ues for hydrated inorganic salts. More significant is the observation that the trend of the displacement magnitudes is in agreement with what would be expected from the structure. The oxygens with the most ligands (O(1)–O(3)) have the smallest displacements, O(4)–O(6) are intermediate, and O(7)–O(12), with the fewest ligands, have the largest amplitudes of motion.

No thermal motion data could be found for a salt which loses water of hydration as readily as $Na_3(CrMo_6O_{24}H_6)\cdot 8H_2O$. It is reasonable to expect the water molecules to have equal or greater freedom of motion than any anion oxygen. This is observed to be the case. In view of the generally good agreement with other structures of the magnitudes of thermal motion of the other atoms in the salt it must be concluded that the values for the displacements of the water molecules are of comparable accuracy.

The anisotropy of the computed thermal ellipsoids appears to be real. In all cases the maximum principal axis is orientated in a direction which could be predicted from the observed structure. For example, the anion oxygens which are bonded to only one Mo atom (O(7)–O(12)) would be predicted to have the maximum displacement approximately normal to the Mo–O bond and this is found to be true for all of them. On the basis of the proposed hydrogen-bonding scheme O(15) is coordinated to three atoms. This situation would predict a marked anisotropy with the maximum principal axis approximately normal to the plane defined by the three coordinating atoms and this is what is found. The O(14) atom provides the same situation, but its coordination was chosen to yield agreement. The distorted octahedron around Na(1) has one centrosymmetrically related pair of faces which are appreciably larger than the other octahedral faces. The direction defined by the centers of these large opposing faces would be predicted to be a direction of large thermal displacement. It is observed that Na(1) has a very elongated thermal ellipsoid with the maximum principal axis in the predicted direction. This consistent agreement appears to justify considerable confidence in the accuracy of the present structure determination.

Acknowledgment.—I wish to express my appreciation to Professors L. C. W. Baker and J. V. Silverton of Georgetown University for suggesting the problem and their continued interest and assistance during the solution. Special thanks are due to F. A. Mauer of the National Bureau of Standards for his assistance with the data collection and to Dr. D. E. Appleman of the U. S. Geological Survey for performing the piezoelectric tests.

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The Crystal and Molecular Structure of Acenaphthylenediiron Pentacarbonyl, $C_{12}H_8Fe_2(CO)_5$

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Acenaphthylenediiron pentacarbonyl, $C_{12}H_8Fe_2(CO)_5$, crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (C_{2h}^5; no. 14) with $a = 10.056 \pm 0.007$ Å, $b = 16.089 \pm 0.010$ Å, $c = 9.376 \pm 0.006$ Å, $\beta = 91.53 \pm 0.09°$, $\rho_{obsd} = 1.74 \pm 0.03$ g cm^{-3}, and $\rho_{calcd} = 1.769$ g cm^{-3} for $Z = 4$. A single-crystal X-ray diffraction study of this complex has been completed, using counter data to $\sin\theta = 0.40$ (Mo Kα radiation). All atoms, including hydrogens, have been located, the final discrepancy index being $R_F = 6.71\%$ for 1791 independent nonzero reflections The crystal consists of distinct molecular units of $C_{12}H_8Fe_2(CO)_5$ separated by normal van der Waals distances. The molecule consists of a modified acenaphthylene ligand in which the carbon atoms of the five-membered ring form a π-cyclopentadienyl system which is bonded to an $Fe(CO)_2$ group, while the three atoms C(5), C(10), and C(6) participate in a π-allyl linkage to an $Fe(CO)_3$ group. The two iron atoms are mutually linked *via* a bond 2.769 Å in length.

Introduction

Recent structural studies on the azulene–metal–carbonyl complexes $C_{10}H_8Fe_2(CO)_5$,[2] $C_{10}H_8Mo_2(CO)_6$,[3–5] $[(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5]Mo_2(CO)_6$,[3,6] $[C_{10}H_8Mo(CO)_3CH_3]_2$,[7] $C_{10}H_8Mn_2(CO)_6$,[8] $(C_{10}H_8)_2Fe_4(CO)_{10}$,[9] and $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$[10] have indicated that a dominant feature of azulene-to-metal bonding is the use of

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[1] Research Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967); M. R. Churchill, *Chem. Commun.*, 450 (1966).

[3] M. R. Churchill and P. H. Bird, *ibid.*, 746 (1967).

[4] J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).

[5] A. W. Schlueter and R. A. Jacobsen, *Inorg. Chim. Acta*, **2**, 241 (1968).

[6] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968).

[7] P. H. Bird and M. R. Churchill, *ibid.*, **7**, 349 (1968); P. H. Bird and M. R. Churchill, *Chem. Commun.*, 705 (1967).

[8] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1793 (1968); P. H. Bird and M. R. Churchill, *Chem. Commun.*, 145 (1968).

[9] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **8**, 1941 (1969); M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, **90**, 3241 (1968).

[10] M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, **8**, 1956 (1969); M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, **90**, 800 (1968).

the five-membered ring in a π-cyclopentadienyl→metal linkage. Again, in bis(azulene)iron,[11] the formation of a ferrocene system outweighs a loss of delocalization energy and the creation of steric strain in the seven-membered rings. Since polycyclic aromatic molecules have both more extensive conjugation in their ground states and more rigid carbon skeletons, structural studies of their metal–carbonyl complexes should provide some indication of the extent to which metal–carbon bonding will compensate for electronic and steric distortions from the ground state of the native ligand.

