Structure—Redox Potential Relations of some Tris(β-dicarbonylato)iron(III) Chelates

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Abstract

The polarographic behaviour of a series of tris(β-dicarbonylato)iron(III) chelates is reported. Conventional polarography and voltametric studies in acetonitrile revealed that these complexes undergo a one-electron reduction process at the Hg and carbon fibre electrodes. The influence of substituents within the β-dicarbonylato moiety is discussed in terms of Hammett σ functions. Reduction potentials are related to Racah's interelectronic repulsion parameter B and to the energy of the spin-forbidden transition $^4T_{2g} \leftarrow {}^6A_{1g}$. The polarographic behaviour of binary mixtures indicates that ligand exchange in solution is a fast process and formation of mixed-ligand chelates in solution with predetermined stoichiometry is unlikely.

Introduction

The redox properties of metal transition complexes is a topic of current interest since they are associated with photochemically as well as biologically important electron transfer reactions [1–4]. In a great many complexes the redox properties are associated with the metal orbitals since they usually constitute the frontier orbitals involved in the electron transfer processes. Chelation changes the energies of the electrons on the central atom and when a closely related set of organic ligands encompassing a large group of substituents is available it is possible to observe relatively subtle effects of remote groups [5–9]. Electrochemical as well as photophysical studies have established that for a given oxidation state and coordination geometry both the central atom and the ligand substituents affect the redox potential [10–11]. Such studies help to elucidate the factors influencing the redox potentials of the metal complexes and augment the predictive capabilities for the synthesis of chelates with predetermined redox characteristics [12, 13].

The β-diketonato complexes are particularly suitable for electrochemical studies since they are easily prepared and readily soluble in a great variety of organic solvents. Moreover there is a wealth of information regarding their spectral and structural characteristics. In addition the electrochemical behaviour of the corresponding complexes of chromium(III), cobalt(III), copper(II) and ruthenium(III) has been the focus of thorough investigations [5–10]. The tris(β-diketonato)iron(III) chelates have not attracted similar attention and the existing results refer to a few complexes and their behaviour in solution at the platinum and mercury electrodes [14]. In this report the electron-transfer behaviour of the aforementioned complexes is investigated with the use of electrochemical techniques.

In particular fifteen tris(β-dicarbonylato)iron(III) chelates corresponding to the general formula I and three square pyramidal complexes having the general formula II were prepared and their electrochemical behaviour in acetonitrile solution was investigated by conventional polarography and cyclic voltametry at the mercury and carbon fibre electrodes. The complexes employed are listed in Table I.

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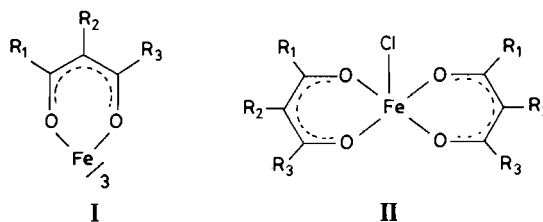
Experimental

Preparation of Compounds

Tris(1,3-dicarbonylato)iron(III) chelates

Most of the ligands were obtained commercially. The ligands not commercially available were synthesized by the condensation of an ester and a ketone according to the method of Collman *et al.* [15]. The tris(β-diketonato)iron(III) complexes were prepared as described in the literature [16] and, when feasible, were purified by sublimation under

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TABLE I. Names and Abbreviations of the Compounds Investigated

