

SPECTROSCOPIC AND THERMAL STUDIES OF THE REACTION OF IODINE WITH COBALT(II) AND COPPER(II) ACETYLACETONATE

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Abstract

A spectrophotometric study of 1:1 charge-transfer complexes derived from two metal acetylacetonates (Co(II) and Cu(II) acetylacetonates) donor and iodine (σ -acceptor) has been carried out. The equilibrium constants (K) and absorptivity (ϵ) for the formation of the chelate-iodine complexes have been evaluated. The suggested structure of the two solid triiodide charge-transfer complexes reported in this study is further supported by thermal analysis and far and mid infrared measurements.

Resumen

En este trabajo se realizó un estudio espectrofotométrico de complejos 1:1 de transferencia de carga derivados de dos acetilacetatos metálicos (acetilacetatos de Co(II) y Cu(II)) donores, y de yodo (aceptor σ). Se evaluaron la constante de equilibrio (K) y la absorptividad (ϵ) para la formación de los correspondientes complejos quelados con yodo. Se sugieren estructuras para dos complejos sólidos de transferencia de carga del triyoduro, las cuales fueron verificadas mediante análisis térmico y espectroscopía en el infrarrojo medio y cercano.

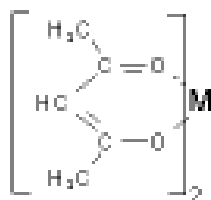
Introduction

The formation of stable charge-transfer complexes between iodine and several types of electron donors like cyclic polyamines, cyclic polysulphur and mixed oxygen-nitrogen cyclic bases are well known [1-7], in view of their good electrical conductivity. The formation of CT- complexes depends strongly on the type and nature of the donor bases as well as the electron acceptors.

Studies on the nature of the reaction of iodine with metal acetylacetonates $[M(acac)_n]$ are rare in the literature and the available investigations [8-13] show that these complexes are similar to those formed by aromatic hydrocarbons with I_2 and that $[M(acac)_n]$ compounds behave as π -electron donors. The interaction of iodine with metal acetylacetonate compounds were demonstrated by measurements of the electronic spectra, dielectric constants and refractive indices of solutions containing mixtures of the components.

The aim of present work is to investigate the new solid CT- complexes formed on the reaction of cobalt(II) and copper(II) acetylacetonates shown in Scheme (I) with iodine

in chloroform using electronic absorption spectroscopy, infrared spectra as well as thermogravimetric (TG) and differential thermogravimetric analysis (DTG).



Scheme (I), M= Co(II) or Cu(II)

Experimental

All chemicals used were of high grade and used without further purification. The cobalt(II)acetylacetonate, $\text{Co}(\text{acac})_2$ was obtained from Merck Chemical Co. and R. G. quality iodine (Hayashi Pure Chemical Industries Ltd.) was used and its concentration in solution was checked spectrophotometrically. The copper(II) acetylacetonate was prepared [14] by using the general method that involves adding an ammoniacal solution of copper(II) nitrate or copper(II) acetate to an alcoholic solution of a 1,3-diketone. The precipitated chelates were filtered and recrystallized.

The $[\text{Cu}(\text{acac})_2]_2\text{-I}_2$ CT-complex with the general formula $[(\text{Cu}(\text{acac})_2)_2\text{I}^+ \cdot \text{I}_3^-]$, was isolated as a greenish brown solid by the addition of an excess of saturated iodine solution (50 ml) to a saturated solution (10 ml) of the $[\text{Cu}(\text{acac})_2]$ in chloroform with constant stirring for about 25 min. The solid precipitate formed was filtered off immediately and washed several times with a little amount of CHCl_3 and dried under vacuum. The solid brown complex with the general formula $[(\text{Co}(\text{acac})_2)_2\text{I}^+ \cdot \text{I}_3^- \cdot 2\text{H}_2\text{O}]$, was prepared in a similar way to that described above by the reaction of $[\text{Co}(\text{acac})_2]$ with iodine using chloroform as a medium. The iodine solid reaction products were characterized by elemental analysis, infrared spectra, electronic absorption bands and thermal analysis data. The elemental analysis data of the solid reaction products were summarized and given as follow: $[\text{Cu}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$: C, 22.97% (23.28%); H, 2.82% (2.71%); Cu, 12.53% (12.32%); I, 50.13% (49.24%), $[(\text{Co}(\text{acac})_2)_2\text{I}^+ \cdot \text{I}_3^- \cdot 2\text{H}_2\text{O}]$: C, 22.41% (22.69%); H, 2.96% (3.02%); Co, 11.75% (11.14%); I, 49.03% (48.00%) (calculated values are shown in parentheses).

