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ESCA and Mössbauer Spectra of some Iron(III) Betadiketonates and Tetraphenylporphyrin Iron(III) Chloride

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X-ray photoelectron spectra and Mössbauer spectra have been recorded for the complexes Fe(1-phenyl-1,3-butanedionate)$_3$, Fe(1,3-diphenyl-1,3-propanedionate)$_3$, Fe(3-phenyl-2,4-pentanedionate)$_3$ and meso-tetraphenylporphyrin iron(III) chloride. As an auxiliary tool in the study the IR absorption intensity of the ν_{CH} vibrations of the phenyl groups present in the complexes was measured. By a combination of the XPS binding energies and the IR intensities with previously established relations between these entities and the effective charge of atoms and groups, a rather complete mapping of the charge distribution of the complexes was achieved. By a combination of the XPS data with the Mössbauer data it was possible to describe the electron population in the (3d, 4s, 4p) orbitals of the central iron atom.

Introduction

In a project aiming at interrelating ESCA and Mössbauer data for a series of iron compounds and starting with papers [1, 2] it is required that the compounds should contain phenyl groups in one way or another. This condition was set up because it should be possible to calibrate the ESCA spectra in the way that had been introduced previously [3], *viz.*, using the C_{1s} binding energy, $E_b(C_{1s})$, as an internal standard. That method has been applied to ESCA investigations on other metal complexes, *e.g.* [4, 5].

$E_b(C_{1s})$ of the phenyl group is assigned from a measurement of the infrared absorption intensity of the C–H stretching vibrations of the phenyl group [3]. It has also been shown in another paper [6] that the same intensity value can be used to estimate the effective charge of the phenyl group.

The aim of this work is to map the charge distribution within some iron(III) complexes in terms of effective charges on the atoms. Because of the above-mentioned requirement the phenyl substituted iron(III) betadiketonates and tetraphenylporphyrin Fe(III) chloride were chosen as test systems to probe the potentialities of the technique. Unfortunately it is not possible to determine the effective charge of the hydrogen atoms with the ESCA method. Therefore it is in principle not possible to determine the effective charge of iron, q_{Fe}, and to couple the data with Mössbauer isomer shift to determine the population of the iron atom in the way discussed in [7].

This treatment implies [1, 7] the solution of the system of equations:

$$E_b\,(\text{Fe 2p}) = f_1\,(n(3d), n(4s), n(4p)) \quad (1)$$

$$\delta(\text{Fe}) = f_2(n(3d), n(4s), n(4p)) \quad (2)$$

$$q_{Fe} = 8 - n(3d) - n(4s) - n(4p) \quad (3)$$

This partitioning of the metal charge into s, p and d populations will hopefully give a more complete picture of the metal–ligand interaction.

In the present case, eqns. (1) and (2) were calibrated against extended Hückel SCC calculations with the additional (rather arbitrary) requirement that q_{Fe} was set to twice the value obtained from the calculations. This rule of thumb was found to hold rather well for the iron complexes investigated in [1].

The proposed procedure requires in a strict sense independent knowledge of q_{Fe}, E_b (Fe 2p) and the isomer shift δ(Fe). As indicated above this condition is not fulfilled for the present complexes. Nevertheless we feel that the close relation of δ to the 4s population and that of E_b (Fe 2p) to the 3d population [1, 7] will give a useful description of the status of the central atom in the complexes. One could therefore attempt to use for q_{Fe} that value which results from the experimentally obtained, rather

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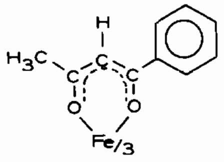

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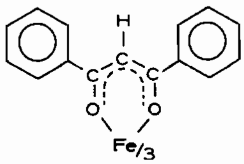

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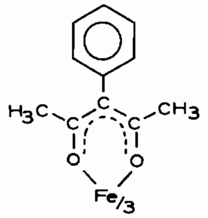

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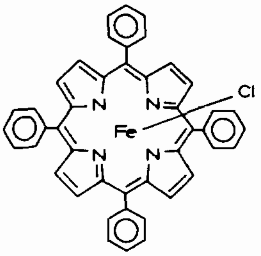