	Compound	R_1	R_2	R_3	Name	Melting point (°C)		References
						Found	Literature	
1	Fe(bdo)$_3$	H	H	CH$_3$	tris(1,3-butanedionato)iron(III)	134–136	135–137	16
2	Fe(ppdo)$_3$	Ph	H	H	tris(1-phenyl-1,3-propanedionato)iron(III)	172	171–172	16
3	Fe(bpdo)$_3$	CMe$_3$	H	H	tris(4,4-dimethyl-1,3-pentanedionato)iron(III)	102–104	104	16
4	Fe(acac)$_3$	CH$_3$	H	CH$_3$	tris(2,4-pentanedionato)iron(III)	189	189	16
5	Fe(acac-Cl)$_3$	CH$_3$	Cl	CH$_3$	tris(3-chloro-2,4-pentanedionato)iron(III)	153–155	154	17
6	Fe(acac-CN)$_3$	CH$_3$	CN	CH$_3$	tris(3-cyano-2,4-pentanedionato)iron(III)	244	244	18
7	Fe(acac-NO$_2$)$_3$	CH$_3$	NO$_2$	CH$_3$	tris(3-nitro-2,4-pentanedionato)iron(III)	196	196	17
8	Fe(bzac)$_3$	Ph	H	CH$_3$	tris(1-phenyl-1,3-butanedionato)iron(III)	211	211	16
9	Fe(tfac)$_3$	CF$_3$	H	CH$_3$	tris(1,1,1-trifluoro-2,4-pentanedionato)iron(III)	114	114	16
10	Fe(btfac)$_3$	CF$_3$	H	Ph	tris(1-phenyl-4,4,4-trifluoro-1,3-butanedionato)iron(III)	140	140	16
11	Fe(hfac)$_3$	CF$_3$	H	CF$_3$	tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(III)	47	47	16
12	Fe(dpmo)$_3$	CMe$_3$	H	CMe$_3$	tris(2,2,6,6-tetramethyl-3,5-heptanedionato)iron(III)	162–163	163	16
13	Fe(dzpmo)$_3$	CMe$_3$	H	Ph	tris(1-phenyl-4,4-dimethyl-1,3-pentanedionato)iron(III)	157		this work
14	Fe(dbmo)$_3$	Ph	H	Ph	tris(1,3-diphenyl-1,3-propanedionato)iron(III)	263–264	265	16
15	Fe(tert-Bu-tfa)$_3$	CF$_3$	H	CMe$_3$	tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)iron(III)	65(dec.)[a]		this work
16	Fe(acac)$_2$Cl	CH$_3$	H	CH$_3$	bis(2,4-pentanedionato)iron(III) chloride	171		20
17	Fe(bzac)$_2$Cl	Ph	H	CH$_3$	bis(1-phenyl-1,3-butanedionato)iron(III) chloride	192		20
18	Fe(dbmo)$_2$Cl	Ph	H	Ph	bis(1,3-diphenyl-1,3-propanedionato)iron(II) chloride	231		20

[a]dec., decomposition.

vacuum. Further purification of the non-fluorinated complexes was obtained by recrystallization, initially from CCl_4 and subsequently from acetonitrile.

The 2-substituted derivatives of $Fe(acac)_3$ were prepared as suggested by Dose and coworkers [17] while the corresponding 2-cyano compound was obtained according to the procedure described by Fackler [18].

Bis(1,3-diketonato)iron(III) chlorides

The square pyramidal complex $Fe(acac)_2Cl$ was prepared by reacting the tris-chelate, $Fe(acac)_3$, with the stoichiometrically required amount of concentrated hydrochloric acid (37%) in chloroform solution at room temperature under vigorous stirring. The same product was obtained following the method of Takeda *et al.* [19]. The complexes $Fe(bzac)_2Cl$ and $Fe(dbmo)_2Cl$ were prepared as suggested by Cox and collaborators [20].

The reaction of Fe(acac)₂Cl with Nabtfac

A quantity of the sodium salt of 1-phenyl-4,4,4-trifluoro-1,3-butanedione, Nabtfac, dissolved in ethanol is added dropwise under continuous stirring to an ethanolic solution of equimolar quantity of $Fe(acac)_2Cl$. Then small amounts of water are added carefully to separate the reaction product. After grinding to a fine powder the amorphous precipitate is washed with H_2O and is then dried under vacuum. Yield 70%.

Apparatus and Electrodes

All polarographic measurements were made on a Metrohm E536 polarography apparatus. The voltametric unit employed was a BANK AG model 17. The current—voltage curves were recorded using a servoscribe X—Y recorder. The cell system was carefully selected to avoid contamination by water and oxygen. The working electrode was either an ordinary hanging Hg-electrode (Metrohm) or a carbon fibre one (Celion GY-70SE) obtained from Celanese, U.S.A. The cell contained a platinum wire auxiliary electrode. A calomel electrode saturated with NaCl (SCE) served as reference electrode. It was connected to the cell by means of a porous Vicor rod to prevent water contamination. This three-electrode arrangement permitted compensation for cell resistance.

Electrochemical Measurements

The techniques of conventional DC polarography and cyclic voltametry (CV) were employed in the present study. The solutions were 0.1 M with respect to the supporting electrolyte, Et_4NClO_4 (TEAP), whereas the concentration of the iron(III) chelate was 5×10^{-4} M. Chelates having the $-C(CH_3)_3$ group were poorly soluble in CH_3CN and the maximum concentration attained in saturated solution was in these cases in the order of 10^{-4} M. Oxygen

was excluded by purging the solution with pre-purified nitrogen which was pre-saturated with solvent. The electronic spectra of the complexes were obtained before and after the electrochemical measurements and were examined for solvolysis or decomposition. There was some change in the UV—Vis spectrum of the fluorinated compounds when the acetonitrile solutions were kept for long time. The change consisted of a blue shift of the first change transfer band and a lowering of the extinction coefficient at the band maximum. Such variations were not noticeable immediately after the dissolution of the complexes. For this reason solutions of the fluorinated compounds were made just before measurements. In addition, measurements were made in propylene carbonate since the stability of the iron(III) chelates in this solvent is greater.