We now report the results of an X-ray structural investigation of acenaphthylenediiron pentacarbonyl. A brief account of this work has appeared previously.[12]

Experimental Section

A solution of $Fe(CO)_5$ (20 ml) and acenaphthylene (8 g, Aldrich technical grade, recrystallized twice from methanol–water) in 125 ml of thiophene-free benzene was irradiated with a sunlamp for 18 hr, refluxing under N_2. The solvent was evaporated and the solid residue redissolved in hexane and chromatographed in batches on a 30-cm alumina column (Woelm, activity grade no. 3). The reddish brown band was isolated and concentrated to yield crystals at −78°; yield, 1.5 g of purple-brown crystals (18%, based on acenaphthylene).

Mass spectral analysis showed the parent ion peak at *m/e* 404 and strong peaks at *m/e* 376, 348, 320, 292, 264 [corresponding to $C_{12}H_8Fe_2(CO)_{5-n}^+$ (n = 1–5)], 208 [$C_{12}H_8Fe^+$], 152 [$C_{12}H_8^+$], 56 [Fe^+], and 28 [CO^+]. The infrared spectrum of the complex showed carbonyl stretching frequencies at 2036 and 1984 cm^{-1} ($CHCl_3$ solution). The product thus appears to be identical with that prepared by King and Stone[13,14] (which had initially been reported as $C_{12}H_8Fe_2(CO)_6$[13] and subsequently correctly reformulated as $C_{12}H_8Fe_2(CO)_5$[14]).

Crystals suitable for X-ray diffraction studies were grown by the gradual cooling of a saturated solution of the complex in 50:50 ether–petroleum ether.

Unit Cell and Space Group

Optical examination of the crystals and the observed reciprocal lattice symmetry (C_{2h}; 2/m) indicated a monoclinic system. Unit cell dimensions, obtained by a least-squares analysis of high-angle precession data, taken with Mo Kα radiation (λ 0.7107 Å) at room temperature (*ca.* 23 ± 2°) and calibrated with sodium chloride (a_{NaCl} = 5.640 Å), are $a = 10.056 \pm 0.007$ Å, $b = 16.089 \pm 0.010$ Å, $c = 9.376 \pm 0.006$ Å, and $\beta = 91.53 \pm 0.09°$. The unit cell volume is 1516.4 Å³.

A careful survey of $0kl$ and $1kl$ Weissenberg and $h0l$, $h1l$, $hk0$, and $hk1$ precession photographs revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, compatible only with space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (C_{2h}^5; no. 14)[15] having the equipoints $\pm(x, y, z)$, $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

The observed density ($\rho_{obsd} = 1.74 \pm 0.03$ g cm^{-3} by flotation in aqueous zinc iodide solution) is consistent with four molecules per unit cell (ρ_{calcd} = 1.769 g cm^{-3} for mol wt 404, Z = 4). The space group thus imposes no specific symmetry on the molecule.

Collection and Reduction of the X-Ray Diffraction Data

Intensity data (Mo Kα radiation) were collected on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer, using the "stationary-background, ω-scan, stationary-background" counting sequence which has been described in detail previously.[16] Experimental details specific to the present investigation include the following. (i) The X-ray generator was stabilized at 49.0 kV/19.3 mA. (ii) The angle scanned was $\omega(hkl) = [2.0 + (1.0/L(hkl))]$, where $1/L(hkl)$ is the Lorentz factor for the reflection hkl. (iii) The scan speed was 2°/min. (iv) Initial and final backgrounds [$B_1(hkl)$ and $B_2(hkl)$] were each measured for one-fourth the time of the main scan [$C(hkl)$ counts]. (v) Within each level a carefully preselected check reflection was remeasured after each batch of 20 reflections had been collected. No significant (*i.e.*, >2%) variations from the mean were detected, thus confirming the stability of the counter electronics and the continued alignment of the crystal. (vi) The intensity of the reflection hkl was calculated as $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$.

Using equiinclination Weissenberg geometry, data for the quadrants hKl and $\bar{h}Kl$ (K = 0–9) were collected from a b-mounted crystal of dimensions 0.30 × 0.39 × 0.48 mm (referred sequentially to the directions normal to the well-developed (011), (01$\bar{1}$), and (110) faces). Data were similarly collected for the quadrants hkL and $\bar{h}kL$ (L = 0–10) from a c-mounted crystal of dimensions 0.18 × 0.26 × 0.54 mm (referred to (110), ($\bar{1}$10), and (101)).

This second set of data is complete to $\sin\theta = 0.40$, save for the few reflections in the range $0 \leq \theta \leq 4°$ which are shielded from the counter by a Pb backstop. [Long-exposure Weissenberg photographs had previously shown that there were few observable reflections beyond $\sin\theta = 0.40$.]

Data were assigned standard deviations according to the following scheme, where $\delta(hkl) = 3[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$ and is the maximum probable error in $I(hkl)$ based *solely* on counting statistics: $I(hkl) \geq 1225$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $1225 > I(hkl) \geq \delta(hkl)$, $\sigma\{I(hkl)\} = 3.5[I(hkl)]^{1/2}$; $I(hkl) < \delta(hkl)$, reflection rejected.

Of the 1670 reflections obtained from the b-mounted crystal, 338 were rejected; of the 2375 reflections (which include equivalent $hk0$ and $\bar{h}k0$ data) from the c-mounted crystal, 559 were rejected. Intensities were corrected for Lorentz and polarization effects [$(Lp)^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)$] and absorption corrections were applied.[17] [With μ = 19.538 cm^{-1} for Mo Kα radiation, transmission factors ranged from 0.406 to 0.635 for the b-mounted crystal of volume 0.0489 mm³ and from 0.614 to 0.740 for the c-mounted crystal of volume 0.0246 mm³.] The 21 zones of data were

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(11) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 716 (1969); M. R. Churchill and J. Wormald, *Chem. Commun.*, 1033 (1968).

