Journal of Molecular Structure
Elsevier Publishing Company, Amsterdam. Printed in the Netherlands

IR SPECTROSCOPIC STUDY OF FERRICINIUM SALTS

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(Received October 9th, 1968)

SUMMARY

Complex ferricinium salts, some not yet described in the literature, have been prepared by the oxidation of ferrocene. An IR study of these salts allowed the still dubious structure of the ferricinium cation to be unequivocally revealed. In the spectral region 4000 to 500 cm^{-1}, all these compounds have but four intense bands, and it therefore follows that their cyclopentadienyl rings conform to a D_{5h} symmetry and that there is no coupling of vibrations between them. This, and their chemical composition, support the view that the valencies of the central iron atom are directed tetrahedrally and therefore, in contradistinction to ferrocene, the planes of the cyclopentadienyl rings are not parallel.

INTRODUCTION

In the nineteen-fifties, Winter et al.[1] and Lippincott and Nelson[2-4] elucidated the structures of several cyclopentadienyl–metal compounds from their IR and Raman spectra. On the basis of the spectral data it was shown that the central metal atom joins, by a sandwich bonding, two cyclopentadienyl rings to give a structure with D_{5d} symmetry in which the metal atom assumes a krypton-like electron configuration. In accordance with this structure, the fundamental vibrations are divided as follows*:

$$\Gamma = 4\,a_{1g}(\mathrm{R, ia})+2\,a_{1u}(\mathrm{t, ia})+ a_{2g}(\mathrm{t, ia})+4\,a_{2u}(\mathrm{t, IR})+ 5e_{1g}(\mathrm{R, ia})+6\,e_{1u}(\mathrm{t, IR}) +6\,e_{2g}(\mathrm{R, ia})+6\,e_{2u}(\mathrm{t, ia})$$

Thus the emergence of ten active IR fundamentals was predictable and these have been recorded (Table I). There are fifteen Raman-active vibrations.

An important representative of this group of compounds is ferrocene, which can be oxidised to a ferricinium cation. Though the preparation, and the study of

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* R = Raman active, ia = IR inactive, t = Raman inactive, IR = IR active.

TABLE 1

FREQUENCIES OF THE NORMAL IR-ACTIVE VIBRATIONS OF FERROCENE

Vibration type	*Frequency* (cm^{-1})	*Species*
ν(CH)	3085, 3075	a_{2u}, e_{1u}
ν(CC)	1411, 1108	a_{2u}, e_{1u}
β(CH)	1002	e_{1u}
γ(CH)	834, 811	a_{2u}, e_{1u}
$\nu_{as}(Fe\pi_6)$	478	a_{2u}
$\gamma_{as}(\pi_6\pi_6)$		
tilt-vibration of rings	492	e_{1u}
$\delta(Fe\pi_6)$	170	e_{1u}

the structure of ferricinium salts has been the subject of many communications, no consensus of opinion about their structure obtains as yet. To elucidate this problem, we have prepared several of these compounds and studied their IR spectra.

PREPARATIVE STUDIES

Kealy and Pauson[5] discovered ferrocene and found that in concentrated sulphuric acid it dissolved to give a blue colour. Wilkinson et al.[6] explained this phenomenon as being the consequence of the oxidation of ferrocene, since the ferricinium cation thus produced has an unpaired electron which is easily brought into an excited state.

Generally, ferricinium salts have a complex structure characterized by the empirical formula $((C_5H_5)_2Fe)_n\ MX_4$, where $n = 1$ or 2, M is a metal (e.g. Fe, Ga, Ge, Hg) and X is a univalent anion. Among the salts formed with inorganic acids only ferricinium chloride (I), synthesised in 1965 by Nesmeyanov et al.[7] has been reported in the literature, and it was not considered to have a complex structure.

