Journal of Organometallic Chemistry 144 (1978) 205—213

THE CRYSTAL AND MOLECULAR STRUCTURE OF FERRICINIUM TETRACHLOROFERRATE

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(Received April 6th, 1977)

Summary

The crystal and molecular structure of ferricinium tetrachloroferrate was studied by X-ray diffraction. The compound crystallizes in space group $Pna2_1$ with 4 molecules $C_{10}H_{10}Cl_4Fe_2$ per unit cell. Data analysis was relatively difficult and direct methods of phase determination were very useful in the interpretation of the Patterson synthesis. The two rings in ferricinium are nearly parallel. The structural parameters are very similar to those previously published by others for ferrocene. This molecular structure and its vibrational properties seem to be in contrast to a general rule previously formulated by others for the infrared spectra of cyclopentadienyl compounds.

Introduction

In 1964 Fritz and Schäfer [1] synthesized a compound with the sum formula $C_{10}H_{10}Cl_4Fe_2$ (I) by the reaction of ferrocene, $Fe(C_5H_5)_2$, with hexachlorocyclopentadiene, C_5Cl_6. This compound had an infrared spectrum which was totally different from the type of spectrum observed for ferrocene or ferricinium and very similar to the type of spectrum observed for compounds such as $C_5H_5CrCl_2$. The very intense 1104 cm^{-1} ferrocene band, for example, was found to be almost imperceptably weak (at 1114 cm^{-1}) in the spectrum of I. The decrease in intensity of this band in the spectra of cyclopentadienylmetal compounds has often been interpreted [2] as an indication of the decreasing covalent character of such complexes.

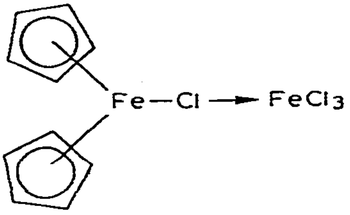
The infrared spectra of both ferrocene and ferricinium are also characterized by the appearance of two significant bands in the 500 cm^{-1} range [2] (at 490 and 478 cm^{-1} in the case of ferrocene; at 510 and 423 cm^{-1} in the case of ferricinium). In the spectrum of I only one band was found in this approximate range (at 379 cm^{-1} [1]) in which one must also expect the appearance of Fe—Cl vibrations. Because of these features, the observed infrared spectrum of I seemed to rule out the structure of ferricinium tetrachloroferrate (A) for this compound. Structure B was therefore tentatively proposed [1] to explain the formula and spectrum of I.

$[Fe(C_5H_5)_2]^+ \; [FeCl_4]^-$

(A)

$[C_5H_5FeCl_2]_2$

(B)



(C)

In subsequent investigations of I it was found [3] that its chemical properties were not consistent with B but indicated a ferricinium type system. On the basis of very thorough investigations Maitlis and Brown [3] therefore proposed structure C to explain the chemical and physical properties of I. The characteristic features of C included a bent framework [3] in which the rings were no longer parallel as in ferrocene but at an angle to each other. Steric hindrance in such a structure was expected [3] to lengthen and to weaken the metal—cyclopentadienyl ring bonds. This was expected to explain the lowering of intensity of the 1114 cm^{-1} band in agreement with Fritz [2] as due to increased ionicity of the metal—ring bond.

The ionicity of Fe in ferricinium was recently found [4] on the basis of ab initio calculations to be not significantly different than the ionicity of Fe in ferrocene. Bagus, Walgren and Almlöf [4] used a double ζ basis set in their calculations to determine the Mulliken gross population of ferricinium and of ferrocene. They found values of +1.47 and +1.39 for the ionicity of Fe in the ion and in ferrocene, respectively. This did not correspond to a significant difference in the ionicity of the bond, since the Fe-ionicity difference amounted to less than 0.1 electrons, while a value of close to one would have been expected.

