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Spectrochimica Acta Part A 60 (2004) 1579–1586

SPECTROCHIMICA ACTA PART A

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Spectroscopic studies on charge-transfer complexes formed in the reaction of ferric(III) acetylacetonate with σ- and π-acceptors

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Received 17 July 2003; accepted 19 August 2003

Abstract

The reaction of ferric(III) acetylacetonate (donor), Fe(acac)$_3$, with iodine as a σ-acceptor and with other different π-acceptors have been studied spectrophotometrically at room temperature in chloroform. The π-acceptors used in this investigation are 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *p*-chloranil and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ). The results indicate the formation of 1:1 charge-transfer complexes with a general formula, [Fe(acac)$_3$ (acceptors)]. The iodine complex was shown to contain the triiodide species, $[\mathrm{Fe(acac)_3}]_2\mathrm{I}^+\mathrm{I_3}^-$, based on the electronic absorptions as well as on the Far-infrared absorption bands characteristic for the non-linear triiodide species, $\mathrm{I_3}^-$, with C_{2v} symmetry. The proposed structure of this complex is further supported by thermal and middle infrared measurements.

Keywords: Charge-transfer; Far-infrared; Ferric(III) acetylacetonate; Triiodide; π-Acceptors

1. Introduction

The study of the charge-transfer complexes formed in the reaction of aromatic electron acceptors (π-acceptors) with various electron donors have attracted considerable interests and growing importance owing to their significant physical and chemical properties [1–6]. In previous studies [7–12], it has been stated that iodine reacts with bases like cyclic polyamines, polysulpher and mixed oxygen-nitrogen to form stable charge-transfer complexes with the formation of polyiodide ions. $\mathrm{I}_n{}^-$ ($n = 3$, 5, 7, and 9).

Some of charge-transfer complexes show very interesting applications in the field of analytical chemistry [13,14]. Polyiodide charge-transfer complexes are of special interest and importance. This is because some of these complexes have shown interesting properties such as electrical conductivity. The highly conducting complex $[(\mathrm{TTT})_2]^+\mathrm{I_3}^-$ is reported [15] to be formed in the reaction of iodine with the sulphur containing base tetrathiotetracene (TTT).

One interesting aspect of the chemistry of metal acetylacetonates $[\mathrm{M(acac)}_n]$ concerns the pseudo aromatic π-electron delocalization in the M(acac) rings [16]. In all previous studies [17–20] concerning the interaction of iodine with metal acetylacetonates, it has been found out that the authors who approached this topic have been ignored the formation of $\mathrm{I_3}^-$ with its characteristic absorptions around 290 and 360 nm. Remarkably, in their studies of the interaction of iodine with metal acetylacetonates, Kulevsky and Butamina [20], wrongly claimed that the 360 nm band was assigned to the blue shifted $\mathrm{I_2}$ band, while the lower peak around 290 nm was attributed to the intermolecular charge-transfer in $\mathrm{M(acac)}_n$–$\mathrm{I_2}$. In another study by Singh and Singh and Sahai [17], the formation of a new absorption band around 360 nm was interpreted as a charge-transfer (CT) band of the $\mathrm{M(acac)}_n$–$\mathrm{I_2}$ molecular complex.

In this paper, we report the formation of new CT-complexes formed on the reaction of ferric(III) acetylacetonate, Fe(acac)$_3$, with different types of σ- and π-electron acceptors. The σ-acceptor used is iodine and the π-acceptors are 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-*p*-benzo-quione (*p*-chloranil) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ). All reactions were carried out in chloroform as a solvent. The obtained results enable

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doi:10.1016/j.saa.2003.08.018

us to investigate the nature of bonding and structure inherent in these new complexes.

2. Experimental

All chemicals used in this study were of analytical reagent grade and used without further purification. Ferric(III) acetylacetonate was obtained from Merck Chemical Co., while 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, tetrachloro-*p*-benzoquinone (*p*-chloranil) and 7,7′,8,8′-tetracyanoquinodimethane was purchased from Aldrich Chemical Co., and iodine was obtained from BDH.

The solid donor–acceptor complexes were isolated as follows. Excess saturated solution for each of the acceptors in chloroform (40 ml) was added to a saturated solution (10 ml) of the ferric(III) acetylacetonate in chloroform. The mixture in each case was stirred for about 10–20 min. The brown $[(Fe(acac)_3]_2I^+I_3^-$, dark brown $[Fe(acac)_3(DDQ)]$, redish yellow $[Fe(acac)_3(p\text{-chloranil})]$ and greenish $[Fe(acac)_3(TCNQ)]$ solid CT-complexes formed were filtered immediately and washed several times with minimum amounts of chloroform (2–5 ml) and dried under vacuum. The formed complexes were characterized by their elemental analysis, vibrational and electronic absorption spectroscopy. The analysis data were obtained as follows, $[Fe(acac)_3]_2I^+I_3^-$: C, 29.31% (29.65%); H, 3.25% (3.46%); Fe, 8.98% (9.20%); I, 41.87% (41.80); $[Fe(acac)_3(DDQ)]$: C, 47.18% (47.57%); H, 3.39% (3.62%); N, 4.75% (4.83); Cl, 11.97% (12.24%); Fe, 9.60% (9.63%); $[Fe(acac)_3(p\text{-chloranil})]$: C, 41.93% (42.07%); H, 3.48% (3.51%); Cl, 23.45% (23.70%); Fe, 9.17% (9.32%); and $[Fe(acac)_3(TCNQ)]$: C, 57.96% (58.13%); H, 4.40% (4.49%); N, 9.89% (10.05%); Fe, 9.93% (10.02%) (the calculated values are shown in parentheses).