$(C_5H_5)_2FeCl$ (I)

However, this compound was prepared by *oxidation of ferrocene* with quinone in the presence of hydrochloric acid. While showing the bands said by Pavlik and Klikorka[8] to be characteristic of the ferricinium cation, the IR spectrum points to a substantial contamination by hydroquinone. OH-bands appear in the spectrum, and also the bands characteristic of para-disubstituted aromatic rings. Analytical results support the view that hydroquinone is present, while they also show a chlorine content near to theory but far less iron is found than the calculated amount. In the literature, only the chlorine content of the supposed ferricinium chloride is given[7]. Thus, by its apparent agreement with the calculated composition, these workers were obviously misled. According to Nesmeyanov et al.[7], the crude salt cannot be recrystallized without decomposition, so we used repeated extraction with ether to purify it. The analysis of the residue, however, suggested it to be ferricinium tetrachloroferrate (II), known in the literature[7,9-11], and was identified with it on the basis of its spectrum.

$$(C_5H_5)_2Fe_2X_4$$

(II), $X = Cl$; (III), $X = Br$; (IV), $X = I$; (V), $X = \frac{1}{2}SO_4^{2-}$; (VI), $4X = 2\,HSO_4^- + SO_4^{2-}$

Since there was the likelihood that this complex salt was the result of some decomposition that occurred during the repeated treatment with ether, we attempted the synthesis of ferricinium chloride by a different route. Ferrocene was dissolved in conc. H_2SO_4[8], then the diluted solution was treated with $BaCl_2$ equivalent to the H_2SO_4 present. However, the analyses of the ferricinium chloride thus obtained (and of the bromide, and iodide prepared similarly) again suggested a composition in agreement only with the respective complex salt, (II), (III) or (IV). Among the three salts, ferricinium tetraiodoferrate (IV), not yet described in the literature, is very sparingly soluble in cold water, so it could be obtained by treating a solution of ferricinium sulphate with potassium iodide. This latter observation allows the conclusion to be drawn that, in the course of oxidation by sulphuric acid, a complex salt (V) is also formed directly. In a careful processing of the oxidation mixture an amorphous substance was obtained, the analysis of which points to structure (VI).

For further studies we prepared the known ferricinium tetraiodomercurate (VII) besides the tetrachloro- and tetrabromomercurates, (VIII) and (IX), not yet described in the literature.

$$((C_5H_5)_2Fe)_2HgX_4$$

(VII), $X = I$; (VIII), $X = Cl$; (IX), $X = Br$.

SPECTROSCOPIC STUDIES

Pavlik et al.[8,12] draw from the IR spectra of ferrocene and ferricinium salts — according to them analogous — the conclusion that the molecular symmetry remains the same, i.e. that ferricinium salts are characterized by the structure shown in Fig. 1.

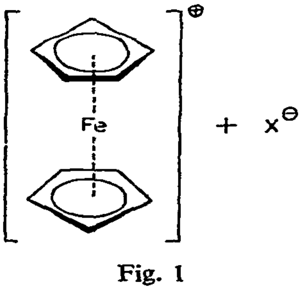


Fig. 1

Contrary to this, Fritz and Schäfer[13] aver that the spectrum of ferrocene and that of the compound later on proven to be ferricinium tetrachloroferrate, are essentially different. On this basis, and without giving detailed reasons, they also suppose that the structures are different, that ferricinium tetrachloroferrate is a dimer (Fig. 2) and that, in consequence, the arrangement according to Fig. 1, with X = $FeCl_4^-$, cannot exist. Furthermore, they find that the intensity of the band at 1114 cm^{-1} is significantly lower when compared to the maximum at 1108 cm^{-1} in the spectrum of ferrocene, and from this they deduce, without giving the reason why or giving an assignment for this band (which incidentally is a skeleton stretching vibration), that the covalent character of the ring–iron (π_6–Fe) bonding is relegated to the background when compared to ferrocene and to the hypothetical ferricinium cation of the structure shown in Fig. 1. According to them, the assignment of the band at 379 cm^{-1} is not certain, and might be attributed to ν(FeCl) or ν(Feπ_6) vibrations or to a superposition of these two.