The cyclic voltammograms on the carbon fibre electrodes were recorded up to *ca.* -2 V *vs.* SCE (NaCl) because of the intercalation of the $(C_3H_5)_4N^+$ ions in the graphite lattice of the fibres at more negative potentials [21]. The current values given in the voltamograms refer to a hanging Hg electrode of 3.5 mm^2 surface area and to the unit of the effective area of the carbon fibres. The effective fibre area in acetonitrile solution was determined experimentally by means of the reversible $Fe(CN)_6^{4-} - e \rightleftharpoons Fe(CN)_6^{3-}$ system. The peak currents for this system obtained at the carbon fibres in acetonitrile solutions were compared to the corresponding currents at a smooth Pt wire of known real surface area, in the same solutions.

Physical Measurements

The electronic absorption spectra in acetonitrile solution were measured on a Perkin-Elmer Hitachi 200 recording spectrophotometer. The infrared spectra in the region 4000—300 cm^{-1} were recorded on a Perkin-Elmer 467 spectrophotometer. The KBr matrix method was employed for the preparation of the sample. Wavenumber calibration was made with polystyrene film.

Results and Discussion

Most of the complexes prepared (Table I) are known and there were no difficulties in their preparation and purification. The d.c. polarograms of the tris(β-dicarbonylato)iron(III) chelates showed only one reduction wave as observed by Murray and Hiller [22], Bond and coworkers [23] and other independent investigators [10, 24, 25] in the case of $Fe(acac)_3$. Sampled d.c. polarograms obtained for the present series were analysed by plotting $\log(i_1 - i_a)$ against E, where i_a denotes the current at potential E and i_1 the limiting current. The relationship was linear with a correlation coefficient better than
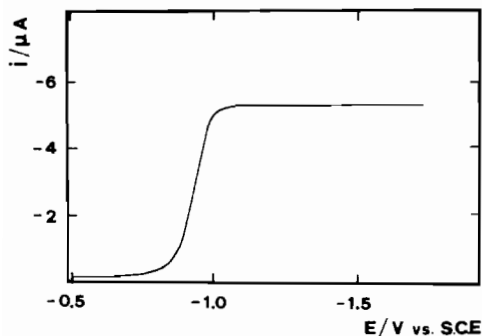
Fig. 1. DC polarogram of 10^{-3} M Fe(dpmo)$_3$ in acetonitrile with 0.1 M TEAP as supporting electrolyte.

0.98 and slope 58 mV which are consistent with a one-electron-transfer process. The 56 mV value of $E_{3/4} - E_{1/4}$ obtained for most complexes was considered sufficient evidence for reversibility. Small deviations from this value were found in the case of Fe(dbmo)$_3$ which is surprising since in most other cases of M(β-diko)$_3$ the presence of phenyl groups confers reversibility [9].

The fluorinated iron(III) β-dicarbonyls are not so stable in acetonitrile solution as are the non-fluorinated ones and deterioration evidenced by spectral changes was observed. However, experiments carried out to examine the kinetics of deterioration indicated that the reaction was too slow within the timescale of the experiments and, therefore, no concentration dependence could be established. In addition to carrying out the experiments in fresh acetonitrile solutions, other solvents were also tried. It was found that the reduction potentials determined in acetonitrile solution were identical to those obtained in propylene carbonate and in the case of complexes containing the trifluoromethyl group the results were more consistent. Insertion of trifluoromethyl groups in the β-diketonato moiety not only affected the stability of the corresponding complexes in solution but also influenced the polarographic behaviour of the corresponding iron(III) chelates by affecting the reversibility of the electron transfer reaction. The divergence from reversibility which is almost insignificant in Fe(bzfac)$_3$ is barely evident in Fe(tfac)$_3$ and becomes more pronounced in Fe(hfac)$_3$. The potential at which reduction of solutions containing Fe(hfac)$_3$ occurs is within the limit of the working range of the dropping mercury electrode (DME) and the accuracy of this value is doubtful.