The electronic absorption spectra of the donor $[\text{M}(\text{acac})_2]$ (M = Co(II) or Cu(II)), acceptors (iodine) 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 a quartz cell of 1 cm path length. The mid infrared spectra of the reactants and the formed CT-complexes were recorded with KBr discs using a Genesis II FT-IR, while the far infrared spectra for the donor $[\text{M}(\text{acac})_2]$ and the iodine complexes were recorded from Nujol mulls dispersed on polyethylene windows in the region $50\text{-}300\text{ cm}^{-1}$ using a Mattson Infinity series FT-IR spectrometer. Thermogravimetric (TG) and differential thermo- gravimetric analysis (DTG) were carried out under a N_2 -atmosphere using a detector model Shimadzu

TG-50 H. Photometric titrations were performed [15] at 25°C for the reactions of M(II) acetylacetonate with the acceptor in chloroform as follows. The concentrations of the donor $[M(acac)_2]$ in the reaction mixtures was kept fixed at $(0.5 \times 10^{-4} M)$, while the concentrations of the acceptor were changed over the range from 0.125×10^{-4} to 1.5×10^{-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): $[Co(acac)_2]_2I^+ \cdot I_3^- \cdot 2H_2O$ and (B): $[Cu(acac)_2]_2I^+ \cdot I_3^-$ respectively in $CHCl_3$.

(A)

X ml of I_2	(Base : I_2) ratio	Absorbance at 364 nm
0.25	1 : 0.25	0.350
0.50	1 : 0.50	0.481
0.75	1 : 0.75	0.599
1.00	1 : 1.00	0.722
1.50	1 : 1.50	0.844
2.00	1 : 2.00	1.028
2.50	1 : 2.50	1.124
3.00	1 : 3.00	1.252

(B)

X ml of I_2	(Base : I_2) ratio	Absorbance at 361 nm
0.25	1 : 0.25	0.316
0.50	1 : 0.50	0.450
0.75	1 : 0.75	0.568
1.00	1 : 1.00	0.715
1.50	1 : 1.50	0.811
2.00	1 : 2.00	0.962
2.50	1 : 2.50	1.037
3.00	1 : 3.00	1.123

$$1ml \text{ donor } (5 \times 10^{-4} M) + X ml \text{ of } (I_2) (5 \times 10^{-4} M) + Y ml \text{ solvent} = 10 ml$$

Results and Discussion

The electronic absorption spectra of the reactants (cobalt(II), $[Co(acac)_2]$ or copper(II) acetylacetonates, $[Cu(acac)_2]$) ($1 \times 10^{-4} M$) with iodine as σ -acceptor ($1 \times 10^{-4} M$) in $CHCl_3$ along with those of the obtained 1:1 CT-complexes are shown in Figure 1 (A and B respectively).

