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Spectoscopic and structural studies on charge-transfer complexes of lanthanum(III)acetylacetonate with σ-acceptor iodine and π-acceptor DDQ

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ABSTRACT

The interaction of the donor La(III)acetylacetonate, [La(acac)$_3$], with iodine as a σ-acceptor and with 2,3-dichloro-5,6 dicyano-1,4-benzoquinone, (DDQ) as a π-acceptor have been studied in the solvents CH_2Cl_2, $CHCl_3$ and CCl_4 at room temperature. The obtained results indicate the formation of 1:1 charge-transfer complexes. The electronic and infrared absorptions and elemental analysis of the formed complexes indicate that the complexes are formulated as the triiodide $[(La(acac)_3)_2I]^+ \cdot I_3^-$ and [La(acac)$_3$(DDQ)]. Far-infrared spectrum shows that the triiodide ion is nonlinear with C_{2v} symmetry. The values of the equilibrium constants (K) and obsorptivities (ε) for both the formed CT-complexes are calculated and discussed in term of reaction stoichiometry values and molecular steric hindrance. Mid infrared spectra suggest that the electron donation from [La(acac)$_3$] to the donors I_2 or DDQ could mainly take place through the oxygen atoms in addition to the acac ring π-molecular orbitals.

1. Introduction

The study of the properties of charge-transfer complexes formed in the reaction of electron acceptors and many compounds containing nitrogen, sulfur and oxygen donor atoms have attracted considerable attention and growing importance [1–14]. This is owing to the important role of charge transfer processes play in biological systems as well as significant physical properties of CT-products such as electrical conductivities and the use of some in many forms of electronic and solar cells and in the analysis of some drugs and pharmaceutical preparations [15–21].

Metal acetylacetonates [M(acac)$_{n=2,\ 3\ \text{or}\ 4}$] show π-electron delocalization in their rings and, therefore, show ability to form molecular complexes with σ-donors like iodine [22–25].

Such an ability of complexation has been taken as strong evidence for such π-delocalization. It has been proposed [24] that the formation of these complexes are similar to those formed by aromatic hydrocarbons with σ-acceptors like iodine as well as π-acceptors like DDQ. However, in these studies on other related systems, the formation of the triiodide complex with its well known characteristic absorptions [2,11,26–28] around 360 and 290 nm were ignored or wrongly assigned either to the blue-shift of I_2 band or to CT band of $[M(acac)_n] \cdot I_2$ complex [24,25].

To continue or investigation in this research area [2–13], we report here the formation of the two new CT-complexes $[(La(acac)_3)_2I]^+ \cdot I_3^-$ and [La(acac)$_3$(DDQ) formed in the reaction of [La(acac)$_3$] with iodine and DDQ, respectively. The aim of the work is to determine the reaction stoichiometries, characterize the new products and make on an assessment of the correct nature of bonding and structure inherent in each of them.

2. Experimental

All chemicals used in this study were of high grade, iodine was obtained from BDH while 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was obtained from Aldrich Chemical Co., while the lanthanum(III)acetylacetonate, $[La(acac)_3] \cdot 6H_2O$ was prepared according to the known method [28] as follows. Lanthanum(III) oxide (1.5 g) was dissolved in the least amount of dilute hydrochloric acid solution, and the excess acid was removed by evaporation. The resulting chloride solution was dissolved in 100 mL volume of 1:1 water-purified dioxin solution containing a slight excess of a acetylacetone. The pH value of the vigorously stirred solution was adjusted at 7.8 by the dropwise addition of aqueous ammonia to just below those of hydroxide precipitation and the solution was stirred for about 20 h. The crystalline product was filtered off, washed with successive portions of ethanol and dried over P_2O_5 under vacuo. The solid $[(La(acac)_3)_2I]^+ \cdot I_3^-$ complex was isolated as a dark brown solid by mixing a saturated solution (20 mL) of [La(acac)$_3$] to a saturated solution (50 mL) of iodine in CH_2Cl_2.