(12) M. R. Churchill and J. Wormald, *ibid.*, 1597 (1968).

(13) R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 4557 (1960).

(14) R. B. King, *ibid.*, **88**, 2075 (1966).

(15) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

(16) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

(17) Using a locally modified version of Burnham's GNABS: C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

merged to a common scale by a least-squares analysis of common reflections,[18] and the resulting 1791 independent, nonzero reflections were used in a Wilson plot,[19] from which the approximate absolute scale and the overall thermal parameter ($B = 2.08$ Å^2) were obtained.

Elucidation and Refinement of the Structure

All crystallographic routines were (unless otherwise stated) performed under the CRYRM system[20] using the Harvard University IBM 7094 computer. The function minimized during least-squares refinement procedures was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\}$ is derived from $\sigma\{I(hkl)\}$ by appropriate adjustment for Lorentz, polarization, absorption, and scale factors. Scattering curves for neutral oxygen, carbon, and hydrogen were taken from the compilation of Ibers.[21a] The Thomas–Fermi–Dirac values for neutral iron[21b] were corrected for the real ($\Delta f' = +0.4$ e$^-$) but not for the imaginary component of dispersion.[21c]

Discrepancy indices used within the text are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

Positions for the two crystallographically independent iron atoms were found from a three-dimensional Patterson synthesis which had been sharpened such that the average intensity was invariant with θ. A subsequent three-dimensional difference-Fourier synthesis, phased only by the two iron atoms, revealed each of the remaining nonhydrogen atoms. Full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for the iron atom, and isotropic thermal parameters for the remaining nonhydrogen atoms led to convergence at $R_F = 9.47\%$, $R_{wF^2} = 6.89\%$.

A difference-Fourier synthesis now revealed the eight hydrogen atoms of the molecule, with peak heights ranging from 0.43 to 0.88 e$^-$ Å^{-3}. The hydrogen atoms were each assigned an isotropic thermal parameter of 3.0 Å^2; both their positions and their thermal parameters were kept fixed during a cycle of full-matrix refinement of positional and anisotropic thermal parameters for all 24 nonhydrogen atoms. This process of locating the hydrogen atoms on a difference Fourier map and refining all parameters of the nonhydrogen atoms was repeated twice more, using two cycles of refinement between successive difference-Fourier maps. The final discrepancy indices were $R_F = 6.71\%$ and $R_{wF^2} = 3.96\%$ (*cf.* $R_F = 7.12\%$ and $R_{wF^2} = 4.61\%$ with hydrogen atoms omitted from structure factor calculations).

This method of positioning hydrogen atoms did not allow great precision as is evidenced by the resulting C–H bond distances which range from 0.78 to 1.33 Å. However, this disadvantage is more than outweighed by the realistic picture obtained for the ligand—as may be seen in Figure 1, all hydrogen atoms lie out of the plane of the acenaphthylene carbon atoms and are displaced *away from* the two iron atoms.

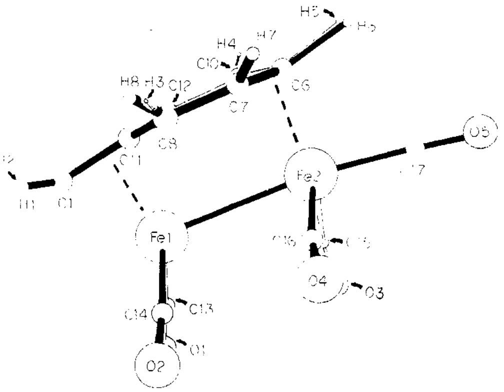

Figure 1.—The $C_{12}H_8Fe_2(CO)_5$ molecule, showing the hydrogen atom positions relative to the carbon atoms of the acenaphthylene ligand.

Application of Hamilton R factor ratio tests[22] indicate that (i) anisotropic refinement of carbon and oxygen atoms and (ii) inclusion of hydrogen atoms are each processes significant at a confidence level greater than 99%.

At the completion of the analysis the standard error in an observation of unit weight was 2.59.

Observed and calculated structure factors are collected in Table I. Final atomic positions are collected in Table II. Anisotropic thermal parameters are given in Table III; their associated atomic vibration ellipsoids are depicted in Figure 2.

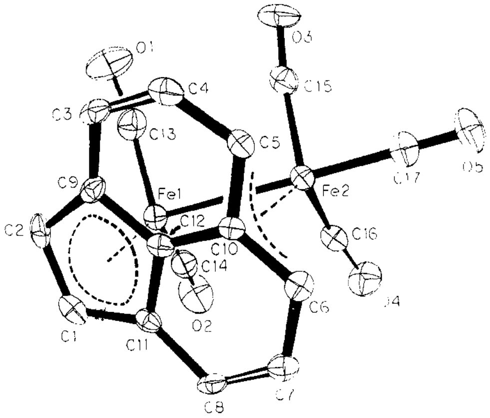

Figure 2.—The 68% probability envelopes for the atomic vibration ellipsoids in $C_{12}H_8Fe_2(CO)_5$.

The Molecular Structure

Interatomic distances, with their estimated standard deviations (esd's), are collected in Table IV; bond angles (with esd's) are shown in Table V. The scheme for numbering atoms is shown in Figures 1–3.

