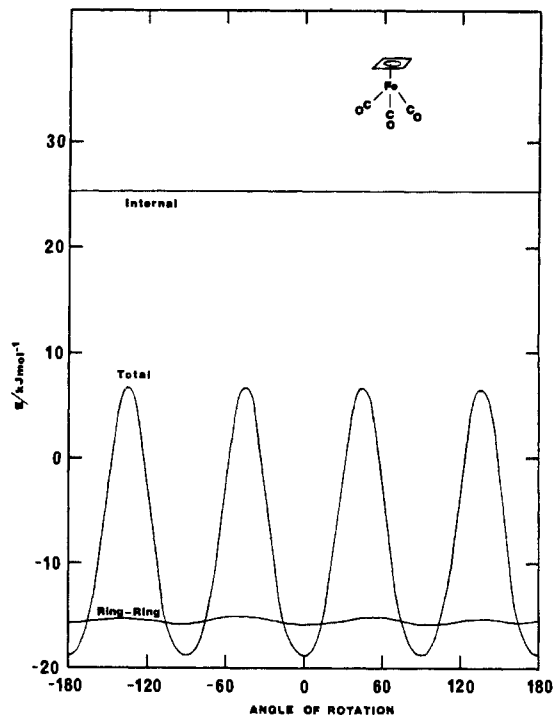


Figure 3. Angular dependence of the total potential energy of the molecule.

Cole-Davidson distribution $G(\tau) = [(\sin(\alpha\tau))/\pi](\tau/\tau' - \tau)$ for $\tau < \tau'$ and $G(\tau) = 0$ for $\tau > \tau'$, where α is a width parameter and τ is the mean jump time. Fitting the experimental results to the appropriate equation¹⁷ for T_1 gives as good a fit with four variables as the earlier results did when six parameters were varied. The barrier to rotation is 22.6 kJ mol⁻¹, with $\tau_0 = 1.6 \times 10^{-15}$ s and $\alpha = 0.66$. This barrier is significantly greater than those observed for the larger arene rings in other metal tricarbonyl complexes.¹⁸⁻²⁰

Since the details of the crystal structure are now known, it is possible to use nonbonded atom-atom potential energy calculations to examine the different contributions to the potential energy environment.²¹ These calculations took a given molecule in the crystal and computed all atom-atom interactions between it and all other atoms within 10 Å of it. The individual energies of interatomic interaction were assumed to be additive.²⁰ The potential energy is calculated as a function of the angle of rotation of the cyclobutadienyl ring, and the barrier height is obtained from the difference between the maximum and minimum energies. Using the crystal coordinates as direct input to the computations

(17) Connor, T. M. *Trans. Faraday Soc.* **1960**, *60*, 1574.

(18) Gilson, D. F. R.; Gomez, G.; Butler, I. S.; Fitzpatrick, P. J. *Can J. Chem.* **1983**, *61*, 737-742.

(19) Delisle, P.; Allegra, G.; Mognasecki, E. R.; Chierico, A. J. *J. Chem. Soc. Faraday Trans. 2* **1975**, *71*, 207-214.

(20) Harvey, P. D.; Butler, I. S.; Gilson, D. F. R. *Inorg. Chem.* **1987**, *26*, 32-38.

(21) Further details are given in ref 18 and 20.

(16) Dodge, R. P.; Schomaker, V. *Acta Crystallogr.* **1965**, *18*, 614-616.

Table IV. Symmetry Correlations

molecular sym C_{3v}	site sym C_s	factor group sym D_{2h}
a_1 a_2 e	a' a''	a_g (Raman)
		b_{2g} (Raman)
		b_{1u} (IR)
		b_{3u} (IR)
		a_g (inact)
		b_{1g} (Raman)
		b_{3g} (Raman)
		b_{2u} (IR)

gave a calculated barrier of 23–27 kJ mol⁻¹, arising almost entirely from intermolecular interactions. The variation results from a superimposed 2-fold barrier caused by the crystallographic mirror plane and the nonequivalence of the two carbonyl groups. The calculations were repeated, therefore, with coordinates adjusted for an idealized molecule with 4- and 3-fold symmetries for the ring and carbonyl groups, respectively. The 2-fold contribution to the barrier disappears in this case to give a barrier of 25.6 kJ mol⁻¹, which is in good agreement with the experimental value for calculations of this type. The angular dependence of the total potential energy is shown in Figure 3, together with the different contributions from ring–ring and internal sources. The nonbonded contribution to the internal barrier is zero, in agreement with predictions that very small barriers should exist in arene–metal tricarbonyl complexes.^{22,23} Almost the entire barrier arises from

(22) Albright, T. A.; Hofmann, P.; Hofmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546–7557.

ring–carbonyl interactions; therefore, cooperative motions between rings is unlikely.