The electronic absorption spectra of the donor $[Fe(acac)_3]$, acceptors (iodine, DDQ, *p*-chloranil and TCNQ) and the formed CT-complexes in chloroform were recorded in the region of 700-200 nm using a Shimadzu UV-spectrophotometer model 1601 PC with quartz cell of 1 cm path length. The mid infrared spectra of the reactants and the formed CT-complexes were recorded from KBr discs using a Genesis II FT-IR, while the far-infrared spectra for the donor $[Fe(acac)_3]$ and the iodine complex were recorded from Nujol mulls dispersed on polyethylene windows in the region 50–300 cm^{-1} using a Mattson infinity series FT-IR spectrometer. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under N_2-atmosphere using two detectors model Shimadzu TG-50 H and Shimadzu DTA-50, respectively. Photometric titration were performed [21] at 25 °C for the reactions of Fe(III) acetylacetonate with the acceptors in chloroform as follow. The concentrations of the donor $[Fe(acac)_3]$ in the reaction mixtures was kept fixed at (1×10^{-4} M), while the concentrations of the acceptors were changed over the range from 0.25×10^{-4} to 3.0×10^{-4} and these produced solutions with donor: acceptor ratios varying from 1:0.25 to 1:3, as shown in Table 1.

Table 1
The electronic absorption spectral data for (A) $[Fe(acac)_3]_2I^+I_3$; (B) $[Fe(acac)_3(DDQ)]$; (C) $[Fe(acac)_3(p\text{-chloranil})]$; and (D) $[Fe(acac)_3\text{-}(TCNQ)]$ complexes, respectively in $CHCl_3$

X ml of I_2	Base:I_2 ratio	Absorbance at 357 nm
(A)		
0.25	1:0.25	0.086
0.50	1:0.50	0.149
0.75	1:0.75	0.205
1.00	1:1.00	0.250
1.50	1:1.50	0.286
2.00	1:2.00	0.320
2.50	1:2.50	0.357
3.00	1:3.00	0.368
X ml of DDQ	Base:DDQ ratio	Absorbance at 346 nm
(B)		
0.25	1:0.25	0.148
0.50	1:0.50	0.244
0.75	1:0.75	0.328
1.00	1:1.00	0.402
1.50	1:1.50	0.480
2.00	1:2.00	0.520
2.50	1:2.50	0.576
3.00	1:3.00	0.600
X ml of *p*-chloranil	Base:*p*-chloranil ratio	Absorbance at 353 nm
(C)		
0.25	1:0.25	0.128
0.50	1:0.50	0.220
0.75	1:0.75	0.260
1.00	1:1.00	0.360
1.50	1:1.50	0.420
2.00	1:2.00	0.484
2.50	1:2.50	0.548
3.00	1:3.00	0.580
X ml of TCNQ	Base:TCNQ ratio	Absorbance at 408 nm
(D)		
0.25	1:0.25	0.998
0.50	1:0.50	1.950
0.75	1:0.75	2.599
1.00	1:1.00	3.151
1.50	1:1.50	4.096
2.00	1:2.00	4.748
2.50	1:2.50	5.501
3.00	1:3.00	5.993

1 ml base (5×10^{-4} M) + X ml of (I_2, DDQ, *p*-chloranil, and TCNQ) (5×10^{-4} M) + Y ml solvent = 5 ml.

3. Results and discussion

The electronic absorption spectra of the reactants, ferric(III) acetylacetonate, $[Fe(acac)_3]$, (1×10^{-4} M) and acceptors (iodine, DDQ, *p*-chloranil and TCNQ) (1×10^{-4} M) in $CHCl_3$ along with those of the obtained 1:1 CT-complexes are shown in Fig. 1 (A–D, respectively). The