This result again cast some doubt on the accuracy of the structural details proposed for I, or on the general validity of the bond-ionicity to 1114 cm^{-1}-low-intensity correlation. We, therefore, decided to start the present X-ray diffraction study of I. Its results, which are described in the following, indicate that I is indeed ferricinium but neither B nor C are correct proposals for its structure. The rings are very nearly parallel, there is no significantly increased steric hindrance compared to ferrocene, the inter-ring distance is, within error limits, the same as in ferrocene [5—7], and the crystal lattice is explained best by alternating ionic layers of $Fe(C_5H_5)_2^+$ and $FeCl_4^-$.

This study was originally started using photographic data and Patterson methods. The solution of the structural problem then turned out to be very difficult and the analysis was not completed. It is, therefore, an additional interesting aspect of the present study that its results were to a large extent made possible by the availability of a computer-controlled diffractometer and because the data analysis involved direct methods of phase determination.

Experimental and data analysis

Crystals of $C_{10}H_{10}Cl_4Fe_2$ were produced by diffusion of C_6H_5Br into a CH_2Cl_2 solution of the compound. For the structural analysis a crystal with dimensions of 0.4 × 0.3 × 0.2 mm^3 was chosen and sealed in a capillary tube to protect it from atmospheric influences and to facilitate its handling.

The compound crystallized in space group $Pna2_1$ (orthorhombic, non centrosymmetric) with 4 molecules $C_{10}H_{10}Cl_4Fe_2$ (mol. wt. 383.7) per unit cell (cell constants a 13.837(5), b 11.966 (4) and c 8.762 (2) Å; standard deviations are given in parentheses and in units of the last digit). With the cell volume of 1450.8 $Å^3$ the crystallographic density was calculated to be 1.757 g cm^{-3}. Experimental value (determined by suspension in a $HCBr_3/CCl_4$ mixture) was 1.75 g cm^{-3}. Identification of the non-centrosymmetric space group $Pna2_1$ was supported by the E statistics (Table 1).

The cell constants were determined from 87 reflections ($\theta > 8°$; Mo-K_α radiation) by a least-squares refinement. The data were recorded on a computer controlled Siemens diffractometer without manual adjustment of the crystal using a computer program which was also used in previous studies [8]. The data used for the structural analysis were recorded on the same diffractometer (on line operation; procedure by Hoppe [9]. Mo-K_α radiation; θ_{max} 28°). 1579 out of 1870 independent reflections, which had a minimum intensity of 5 counts/sec, were selected for further analysis.

The analysis of the diffraction data was based on the direct methods of phase determination of Germain et al. [10,11]. The program package of the University of York [12] was used for these calculations.

At the beginning of the data refinement, the positions of two heavy atoms (coordinates consistent with space group $Pna2_1$) were determined from a Patterson synthesis. This Patterson synthesis would not have been so easily interpretable without the additional information which was available from the direct methods of phase determination, since the main Fe-contributions were found at quite special positions in the vector space (Table 2). The results from the direct methods were generally of great importance in the search for a solution of the structural problem, which was finally found by successive Fourier and difference-Fourier syntheses of the electron density and by least-squares refinements of the atom parameters. The coordinates of the chlorine atoms were found later than those of the carbon atoms because of their relatively large temperature factors. The coordinates of the hydrogen atoms could not be determined at all by this analysis. Their contributions to the diffraction pattern were therefore neglected in all parts of our study.

TABLE 1

THE E-STATISTICS FOR $C_{10}H_{10}Cl_4Fe_2$

	Calculated	Non-centrosymmetric	Centrosymmetric
$\overline{(E^2-1)}$	0.731	0.736	0.968
$\overline{\|E\|}$	0.886	0.886	0.798

TABLE 2

THE GREATEST MAXIMA IN THE VECTOR SPACE

u	v	w	Peak-height
0.5	0.0	0.0	7410
0.0	0.5	0.5	7220
0.5	0.5	0.5	4640
0.253	0.0	0.5	3470
0.297	0.5	0.0	3220
0.204	0.5	0.0	2860
0.251	0.5	0.5	2610
0.249	0.0	0.374	1760