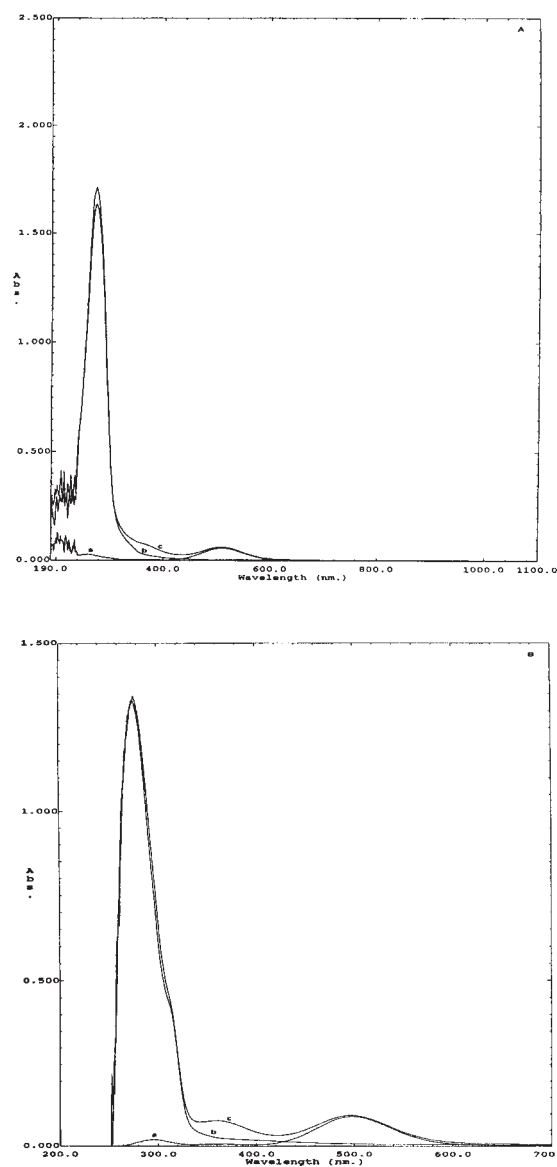


Figure 1: Electronic absorption spectra of (A) $[\text{Co}(\text{acac})_2]$ -iodine reaction in CHCl_3 , (B) $[\text{Cu}(\text{acac})_2]$ -iodine reaction in CHCl_3 , (a) = acceptor ($1 \times 10^{-4} \text{ M}$), (b) = donor ($1 \times 10^{-4} \text{ M}$), (c) = donor-acceptor CT-complex

The spectra show that the formed CT-complexes have a real strong absorption band around 360 nm for the two new triiodide CT-complexes $[\text{Co}(\text{acac})_2]_2\text{I}_3^- \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{acac})_2]_2\text{I}_3^-$. The stoichiometry of the $[\text{M}(\text{acac})_2(\text{iodine})]$ (where $\text{M} = \text{Co}(\text{II})$ or $\text{Cu}(\text{II})$) reactions were shown in all cases to be of 1:1 ratio. This was proposed on the base of the obtained elemental analysis data of the isolated solid CT-complexes as well as from the complexes infrared spectra, Figure 2 and Table 2, which indicate the existence of shifts in bands characteristic for both the $[\text{Co}(\text{acac})_2]$ and $[\text{Cu}(\text{acac})_2]$ chelates.