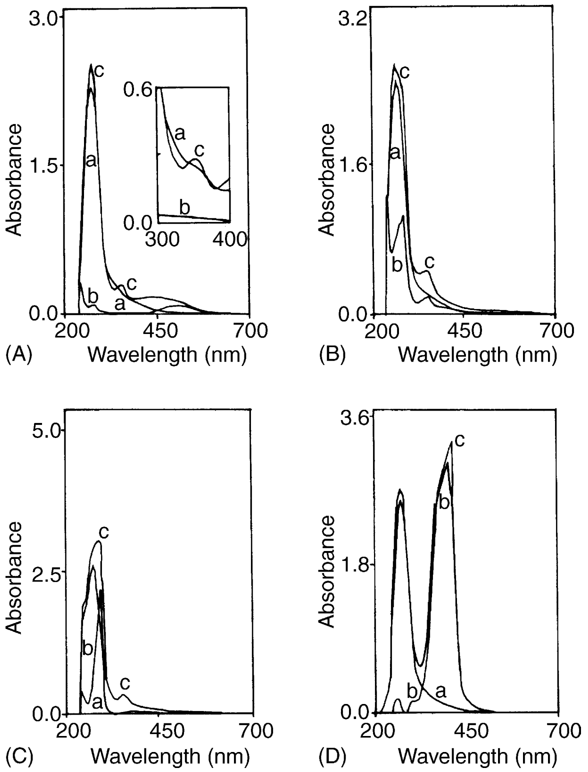

Fig. 1. Electronic absorption spectra of: (A) $[Fe(acac)_3]$–I_2 reaction in $CHCl_3$; (B) $[Fe(acac)_3]$–DDQ reaction in $CHCl_3$; (C) $[Fe(acac)_3]$–*p*-chloranil reaction in $CHCl_3$; and (D) $[Fe(acac)_3]$–TCNQ reaction in $CHCl_3$. (a) Donor (1×10^{-4} M), (b) acceptor (1×10^{-4} M), and (c) donor–acceptor CT-complex.

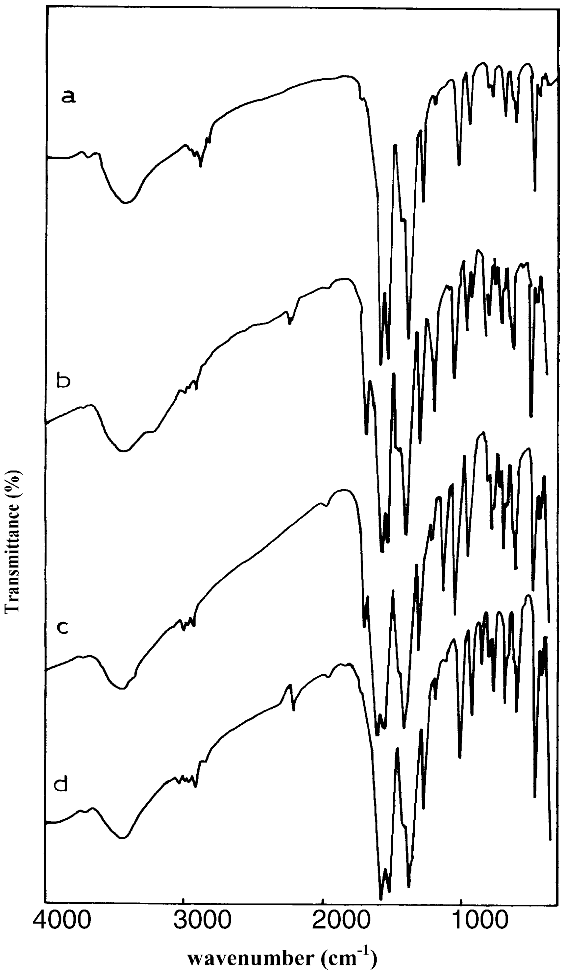

Fig. 2. Infrared spectra of: (a) $[Fe(acac)_3]_2I^+I_3^-$ complex; (b) $[Fe(acac)_3(DDQ)]$ complex; (c) $[Fe(acac)_3(p\text{-chloranil})]$ complex; and (d) $[Fe(acac)_3(TCNQ)]$ complex.

spectra demonstrate that the formed CT-complexes have a real strong absorption bands around 357 and 286 nm for $[(Fe(acac)_3]_2I^+I_3^-$, 346 and 268 nm for $[Fe(acac)_3(DDQ)]$, 353 and 290 nm for $[Fe(acac)_3(p\text{-chloranil})]$ and at 408 nm for $[Fe(acac)_3(TCNQ)]$. The stoichiometry of the $[Fe(acac)_3(acceptor)]$ reactions were shown in all cases to be of 1:1 ratio. This was proposed on the bases of the obtained elemental analysis data of the isolated solid CT-complexes as well as from the complexes infrared spectra, Fig. 2 and Table 2, which indicate the existence of the bands characteristic for both the $[Fe(acac)_3]$ and the acceptors. The stoichiometry of 1:1 is also strongly supported by photometric titration measurements. These measurements were based on the CT absorption bands exhibited by the spectra for each of the $[Fe(acac)_3(acceptor)]$ systems (indicated above) and are given in Fig. 3. The $Fe(acac)_3(acceptors)$ equivalence points indicate that the donor/acceptor ratio in all cases is 1:1 and this result agrees quite well with the elemental analysis and infrared spectra of the solid CT-complexes. Accordingly, the formed CT-complexes upon the reaction of $[Fe(acac)_3]$ as a donor with the σ- and π-acceptors under investigation in chloroform have the general formula $[Fe(acac)_3(acceptor)]$. The 1:1 modified Benesi-Hildebrand equation [22], was used to calculate the values of the equilibrium constant, K ($l\,mol^{-1}$) and the extinction coefficient, ε ($l\,mol^{-1}\,cm^{-1}$).