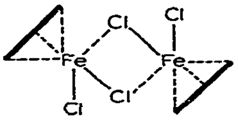


Fig. 2

A year later, Maitlis and Brown[14] suggested another structure (Fig. 3) based on their ligand exchange studies, and on the fact that reduction of ferricinium tetrachloroferrate with sodium borohydride yields ferrocene quantitatively. Both sets of results were incompatible with the structure shown in Fig. 2.

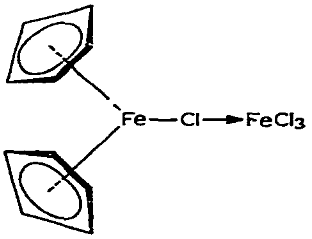


Fig. 3

The loss of intensity in the band at 1114 cm^{-1}, plus the shift towards lower frequencies of the bands at 492 and 479 cm^{-1} in the ferrocene spectra, led them to conclude, again without reason, that the cyclopentadienyl rings cannot be parallel as in ferrocene, but that the planes of the two rings intersect at a given angle. We may note in passing, that they erroneously assign the maxima at 492 and 479 cm^{-1} equally to ν(Feπ_6) vibrations while the latter belongs to the antisymmetric tilt-vibrations of the two rings[1].

Our idea is that because of the angle formed by the Fe–π_6 bonds in the case of the ferricinium salts studied by us, the coupling of the vibrations of the cyclopentadienyl rings ceases and the rings become, from a point of view of vibrations, independent units within the molecule.

The cyclopentadienyl ring, with D_{5h} symmetry, has 14 fundamental frequencies and since 10 of these are doubly degenerate, the number of normal vibrations is 24. These have been illustrated by Fritz[21]:

$$2a_1'+0a_1''+1a_2'+1a_2''+3e_1'+1e_1''+4e_2'+2e_2''$$

Since only species a_2'' and e_1' are active in the IR, the emergence of only 4 bands can be expected in the IR spectrum (the number of Raman bands is 7).

Fritz and Schäfer have studied the IR spectra of several metal salts of the cyclopentadienyl anion $[C_5H_5]^-M^+$, where M = alkali metal. According to their data[15], the number of relatively intense bands is considerably higher than four. The theoretical frequency values given by Billes[16] are in good agreement with experimental results. We think that the cause for this may be that, in the crystal aggregates, a polymer-chain association by sandwich bonds (Fig. 4) develops, and that in this association the vibrations of two cyclopentadienyl rings arranged in parallel become coupled. Similar coupling within associated chains has been observed[18] in other cases whereas such association structures have been postulated for imidazole and pyrazole derivatives in order to explain the diffuse structure and the low frequency of the ν(NH) band[17].

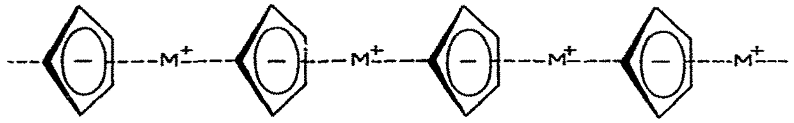
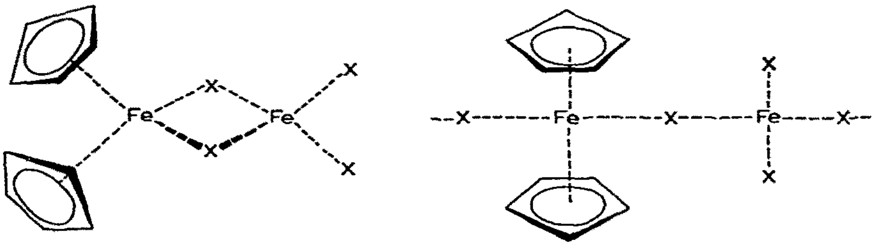


Fig. 4

According to our supposition, for ferricinium salts a tetragonal structure (Fig. 5a) exists, and this structure may become more or less deformed, as a function of the electronegativity and of space filling of the anions, so as to approach the planar arrangement shown in Fig. 5b.