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The mixture was stirred for 10 min, at room temperature and the precipitate was filtered off, washed with minimum amounts of CH_2Cl_2 and dired under vacuo over P_2O_5. The 1:1 dark green charge-transfer complex [La(acac)$_3$(DDQ)] was prepared by mixing a saturated solution (10 mL) of [La(acac)$_3$] with a saturated solution (50 mL) of DDQ in CH_2Cl_2. The reaction mixture was stirred at room temperature for about 45 min. The precipitate was filtered off and washed several times with the minimum amounts of CH_2Cl_2 and dried over P_2O_5 under vacuo. The new prepared solid complexes were characterized through their vibrational and electronic absorption spectra as well aselemental analysis (calculated values are shown in brackets). Analysis; $[(La(acac)_3)_2I]^+ \cdot I_3^- \cdot 12H_2O$, (M/W: 1596.4 g); C, 21.87 (22.57); H, 4.62 (4.17); I, 31.11 (31.79) and La, 17.12% (17.40%). $[La(acac)_3(DDQ)] \cdot 6H_2O$, (M/W: 770.9 g); C, 34.92 (35.80); H, 4.34 (4.28); N, 3.50 (3.63); Cl, 8.76 (9.21) and La, 18.10% (18.03%). Elemental analysis (CHN) were performed by the microanalytical unit, Cairo University while La contents were determined using atomic absorption spectrometer model Pye-Unicam SP 1900. The content of the water of crystallization in both CT-complexes $[(La(acac)_3)_2I]^+ \cdot I_3^- \cdot 12H_2O$ and $[La(acac)_3(DDQ)] \cdot 6H_2O$ were determined by gravimetric means. Each complex sample was heated in an open air crucible at 155–160 °C for a time to reach in each case a constant weight. The heating was controlled to a maximum of 160 °C to avoid any iodine losses since the $I^+ \cdot I_3^-$ unit in a number of CT-complexes undergoes thermal decomposition at a temperature range of 180–200 °C [13,29]. The complete loss of water molecules were checked from IR-spectra of the complex samples in Nujol mulls in order to prevent possible water contamination from air or from KBr. The obtained data agree quite well with the proposed formula; H_2O, 13.14% (13.54%) for the complex $[(La(acac)_3)_2I]^+ \cdot I_3^- \cdot 12H_2O$ and 14.36% (14.01%) for the complex $[La(acac)_3(DDQ)] \cdot 6H_2O$ (calculated values of H_2O are shown in brackets).

The electronic absorption spectra of the donor [La(acac)$_3$] and the acceptors iodine and DDQ and the formed CT-complexes were recorded in CH_2Cl_2 in the region 700–200 nm using a Perkin–Elmer double beam spectrometer model EZ-210 fitted with a quartz cell of 1.0 cm path length.

In order to determine the stoichiometry of the formed CT-complexes, photometric titrations were performed in each of the solvents CH_2Cl_2, $CHCl_3$ and CCl_4 for the reactions of the [La(acac)$_3$] with the each of iodine and DDQ at 25 °C according to the known method [29,30]. These concentration of [La(acac)$_3$] was kept fixed at 5×10^{-5} and 1×10^{-4} mol L^{-1} in the case of the reactions with iodine and DDQ, respectively. The iodine concentration was changed over the range from 1.25×10^{-5} to 15×10^{-5} mol L^{-1} while that of DDQ was changed over the range from 0.25×10^{-4} to 3.0×10^{-4} mol L^{-1}. In these reactions, the donor:acceptor ratio varying from 1:0.25 to 1:3. The photometric titration measurements were based on the characteristic absorptions at 362 and 290 nm for the formed [La(acac)$_3$]–iodine complex and at 407 and 309 nm for the formed [La(acac)$_3$]–DDQ complex. Infrared spectra in the region 4000–500 cm^{-1} for the free reactants and the formed CT-complexes were recorded from KBr disks using a Niclolet FT-IR spectrometer model 670 while the far-infrared spectrum (200–50 cm^{-1}) for the solid iodine complex was recorded from a Nujol mull dispressed on polyethylene windows using a Nicolet FT-IR spectrometer model 760.

3. Results and discussion

3.1. Reaction of La(acac)$_3$ with iodine

The electronic absorption spectra of the [La(acac)$_3$]–iodine complex were measured in various solvents such as CCl_4, $CHCl_3$ and CH_2Cl_2. The spectrum of 1:1 [La(acac)$_3$]–iodine mixture of a concentration of 5×10^{-5} mol L^{-1} of each reactant in CH_2Cl_2 is shown in Fig. 1.