$$\frac{C_a^0 C_d^0 l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^0 + C_d^0}{\varepsilon}$$

where C_a^0 and C_d^0 are the initial concentrations of the acceptors (iodine, DDQ, *p*-chloranil and TCNQ) and the donor $[Fe(acac)_3]$, respectively, while A is the absorbance of the strong bands at 357 and 286 nm for $[Fe(acac)_3]_2I^+I_3^-$, 346 and 268 nm for $[Fe(acac)_3(DDQ)]$, 353 and 290 nm for $[Fe(acac)_3(p\text{-chloranil})]$ and 408 nm for $[Fe(acac)_3(TCNQ)]$ complexes. The data obtained throughout these calculations are given in Table 3. Blotting the values of $C_a^0C_d^0/A$ against $C_a^0 + C_d^0$ values for each acceptor, a straight line is obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Fig. 4. The values of both K and ε associated with these complexes are given in Table 4. These complexes show high values of both the formation constant (K) and the extinction coefficients (ε). These high values of K confirm the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the ferric(III) acetylacetonate. The

Table 2
Infrared frequencies[a] (cm^{-1}) and tentative assignments for DDQ, *p*-chloranil, TCNQ, $[Fe(acac)_3]_2I^+I_3^-$, $[Fe(acac)_3(DDQ)]$, $[Fe(acac)_3(p\text{-chloranil})]$, and $[Fe(acac)_3(TCNQ)]$ complexes

DDQ	*p*-Chloranil	TCNQ	$[Fe(acac)_3]_2I^+I_3^{-1}$	$[Fe(acac)_3(\pi\text{-acceptor})]$			Assignments[b]
				DDQ	TCNQ	*p*-Chloranil	
3458 s,br	3486 br	3406 w,br	3415 s,br	3441 s,br	3455 s,br	3455 s,br	$\nu_{(O-H)}$; H_2O of KBr
3347 vw	3292 ms		3236 sh	3234 sh	3125 vw	3360 sh	
3250 w,br							
–	–	3137 ms	2984 vw	3005 w	3005 w	3083 vw	$\nu_{(C-H)}$; $Fe(acac)_3$ and TCNQ
		3050 vs	2952 vw	2910 w	3002 vw	3000 w	
		2969 mw	2925 ms	2866 vw	2957 vw	2958 vw	
		2851 mw	2844 w		2917 w	2930 w	$\nu_{(CH_3)}$; $Fe(acac)_3$
–	–				2830 vw	2861 w	
2250 vw	–	2220 vs	–	2239 ms	2202 s	–	$\nu_{(C\equiv N)}$; DDQ and TCNQ
2236 ms				2205 w			
1680 vs	1680 vs	–	1566 vs	1665 vs	1708 w	1690 s	$\nu_{(C=O)}$; $Fe(acac)_3$, DDQ, and *p*-chloranil
1555 vs	1583 vs	1670 s	1528 vs	1566 vs	1569 vs	1572 vs	$\nu_{(C=C)}$; $Fe(acac)_3$, DDQ, *p*-chloranil, and TCNQ
1458 mw	1555 w,sh	1539 vs	1400 vw	1519 vs	1525 vs	1530 vs	$\nu_{(C=O)}$; $Fe(acac)_3$
1430 mw	1528 vw			1444 w	1416 vw	1416 vw	$\delta_{(CH)}$; $Fe(acac)_3$
	1458 vw			1436 vw			
1389 vw	1319 vw	1352 s	1278 vs	1380 vs	1377 vs	1375 vs	$\nu_{(C-C)}$; $Fe(acac)_3$, DDQ, *p*-chloranil and TCNQ
1250 s	1277 s	1285 w		1278 vs	1345 sh	1278 vs	$\delta_{(CH_3)}$; $Fe(acac)_3$
1166 vs	1236 ms	1205 w		1167 vs	1266 vs	1250 vw	$\nu_{(C\text{-}CH_3)} + \delta_{(CH)}$, in-plane bend
1083 vw	1194 vw	1118 s	1094 vw	1059 w	1178 s	1190 ms	$\delta_{(CH_3)}$, rock; $Fe(acac)_3$
	1097 vs	1044 w	1010 vs	1020 vs	1126 w	1115 vs	
					1029 vs	1025 vs	
902 s	986 vw	996 w	930 s	884 vs			
778 vs	916 s	962 w		866 s	930 vs	950 vs	$\nu_{(C\text{-}CH_3)} + \nu_{(C-O)}$; $Fe(acac)_3$
		859 vs		799 vs	847 s	792 w	CH-deformation; DDQ, *p*-chloranil and TCNQ
		808 w			792 ms		
708 s	764 s	772 vw	775 vw	765 s	750 s	766 s	$\delta(_{CH})$, out-of-plane bend + Ring def. + $\nu_{(M-O)} + \delta_{(C\text{-}CH_3)}$ bend; $Fe(acac)_3$
611 mw	722 s	621 mw	736 ms	706 ms	654 vs	710 ms	
			655 s	688 vs		667 vs	
			569 s				
							$\nu_{(C-Cl)}$; DDQ and *p*-chloranil CH, in-plane bend; TCNQ skeletal vibration
528 mw	472 mw	555 vw	442 vs	596 vs	580 vs	570 vs	Ring def. + $\nu_{(M-O)}$; $Fe(acac)_3$
458 mw	430 vw	472 vs	425 ms	542 vw	446 vs	446 vs	CH, out-of-plane bend; TCNQ.
				457 vs	377 ms	390 s	Skeletal vibration
				416 ms			

[a] s: strong; w: weak; m: medium; sh: shoulder; v: very; and br: broad.
[b] ν: stretching; and δ: bending.

equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it such as cyano and halo groups.