The final refinement led to a weighted crystallographic R value of 4.8% ($R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} \times 100\%$; 1579 reflections, and 144 refined parameters corresponding to 1435 degrees of freedom; w is the weighting function $F_o^2/[s(F_o^2)]$; $s(F_o^2)$ is the standard deviation of F_o^2 according to the statis-

(continued on p. 211)

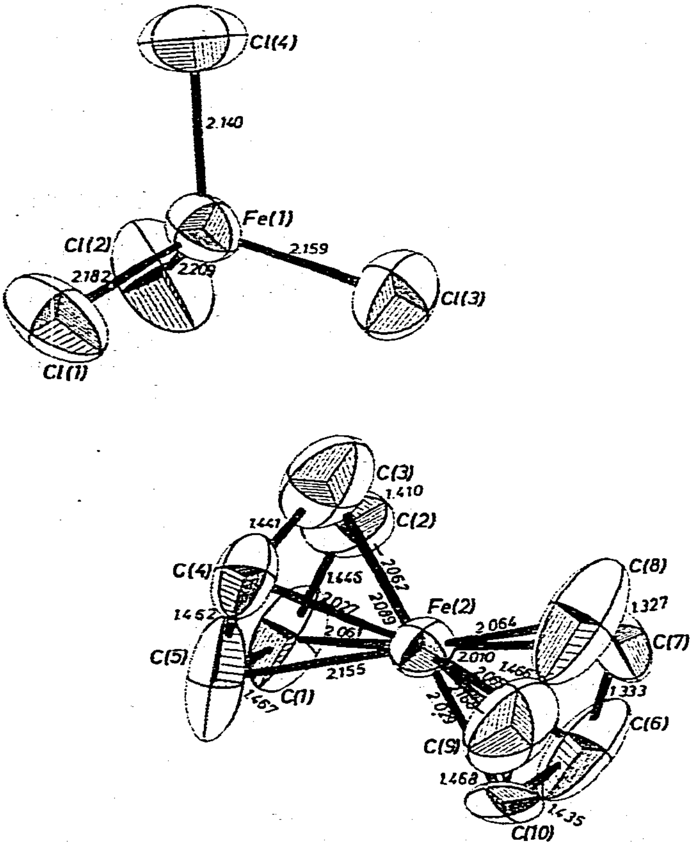


Fig. 1. Bond lengths of ferricinium tetrachloroferrate. Standard deviations $\bar{\sigma}$: Fe—Cl, 0.005; Fe—C, 0.02; C—C, 0.04; all values in Å.

TABLE 3

ATOM COORDINATES FOR $C_{10}H_{10}Cl_4Fe_2$

(The coordinates are given in the units of the cell constants. The numbers in parentheses are the standard deviations in units of the last decimal place of each coordinate.)

Atoms	*X*	*Y*	*Z*
Fe(1)	0.29324(6)	0.78657(8)	0.95195[a]
Fe(2)	0.48972(6)	0.25001(5)	0.9520(7)
Cl(1)	0.4504(1)	0.7708(2)	0.9538(14)
Cl(2)	0.2499(5)	0.8724(8)	1.1643(10)
Cl(3)	0.2303(2)	0.6215(2)	0.9482(16)
Cl(4)	0.2476(6)	0.8809(7)	0.7574(10)
C(1)	0.501(2)	0.394(2)	1.080(2)
C(2)	0.439(1)	0.412(1)	0.949(4)
C(3)	0.487(2)	0.390(2)	0.810(3)
C(4)	0.582(1)	0.366(2)	0.868(2)
C(5)	0.599(2)	0.364(2)	1.033(3)
C(6)	0.417(2)	0.124(2)	1.065(2)
C(7)	0.380(1)	0.141(2)	0.926(4)
C(8)	0.442(3)	0.122(2)	0.813(3)
C(9)	0.534(2)	0.085(2)	0.879(4)
C(10)	0.517(2)	0.098(1)	1.043(4)

[a] This coordinate was kept constant during refinement as the reference *Z*-coordinate of the space group.