(a) (b)

Fig. 5

The structure shown in Fig. 5b has D_{5d} symmetry, thus the emergence of 10 IR bands* would be in accord. There is no coupling between vibrations of the cyclopentadienyl rings in a structure such as Fig. 5a; thus here, with D_{5h} symmetry,

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* These conclusions are not affected by the theoretical possibility of ferrocene forming a structure with D_{5h} symmetry because of the low energy barrier to internal rotation, since in this case 10 IR-active vibrations would also appear.

4 IR bands would be produced. Vibrations of the Fe–π_6 and Fe–X bonds absorb in a region below 500 cm^{-1}. Among these, the frequencies of ν_{as}(Feπ_6) and ν_s(Feπ_6), and of ν_{as}(FeX) and ν_s(FeX), have nearly the same value while those of δ(Feπ_6) and δ(FeX) fall outside the measurable spectral domain. Thus when a structure such as Fig. 5a obtains, the emergence of only four IR bands can be expected in the region between 4000 and 500 cm^{-1}.

Our suppositions concerning the formation of the structure shown in Fig. 5a are definitely supported by the IR spectra of the ferricinium salts obtained by us, in so far as 4 intense bands emerge between 4000 and 500 cm^{-1}, the frequencies of which correspond to the ν_4–ν_7 type[21] vibrations expected to be active in the IR on the basis of a D_{5h} symmetry. To the $\nu_4-\nu_7$ vibrations (viz. to γ(CH), ν(CH), β(CH) and ν(CC), in this sequence) the bands at 850, 3100, 1010 and 1420 cm^{-1} can be assigned.

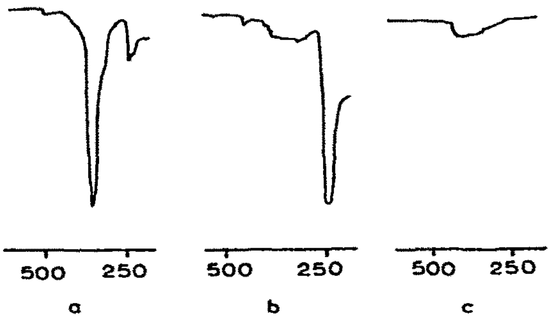

Fig. 6. Spectra of ferricinium tetrahalogenoferrates between 500 and 250 cm^{-1}. (a) chloro, (b) bromo, (c) iodo compound.

At 380 cm^{-1} and at 290 cm^{-1}, respectively, in the spectra of ferricinium tetrachloroferrate ((II), Fig. 6a) and of the tetrabromoferrate ((III), Fig. 6b) the ν(FeX) vibration is manifested by a highly intense band. The ν(FeI) band of ferricinium tetraiodoferrate ((IV), Fig. 6c) lies outside the measurable 4000 to 250 cm^{-1} domain. For (III) and (IV), the weak and diffuse ν(Feπ_6) band could also be identified between 450 and 300 cm^{-1} but for compound (II) this band coalesces with ν(FeCl) (Fig. 6). That the ν(Feπ_6) frequency is lower than that in ferrocene, where it is 478 cm^{-1}, is in good agreement with the contraction of the $\widehat{\pi_6\text{Fe}\pi_6}$ angle.

The deviations of the spectrum of structure 5a from the spectra of ferrocene and ferricinium salts therefore have a theoretical interpretation and, on this basis, the correctness of structure 5a cannot only be assumed, but can be said to be unequivocally proven in opposition to structures 1 and 5b. As far a sthe structure of Maitlis and Brown[14] is concerned (Fig. 3) the arrangement of the cyclopentadienyl rings is similar to 5a and differs from it in the configuration of the iron atoms only. Since the configuration in Fe^{III}-compounds is known to be tetrahedral, structure 3 is improbable all the more, because the differences in the spectra mentioned above, could not be interpreted by this structure.

The structure of Fig. 2 can be disregarded on the basis of the preparative studies described earlier[14]. However, if spectroscopic evidence is considered exclusively, only the appearance of the $\nu_{as}(Fe\pi_6)$, $\nu_s(Fe\pi_6)$ pair of bands would speak against it. But, since no splitting occurs in ferricinium tetrachloromercurates where it is certain that two cyclopentadienyl rings are linked to the same iron atom, the absence of splitting can never be regarded as an indication that would exclude structure 5a.