The appearance of the two absorption bands around 360 and 285 nm are well known [23–25] to be characteristic for the formation of the triiodide ion (I_3^-). This was also supported by the far-infrared spectrum of the iodine complex, Table 5. This spectrum shows the characteristic bands for the triiodide ion at 150, 102, and 76 cm^{-1}, which are assigned to ν_{as} (I–I), ν_s (I–I) and δ (I_3^-), respectively. These three absorptions do not exist in the spectrum of the donor. However, the I_3^- ion may be linear ($D_{\infty h}$) or non-linear (C_{2v}). Group theoretical analysis indicates that the I_3^- with C_{2v} symmetry displays three vibrations ν_s (I–I); A_1, ν_{as} (I–I); B_2 and δ (I_3^-); A_1, all are infrared active in good agreement [23,26–29] with the observed three infrared bands for $[Fe(acac)_3]_2I^+I_3^-$ as shown in Table 5.

According to the foregoing discussion, a general mechanism is proposed for the formation of $[Fe(acac)_3]_2I^+I_3^-$ complexes as follows:

$$2[Fe(acac)_3] + I_2 \rightarrow [Fe(acac)_3]_2I^+I^-$$

$$[Fe(acac)_3]_2I^+I^- + I_2 \rightarrow [Fe(acac)_3]_2I^+I_3^-$$

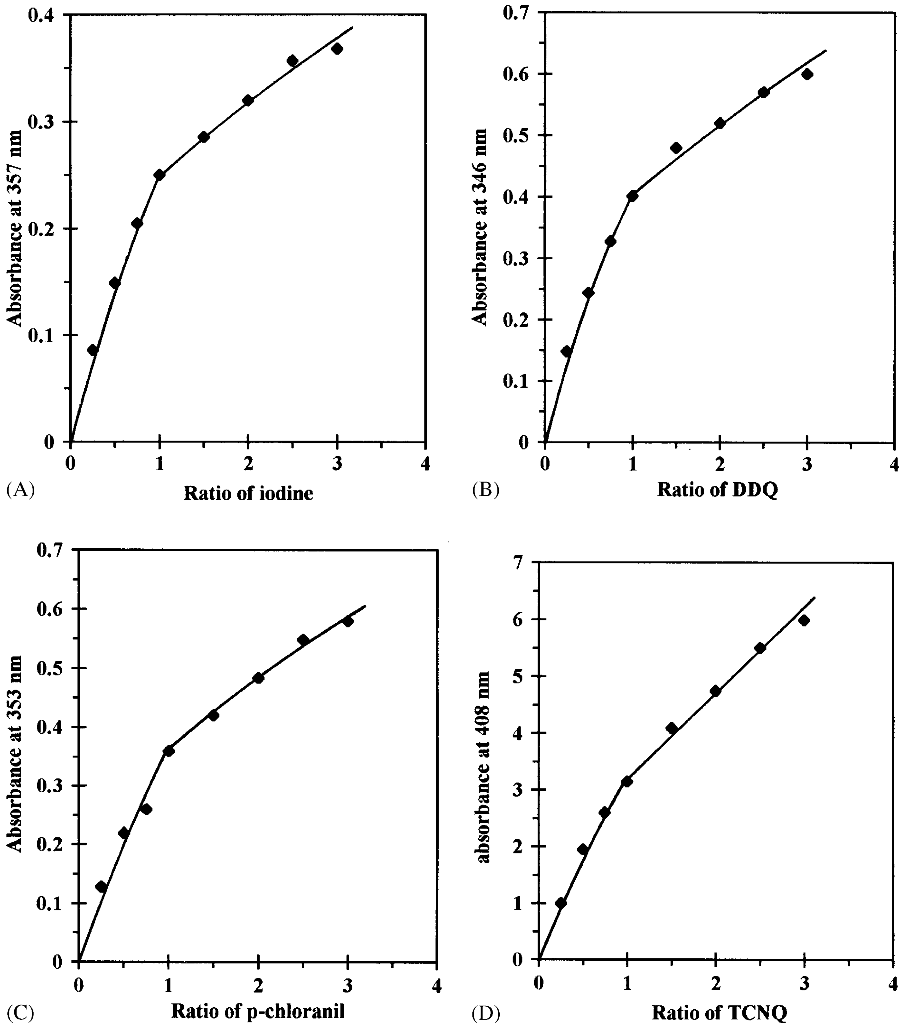

Fig. 3. Photometric titration curves for the [Fe(acac)$_3$]–acceptor reactions in CHCl$_3$: (A) [Fe(acac)$_3$]–iodine reaction at 357 nm; (B) [Fe(acac)$_3$]–DDQ reaction at 346 nm; (C) [Fe(acac)$_3$]–*p*-chloranil reaction at 353 nm; and (D) [Fe(acac)$_3$]–TCNQ reaction at 408 nm.