The nature of the metal-to-ligand bonding is illustrated in Figure 2; the approximate C_s symmetry of

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[18] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[19] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

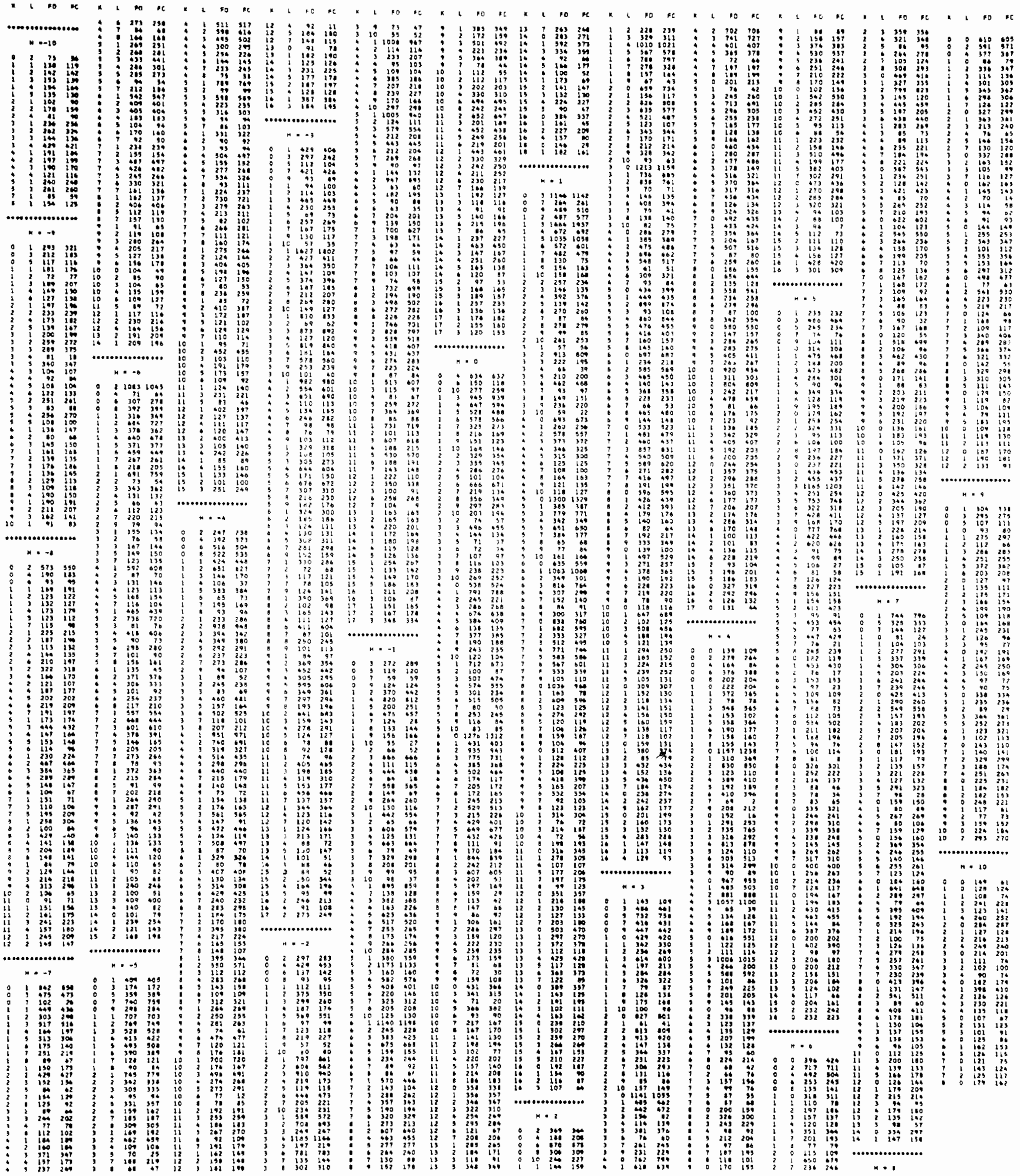
[20] CRYRM is an integrated sequence of crystallographic routines for the IBM 7094 developed by Professor R. E. Marsh and his coworkers.

[21] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

[22] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN e$^-$ × 5.00) FOR $C_{12}H_8Fe_2(CO)_5$



the $C_{12}H_8Fe_2(CO)_5$ molecule is demonstrated in Figure 3.

One iron atom, Fe(1), is bonded symmetrically to the carbon atoms of the five-membered ring *via* a π-cyclopentadienyl→metal linkage. The five carbon atoms C(1), C(2), C(9), C(12), and C(11) have a root-mean-square deviation of only 0.005 Å from the least-squares plane $0.6305X + 0.5050Y + 0.5892Z - 8.3025 = 0$ (see Table VI). Individual carbon–carbon bond distances within this π-cyclopentadienyl system vary from 1.415 (13) to 1.441 (12) Å, averaging 1.431 Å. The C–C–C bond angles vary from 104.9 (7) to 110.6 (7)°, averaging 108.0°. Fe(1) lies 1.725 Å below the plane of the ring, with individual Fe–C distances ranging from 2.078 (9) to 2.140 (8) Å, averaging 2.112 Å. There are two carbonyl ligands attached to Fe(1).