When structure 5a is distorted into structure 5b, some of the plus-bands forbidden in structure 5a but allowed in 5b may appear with low intensities due to perturbation effects. These bands corresponding to forbidden transitions are the more intense the stronger the perturbation effects become, i.e. the nearer structure 5a becomes structure 5b.

The stronger the repulsion between atoms X in the $(C_5H_5)_2Fe_2X_4$ molecule, the wider the $\widehat{XFeX}$ and the $\widehat{\pi_6Fe\pi_6}$ angle will become, thus the more structure 5a will be distorted.

In conformity with this, is the fact that the intensity of "forbidden bands" increases in the X = Cl, Br, I order within the (II)–(IV) series. In the spectrum of (II) and of (III), the relative intensity of the bands in question show mimina at 1110, and 1055 cm^{-1}, respectively, while these intensities are commensurable with those of the other bands in the case of ferricinium tetraiodoferrate (IV).

In ferricinium tetrahalomercurates, (VII)–(IX), a mercury atom is substituted for one of the iron atoms. As far as perturbation effects are concerned, in these compounds the differences between chloro-, bromo-, and iodo-compounds are smaller; this is shown by the fact that scarcely any change of intensity of "forbidden bands" is perceivable. Therefore, in a comparison of haloferrates with halomercurates, the most conspicious deviation appears for the iodo-compounds since, referred to the corresponding iodoferrates, iodomercurates show a far lower intensity in their "forbidden bands".

Since in all the spectra of the ferricinium salts* studied by us the four IR-active normal vibrations (in accordance with the D_{5h} symmetry of cyclopentadienyl rings) appear at the same frequency and relative intensity, we think it justified to assume that all these salts have the structure shown in Fig. 5a.

EXPERIMENTAL

Ferrocene

$FeSO_4 \cdot 4\,H_2O$ (50 g) is dehydrated on a bath (200°) under reduced pressure (20 torr) in a nitrogen gas stream until nearly all of the water is removed. The

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* On the basis of data in the literature, besides those discussed, we have prepared other ferricinium salts, e.g. picrate, molybdenate, reineckate, and the spectra of these were without exception of an analogous pattern.

temperature of the bath is then raised to 260° for 15 minutes. After cooling, the almost white residue is stirred with cyclopentadiene (42 ml) while cooled with ice, and then triethylamine (100 ml) is added. The suspension is stirred for 24 hours at room temperature, then processed as described in the literature[19]. Yield of ferrocene is 31.5 g or 68 %. M.p. 172–174°. Lit.[20] m.p. 173–174°.

Ferricinium tetrachloroferrate (II)

1. "Ferricinium chloride"[7] (calc. for $C_{10}H_{10}FeCl$: Fe 25.2, Cl 16.1 %; found: Fe 16.0, Cl 14.6 %) is boiled on a water bath with dry ether; then the solvent is decanted without cooling. After six repetitions of this treatment 0.3 g substance remains from the 1 g originally taken. Calc. for $C_{10}H_{10}Fe_2Cl_4$: Fe 29.11, Cl 36.96 %; found: Fe 28.10, Cl 35.31 %.

2. Through the dark blue solution of ferrocene (0.95 g) in conc. sulphuric acid (2.5 ml) a stream of oxygen is bubbled for 2 hours at steam bath temperature. After cooling, the reaction mixture is diluted to 50 ml with water, and the sulphate is removed with a 5 *N* solution of barium chloride. The filtrate is evaporated in vacuo at 30°, the solid residue is suspended in isopropanol, and washed with isopropanol and ether. The final residue is a grey-green powder (0.45 g). Found: Fe 26.4 % and Cl 33.3 %.

The crude chloroferrate (II) is recrystallized from ethanol (50 ml) to yield dark blue crystals. Found: Fe 28.35 % and Cl 36.62 %.