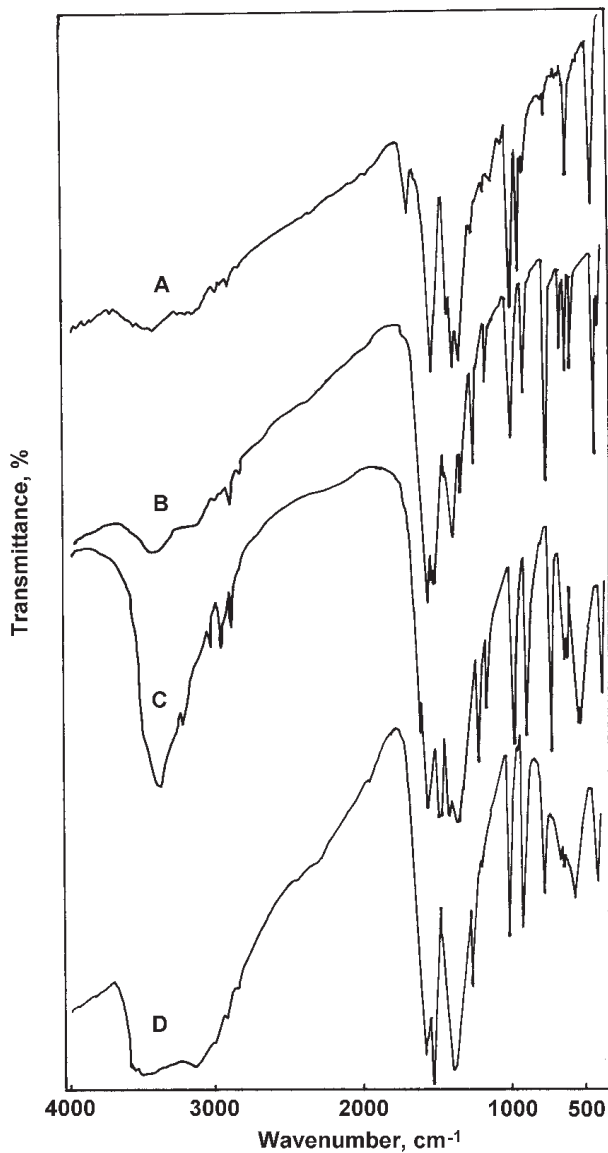


Figure 2: Infrared spectra of : (A) $\text{Cu}(\text{acac})_2$ (B) $[\text{Cu}(\text{acac})_2]_2\text{I}^+\cdot\text{I}_3^-$ complex
(C) $\text{Co}(\text{acac})_2$, (D) $[\text{Co}(\text{acac})_2]_2\text{I}^+\cdot\text{I}_3^- \cdot 2\text{H}_2\text{O}$ complex

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 $[\text{M}(\text{acac})_2]$ -(iodine) $[\text{M} = \text{Co}$ or $\text{Cu}]$ systems (indicated above) and are given in Figure 3. The $\text{M}(\text{acac})_2$ -iodine 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.

Table 2. Infrared frequencies^(a) (cm^{-1}) and tentative assignments (A): $\text{Co}(\text{acac})_2$, (B): $\text{Cu}(\text{acac})_2$, (C): $[\text{Co}(\text{acac})_2]_2\text{I}^+\cdot\text{I}_3^- \cdot 2\text{H}_2\text{O}$ and (D): $[\text{Cu}(\text{acac})_2]_2\text{I}^+\cdot\text{I}_3^-$

(A)	(B)	(C)	(D)	Assignments ^(b)
—	—	3564 w 3500 w	—	$\nu_{(\text{O-H})}$; uncord. H_2O
3425 mbr	3460 mbr	3450 vw	3454 mbr	$\nu_{(\text{O-H})}$; H_2O of KBr
3255 w 3082 m 2995 ms 2930 ms 2850 w	3300 vw 3210 vw 3008 w 2925 vw 2856 m	3286 mbr 3130 mbr 3003 vw 2930 vw 2856 vw	3160 mbr 3087 vw 3024 vw 2972 w 2930 m 2856 w	$\nu_{(\text{C-H})}$; CH_3
1657 m 1604 vs	1709 ms 1662 sh 1604 sh 1552 vs	1589 ms 1564 sh	1583 vs 1557 ms	$\nu_{(\text{C=O})}$ $\nu_{(\text{C=C})}$
1520 vs 1463 m	1515 sh 1442 m	1530 vs 1442 sh	1536 ms 1458 sh	$\nu_{(\text{C=O})}$ $\delta_{(\text{CH})}$
1400 s 1358 sh	1410 s 1374 s	1390 vs	1410 s 1358 s	$\delta_{(\text{CH}_3)}$
1264 vs 1200 s	1280 w 1196 m	1264 s 1206 s	1274 s 1190 s	$\nu_{(\text{C-C})} + \nu_{(\text{C-CH}_3)}$ $\delta_{(\text{CH})}$, in-plane bend
1133 sh 1023 vs	1149 m 1075 m 1023 vs	1142 sh 1023 vs	1128 vw 1023 vs	$\delta_{(\text{CH}_3)}$, rock
934 vs 834 vw	965 vs 928 m 824 vw	965 vw 928 vs	939 s 860 sh	$\nu_{(\text{C-CH}_3)} + \nu_{(\text{C-O})}$
771 vs	777 m	777 s	782 vs	$\delta_{(\text{CH})}$, out-of-plane bend
672 m	698 w 685 w	672 m 651 m	682 ms	Ring def. + $\nu_{(\text{M-O})}$
660 m	656 vw 635 s	614 sh	656 s 614 s	$\delta(\text{C-CH}_3)$; bend + $\nu_{(\text{M-O})}$
583 m 567 m 426 vs	557 vw 504 vw 462 vs	577 ms 420 s	457 vs 431 ms	Ring def. + $\nu_{(\text{M-O})}$ Skeletal vibration

(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.

(b): ν , stretching; δ , bending.