Fe(2) is associated with three carbonyl ligands and bonds to three atoms of the acenaphthylene ligand *via* a π-allyl→metal linkage, in which Fe(2)–C(5) = 2.241 (8), Fe(2)–C(10) = 2.051 (7), and Fe(2)–C(6) = 2.242 (8) Å. [It should be noted that the Fe(2)···C(12) distance of 2.652 (8) Å is essentially nonbonding.] Carbon–carbon distances within the π-allyl system, C(5)–C(10) = 1.431 (11) and C(10)–C(6) = 1.431 (12) Å, are in keeping with previously reported values.[23]

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(23) M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 105 (1967), and references therein.

TABLE II

FINAL ATOMIC POSITIONS, WITH ESTIMATED STANDARD DEVIATIONS, FOR $C_{12}H_8Fe_2(CO)_5$

Atom	x	y	z
Fe(1)	0.24631 (11)	0.41773 (8)	0.30206 (10)
Fe(2)	0.38623 (10)	0.27104 (8)	0.26924 (11)
C(1)	0.2664 (9)	0.4995 (6)	0.4749 (10)
C(2)	0.3268 (9)	0.5332 (6)	0.3531 (9)
C(3)	0.5258 (9)	0.4782 (7)	0.1985 (8)
C(4)	0.5976 (10)	0.4079 (8)	0.1815 (9)
C(5)	0.5858 (8)	0.3330 (6)	0.2687 (8)
C(6)	0.4812 (8)	0.2733 (6)	0.4883 (9)
C(7)	0.3917 (9)	0.2885 (7)	0.6075 (9)
C(8)	0.3232 (8)	0.3593 (6)	0.6192 (7)
C(9)	0.4340 (8)	0.4805 (6)	0.3088 (8)
C(10)	0.5118 (7)	0.3413 (6)	0.3962 (7)
C(11)	0.3349 (8)	0.4239 (6)	0.5119 (8)
C(12)	0.4345 (8)	0.4124 (6)	0.4064 (8)
C(13)	0.1999 (10)	0.4421 (7)	0.1259 (10)
C(14)	0.0802 (10)	0.3887 (6)	0.3380 (9)
C(15)	0.3424 (9)	0.2908 (7)	0.0862 (10)
C(16)	0.2291 (9)	0.2388 (6)	0.3302 (9)
C(17)	0.4563 (9)	0.1703 (8)	0.2370 (10)
O(1)	0.1725 (9)	0.4648 (7)	0.0123 (8)
O(2)	−0.0298 (7)	0.3767 (5)	0.3583 (9)
O(3)	0.3204 (8)	0.2964 (6)	−0.0329 (6)
O(4)	0.1331 (6)	0.2077 (5)	0.3741 (7)
O(5)	0.4976 (8)	0.1062 (6)	0.2149 (10)
H(1)	0.2290	0.5280	0.5280
H(2)	0.3500	0.5980	0.2880
H(3)	0.5800	0.5110	0.1490
H(4)	0.6750	0.4190	0.1400
H(5)	0.6900	0.2870	0.2440
H(6)	0.5720	0.2130	0.4870
H(7)	0.4200	0.2610	0.6710
H(8)	0.3200	0.3830	0.7000

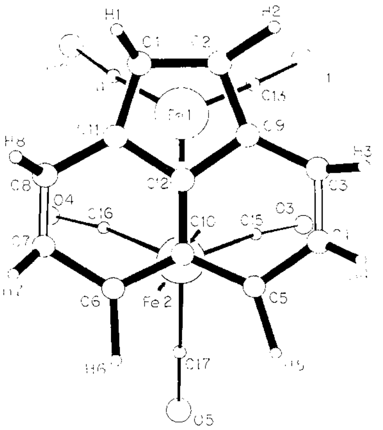

Figure 3.—The $C_{12}H_8Fe_2(CO)_5$ molecule, projected onto the plane of the five-membered ring. Note the approximate C_s symmetry of the molecule.

TABLE III

ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^4$) FOR NONHYDROGEN ATOMS IN $C_{12}H_8Fe_2(CO)_5$[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	70.7 (1.4)	27.7 (0.7)	89.6 (1.5)	1.6 (1.3)	−22.5 (2.0)	−3.1 (1.4)
Fe(2)	66.3 (1.4)	29.3 (0.7)	96.8 (1.5)	−5.4 (1.2)	15.2 (2.0)	−15.9 (1.3)
C(1)	97 (11)	43 (5)	134 (11)	4 (11)	1 (17)	−65 (11)
C(2)	125 (12)	22 (4)	161 (12)	−17 (11)	−58 (19)	−32 (11)
C(3)	134 (12)	48 (6)	88 (9)	−98 (13)	−10 (16)	13 (12)
C(4)	115 (11)	64 (6)	119 (10)	−100 (13)	36 (17)	−55 (13)
C(5)	65 (9)	38 (5)	136 (11)	−27 (10)	48 (14)	−38 (11)
C(6)	65 (9)	42 (5)	129 (10)	20 (10)	−27 (15)	11 (11)
C(7)	101 (10)	50 (6)	95 (10)	7 (12)	−40 (15)	11 (11)
C(8)	97 (10)	46 (5)	57 (7)	−46 (11)	0 (13)	4 (10)
C(9)	104 (10)	32 (4)	94 (9)	−44 (11)	−34 (15)	18 (11)
C(10)	61 (8)	37 (5)	77 (8)	−11 (9)	3 (12)	−8 (9)
C(11)	71 (8)	34 (4)	85 (8)	−14 (9)	−2 (13)	−31 (9)
C(12)	56 (7)	38 (5)	73 (7)	−21 (9)	−34 (12)	−18 (9)
C(13)	110 (12)	42 (5)	132 (13)	11 (12)	−52 (18)	16 (13)
C(14)	110 (12)	34 (5)	110 (10)	15 (12)	−21 (17)	−12 (11)
C(15)	95 (10)	42 (5)	128 (12)	−29 (11)	36 (17)	−33 (12)
C(16)	84 (10)	37 (5)	98 (9)	4 (11)	8 (15)	−26 (11)
C(17)	84 (10)	43 (6)	173 (14)	−11 (12)	−14 (18)	−17 (15)
O(1)	199 (13)	107 (7)	128 (10)	1 (14)	−93 (16)	97 (12)
O(2)	88 (9)	61 (5)	249 (12)	−29 (9)	62 (17)	−55 (12)
O(3)	172 (11)	92 (6)	75 (8)	−27 (12)	13 (13)	−21 (9)
O(4)	91 (8)	54 (4)	187 (10)	−34 (9)	52 (14)	13 (10)
O(5)	131 (10)	49 (5)	302 (16)	24 (11)	52 (19)	−94 (13)