The cyclic voltammetric curves were determined by scanning the potential initially in the cathodic direction. Only one reduction peak (a) was observed associated with the anodic response (a') (Fig. 2). For these complexes, and specially the non-fluorinated ones, the difference between the cathodic and the anodic peak potentials, $E_{pc} - E_{pa}$, is
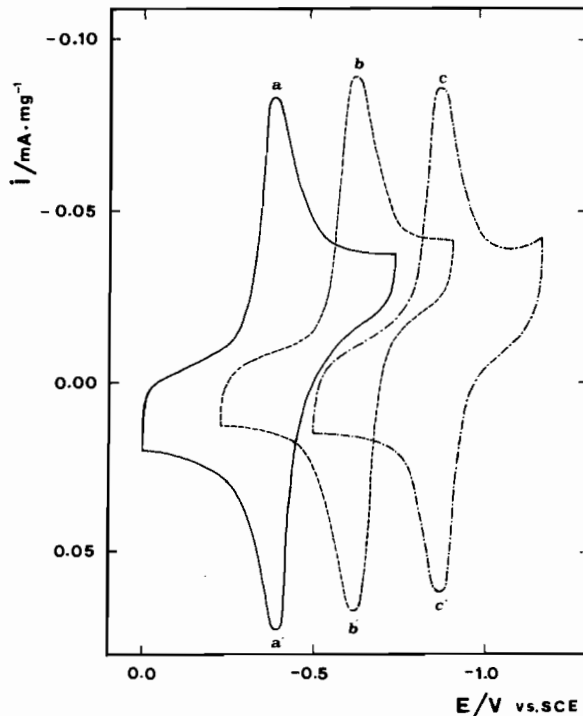

Fig. 2. Cyclic voltamograms of (a) Fe(ppdo)$_3$, (b) Fe-(bzpmo)$_3$, and (c) Fe(dpmo)$_3$ in acetonitrile with 0.1 M TEAP as supporting electrolyte.

50–60 mV (Table II) confirming the earlier findings that the first step in the reduction of Fe(β-diko)$_3$ is a one-electron process, under the conditions described. Spectral changes occurring in the visible upon prolonged electrolysis suggest that the electron acquired occupies an orbital localized in the central atom thus confirming previous suggestions that the electrochemical reduction is a metal centred process [24]. The variation in reduction potential supports the suggestion that these orbitals have appreciable ligand character [10].

In the non-fluorinated chelates the heights of the anodic and the cathodic peaks are almost equal confirming the reversibility of the electron transfer process as found by the polarographic measurements. This also suggests that the species reduced in the forward sweep are then oxidized in the backward sweep and implies that the chemical reaction accompanying the fast electron transfer process is slow.

$$Fe(\beta\text{-diko})_3 + e^- \xrightarrow{\text{fast}} Fe(\beta\text{-diko})_3^- \xrightarrow{\text{slow}} \text{products}$$
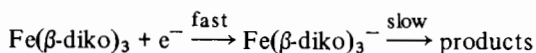
The slight deviation from reversibility observed previously for Fe(dbmo)$_3$ was not confirmed by the cyclovoltammetric measurements. Cyclic voltammetric tests carried out at potential scan rates in the range 0.05–100 V s^{-1} revealed that the behaviour of these iron(III) complexes remains typical for a reversible one-electron process. The $i_p/v^{1/2}$ ratio remained

TABLE II. Reduction Potentials, Cyclovoltametric Anodic and Cathodic Peak Values, Spectral Data and Hammett $\Sigma\sigma$ and $\Sigma\sigma^+$ Functions for Tris(β-dicarbonylato)iron(III) Chelates

Compound	$E_{1/2}$ (V)	E_{pa} (V)	E_{pc} (V)	$(E_{pa} + E_{pc})/2$ [a] (V)	$\nu(^4T_{2g} \leftarrow {}^6A_{1g})$ (μm^{-1})	B (cm^{-1})	$\Sigma\sigma$	$\Sigma\sigma^+$
1 Fe(bdo)$_3$	−0.50	−0.48	−0.52	−0.50	1.316	548	−0.17	−0.31
2 Fe(ppdo)$_3$	−0.45	−0.37	−0.40	−0.39	1.307	483	0.01	−0.18
3 Fe(bpdo)$_3$	−0.61	−0.60	−0.63	−0.61	1.299	573	−0.20	−0.26
4 Fe(acac)$_3$	−0.68	−0.59	−0.63	−0.62	1.333	536	−0.34	−0.62
5 Fe(acac-Cl)$_3$	−0.38	−0.33	−0.36	−0.34	1.336	530	0.03	−0.22
6 Fe(acac-CN)$_3$	0.03	0.12	0.06	0.09	1.320	525	0.34	−0.06
7 Fe(acac-NO$_2$)$_3$	0.10	0.13	0.08	0.11	1.310	510	0.37	0.05
8 Fe(bzac)$_3$	−0.61	−0.54	−0.56	−0.55	1.307	503	−0.16	−0.49
9 Fe(tfac)$_3$	−0.02	0.00	−0.04	−0.02	1.330	513	0.38	0.30
10 Fe(btfac)$_3$	0.02	0.04	0.00	0.02	1.307	503	0.56	0.43
11 Fe(hfac)$_3$		0.80	0.65	0.73	1.333	493	1.1	1.22
12 Fe(dpmo)$_3$	−0.91	−0.85	−0.88	−0.87	1.342	554	−0.40	−0.52
13 Fe(bzpmo)$_3$	−0.70	−0.69	−0.73	−0.71	1.355	550	−0.19	−0.44
14 Fe(dbmo)$_3$	−0.55	−0.47	−0.50	−0.49	1.290	453	0.02	0.02
15 Fe(tert-Bu-tfa)$_3$	−0.10	−0.07	−0.12	−0.10	1.316	520	0.35	0.35

[a]Equivalent to $E'_{1/2}$.

invariable over the scan rates investigated suggesting a diffusion controlled charge transfer.