The spectrum of the formed complex shows real absorptions at 362 and 290 nm which are not present in spectra of both free reactants, iodine and [La(acac)$_3$]. Photometric titration curves for the reaction based on the two characteristic absorptions for the new iodine complex at 362 and 290 nm in CH_2Cl_2 are shown in Fig. 2. The curves of the two absorptions show the same point of inflections clearly indicate two facts that the two absorptions belong to one species and that the stoichiometry of [La(acac)$_3$]–iodine reaction is 1:1 This stoichiometry of the reaction in the solvents $CHCl_3$, CH_2Cl_2 and CCl_4 is shown to be the same, 1:1. The formation of this 1:1 complex is supported by elemental analysis data. Taking these facts into consideration beside that the two absorptions of the formed iodine complex around 362 and 290 nm are well know [9,14,27] to be characteristic for the formation of triiodide ion, I_3^-, we conclude that the formed iodine complex is formulated as $[(La(acac)_3)_2I]^+ \cdot I_3^-$. These two absorptions around 360 and 290 nm were wrongly assigned in many other related iodine [M(acac)$_{n=2,\ 3\ \text{or}\ 4}$] systems [24] where the 290 nm band was assigned to the blue shifted I_2 band and the other band around 360 is attributed to the intermolecular charge transfer upon complexation. Here, it was wrongly assumed [24] the formation of simple complex-iodine type, [La(acac)$_3$]–I_2 rather than our findings of the formation of the triiodide product, $[(La(acac)_3)_2I]^+ \cdot I_3^-$. It is known that the 510 nm band of iodine in CH_2Cl_2 is assigned to the electronic transition of the type 4π–$10\sigma^*$. The split of this iodine band with blue shifts upon complexation with [La(acac)$_3$] resulted in the two observed bands at 362 and 290 nm upon the formation of the triiodide ion, I_3^-. Such blue shifts of the iodine band upon complexation is obviously due to the perturbation of the $10\sigma^*$ molecular orbital of iodine and should be assigned to

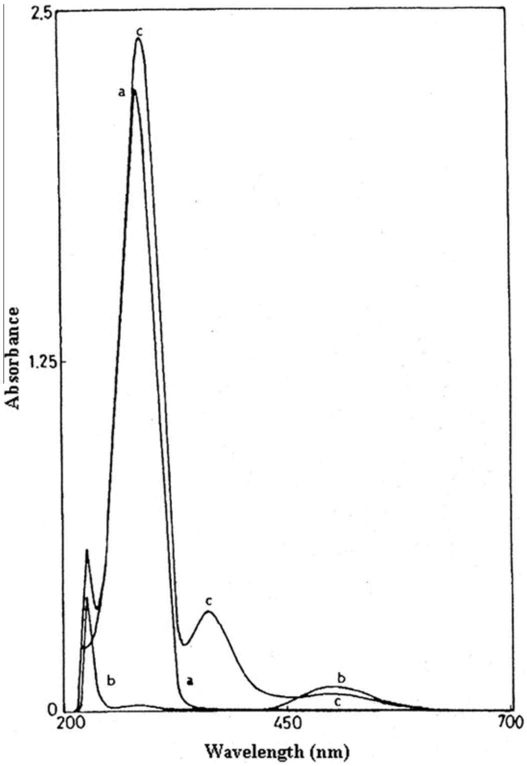

Fig. 1. Electronic absorption spectra of (a) [I_2] = 5×10^{-5} mol L^{-1}, (b) [La(acac)$_3$] = 5×10^{-5} mol L^{-1}, (c) I_2–[La(acac)$_3$] mixture [I_2] = [La(acac)$_3$] = 5×10^{-5} mol L^{-1}.