IV

Fig. 1. The formal structure of the complexes under investigation. I: Fe(1-phenyl-1,3-butanedionate)$_3$; II: Fe(1,3-diphenyl-1,3-propanedionate)$_3$; III: Fe(3-phenyl-2,4-pentanedionate)$_3$; IV: meso-tetraphenylporphyrin Fe(III) chloride.

approximate, relation between E_b (Fe 2p) and q_{Fe} described in [2], *viz.*,

$$E_b(\text{Fe 2p}) = 6.5\, q_{Fe} + 704.2 \qquad (4)$$

It is of course not quite consistent to use the 2p core level shift in two different ways. However, the domination of δ and E_b(Fe 2p) in determining the 4s and 3d populations, respectively, has been noted above. This will mean that an error in the charge (caused by the application of eqn. (4)) will be reflected mainly as an error in the 4p population. With this limitation the results might be used for comparisons between complexes of similar type.

To aid the following discussion we reproduce the formula of the complexes in Fig. 1.

Experimental

Infrared spectra were recorded with a PE 580 spectrophotometer in the range 3400–2800 cm^{-1}. They were run repeatedly, and data were accumulated and treated on a PE Data Station. The area of the bands corresponding to the aromatic C–H vibrations were measured with a planimeter after the spectra (properly magnified) had been displayed again on paper. The samples were dissolved in $DCCl_3$ and measured in 0.1 mm CaF_2 cells.

The ESCA spectra were recorded with an AEI ES 200 spectrometer as described in detail elsewhere [4]. The binding energies were calibrated relative to the C_{1s} value $E_b\,(C_{1s})_{phenyl}$ obtained from the IR intensity (A_{CH}) just mentioned using the formula (5) representing the line of Fig. 2 in the first paper [3] on the methodology of the present series of XPS investigations.

$$E_b(C_{1s})_{phenyl} = -6.82\cdot 10^{-4}\, A_{CH} + 285.9 \qquad (5)$$

The Mössbauer spectra were recorded in the same way as described in [2].

The betadiketonates were prepared following literature prescriptions [8]. Results of elemental analysis were:

I: H found 5.1%, calc. 5.0%; C found 66.3%, calc. 66.6%; Fe found 9.9%, calc. 10.5%; m.p. found 218 °C, reported 218 °C.

II: H found 4.5%, calc. 4.55%; C found 70.9%, calc. 75.5%; Fe found 7.3%, calc. 7.7%; m.p., found *ca.* 270 °C, reported 262 °C.

III: H found 5.8%, calc. 5.72%; C found 68.4%, calc. 68.2%; Fe found 9.1%, calc. 9.6%; m.p., found *ca.* 250 °C.

The tetraphenylporphyrin iron(IIII) chloride was a commercial preparation, and was used without further purification.

As the HC=CH absorption of the pyrrol-related rings in the porphyrin structure coincides with that of the phenyl C–H stretching, the following procedure was undertaken: The spectra of 2.5-dimethylpyrrole and 3-pyrroline were measured and the C–H stretch absorption intensity was determined for each of the substances. As the structure related to each of them is formally present in the porphyrin molecule twice, the measured intensity of the porphyrin phenyl group was decreased with the mean value of A_{CH} of the model molecules.

Results

ESCA Investigation

The relevant data are collected in Table I. The C_{1s} spectra of the three diketonates are given in Fig. 2. Within the resolution of our spectrometer one can

TABLE 1. Experimental Values of IR Intensity, Binding Energies and Mössbauer Parameters. A_{CH} is given per phenyl group. The upper row of binding energies represents the original data, the second row represents the corrected values.

Complex	$A_{CH}\cdot 10^{-2}$ M^{-1} cm^{-2}	Ref C_{1s}	Fe $2p_{3/2}$/eV	C_{1s}			O_{1s}/eV	N_{1s}/eV	Cl_{2p}/eV	δ/mm s^{-1}	Δ/mm s^{-1}
				terminal	phenyl/methyl	central					
			711.8	287.4	285.3	284.3	532.0				
I	14.3	284.9	711.4	287.0	284.9	283.9	531.6			0.259	0.761
			710.9	287.0	284.9	283.0	531.4				
II	13.8	285.0	711.0	287.1	285.0	283.1	531.5			0.274	0.00
			711.9	287.4	285.5	284.6	532.1			0.232	0.787
III	21.4	284.4	710.8	286.3	284.4	287.5	531.0			0.681	0.004
IV	18.7*		708.7	283.4				397.1	197.3		
2.5-dimethylpyrrole	1.6										
3-pyrroline	2.9										
IV	16.5**	284.8	710.1	284.8				398.5	198.7	−0.041	0.00