The tris(β-diketonato)iron(III) chelates containing trifluoromethyl groups do not exactly follow the pattern established by the other members of this series but rather exhibit a behaviour approaching that demonstrated in polarography. Thus, a slight deviation from the $(E_{pc} - E_{pa})$ criterion for reversibility was observed and the divergence from the $E_{1/2}$ values increased on moving from Fe(btfac)$_3$ to Fe(tfac)$_3$ to Fe(hfac)$_3$. Furthermore the constancy of the $i_p/\nu^{1/2}$ ratio changes on moving to Fe(tfac)$_3$ and the increase with increasing scan rates became more prominent again in the case of Fe-(hfac)$_3$. A plot of i_p against $\nu^{1/2}$ although it did not pass through the origin, nevertheless indicated that no absorption occurs on the carbon fibres.

The $E_{1/2}$ value for Fe(acac)$_3$ agrees well with values reported in the literature for reversible processes in acetonitrile solution [21, 22–24]. Concordance in $E_{1/2}$ values pertains even to cases in which the reference electrode is other than the SCE one [8]. The electrochemical data for the other iron(III) complexes of this series are very few and indicate that the reduction potentials depend on the experimental conditions [11, 25]. Solvents other than acetonitrile or propylene carbonate may introduce solvation effects and are likely to influence the mechanism of electron transfer. Indeed, Endo and coworkers [14] have established that the cyclic voltametric reduction of Fe(acac)$_3$ in *N,N*-dimethylformamide is irreversible; irreversibility of charge transfer is also evident in eight other tris(β-diketonato)iron(III) chelates which these investigators have studied. From these results it becomes

difficult to form a clear picture of the factors affecting the reduction potentials.

The $E_{1/2}$ values ranged from −0.91 V for Fe-(dpmo)$_3$ to about +0.70 for Fe(hfac)$_3$, a range of 1.6 V. Significant variations in $E_{1/2}$ are also evident in the case of the Fe(X-acac)$_3$ compounds. Since the chelate ring formed upon coordination is invariably the same this implies that the substituents attached to the β-dicarbonylato moiety have a profound effect on the reduction potential of these complexes. From the results of Endo *et al.* [14] and the data listed in Table II it becomes evident that electron-donating groups, e.g. −C(CH$_3$)$_3$, shift the reduction potential to more negative values whilst electron-attracting substituents have the opposite effect and the corresponding chelates become better oxidizing agents. The more electron-attracting the substituents the more positive the potential.

The reactivity and the physicochemical properties of the β-diketonato complexes have been explained in terms of 'quasi-aromaticity' of the chelate ring [26]. Electronic effects engendered by the substituents are expected to influence the electron distribution and, subsequently, the energy levels of these iron(III) chelates. Previous spectral and electrochemical studies [7, 9, 27, 28] of β-diketonato transition metal chelates have established that the nature of the electronic effects engendered by the substitution within the β-diketonato moiety is mainly inductive and that the parameters best describing these effects are Hammett's σ functions. Lintvedt and coworkers [7] in the electrochemical study of bis(1,3-diketonato)copper(II) chelates have found that the σ parameters describing the dependence of $E_{1/2}$ on the substituents are determined by their