The formation of the iodine intermediate [Fe(acac)$_3$]$_2$I$^+$I$_3$$^-$ is well known to be formed between iodine and cyclic polyamines [12,26]. To confirm the proposed formula and structure for the new [Fe(acac)$_3$]$_2$I$^+$I$_3$$^-$ complex, thermogravimetric and differential thermal analysis were carried out for this complex under N$_2$ flow. DTA thermograms and TGA curves are shown in Fig. 5. Table 6 gives the maximum temperature values, $T_{\max}$ (°C), together with the corresponding weight loss for each step of the decomposition reactions of this complex. The obtained data strongly support the structure proposed for the iodine complex and indicate that, the thermal decomposition of this complex in inert atmosphere proceeds approximately with two main degradation steps (Fig. 5). The first stage of degradation occurs within a temperature range of 184–230 °C. The found weight loss associated with this stage of decomposition is 41.3% and may be attributed to the loss of the two iodine molecules, which is in good agreement with the calculated value of 41.81%. The second stage of decomposition occurs at a three different maximum temperature of 258, 372, and 400 °C with a weight loss of 44.73% and may correspond to the loss of $14C_2H_2 + 2CO_2 + 5H_2O + 2H_2$ molecules. The calculated weight loss associated with the loss of these species is 44.98% and agrees quite well with obtained value. The weight found for the residue after decomposition is 13.97% giving an actual total weight loss of 86.03%. However, the calculated total weight loss (86.79%) supports our conclusion about the thermal decomposition mode of the complex, [Fe(acac)$_3$]$_2$I$^+$I$_3$$^-$. Finally, the thermal decomposition reactions of the complex can be summarized as follows:

$$[Fe(CH_3COCH{=}C(O)CH_3)_3]_2I^+I_3^-$$
$$\xrightarrow{164\text{--}222\,^{\circ}C} 2[Fe(CH_3COCH{=}C(O)CH_3)_3] + 2I_2$$

$$2[Fe(CH_3COCH{=}C(O)CH_3)_3]_2 \xrightarrow{\geq} Fe_2O_3 + 14C_2H_2$$
$$+2CO_2 + 5H_2O + 2H_2$$

The infrared spectra of the formed CT-complexes, [Fe(acac)$_3$(acceptor)] (acceptors: iodine, DDQ, *p*-chloranil,

Table 3
The values C_d^0+, C_a^0, $C_d^0+C_a^0$ and $C_d^0+C_a^0/A$, for (A) [Fe(acac)$_3$]$_2$I$^+$I$_3{}^-$; (B) [Fe(acac)$_3$(DDQ)]; (C) [Fe(acac)$_3$(*p*-chloranil)]; and (D) [Fe(acac)$_3$(TCNQ)] complexes, respectively, in CHCl$_3$

Base:I$_2$ ratio	$C_d^0 \times 10^{-4}$	$C_a^0 \times 10^{-4}$	Absorbance at 357 nm	$(C_d^0 + C_a^0) \times 10^{-6}$	$(C_d^0 C_a^0) \times 10^{-8}$	$(C_d^0 C_a^0/A) \times 10^{-8}$ at 357 nm
(A)						
1:0.25	1.00	0.25	0.086	125	0.25	2.90
1:0.50	1.00	0.50	0.149	150	0.50	3.35
1:0.75	1.00	0.75	0.205	175	0.75	3.65
1:1.00	1.00	1.00	0.250	200	1.00	4.00
1:1.50	1.00	1.50	0.286	250	1.50	5.25
1:2.00	1.00	2.00	0.320	300	2.00	6.25
1:2.50	1.00	2.50	0.357	350	2.50	7.00
1:3.00	1.00	3.00	0.368	400	3.00	8.15
Base:DDQ ratio			Absorbance at 346 nm			$(C_d^o \cdot C_a^o/A) \times 10^{-8}$ at 346 nm
(A)						
1:0.25	1.00	0.25	0.148	125	0.25	1.689
1:0.50	1.00	0.50	0.244	150	0.50	2.049
1:0.75	1.00	0.75	0.328	175	0.75	2.287
1:1.00	1.00	1.00	0.402	200	1.00	2.488
1:1.50	1.00	1.50	0.480	250	1.50	3.125
1:2.00	1.00	2.00	0.520	300	2.00	3.846
1:2.50	1.00	2.50	0.576	350	2.50	4.340
1:3.00	1.00	3.00	0.600	400	3.00	5.000
Base:*p*-chloranil ratio			Absorbance at 353 nm			$(C_d^o \cdot C_a^o/A) \times 10^{-8}$ at 353 nm
(C)						
1:0.25	1.00	0.25	0.128	125	0.25	1.953
1:0.50	1.00	0.50	0.220	150	0.50	2.273
1:0.75	1.00	0.75	0.260	175	0.75	2.885
1:1.00	1.00	1.00	0.360	200	1.00	2.778
1:1.50	1.00	1.50	0.420	250	1.50	3.571
1:2.00	1.00	2.00	0.484	300	2.00	4.132
1:2.50	1.00	2.50	0.548	350	2.50	4.562
1:3.00	1.00	3.00	0.580	400	3.00	5.172
Base:TCNQ ratio			Absorbance at 408 nm			$(C_d^0 C_a^0/A) \times 10^{-8}$ at 408 nm
(D)						
1:0.25	1.00	0.25	0.998	125	0.25	0.251
1:0.50	1.00	0.50	1.950	150	0.50	0.256
1:0.75	1.00	0.75	2.599	175	0.75	0.289
1:1.00	1.00	1.00	3.151	200	1.00	0.317
1:1.50	1.00	1.50	4.096	250	1.50	0.366
1:2.00	1.00	2.00	4.748	300	2.00	0.421
1:2.50	1.00	2.50	5.501	350	2.50	0.454
1:3.00	1.00	3.00	5.993	400	3.00	0.501

and TCNQ) are shown in Fig. 2, and their band assignments are given in Table 2. These assignments are based on a comparison of the spectra of CT-complexes with those of the reactants. The spectra of the reaction products contain the