[a] The anisotropic thermal parameter is defined as $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$. [b] Hydrogen atoms were each assigned an isotropic thermal parameter of $B = 3.0$ Å^2.

The Fe(1)–Fe(2) distance of 2.769 (3) Å is indicative of a metal–metal bond (*cf.* 2.782 Å for the iron–iron bond in azulenediiron pentacarbonyl[2]); each iron atom thus attains the appropriate inert gas configuration, in keeping with the observed diamagnetism of the compound.

The acenaphthylene system retains two uncoordinated double bonds, C(3)–C(4) = 1.352 (13) Å and C(7)–C(8) = 1.337 (12) Å. The bonds joining the various unsaturated systems, *viz.*, C(9)–C(3) = 1.405 (12) Å, C(4)–C(5) = 1.463 (13) Å, C(6)–C(7) = 1.473 (12) Å, C(8)–C(11) = 1.453 (11) Å, C(12)–C(10) = 1.388 (11) Å, may be compared with the accepted C(sp^2)–C(sp^2) single-bond length of 1.465 ± 0.005 Å.[24] The organic ligand is no longer *strictly* planar, as may clearly be seen from Figure 1. Referred to the least-squares

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(24) "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959," Special Publication No. 18, The Chemical Society, London, 1965, p S15s.

TABLE IV

INTRAMOLECULAR DISTANCES, WITH ESTIMATED STANDARD DEVIATIONS,[a] FOR $C_{12}H_8Fe_2(CO)_5$

Atoms	Dist, Å	Atoms	Dist, Å
(a) The Iron–Iron Linkage			
Fe(1)–Fe(2)	2.769 (3)		
(b) Iron–Acenaphthylene Distances			
Fe(1)–C(1)	2.093 (9)	Fe(2)–C(5)	2.241 (8)
Fe(1)–C(2)	2.078 (9)	Fe(2)–C(10)	2.051 (7)
Fe(1)–C(9)	2.139 (8)	Fe(2)–C(6)	2.242 (8)
Fe(1)–C(12)	2.109 (7)	Fe(2)···C(12)	2.652 (8)
Fe(1)–C(11)	2.140 (8)		
(c) Carbon–Carbon Distances within the Acenaphthylene Ligand			
C(1)–C(2)	1.415 (13)	C(4)–C(5)	1.463 (11)
C(2)–C(9)	1.441 (12)	C(5)–C(10)	1.431 (11)
C(9)–C(12)	1.426 (11)	C(10)–C(6)	1.431 (11)
C(12)–C(11)	1.437 (11)	C(6)–C(7)	1.473 (12)
C(11)–C(1)	1.435 (12)	C(7)–C(8)	1.337 (12)
C(9)–C(3)	1.405 (12)	C(8)–C(11)	1.453 (11)
C(3)–C(4)	1.352 (13)	C(10)–C(12)	1.388 (11)
(d) The Iron–Carbonyl Systems			
Fe(1)–C(13)	1.748 (10)	C(13)–O(1)	1.152 (13)
Fe(1)–C(14)	1.775 (9)	C(14)–O(2)	1.143 (12)
Fe(2)–C(15)	1.789 (9)	C(15)–O(3)	1.135 (12)
Fe(2)–C(16)	1.772 (8)	C(16)–O(4)	1.170 (11)
Fe(2)–C(17)	1.796 (10)	C(17)–O(5)	1.132 (13)
(e) Carbon–Hydrogen Distances			
C(1)–H(1)	0.78	C(5)–H(5)	1.31
C(2)–H(2)	1.23	C(6)–H(6)	1.33
C(3)–H(3)	0.90	C(7)–H(7)	0.79
C(4)–H(4)	0.90	C(8)–H(8)	0.85

[a] Estimated standard deviations, shown in parentheses, include contributions from posible errors in unit cell dimensions.

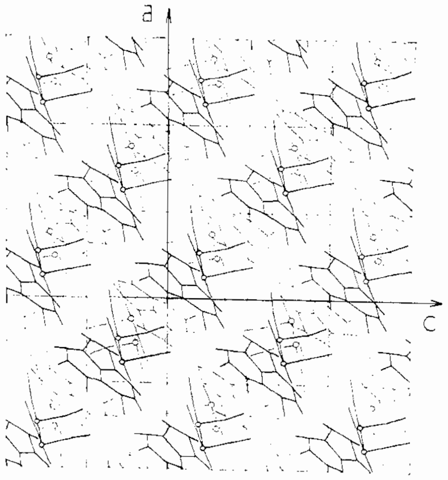


Figure 4.—Packing of $C_{12}H_8Fe_2(CO)_5$ molecules, viewed down *b*.

plane of the five-membered ring, the remaining carbon atoms of the acenaphthylene ligand are displaced toward the iron atoms to the following extents: C(3) by 0.017 Å and C(8) by 0.011 Å; C(4) by 0.224 Å and C(7) by 0.215 Å; C(5) by 0.440 Å and C(6) by 0.411 Å; and C(10) by 0.158 Å. These pairs of figures, taken with others in Table VI, serve to illustrate that the molecule has approximate C_s symmetry.