Ferricinium tetrabromoferrate (III)

As in the preceding sulphuric acid oxidation but with barium bromide treatment, 0.7 g crude bromoferrate (III) is obtained which, after recrystallization from ethanol, yields a brown powder. Calc. tor $C_{10}H_{10}Fe_2Br_4$: Fe 19.89, Br 56.93 %; found: Fe 19.72, Br 56.14 %.

Ferricinium tetraiodoferrate (IV)

1. The oxidation mixture described above is treated in a similar way with a 5 *N* solution of barium iodide. The iodoferrate salt (IV) precipitates together with barium sulphate in the form of a light grey powder. This is collected by filtration, washed with water, then boiled in a 1 *N* solution of hydrogen iodide (50 ml) and filtered while hot. On cooling, a crystalline substance (0.1 g) separates from the filtrate. This is the same substance as prepared by methods 2 and 3.

2. To the dilute sulphuric acid solution, potassium iodide (10 g) dissolved in water (20 ml) is added, the precipitate is filtered off and washed with water, ethanol, and ether. The grey powder (0.8 g), when recrystallized from ethanol, yields violet needles. Calc. for $C_{10}H_{10}Fe_2I_4$: Fe 14.9, I 67.73 %; found: Fe 14.45, I 68.19 %.

3. To ferrocene (1.9 g) dissolved in carbon tetrachloride (75 ml), iodine (7 g) is added and the mixture is boiled for one hour on a water bath. The precipitate is filtered from the still hot solution, then washed with carbon tetrachloride, ethanol, and ether. The crude iodoferrate (IV) is boiled in ethanol (200 ml), cooled, filtered and washed with ethanol and ether. A blue-grey substance (2.5 g) is obtained in which 14.67 % Fe and 67.50 % I is found. Nesmeyanov et al.[7] prepared a ferricinium salt containing 67.19 % iodine, but attributed a "tri-iodide" structure, $C_{10}H_{10}FeI_3$, to it.

Ferricinium sulphate (VI)

The reaction mixture obtained in the sulphuric acid oxidation of ferrocene (0.95 g) is diluted, while cooled, with ethanol (110 ml) and then with ether (400 ml). The solvent is decanted off the oil that separates, the residue is redissolved in ethanol and again admixed with ether. The syrup, left after decanting the solvent, solidifies when stirred with isopropanol. After filtration, and washing with isopropanol and ether, a light blue-grey substance (0.3 g) is obtained. Calc. for $C_{10}H_{10}FeSO_4 \cdot 2\,HSO_4$: C 22.55, H 2.27, S 18.08, Fe 20.95 %; found: C 22.12, H 2.38, S 17.20, Fe 20.40 %.

Ferricinium tertrachloromercurate (VIII)

Ferrocene (0.95 g) oxidized in sulphuric acid is diluted, while cooled, to 20 ml with water, then a mixture of $HgCl_2$ (1.35 g) dissolved in water (20 ml) and of KCl (0.8 g) dissolved in water (10 ml) is added. The precipitate, washed with water, ethanol, and ether, is a violet-blue salt (2.4 g), (VIII), which is recrystallized from ethanol (250 g). The pure tetrachloromercurate salt separated in the form of dark blue needles (0.8 g). Calc. for $C_{10}H_{10}FeHgCl_4$: Fe 15.67, Cl 19.84 %; found: Fe 15.33, Cl 19.42 %.

Ferricinium tetrabromomercurate (IX)

With $HgCl_2$ (1.35 g) and KBr (2.4 g) the complex salt is precipitated like the tetraiodomercurate (VIII). The crude tetrabromomercurate (3.7 g), (IX), recrystallized from ethanol (500 ml), gives a dark blue, powdery crystalline substance (0.8 g). Calc. for $C_{10}H_{10}FeHgBr_4$: Fe 12.57, Br 35.81 %; found: Fe 12.10, Br 35.02 %.

IR spectra were recorded of samples in KBr pellets and in suspension in nujol. The records obtained were the same. Between 4000 and 400 cm^{-1}, spectra were recorded with a Zeiss UR-10 (Jena) spectrometer, while between 400 and 250 cm^{-1} a Perkin-Elmer 457 instrument was employed.

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