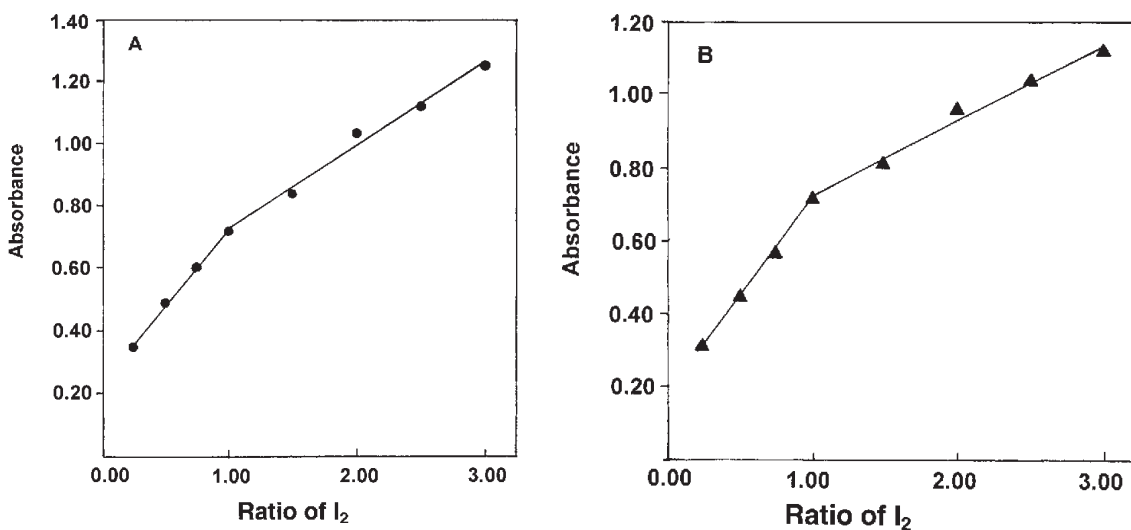


Figure 3: Photometric titration curves for (A): [Co(acac)₂]-I₂ and (B): [Co(acac)₂]-I₂ systems in chloroform at 364 and 361nm respectively.

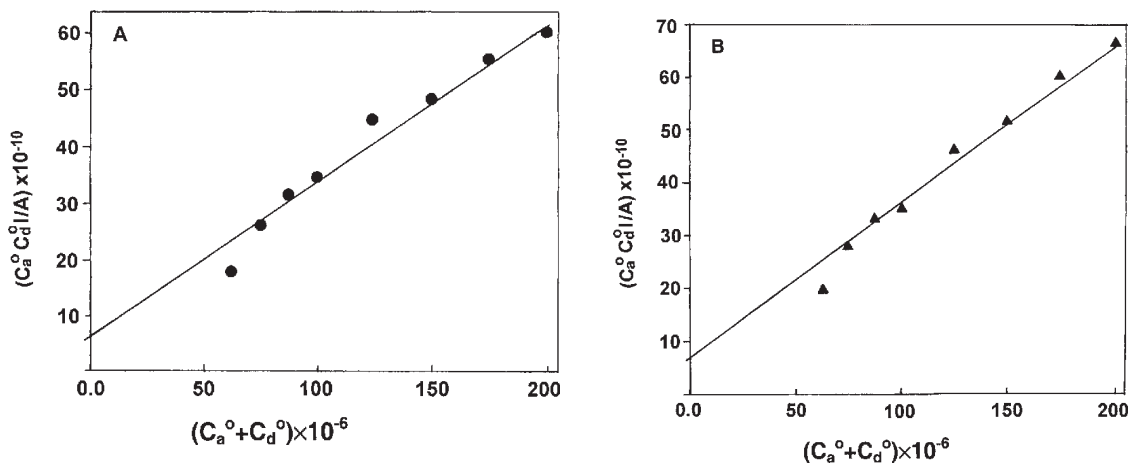


Figure 4: The modified Benesi-Hildebrand plots for (A): Iodine- [Co(acac)₂] and (B): Iodine- [Cu(acac)₂] reactions; C_a^0 , C_d^0 , A and l are the acceptor concentration, donor concentration, absorbance and the pathlength, respectively.