The dihedral angle between the planes of the π-cyclopentadienyl and π-allyl systems is 156° 35′.

TABLE V

BOND ANGLES WITHIN THE $C_{12}H_8Fe_2(CO)_5$ MOLECULE[a]

Atoms	Angle, deg	Atoms	Angle, deg
(a) Within the π-Cyclopentadienyl System			
C(1)–C(2)–C(9)	110.3 (0.8)	C(1)–Fe(1)–C(2)	39.7 (0.4)
C(2)–C(9)–C(12)	104.9 (0.7)	C(2)–Fe(1)–C(9)	39.9 (0.3)
C(9)–C(12)–C(11)	110.6 (0.7)	C(9)–Fe(1)–C(12)	39.2 (0.3)
C(12)–C(11)–C(1)	106.3 (0.7)	C(12)–Fe(1)–C(11)	39.5 (0.3)
C(11)–C(1)–C(2)	107.8 (0.8)	C(11)–Fe(1)–C(1)	39.6 (0.3)
(b) Within the π-Allyl System			
C(5)–Fe(2)–C(10)	38.6 (0.3)	C(10)–Fe(2)–C(6)	38.6 (0.3)
(c) Within the Six-Membered Rings			
C(12)–C(9)–C(3)	117.4 (0.8)	C(8)–C(11)–C(12)	117.1 (0.7)
C(9)–C(3)–C(4)	118.2 (0.9)	C(7)–C(8)–C(11)	120.0 (0.8)
C(3)–C(4)–C(5)	124.8 (0.9)	C(6)–C(7)–C(8)	122.0 (0.8)
C(4)–C(5)–C(10)	116.2 (0.8)	C(10)–C(6)–C(7)	118.3 (0.8)
C(5)–C(10)–C(12)	116.0 (0.7)	C(12)–C(10)–C(6)	117.3 (0.7)
C(10)–C(12)–C(9)	125.5 (0.7)	C(10)–C(12)–C(11)	123.7 (0.7)
(d) External Angles of the Organic Ligand			
C(1)–C(11)–C(8)	136.5 (0.8)	C(2)–C(9)–C(3)	137.6 (0.8)
C(5)–C(10)–C(6)	123.8 (0.7)		
(e) Within the Carbonyl Ligands			
Fe(1)–C(13)–O(1)	174.3 (0.9)	Fe(2)–C(15)–O(3)	173.4 (0.9)
Fe(1)–C(14)–O(2)	174.2 (0.9)	Fe(2)–C(16)–O(4)	171.3 (0.8)
		Fe(2)–C(17)–O(5)	178.2 (1.0)
(f) Angles between Ligands and Iron Atoms			
Cp–Fe(1)–Fe(2)[a]	98.7 (0.3)	C(13)–Fe(1)–Fe(2)	102.1 (0.3)
Cp–Fe(1)–C(13)[a]	127.3 (0.4)	C(14)–Fe(1)–Fe(2)	106.3 (0.3)
Cp–Fe(1)–C(14)[a]	128.6 (0.4)	C(13)–Fe(1)–C(14)	90.5 (0.5)
C(15)–Fe(2)–Fe(1)	80.9 (0.3)	C(15)–Fe(2)–C(16)	99.3 (0.4)
C(16)–Fe(2)–Fe(1)	75.8 (0.3)	C(16)–Fe(2)–C(17)	98.4 (0.4)
C(17)–Fe(2)–Fe(1)	172.1 (0.3)	C(17)–Fe(2)–C(15)	95.0 (0.5)
(g) Angles Involving Hydrogen Atoms			
C(2)–C(1)–H(1)	121	C(4)–C(5)–H(5)	107
C(11)–C(1)–H(1)	125	C(10)–C(5)–H(5)	130
C(1)–C(2)–H(2)	144	C(10)–C(6)–H(6)	113
C(9)–C(2)–H(2)	102	C(7)–C(6)–H(6)	124
C(9)–C(3)–H(3)	142	C(6)–C(7)–H(7)	105
C(4)–C(3)–H(3)	96	C(8)–C(7)–H(7)	126
C(3)–C(4)–H(4)	111	C(7)–C(8)–H(8)	119
C(5)–C(4)–H(4)	119	C(11)–C(8)–H(8)	108

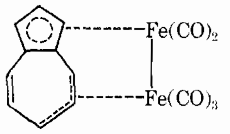
[a] Cp represents the center of gravity of the five-membered ring.

Crystal Packing

The crystal consists of discrete molecular units of $C_{12}H_8Fe_2(CO)_5$, separated by normal van der Waals distances. The closest oxygen···hydrogen contact is 2.51 Å and the closest hydrogen···hydrogen contact is 2.42 Å. The packing of molecules within the crystal is illustrated in Figure 4.