*Total value. **Corrected value (see Experimental).

observe an extra peak at about 2 eV lower kinetic energy and one at about 2 eV higher kinetic energy relative to the main peak. The ratios of these peaks were about 2:7:1, 2:12:1 and 2:8:1 for the complexes I, II and III, respectively. We therefore suggest that they correspond to terminal, phenyl + methyl and central carbon atoms, respectively. As we could not resolve the methyl and the phenyl peaks, these carbon atoms must have about the same binding energy and hence (in our model) about the same effective charge.

To get more precise information on the positions of these three peaks on the energy scale, we performed a computer analysis of the experimental curves. By successively fitting three Gaussian curves [9] we obtained three components as shown in Fig. 2. The ratios of the peak areas are given in the text of the figure. Within the precision of the analysis the area ratios are those expected and we therefore feel confident that we can identify the terminal and central carbons of the chelate ring.

The effective charges on the atoms in the complexes have been estimated from our previously established relations:

$E_b(N_{1s}) = 7.00\, q_N + 401.4$ eV [10]

$E_b(C_{1s}) = 11.5\, q_C + 284.8$ eV [10]

$E_b(Cl_{2p}) = 4.25\, q_{Cl} + 201.2$ eV [4]

$E_b(O_{1s}) = 6.04\, q_O + 535.6$ eV [11]

$E_b(Fe_{2p}) = 6.5\, q_{Fe} + 704.2$ eV [2]

The charge on the entire phenyl group was derived from the relation (6) between $q_{C_6H_5}$ and the intensity of the IR band of CH stretching, *i.e.* the same quantity that has been used above for the calibration of C_{1s} of the phenyl carbons.

The provisional, analytical form of this not yet quite established relation can be written as:

$$q_{C_6H_5} = +5.6 \times 10^{-4}\ A - 0.36$$

$$A < 10 \times 10^{2}\ M^{-1}\ \text{cm}^{-2} \qquad (6a)$$

$$q_{C_6H_5} = -2.52 \times 10^{-4}\ A + 0.51$$

$$A > 10 \times 10^{2}\ M^{-1}\ \text{cm}^{-2} \qquad (6b)$$

The results of these estimations are collected in Table II. The remaining parts of the betadiketonate ligands are the CH_3 groups and the hydrogen atom at the central carbon. In the last columns of Table II, the charges of these groups or atoms are given ('rest charge'). This rest charge is obtained from the difference between zero (= the charge of the entire

TABLE II. Experimental Charges on the Atoms and Groups of the Complexes Investigated.

Complex	q_{Fe}	q_{Ph}	q_C (terminal)	q_C (phenyl/methyl)	q_C (central)	q_O	q_{rest}	q_H (central)	q_H (CH_3)
I	+1.11	+0.15	+0.19	+0.01	–0.08	–0.66	+0.50	+0.23	+0.09
II	+1.05	+0.16	+0.20	+0.02	–0.15	–0.68	+0.44	+0.44	–
III	+1.02	–0.03	+0.13	–0.03	–0.11	–0.76	+1.06	–	+0.19
	q_{Fe}	q_{Cl}	q_N						
IV	+0.91	–0.59	–0.41						

complex) and the sum of all the estimated charges on all other atoms and groups. For the complex III the remaining charge per ligand is that of the two methyl groups. Hence each group would carry a charge of +0.53. The charge of the carbon atom in that CH_3 group is very small and probably about –0.03. We thus find that each H-atom in the CH_3 group would carry a charge of about +0.19. Similarly, for the complex II we arrive directly at q_H = +0.44 for the hydrogen bonded to the central