Table 4
Spectrophotometric results of CT-complexes of [Fe(acac)$_3$]$_2$I$^+\cdot$I$_3^-$, [Fe(acac)$_3$(DDQ)], [Fe(acac)$_3$(*p*-chloranil)], and [Fe(acac)$_3$(TCNQ)] in CHCl$_3$

Acceptor	K (l mol^{-1})	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})
I$_2$	4.222×10^4	357	0.526×10^4
DDQ	4.273×10^4	346	0.851×10^4
p-Chloranil	4.167×10^4	353	0.800×10^4
TCNQ	0.760×10^4	408	10.526×10^4

Table 5
Fundamental vibrations for some triiodide compounds

Compounds	Assignments[a]			References
	$\nu1$	$\nu2$	$\nu3$	
KI$_3$	111		143	[23]
CsI$_3$	103	69	149	[27]
(CH$_3$)$_4$NI$_3$	111	74	138	[27,28]
(C$_2$H$_5$)$_4$NI$_3$	104	72, 66	132	[28]
(TACPD)I$^+$I$_3{}^-$	109	60	132	[26]
(HMTACTD)I$^+$I$_3{}^-$	110	61	144	[26]
[Ni(acac)$_2$]$_2$I$^+$I$_3{}^-$	101	84	132	[29]
[Fe(acac)$_3$]$_2$I$^+$I$_3{}^-$	102	76	150	Present work

[a] ν_1, ν_s (I–I); ν_2, δ (I$_3{}^-$); ν_3, ν_{as} (I–I).

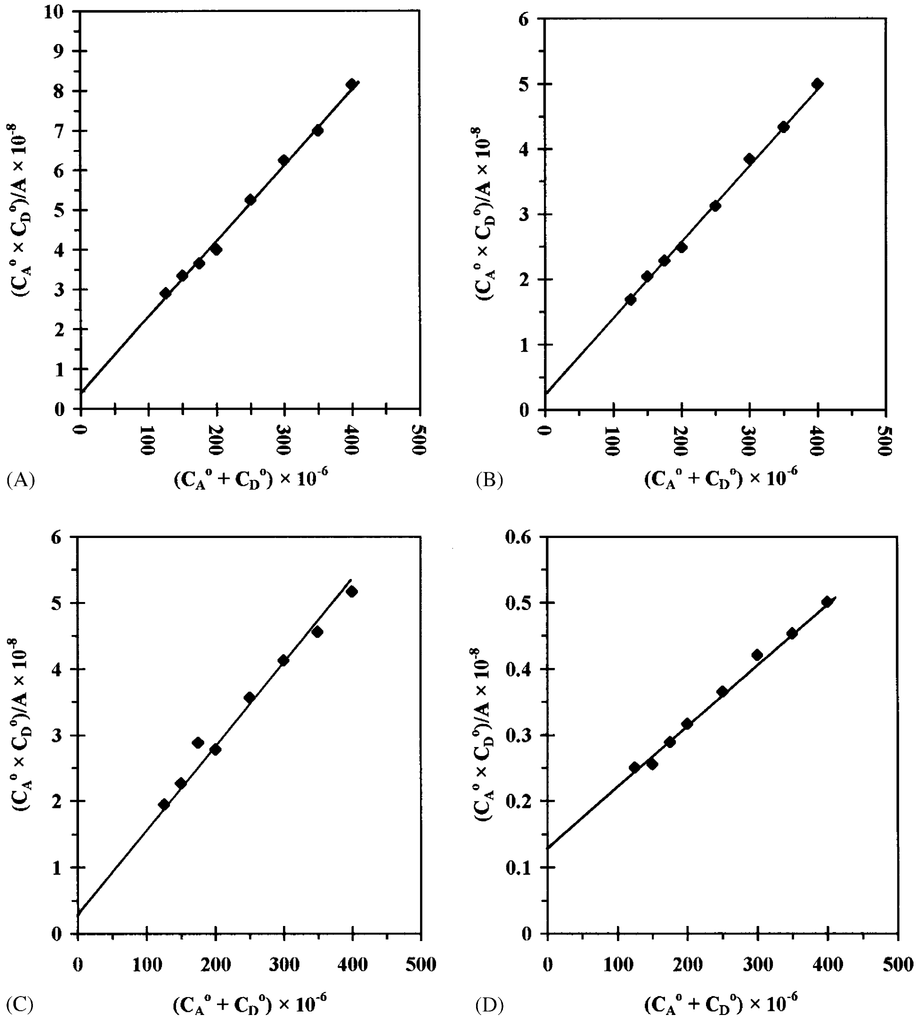

Fig. 4. The plot of $(C_a^0 \times C_d^0/A)$ values against $(C_a^0 + C_d^0)$ values for the [Fe(acac)$_3$]–acceptor reactions in CHCl$_3$: (A) [Fe(acac)$_3$]–iodine reaction at 357 nm; (B) [Fe(acac)$_3$]–DDQ reaction at 346 nm; (C) [Fe(acac)$_3$]–*p*-chloranil reaction at 353 nm; and (D) [Fe(acac)$_3$]–TCNQ reaction at 408 nm.