Reinterpretation of the Vibrational Spectra. Table IV shows the symmetry correlations of the internal vibrational modes for CbFe(CO)₃ between the isolated molecule and the crystal. The low-temperature Raman spectrum in the CO stretching region¹² exhibits four peaks between 2020 and 2040 cm⁻¹ and five in the 1920–1990-cm⁻¹ region; they were originally interpreted for the Fe(CO)₃ moiety as being due to the factor group splitting of the $a_1(\nu_{18})$ and $a_1(\nu_{23}) \nu(\text{CO})$ modes, respectively. For the space group *Pnma*, the factor group is D_{2h} and the correlations among C_{3v} (local symmetry), C_s (site), and D_{2h} should lead to a doublet for the $a_1(\text{CO})$ mode and a quartet for the $e(\text{CO})$ mode in the Raman spectrum. The Raman data are now reinterpreted: a_1 , 2035 and 3036 cm⁻¹; e , 1931, 1944, 1957, and 1988 cm⁻¹. The weaker peaks that appear in these regions are due to combination modes and/or ¹³C satellites. Other splittings occur in the Raman spectrum; the a_1 Fe–CO mode (ν_{19}) gives rise to features at 425 and 428 cm⁻¹ in accord with factor group predictions.

Acknowledgment. This work was supported in part by the National Science Foundation (NSF Grant CHE84-19828, H. B.G.) and in part by the Exxon Educational Foundation (W.P.S.). The low-temperature attachment for the diffractometer was purchased with NSF funds (Grant CHE82-19039). P.D.H. acknowledges the National Research Council of Canada for an NSERC–NATO postdoctoral fellowship.

Registry No. (C₄H₄)Fe(CO)₃, 12078-17-0.

Supplementary Material Available: A complete description of the X-ray data collection and refinement with references and Table VI, anisotropic thermal parameters (3 pages); Table V, observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(23) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149–155.

Contribution from the Department of Chemistry, State University of New York, Plattsburgh, New York 12901, Sandia National Laboratories, Albuquerque, New Mexico 87185, and 3M Corporate Research Laboratories, St. Paul, Minnesota 55144

Magnetic Interactions in a Copper(II) Trimer Encapsulated in a Molecular Metal Oxide Cluster

G. F. Kokoszka,*^{1a} F. Padula,^{1a} A. S. Goldstein,^{1a} E. L. Venturini,*^{1b} L. Azevedo,*^{1b} and A. R. Siedle*^{1c}

Received January 26, 1987

This paper presents EPR and magnetic susceptibility data on the trimeric Cu(II) complex (W₉AsO₃₃)₂Cu₃(H₂O)₂¹²⁻, with emphasis on the intramolecular spin-exchange coupling processes. The exchange interaction arises from the coupling of one unpaired electron centered on each of the three Cu(II) ions, which are arranged in an isosceles triangle (Cu–Cu distances = 4.669 and 4.707 Å). An isotropic antiferromagnetic interaction means that the highest spin state ($S = 3/2$) is above the two $S = 1/2$ states. The observed quartet state is quite normal in its EPR behavior and shows the allowed transitions centered at about 3000 G ($g_{11} = 2.075$, $g_1 = 2.243$, $D = 1.9 \times 10^{-2}$ cm⁻¹, and $E < 30$ g) as well as the two sets of forbidden lines at about one-half and one-third of that field value over the range 10–300 K. The quartet spectrum was observed, with some changes in shape and intensity, down to 2 K. Additional EPR lines are found both below and above the $S = 3/2$ EPR absorptions and have a pronounced temperature dependence with a maximum intensity at about 40 K. The most prominent of these lines is at $g \sim 10$ at both 9 and 53 GHz. The magnetic susceptibility data in the 10–300 K range can be fit with an equation of the form $C/(T + T_c) + A$ with $T_c = 3.3$ K, $C = 2.54 \times 10^{-4}$ cm³ K/g and $A = -8.7 \times 10^{-8}$. This value of C yields a typical Cu(II) g value based on the value of $S = 1/2$ for each of the unpaired electrons centered on three Cu(II) ions. Below 10 K, the magnetic susceptibility deviates from a Curie temperature dependence and can be interpreted with an intramolecular antiferromagnetic coupling with $J = -7.5$ K; intermolecular effects may play a role at the lowest temperature (2 K). The individual trimers in the crystal lattice are arranged in undulating ribbons with a center–center distance of about 10 Å. The shortest intermolecular metal–metal distance is 7.86 Å.

Introduction

We are pursuing a broad synthetic and spectroscopic study of metal oxide cluster chemistry. Such clusters, in addition to their intrinsic interest, can provide tractable, molecular level models

for surface processes on extended phase oxide surfaces whose detailed characterization poses formidable problems.² A general class of surface interactions of particular interest concerns those between groups of paramagnetic ions positioned on an oxide

(1) (a) State University of New York. (b) Sandia National Laboratories. (c) 3M Corporate Research Laboratories.

(2) A comprehensive review of metal oxide clusters is to be found in: Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: New York, 1983.