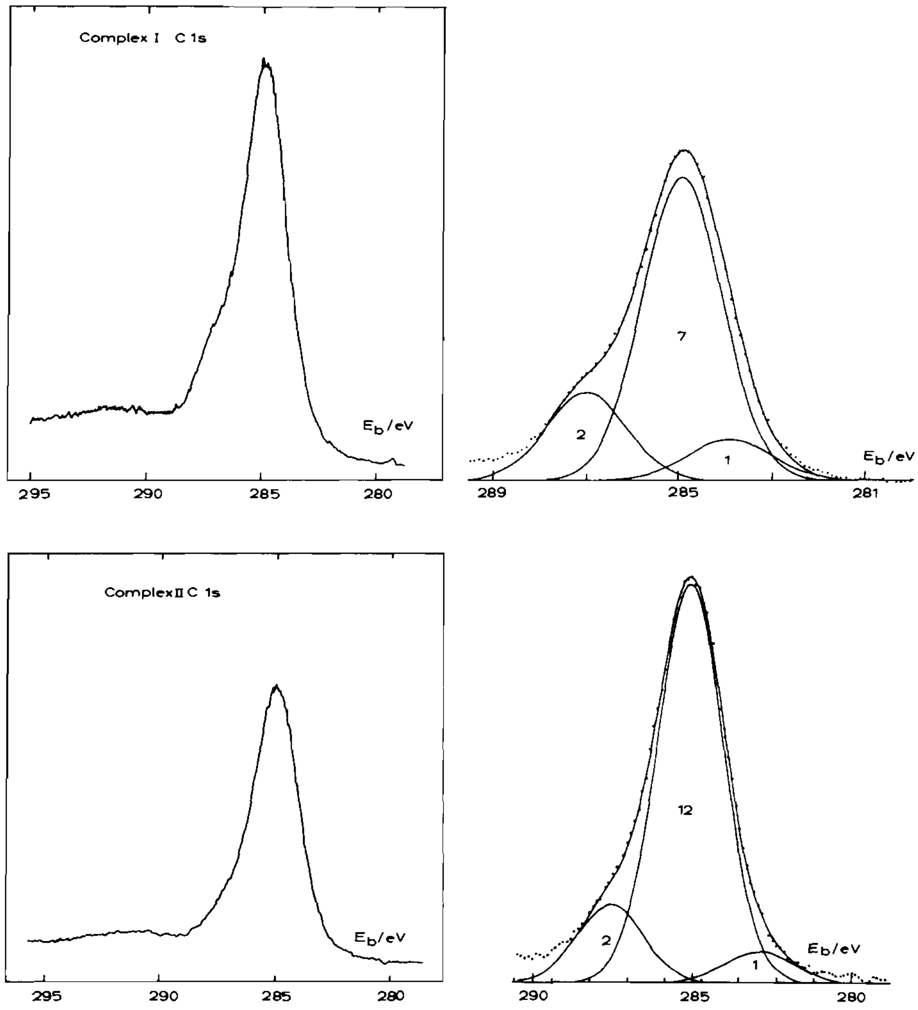

Fig. 2. *(For caption see facing page.)*

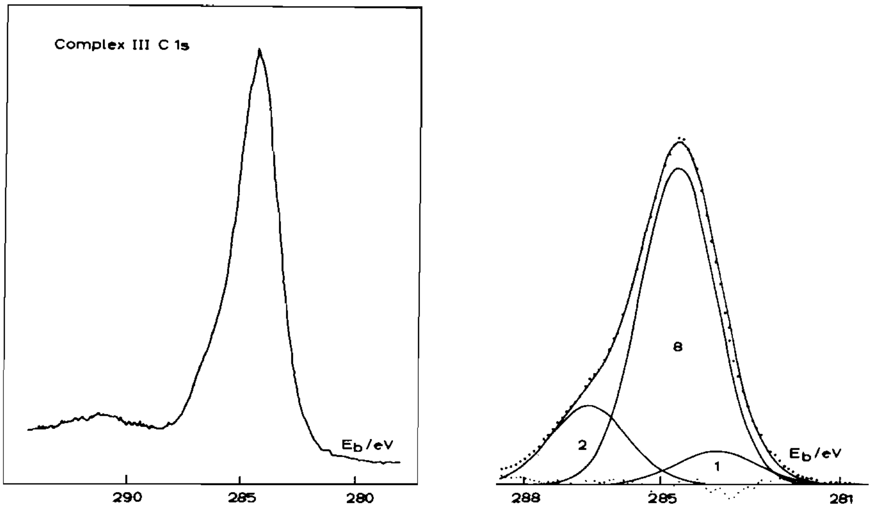

Fig. 2. Curve analysis of the C_{1s} peaks of the complexes I, II and III. The ratios of the areas are (left to right): complex I, 2.1: 7.3:1; complex II, 2.3:12:0.9; complex III, 2:7.9:0.9.