TABLE III. σ_p and σ_m Values for Substituents

|	CH_3	$C(CH_3)_3$	C_6H_5	CF_3	CN	Cl	NO_2
σ_m	−0.07	−0.12	+0.22	+0.41	+0.68	+0.37	+0.71
σ_p	−0.17	−0.20	+0.01	+0.55	+0.66	+0.23	+0.78
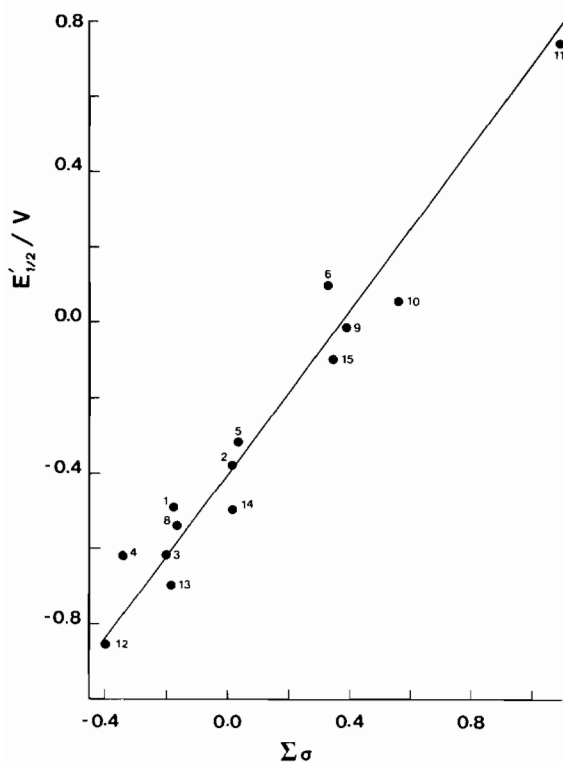
Fig. 3. Plot of $E'_{1/2}$ against the Hammett σ functions of the substituents.

position relative to copper(II) ion. Further studies on other β-diketonato metal chelates provided evidence suggesting transposition of the parameters used i.e. for substituents in position meta to central ion the σ_p values should be employed. The σ_p and σ_m values for the substituents as given by Jaffe [29] are shown in Table III.

Plots of the Hammett constants σ, σ^+ or σ^- against $E_{1/2}$ for the present series of tris(1,3-diketonato)iron(III) chelates allow a more detailed pattern to emerge depicting the influence of the substituents. Figure 3 shows that a good linear correlation for $E_{1/2}$ and $\Sigma\sigma$ is observed whilst the correlations with σ^+ and σ^- are significantly poorer (correlation coefficients, $r = 0.99$, $r = 0.88$). The present results suggest that the influence of the substituents is essentially inductive and that delocalization of electron charge into the chelate ring confers restricted resonance stabilization to the complex.

The additivity of Hammett's σ functions holds quite well throughout the series irrespective of the nature and the position of the substituent groups (Fig. 3). This suggests that more subtle differences in the reduction potentials might be achieved were it possible to prepare mixed-ligand complexes of the general formula FeL_2L', where L, L' denote β-dicarbonyls. Furthermore, such complexes might facilitate the assessment of stereochemical effects, if any.

The formation of a mixed-ligand complex FeL_2L' seems feasible when one considers the reaction of the square-pyramidal complex $Fe(acac)_2Cl$ with the sodium salt of another β-diketone such as the 1-phenyl-4,4,4-trifluoro-1,3-butanedione.

$$Fe(acac)_2Cl + Nabtfac \longrightarrow Fe(acac)_2(btfac) + NaCl$$
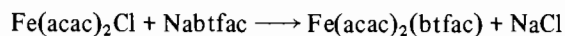
The infrared spectrum of the red product of this reaction was almost identical to that obtained from a 2:1 mixture of $Fe(acac)_3$ and $Fe(btfac)_3$. The polarograms of the reaction product revealed four one-electron reduction waves instead of the expected one since the acquired electron occupies metal localized orbitals. Four separate peaks were also observed in the cyclic voltamograms instead of only one cathodic and the corresponding anodic. In the polarograms, of the four reduction waves one occurs at the potential associated with $Fe(acac)_3$ and an-
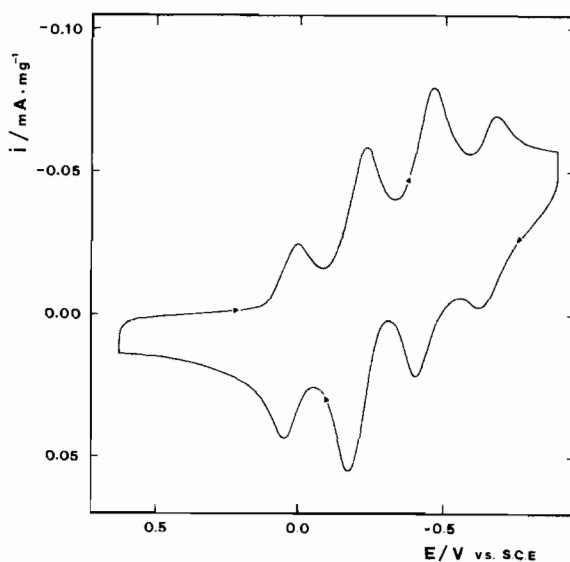

Fig. 4. Cyclic voltammogram of the reaction product (Fe-(acac)$_2$Cl + Nabtfac) in acetonitrile.