TABLE 4

COEFFICIENTS FOR THE ISOTROPIC AND ANISOTROPIC TEMPERATURE FACTORS FOR $C_{10}H_{10}Cl_4Fe_2$

The values of the coefficients of the isotropic temperature factors are those values which were obtained at the start of the refinement of the anisotropic temperature factors. The expression $\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$ holds for the anisotropic factors. The B_{ik}-values given in this table are defined by $B_{ik} = b_{ik} \cdot 4/(a_i^* \cdot a_k^*)$; where a_1^*, a_2^*, a_3^* are the lattice constants of the reciprocal cell a^*, b^*, c^*. Numbers in parentheses (except for the atom numbers) are the standard deviations in units of the last decimal place of each number.

Atoms	B_{iso}[Å^2]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	4.8(1)	4.48(4)	5.96(5)	4.07(4)	−0.12(7)	−0.2(4)	0.0(4)
Fe(2)	3.8(1)	4.24(4)	3.41(3)	3.69(3)	−0.15(6)	0.1(4)	0.0(4)
Cl(1)	7.5(3)	4.55(8)	14.3(2)	5.7(1)	0.5(2)	0.0(8)	−0.3(12)
Cl(2)	4.9(2)	6.8(3)	14.6(5)	6.3(3)	−1.0(6)	1.4(5)	−3.9(6)
Cl(3)	9.4(4)	9.0(1)	5.6(1)	11.7(2)	−1.1(2)	−1.1(12)	0.8(11)
Cl(4)	8.5(6)	9.0(4)	8.3(3)	7.8(3)	1.3(5)	−1.2(5)	3.0(5)
C(1)	5.4(4)	13.3(16)	4.7(8)	3.8(6)	−4(2)	3(2)	−3(1)
C(2)	6.6(3)	9.7(7)	3.6(3)	11.1(13)	1(1)	−4(3)	1(2)
C(3)	7.9(6)	6.6(9)	5.7(9)	14.2(19)	1(1)	2(2)	2(2)
C(4)	5.1(3)	5.6(7)	5.3(7)	5.2(8)	−2(1)	2(1)	0(1)
C(5)	6.6(5)	7.5(9)	6.1(8)	14.6(20)	−4(1)	3(2)	−3(2)
C(6)	5.3(3)	13.9(11)	5.1(8)	5.4(9)	−3(2)	5(2)	0(2)
C(7)	6.3(3)	7.8(7)	6.8(6)	14.5(21)	−3(1)	−7(3)	2(3)
C(8)	5.6(3)	16.7(19)	5.4(10)	8.1(12)	−4(2)	6(3)	−3(2)
C(9)	6.4(4)	10.3(12)	4.3(7)	17.3(24)	0(1)	−1(2)	2(2)
C(10)	5.1(3)	8.5(12)	2.7(5)	11.8(17)	0(1)	−7(3)	3(2)

TABLE 5

BOND ANGLES (in degrees) FOR $C_{10}H_{10}Cl_4Fe_2$

Standard deviations as in the previous tables

Cl(1)—Fe(1)—Cl(2)	107.7(3)
Cl(1)—Fe(1)—Cl(3)	108.8(1)
Cl(1)—Fe(1)—Cl(4)	110.2(3)
Cl(2)—Fe(1)—Cl(3)	109.2(4)
Cl(2)—Fe(1)—Cl(4)	110.2(1)
Cl(3)—Fe(1)—Cl(4)	110.6(4)
C(2)—C(1)—C(5)	111(2)
C(1)—C(2)—C(3)	112(1)
C(2)—C(3)—C(4)	99(2)
C(3)—C(4)—C(5)	119(2)
C(1)—C(5)—C(4)	97(2)
C(7)—C(6)—C(10)	106(2)
C(6)—C(7)—C(8)	114(2)
C(7)—C(8)—C(9)	109(2)
C(8)—C(9)—C(10)	102(2)
C(6)—C(10)—C(9)	108(2)

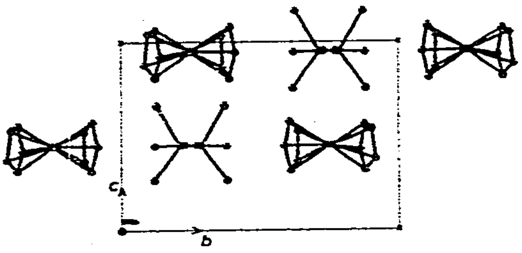


Fig. 2. Unit cell projection of ferricinium tetrachloroferrate along the a-axis.