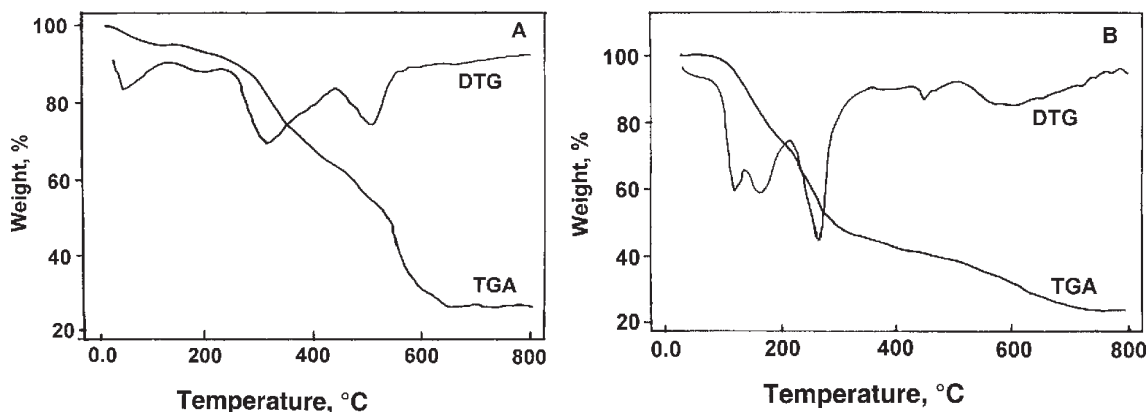


Figure 5: TGA & DTG diagrams of (A): $[\text{Co}(\text{acac})_2]_2\text{I}_3 \cdot 2\text{H}_2\text{O}$ and (B): $[\text{Cu}(\text{acac})_2]_2\text{I}_3$ complexes respectively.

Accordingly, the formed CT-complexes upon the reaction of $[\text{M}(\text{acac})_2]$ as a donor with the π -acceptor under investigation in chloroform have the general formula $[\text{M}(\text{acac})_2]_2\text{I}_3 \cdot \text{I}_3^-$. Benesi-Hildebrand plots [16] and also the modified Benesi-Hildebrand equation (1) was used to calculate the values of the equilibrium constant, K (Lmol^{-1}) and the extinction coefficient, ϵ ($\text{Lmol}^{-1}\text{cm}^{-1}$) which give a straight line by plotting the values of $C_a^0 C_d^0 l/A$ against $C_a^0 + C_d^0$ values in each system showing 1:1 donor-acceptor composition in the charge transfer complexes (Figure 4).

$$\frac{C_a^0 C_d^0 l}{A} = \frac{1}{K\epsilon} + \frac{C_a^0 + C_d^0}{\epsilon} \quad (1)$$

Here C_a^0 and C_d^0 are the initial concentrations of the iodine and the donor $[\text{M}(\text{acac})_2]$ ($\text{M} = \text{Co}$ or Cu), respectively, while A is the absorbance of the strong bands at 364 nm for $[\text{Co}(\text{acac})_2]_2\text{I}_3 \cdot 2\text{H}_2\text{O}$ and 361 nm for $[\text{Cu}(\text{acac})_2]_2\text{I}_3$ complexes. The data obtained throughout these calculations are given in Table 3.

Table 3. The values C_d^0 , C_a^0 , $C_d^0 + C_a^0$ and $C_d^0 \cdot C_a^0 l/A$, for (A): $[\text{Co}(\text{acac})_2]_2\text{I}_3 \cdot 2\text{H}_2\text{O}$ and (B): $[\text{Cu}(\text{acac})_2]_2\text{I}_3$ complexes respectively in CHCl_3 .

(A)

Base: I_2 ratio	C_d^0 $\times 10^{-4}$	C_a^0 $\times 10^{-4}$	Absorbance at 364 nm	$(C_d^0 + C_a^0)$ $\times 10^{-6}$	$(C_d^0 \cdot C_a^0)$ $\times 10^{-10}$	$(C_d^0 \cdot C_a^0 l/A)$ $\times 10^{-10}$ at 361 nm
1 : 0.25	0.5	0.125	0.350	62.5	6.25	17.86
1 : 0.50	0.5	0.250	0.481	75.0	12.50	25.99
1 : 0.75	0.5	0.375	0.599	87.5	18.75	31.30
1 : 1.00	0.5	0.500	0.722	100	25.00	34.63
1 : 1.50	0.5	0.750	0.844	125	37.50	44.43
1 : 2.00	0.5	1.000	1.028	150	50.00	48.64
1 : 2.50	0.5	1.250	1.124	175	62.50	55.60
1 : 3.00	0.5	1.500	1.252	200	75.00	59.90