other appears at the potential at which reduction of Fe(btfac)$_3$ takes place. The remaining two waves occur at potentials between the previous values, at −0.21 and −0.45 V. Since the reduction of Fe-(acac)$_2$Cl occurs at +0.12 V, the observed waves cannot be associated with the square-pyramidal complex. It is easily verified that the observed potentials correspond to

$$E_1 = \frac{1}{3}[(3 - n)E_{1/2}(\text{Fe(acac)}_3) + nE_{1/2}(\text{Fe(btfac)}_3)]$$

$$(1 \leqslant n \leqslant 2)$$

These results suggest that ligand exchange might not necessarily be confined to the replacement of the coordinated chlorine atom. Interestingly enough, mixtures of Fe(acac)$_3$ and Fe(btfac)$_3$, irrespectively of mole ratios, exhibit the same electrochemical behaviour in acetonitrile solution as the aforementioned reaction product. The above results indicate that in solution ligand exchange takes place in the tris(β-diketonato)iron(III) chelates and that mixed-ligand complexes are formed, existing in equilibrium with the plain chelates, i.e.

Fe(btfac)$_3$ + Fe(acac)$_3$ $\longrightarrow$

Fe(acac)$_2$(btfac) + Fe(acac)(btfac)$_2$
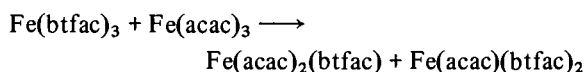
In order to further examine whether the ligand exchange is a general feature of these iron(III) chelates, the electrochemical behaviour of Fe(acac)$_3$ in the presence of Nabtfac was investigated. Addition of Nabtfac and even of the free β-diketone Hbtfac invariably resulted in the enhancement of peaks attributable to Fe(acac)$_2$(btfac), Fe(acac)(btfac)$_2$ and Fe(btfac)$_3$, whereas the opposite effect was observed upon addition of Naacac. Moreover, addition of Fe(acac)$_3$ to a solution of Hbtfac resulted in the disappearance of the polarographic wave at −1.22 V attributed to the enol form of this β-diketone, while the expected peaks of the mixed-ligand complexes emerged. Similarly disappearance of the reduction wave at −0.1 V (attributable to acac$^-$) occurred when Fe(btfac)$_3$ was added to a solution of Kacac. Since the heights of the new peaks remained unaltered with time it is deduced that contrary to previous claims [30] the preparation of mixed-ligand tris(β-diketonato)iron(III) chelates in solution is unlikely.

The reduction of tris(β-diketonato)iron(III) chelates is associated with orbitals localized in the central ion. Since the tris(1,3-diketonato)iron(III) chelates are high-spin and the local symmetry is pseudooctahedral [31], the t_{2g} and e_g orbitals are half-filled. The 'holes' existing in these orbitals offer the possibility of accommodating the electron acquired in the electrochemical reduction but energy considerations favour placement in the HOMO e_g orbitals. Sock and coworkers [24] have found that the absolute reduction potentials of several M(acac)$_3$

chelates are in concordance with the theoretically calculated energies of the acceptor orbitals of these compounds [32]. Since the actual value of the reference electrode, SCE, is $E_{SCE} = -5.06$ [33] the corrected reduction potential of Fe(acac)$_3$ turns out to be $E_{Corr} = -5.74$ eV or -4.63 μm^{-1}. Thus the agreement with the energy of the e_g orbitals calculated by Barnum [32] $E(e_g) = -4.60$ μm^{-1} is excellent.

The agreement between the electrochemically determined energy of the e_g orbitals and the theoretically calculated one for Fe(acac)$_3$ suggests that the energy of the HOMO orbitals in the other tris(β-diketonato)iron(III) chelates depends on Hammett's σ functions of the substituents and the relationship is a linear one. The spectral study [16] of these iron(III) chelates revealed that the energy separation of the half filled e_g and t_{2g} orbitals, 10 Dq, remains virtually unaltered throughout the series (Table II) and any energy change in the e_g orbitals is followed by a similar change in the t_{2g} orbitals. The constancy of the parameter Dq suggests that charge redistribution within the metal localized orbitals does not constitute a reflection of the changes engendered by the substituents. Shifts in band maxima in the near infrared (Table II) corroborate the electrochemical results that the energies of the HOMO orbitals are affected by the substituents. The energies of the ligand field excited states depend on the parameters Dq, B and C and since Dq remains invariable the changes should be sought in the interelectronic repulsion parameters B and C. The free ion values C and B according to Low and Rosengarden [34] are 3990 cm^{-1} and 1081 cm^{-1} respectively. From ref. 16 and Table II it transpires that whereas both B and C are reduced appreciably upon complexation only B decreases as the reduction potentials are shifted to more positive values.