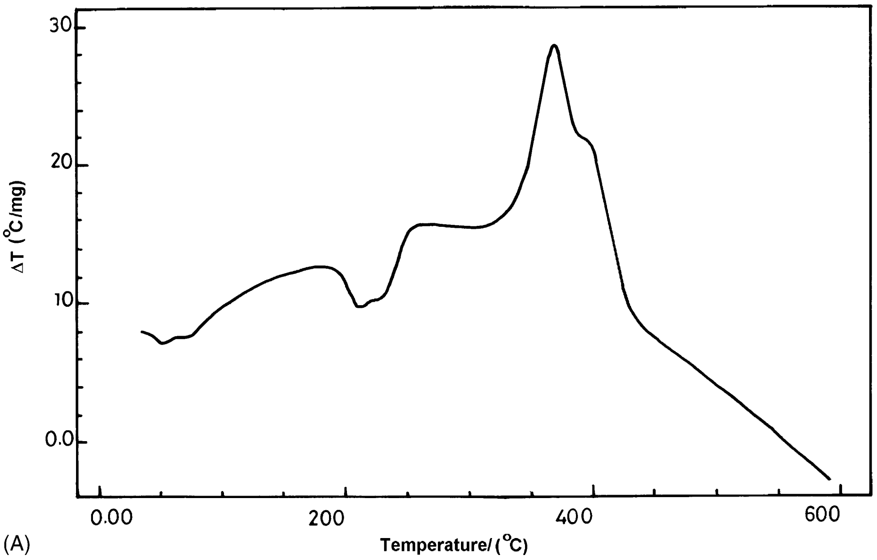

Fig. 5. (A) DTA diagram of [Fe(acac)$_3$]$_2$I$^+$I$_3^-$ complex. (B) TGA diagram of [Fe(acac)$_3$]$_2$I$^+$I$_3^-$ complex.

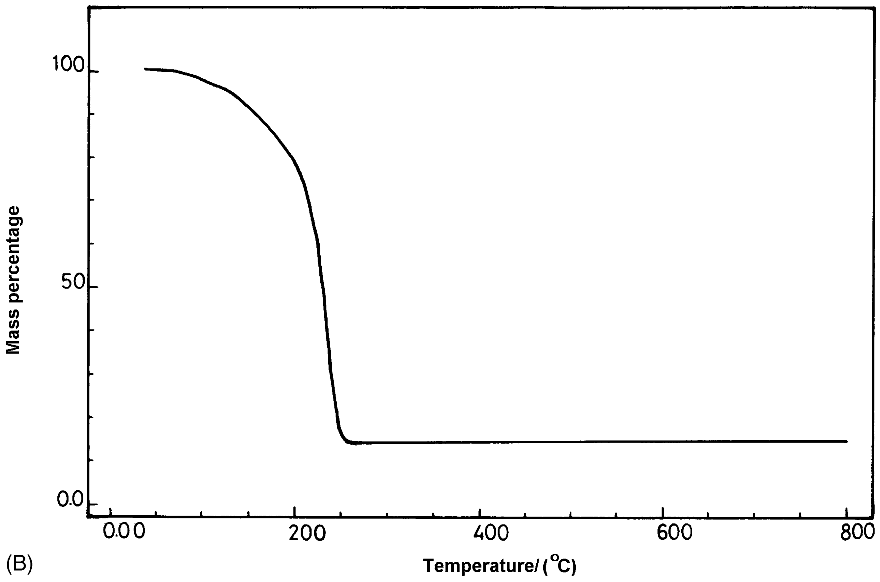

Fig. 5. (*Continued*).

Table 6
The maximum temperature, T_{max} (°C), and weight loss values of the decomposition stages for the $[Fe(acac)_3]_2I^+I_3^-$ complex

Decomposition	T_{max} (°C)	Lost species	% weight losses	
			Found	Calculated
First stage	212, 225 °C	$2I_2$	41.30%	41.81%
Second stage	≥365 °C	$14C_2H_2 + 2CO_2 + 5H_2O + 2H_2$	44.73%	44.98%
Total loss			86.03%	86.79%
Residue			13.97%	13.21%

main bands for both the reactants, however, the bands of the acceptors and [(Fe(acac)$_3$] in the spectra of the complexes show some changes in intensities and in some cases show small shifts in the frequency values compared with those of the free reactants. This could be understood in the basis of symmetry and electronic structure changes in both acceptor and [Fe(acac)$_3$] in the formed CT-complexes compared with those of the free molecules.

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