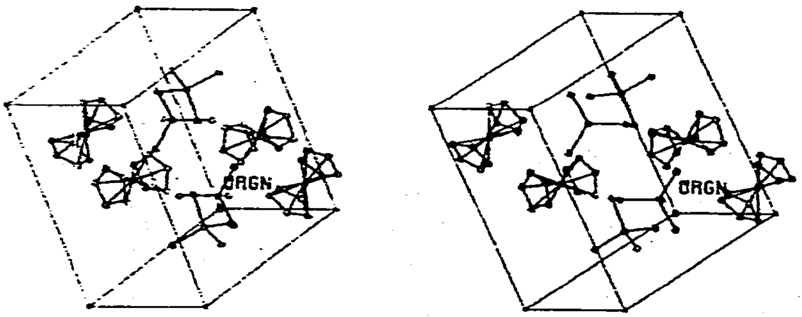


Fig. 3. Stereoscopic representation of the unit cell of ferricinium tetrachloroferrate. The directions of the a- and c-axes are upwards and to the right, respectively, with respect to the origin.

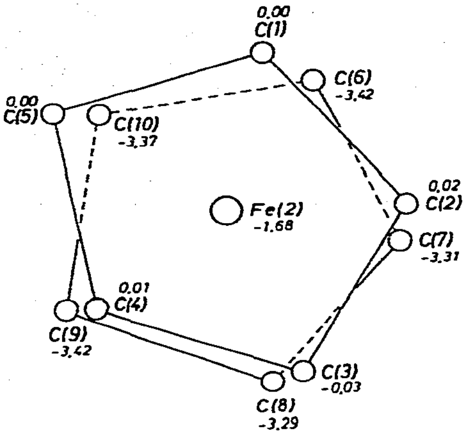


Fig. 4. Projection of the ferricinium cation on the best plane through one cyclopentadienyl-ring [C(1) to C(5)]. Deviations of the atoms from that ring plane are given in Å.

tics of the intensity measurements). The conventional unweighted R value ($R = \Sigma[|F_0| - |F_c|]/(\Sigma|F_0|) \times 100\%$) was 4.9%. The 10 strongest peaks of the final difference synthesis of the electron density were of the order of magnitude of 0.2 to 0.3 e A^{-3} *.

Considering the results presented in this paper one might be inclined to stipulate that the space group of the investigated compound was not $Pna2_1$ but $Pnma$ with special positions of the molecules on mirror planes. The E statistics and the R value of 4.8% contradict this stipulation. We have nevertheless also executed a structure parameter refinement on the basis of space group $Pnma$, which yielded a weighted R value of 15.6%.

All calculations were executed on a Siemens 4004/151 computer. The Hoechst program package developed by Kobelt and Paulus [13] was used. The scattering factors and the corrections for anomalous scattering were taken from the International Tables for X-ray Crystallography [14].

The results of this study are presented in Tables 1—5 and in Fig. 1—4.

Discussion

(a) The structural results

Dunitz, Orgel and Rich [7] studied the X-ray diffraction data of ferrocene in 1956. The most recent gas electron diffraction studies of this compound were reported by Bohn and Haaland [5] and by Haaland and Nilsson [6]. The molecule was found to have a sandwich structure with an inter-ring distance of 3.32 Å.

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* The table of structure factors has been deposited as NAPS Document No. 03168 (11 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

The carbon atoms in opposite cyclopentadienyl rings were found to be staggered in the crystal, while a rather low barrier to internal ring-rotation was determined from the vapor phase data. Willis [15] studied this molecule by neutron diffraction.