The reduction of interelectronic repulsion parameters, termed nephelauxetic effect, is associated with the expansion of metal d orbitals. Since electron acquisition is facilitated by expanded acceptor orbitals it is reasonable to examine the dependence of $E_{1/2}$ on B. Figure 5 shows a linear correlation between $E_{1/2}$ and B exists. This Racah parameter B affects the energies of the ligand field (LF) excited states that are created from electronic transitions involving the metal localized e_g orbitals [35]. Two broad bands in the absorption spectra, one in the near-infrared and the other in the red, have been assigned [14] to LF transitions, namely $^4T_{1g} \leftarrow {}^6A_{1g}$ and $^4T_{2g} \leftarrow {}^6A_{1g}$ in O_h symmetry. Since the ligand field parameter Dq is almost invariant in the tris(β-dicarbonylato)iron(III) series the changes in the energy requirements for these transitions, reflected by the shifts in band maxima, should be largely due to changes in the Racah parameter B. Therefore there might be a correlation between $E_{1/2}$ and the
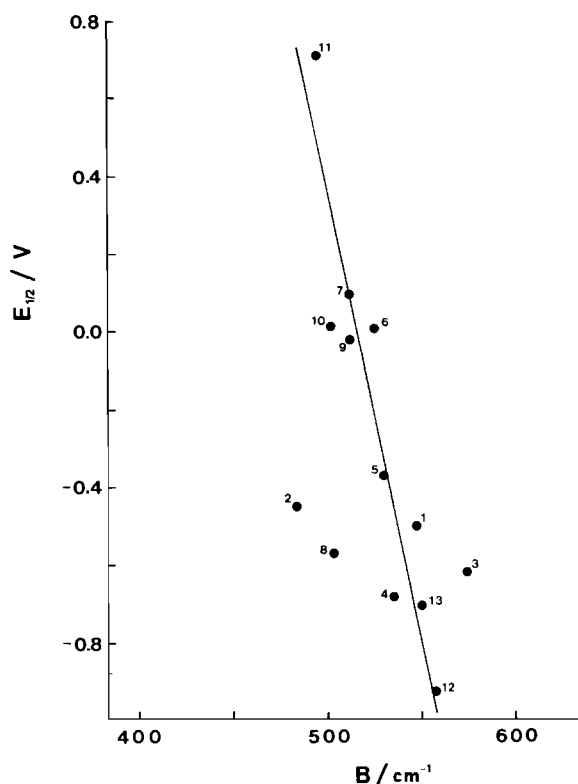
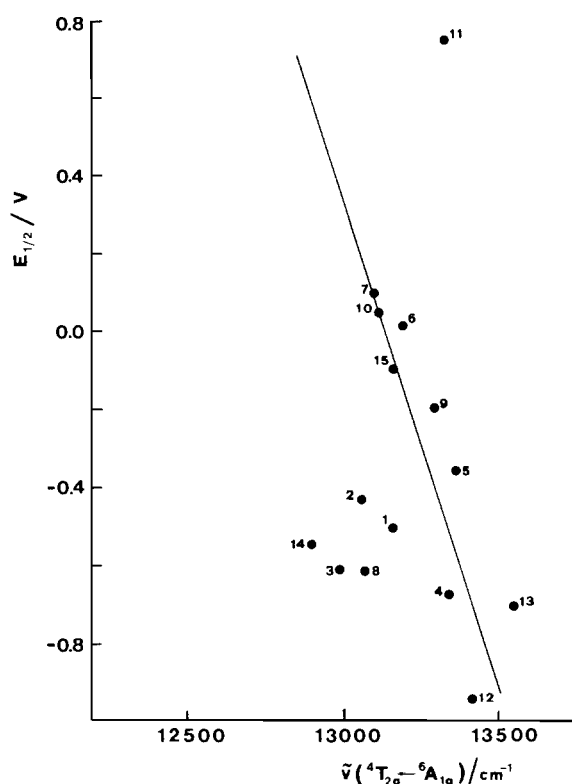Fig. 5. Correlation of $E'_{1/2}$ with the Racah interelectronic repulsion parameter B.

Fig. 6. Dependence of $E'_{1/2}$ on the wavenumber of the spin-forbidden transition $^4T_{2g} \leftarrow {}^6A_{1g}$ of Fe(diko)$_3$.

energies of the LF transitions of this series. The broadness of the bands and the lack of emission spectra at least in this region adds to the uncertainty of the transition energies. Figure 6 indicates that there is some dependence of $E_{1/2}$ on the energy of the $^4T_{2g}(t_{2g}{}^4e_g{}^1)$ state. The energy requirements of the tris(β-dicarbonylato)iron(III) chelates for excitation to higher energy LF states are comparable to those for change transfer transitions. Consequently these spin-forbidden transitions are masked by the more intense charge transfer bands that dominate the visible.

Acknowledgements

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