Discussion

The factoring of π electrons in azulenediiron pentacarbonyl has previously been shown to be that pictured in I. Therefore, on an *a priori* basis the acenaphthylene ligand might be expected to take up the configuration II (which is analogous to I and also conserves a noncoordinated *cis*-butadiene system along with its concomitant delocalization energy); instead, we actually observe configuration III, in which conjugation



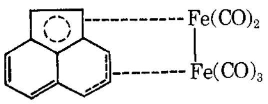
I

TABLE VI

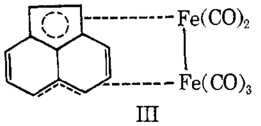
LEAST-SQUARES PLANES WITHIN THE $C_{12}H_8Fe_2(CO)_5$ MOLECULE[a-c]

Atom	Dist, Å	Atom	Dist, Å
(A) $0.6305X + 0.5050Y + 0.5892Z - 8.3025 = 0$			
C(1)*	−0.006 (9)	C(3)	−0.017
C(2)*	−0.003 (9)	C(8)	−0.011
C(9)*	+0.011 (8)	C(4)	−0.224
C(12)*	−0.015 (8)	C(7)	−0.215
C(11)*	+0.013 (8)	C(5)	−0.440
		C(6)	−0.411
Fe(1)	−1.725	C(10)	−0.158
(B) $0.8355X + 0.1618Y + 0.5250Z - 7.0556 = 0$			
C(5)*	0.000	Fe(2)	−1.837
C(10)*	0.000		
C(6)*	0.000		
(C) $-0.4446X - 0.3724Y + 0.8146Z + 1.2650 = 0$			
C(10)*	+0.001 (8)	C(5)	−1.268
C(12)*	−0.001 (8)	C(6)	+1.258
Fe(1)*	0.000 (1)	C(13)	−1.303
Fe(2)*	0.000 (1)	C(14)	+1.196
C(1)	+0.759	O(1)	−2.196
C(2)	−0.656	O(2)	+1.916
C(9)	−1.162	C(15)	−1.341
C(11)	+1.192	C(16)	+1.368
C(3)	−2.414	O(3)	−2.198
C(8)	+2.463	O(4)	+2.323
C(4)	−2.446	C(17)	+0.041
C(7)	+2.490	O(5)	+0.067

[a] All planes are expressed in Cartesian coordinates. The transformations to natural cell coordinates are $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$. [b] A plane is derived using unit weights for atoms marked with asterisks. [c] The angle between planes A and B is 23° 25′.



II



III

within the six-membered rings has been wholly disrupted. The stability of this compound is thus a considerable tribute to the combined strength of π-cyclopentadienyl→iron and π-allyl→iron bonding.

The preference for III over II furthermore demonstrates the importance of steric effects. In azulenediiron pentacarbonyl[2] (I) atoms of the seven-membered ring are bent out of the plane of the five-membered ring by as much as 0.91 Å, and the stereochemistry of the azulene ligand adapts to conform to electronic requirements. In the case of acenaphthylenediiron pentacarbonyl, the organic ligand is more rigid than azulene and the planar configuration III is more in keeping with iron–iron bond length requirements than is the planar configuration II. In this case, then, the electronic requirements are subservient to the steric requirements of the relatively rigid polycyclic acenaphthylene framework. There is some distortion of the ligand from planarity, but Figure 1 shows this to be relatively slight.

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CONTRIBUTION FROM THE
ISTITUTO CHIMICO DELL'UNIVERSITÀ DI NAPOLI, NAPLES, ITALY

The Solid-State Structure of π-Allyldi(thiourea)nickel(II) Chloride

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The crystal structure of π-allyldi(thiourea)nickel(II) chloride has been determined by single-crystal X-ray diffraction methods. The crystals are orthorhombic with space group Pbca and cell parameters $a = 25.24$ (8) Å, $b = 11.17$ (4) Å, $c = 8.63$ (3) Å, with $Z = 8$, $d_{\text{calcd}} = 1.57$ g cm^{-3}, and $d_{\text{obsd}} = 1.5$ g cm^{-3}. With Cu Kα radiation 1113 intensities were measured by standard Weissenberg equiinclination photographic methods. The structure was solved by routine heavy-atom methods and refined by block-diagonal least-squares methods with anisotropic temperature factors for Ni, Cl, and S to a final conventional R factor of 0.096. The structure is made up of molecular ions π-$C_3H_5Ni(SC(NH_2)_2)_2^+$ and chloride ions. The shortest Ni–Cl distance is 3.445 ± 0.004 Å. The coordination of the ligands around the nickel atom in the positive molecular ion may be considered as square planar. The S_1NiS_2 angle (110.9 ± 0.1) is however definitely larger than that expected for a normal square-planar coordination. The carbon–carbon distances of the allyl group are equal within errors. The dihedral angle between the plane containing the carbon atoms of the allyl group and that containing the Ni, S_1, and S_2 atoms is 118 ± 3°. The crystal structure appears to be largely determined by the formation of hydrogen bonds between the NH_2 groups of the thiourea ligands and the chloride ions.

Introduction

The influence of thiourea on the efficiency of π-allylnickel halides as catalysts for the synthesis of dienoic esters was observed and discussed by Chiusoli and Merzoni.[1] They postulated the formation of an intermediate π-allylnickel(II)–thiourea complex. The existence of this complex was confirmed by Guerrieri[2] by the preparation of a series of compounds of the general formula π-alNiLL′X in which al is allyl, methallyl, or crotyl, L and L′ are thiourea, diisopropyl-

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(1) G. P. Chiusoli and S. Merzoni, *Chim Ind.* (*Milan*), **43**, 259 (1961).

(2) F. Guerrieri *Chem. Commun.*, 983 (1968).