A number of ferricinium compounds were studied by X-ray diffraction by Bernstein and Herbstein (ferricinium triiodide [16]), by Pettersen (ferricinium picrate [17]), by Schlueter and Gray (ferricinium tris(trichloroacetic) acid [18]), and by Mammano et al. (ferricinium tetrachlorobismuthate [19]). In the case of the triiodide, the crystal structure was apparently so disordered that no structural details concerning ferricinium could be obtained [16]. In ferricinium picrate [17] the inter-ring distance was reported to be somewhat larger than in ferrocene. In ferricinium tris(trichloroacetic) acid, the two rings were found to be eclipsed rather than staggered and the mean Fe—C distance was 2.048(5) Å [18]. The same value was 2.045(10) in ferrocene [7]. The cyclopentadienide rings were also eclipsed in the bismuthate complex and the average Fe—C distance in this compound was found to be 2.08 Å [19].

As is seen from Fig. 1—4 and the Tables 1—5, our compound is best described as ferricinium tetrachloroferrate (structure A). The rings are nearly eclipsed and nearly parallel (mean angle of inclination is 2.2°). The inter-ring distance is 3.36 Å and therefore identical, within error limits, to the one found for ferrocene. The missing electron does not seem to weaken the Fe—C bond distances (average value 2.07 Å) and the sterical interactions between the rings do not seem to be more strained than in ferrocene. The nearly eclipsed arrangement of the rings in the crystal compared to their nearly unhindered internal rotation in gaseous ferrocene reminds one of the similar situation found for benzenechromium tricarbonyl compounds. In such systems, the arrangement of the ligands can also be eclipsed or staggered in the crystal, while nearly unhindered internal rotation was found for the vapors of benzenechromium tricarbonyl [20]. For the states of ferrocene considered by Bagus, Walgren and Almlöf [4] in their ab initio study, wave functions were obtained for both the eclipsed and staggered conformations of the cyclopentadienyl rings. Both absolute and relative total energies were found to be essentially the same for either conformation [4].

The crystal structure of ferricinium tetrachloroferrate is determined by the $Fe(C_5H_5)_2^+$ and $FeCl_4^-$ ions. Parallel layers $(0\bar{1}1)$ of $FeCl_4^-$ alternate with layers of $Fe(C_5H_5)_2^+$ (Fig. 3). The closest distance between the complexed iron (Fe(2)) and a chlorine atom is >4.0 Å. This should rule out the possibility of bond formation between Fe(2) and a chlorine atom as indicated by structure C.

(b) The vibrational spectrum

As mentioned above, Fritz [2] has correlated the decrease in intensity of the 1100 cm^{-1} band to the decreasing covalent bonding of cyclopentadienylmetal complexes. Our compound (I) is obviously ferricinium. Following Bagus, Walgren and Almlöf [4], Fe in ferricinium is not significantly more ionic than in ferrocene. Yet, compound I has a very low intensity 1100 cm^{-1} band. We have to conclude that the correlation of cyclopentadienyl-ionicity to 1100 cm^{-1}-band-intensity may not be generally applicable and can be misleading, since other factors than those involving bond ionicity must be taken into account. One feels reminded at this point of the dibenzenechromium controversy. For this compound, too, structural details (distortion of complexed benzene to threefold symmetry) were postulated on the basis of intensity considerations of vibrational modes [2]. These postulates could, again, not be confirmed by more thorough investigations [21,22].

The characteristic features of the vibrational spectra of transition-metal complexes can often be significantly influenced by kinematic vibrational coupling phenomena [23—25]. In the course of this study we have, therefore, performed vibrational analyses of I using approximate force fields in order to determine whether vibrational coupling can explain some of the frequency shifts observed in the 500 cm^{-1} range for I compared to ferrocene.

When an $FeCl_4$ oscillator is coupled to an $Fe(C_5H_5)_2$ oscillating system, then one can indeed calculate frequency shifts (compared to the uncoupled systems) which are not due to changes in force constants but to vibrational coupling. In the present case, the frequency shifts obtained by our calculations do not reflect, however, the exact difference pattern observed for the spectra of I and of ferrocene. More detailed conclusions concerning this question will therefore be possible only when more information on the force field of I will be available than is presently the case.

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