(B)

Base:I ₂ ratio	C _d ^o x10 ⁻⁴	C _a ^o x10 ⁻⁴	Absorbance at 361 nm	(C _d ^o +C _a ^o) x10 ⁻⁶	(C _d ^o .C _a ^o) x10 ⁻¹⁰	(C _d ^o .C _a ^o /A) x10 ⁻¹⁰ at 364 nm
1 : 0.25	0.5	0.125	0.316	62.5	6.25	19.78
1 : 0.50	0.5	0.250	0.450	75.0	12.50	27.78
1 : 0.75	0.5	0.375	0.568	87.5	18.75	33.01
1 : 1.00	0.5	0.500	0.715	100	25.00	34.96
1 : 1.50	0.5	0.750	0.811	125	37.50	46.24
1 : 2.00	0.5	1.000	0.962	150	50.00	51.97
1 : 2.50	0.5	1.250	1.037	175	62.50	60.27
1 : 3.00	0.5	1.500	1.123	200	75.00	66.78

A straight line is obtained with a slope of $1/\epsilon$ and intercept of $1/K\epsilon$ as shown in Figure 4. The values of both K and ϵ associated with these complexes are given in Table 4.

Table 4. Spectrophotometric results of CT-complexes of $[\text{Co}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^- \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^-$ in CHCl_3 .

Acceptor/ I_2	K/Lmol ⁻¹	λ_{max} /nm	ϵ_{max} /Lmol ⁻¹ cm ⁻¹
$[\text{Co}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^- \cdot 2\text{H}_2\text{O}$	4.31×10^4	364	3.57×10^4
$[\text{Cu}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^-$	4.23×10^4	361	3.38×10^4

These complexes show large values of both the equilibrium constants (K) and the extinction coefficients (ϵ) indicate the stability of the chelate rings under the conditions employed, and, when considered along with the accompanying facts, support the present interpretation of the 364 or 361 nm absorption bands.

The appearance of the absorption band around 360 nm is well known [17-19] as characteristic for the formation of the triiodide ion (I_3^-). This was also supported by the far infrared spectra of the iodine complexes, Table 5.

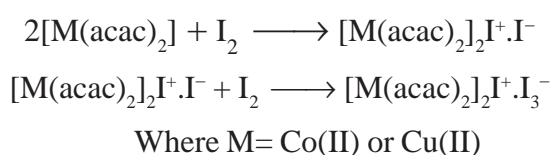
Table 5. Fundamental vibrations for some triiodide compounds.

Compounds	Assignments*			References
	ν_1	ν_2	ν_3	
KI_3	111		143	17
CsI_3	103	69	149	21
$(\text{CH}_3)_4\text{NI}_3$	111	74	138	21, 22
$(\text{C}_2\text{H}_5)_4\text{NI}_3$	104	72, 66	132	22
$(\text{TACPD})\text{I}^+\cdot\text{I}_3^-$	109	60	132	20
$(\text{HMTACTD})\text{I}^+\cdot\text{I}_3^-$	110	61	144	20
$[\text{Ni}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^-$	101	84	132	13
$[\text{Co}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^-$	142	110	76	Present work
$[\text{Cu}(\text{acac})_2]_2\text{I}_3^+\cdot\text{I}_3^-$	138	103	75	Present work

ν_1^* , ν_s (I-I); ν_2 , δ (I_3^-); ν_3 , ν_{as} (I-I).

This spectra show the characteristic bands of the triiodide ion for the two CT-complexes $[\text{Co}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^- \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ at around 140, 106 and 75 cm^{-1} , which are assigned to $\nu_{\text{as}}(\text{I-I})$, $\nu_{\text{s}}(\text{I-I})$ and $\nu(\text{I}_3^-)$, respectively. These three absorptions do not exist in the spectrum of the donor. However, the I_3^- ion may be linear ($\text{D}_{\infty\text{h}}$) or non linear ($\text{C}_{2\text{v}}$). Group theoretical analysis indicates that the I_3^- with $\text{C}_{2\text{v}}$ symmetry displays three vibrations $\nu_{\text{s}}(\text{I-I})$; A_1 , $\nu_{\text{as}}(\text{I-I})$; B_2 and $\nu(\text{I}_3^-)$; A_1 , all are infrared active in good agreement [13, 17, 20-22] with the observed three infrared bands for $[\text{M}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ as shown in Table 5.