carbon atom. In complex I the remaining charge is composed of that for the central H atom and one methyl group. For want of better information we have split it up in proportion using the data from complexes II and III.

$$q_{CH_3} = \frac{0.53}{0.53 + 0.44} \times 0.50 = +0.27$$

$$q_H = \frac{0.44}{0.53 + 0.44} \times 0.50 = +0.23$$

Thus the charge on each H atom of the CH_3 group of complex I is something like $(0.27 - 0.01)/3 = +0.09$.

It might be worth noting that the hydrogen charges thus obtained agree quite well with recently reported q_H values from *ab initio* calculations on methane derivatives [12]. Wiberg thus found [12] that using a conventional population analysis q_H is +(0.10 – 0.15) for many derivatives. Especially interesting here however is the finding that for a positively charged neighbour such as $^+H_3NCH_3$, the carbon is mildly negative and the hydrogens are positive ($q_H = +0.18$). A similar situation holds for the methylcyanides.

As we have based our binding energy–charge correlations on effective charges from population analyses [3, 4, 5, 10], we consider it congruent to make the comparison with that part of Wiberg's work. (The main object of Wiberg's work [12] is, however, to determine charges from electron distribution functions; they are slightly different from those discussed here.)

Furthermore, one can note that the positive character of hydrogen at the central carbon (and the negative charge of this atom) fits with the well-documented electrophilic substitution reactions at this position (*e.g.* Collman [13]). The precise value of the charge on this central hydrogen atom should not be taken too literally, however. It is strongly dependent on errors in the entities used for its calculation. *E.g.*, an error of ±5% in A_{CH} reflects itself as an error in $q_{C_6H_5}$ of about ∓0.01 charge units and therefore in q_H as ±0.02 charge units. For clarity we present the resulting data in a pictorial form in Fig. 3.

For the porphyrin complex we do not have the same possibility of a detailed mapping of charges in the molecule. One can note, however, that the charge on the iron atom is estimated as $q_{Fe} = +0.91$. Similarly $q_{Cl} = -0.59$. The Fe–Cl bond thus has a polarity of the same magnitude as that of other Fe(III) Cl complexes, *e.g.* $FeCl_4^-$ [4, 14]. Possibly the chloride atom is somewhat more negatively charged in the present complex.

Mössbauer Investigation

The data for isomer shifts and quadrupole splittings are reported in Table I. The shifts are given with Fe in Rh as reference substance. A typical spectrum is given in Fig. 4. One notices that the complexes of highest symmetry, complexes II and IV, do not show any quadrupole splitting. The two sets of data obtained for complex III might be related to two different crystallographic positions of the iron atom in relation to the phenyl groups. One of these positions should then be almost as symmetric as those of complexes II and IV. The values of δ and Δ can be compared, *e.g.*, with those reported by Frank and Drickamer [15]. The isomer shifts so determined

TABLE III. Electron Population of the 3d 4s 4p Orbitals of the Complexes I–IV Determined via Eqns. (1)–(4).

Complex	n(d)	n(s)	n(p)	q_{Fe} (from eqn. (3))
I	6.72	0.13	0.59	+0.56
II	6.76	0.13	0.59	+0.52
III	6.77	0.17	0.56	+0.50
IV	6.80	0.39	0.36	+0.45

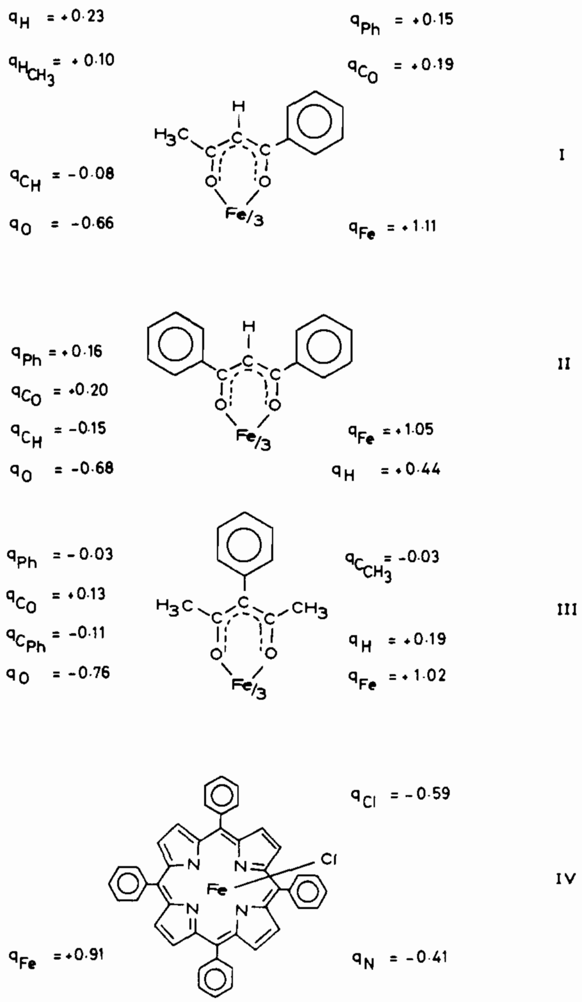

Fig. 3. The charge distribution of the complexes determined 'experimentally' as described in the text.

can now be coupled to the ESCA data and used for the estimation of spd occupation numbers from eqns. (1)–(3). The results of these operations are given in Table III.

One notices at once that the variation of the population profile for the three betadiketonate complexes is very small. Complex III shows the highest value of n(4s), a finding that is related to the fact that this complex has the lowest value of δ of the three compounds. Including the tetraphenylporphyrin in the comparison, one can note a more drastic variation in the 4s and 4p occupation numbers. The s and p orbitals are more evenly populated in this latter complex and the s orbital is the one that has an increased population.

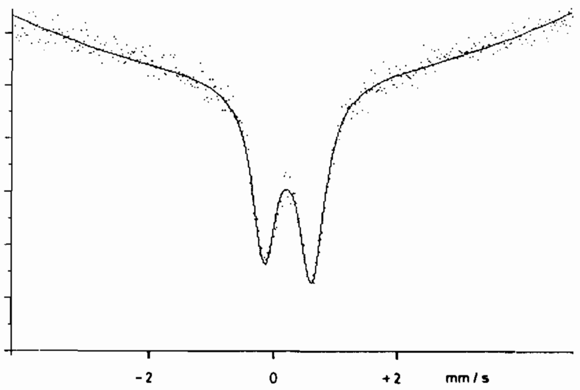

Fig. 4. A representative Mössbauer spectrum of complex I.

This 'experimental' observation can perhaps be seen to reflect the different demands on 3d, 4s and 4p orbitals for an octahedral and a square planar arrangement. For iron dithiolate complexes the 4s and 4p contributions, obtained by extended Hückel calculations, are considerably reduced in the 'octahedral' tris complexes as compared to the planar ones [2]. This analogy is interesting and makes us believe that the experimental calculation of occupation numbers as done here can be useful.

Comparison with Other Investigations

Few all-electron calculations have been published on betadiketonate complexes of iron. Of other metals the work by Schaaf *et al.* [16] on aluminium complexes may be quoted. This system is however not similar to the present ones, as there is no d-orbital participation in the Al(III)–oxygen bonding, whereas the present results show a very strong participation of d-orbitals in the iron(III) oxygen bond. The charge derived by Schaaf *et al.* [16] was q_{Al} = +0.49 (CHELEQ) or q_{Al} = +1.27 (CNDO/2).

π-electron calculations have, however, been performed and the π-densities on the atoms of the chelate ring (of the free ligand) are given by Forster as –0.66, +0.36 and –0.39 for oxygen, peripheral and central carbons, respectively [17]. The same successive change of signs was also found in our present work (Fig. 3).

Experimental determinations of the charge of the metal ion in a series of acetylacetonato complexes have been attempted, however, by Maijs [18] in his studies on the applicability of the Haber–Born–Kapustinskii cycle to elucidate bond properties. One notices that for iron(III) Maijs reports $q_{Fe} = +1.2$ [18]. This value is in very good agreement with our data if one performs an extrapolation from two over one to zero numbers of phenyl groups (*cf.* Table II).

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