According to the foregoing discussion a general mechanism is proposed for the formation of $[\text{M}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ complexes as follows:

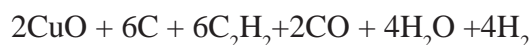
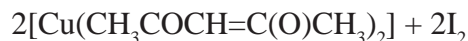
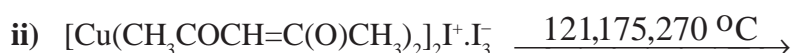
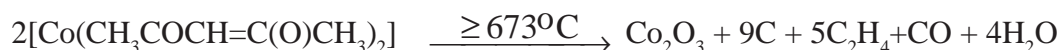
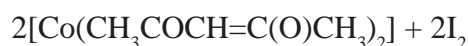
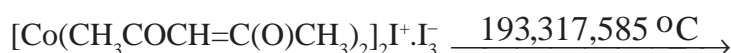


The formation of the iodine intermediate $[\text{M}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ is well known between iodine and cyclic polyamines [20,23]. To confirm the proposed formula and structure for the two new $[\text{Co}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^- \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ complexes, thermogravimetric (TG) and differential thermogravimetric analysis (DTG) were carried out for these complexes under N_2 flow. TG curves are shown in Figure 5 (A and B). Table (6) gives the maximum temperature values, $T_{\text{max}}/^\circ\text{C}$, together with the corresponding weight loss for each step of the decomposition reactions of these complexes.

Table 6. The maximum temperature, $T_{\text{max}}/^\circ\text{C}$, and weight loss values of the decomposition stages for the $[\text{Co}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^- \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ complexes.

Decomposition		$T_{\text{max}}/^\circ\text{C}$	Lost species	%weight losses	
				Found	Calc.
$[\text{Co}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^- \cdot 2\text{H}_2\text{O}$	First stage	85°C	$2\text{H}_2\text{O}$	3.50%	3.40%
	Second stage	193,317,585°C	2I_2	47.60%	48.00%
	Third stage	$\geq 673^\circ\text{C}$	$5\text{C}_2\text{H}_4 + \text{CO} + 4\text{H}_2\text{O}$	21.98%	22.69%
	Total loss			73.08%	74.09%
	Residue			26.92%	25.91%
$[\text{Cu}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$	First stage	121,175,270°C	2I_2	48.55%	49.25%
	Second stage	$\geq 412^\circ\text{C}$	$6\text{C}_2\text{H}_2 + 2\text{CO} + 4\text{H}_2\text{O} + 4\text{H}_2$	28.07%	28.33%
	Total loss			76.62%	77.58%
	Residue			23.38%	22.42%

The data obtained strongly support the structure proposed for the two iodine complexes and indicate that, the thermal decomposition of these complexes in inert atmosphere proceeds approximately with three or two main degradation steps (Figure 5). The thermal decomposition reactions of the complexes can be summarized as follows:



The infrared spectra of the formed $[\text{Co}(\text{acac})_2]_2\text{I}^+\cdot\text{I}_3^-$ and $[\text{Cu}(\text{acac})_2]_2\text{I}^+\cdot\text{I}_3^-$ CT-complexes, are shown in Figure (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 which detected some changes in intensities and in some cases show small shifts in the frequency values compared with those of the free reactants. This can be explained on the basis of symmetry and electronic structure changes in both acceptor and $[\text{M}(\text{acac})_2]$ in the formed CT-complexes compared with those of the free molecules.

Whereas all the metal acetylacetonates used in the present study absorb strongly only in the region 270-300 nm due to $\pi_3 \rightarrow \pi_4$ transitions, a new absorption band between 360 and 366 nm has been observed in the case of each metal acetylacetonate interacting with iodine. This new absorption band is interpreted as a charge-transfer band of the $\text{M}(\text{acac})_n\text{-I}_2$ molecular complex. Since this absorption band falls remarkably close to the region where one of the two characteristic bands (*ca.* 290 and 360 nm) for the triiodide ion is to be found [24,25], an alternative possibility, in which an electrophilic attack by iodine on metal acetylacetonates may produce corresponding iodo chelates and the triiodide ion (resulting from a combination of iodine ion with iodine), must be considered.

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