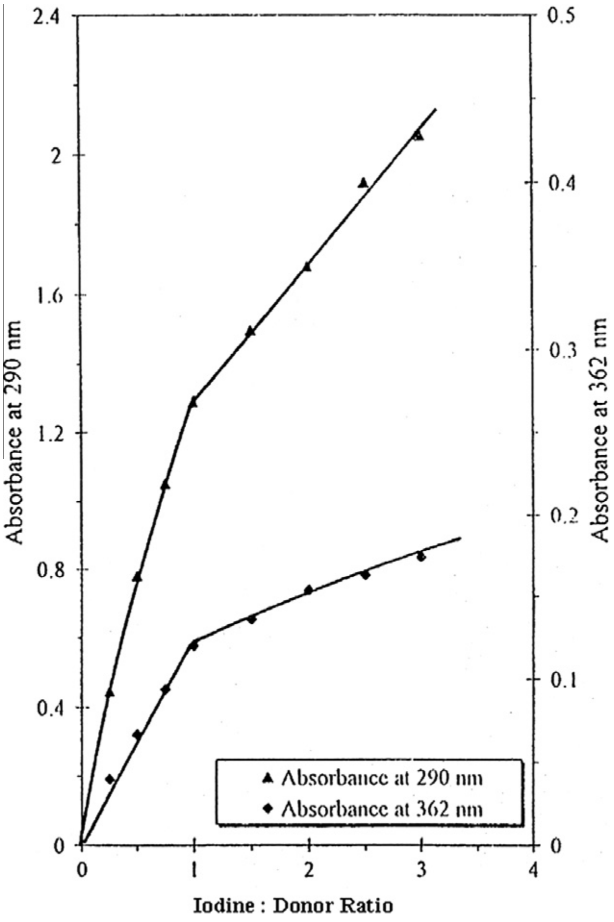

Fig. 2. Photometric titration curves for La(acac)$_3$–I$_2$ mixture.

allowed transitions in the newly formed triiodide ion. The wrong assumption [24] in related systems with different metals of the formation of I$_2$ complex, [M[acac)n]·I$_2$ rather than I_3^- complex lead also to wrong assignments of the observed low wavenumber vibrations of iodine species. The formation of I_3^- ion in our complex under study was further supported by its characteristic far-infrared absorptions, Table 1. The triiodide shows three infrared absorption band at 138, 104 and 76 cm^{-1} assigned to ν_{as}(I–I), ν_s(I–I) and $\delta(I_3^-)$, respectively. Group theoretical analysis indicate that the I_3^- ion in [La(acac)$_3$]$_2$I$^+$·I_3^- is nonlinear with C_{2v} symmetry, where all of the three vibrations should be infrared active. It is of interest to indicate here that the ν(I–I) bond vibrations of I_3^- ion are moved to lower wavenumber values at 138 and 104 cm^{-1} (Table 1) upon complexation compared with that known [31] of free iodine at 180 cm^{-1}. Such a wavenumber decrease may be understood as a result of the electron donation from [La(acac)$_3$] to σ^*-antibonding orbital of iodine lowering the iodine bond strength and hence its bond vibration wavenumber value. This conclusion is in agreement with the known values [32] of the I-I stretching force constants of 0.90 and 1.72 mdyn/°A for the, I_3^- and free I$_2$, respectively. We should indicate here that the assumption of Kulevsky and Butamina [24] of the formation of [M(acac)$_n$]·I$_2$ iodine-complex should display only one infrared band related to ν(I–I) and this is expected to occur at higher value than those observed for the triiodide in [La(acac)$_3$]$_2$I$^+$·I_3^- at 138 and 104 cm^{-1}. The ν(I–I) in the iodine complex [9] [(TTCTD)]·I$_2$ occurs at 154 cm^{-1}; (TTCTD), 1,4,8,11-tetrathiacyclotetradecane. The higher value of iodine vibration in this complex is due to that the charge transfer from the donor (TTCTD) to I$_2$ is relatively low and not enough to form the iodide and hence the triiodie ion. This conclusion is supported by the fact that when substituting the 4S atom in (TTCTD) with stronger donor atoms like nitrogen leads to higher charge transfer value to iodine enough to form the triiodide ion [11] as in [(TACTD)]I$^+$·I_3^-; (TACTD), 1,4,8,11-tetraazacylotetradecane As mentioned before, the donor donates to the σ^*-molecular orbital of iodine lowering its force constant value and then its bond vibration. Accordingly, we conclude here that the magnitude of the decrease of iodine bond vibration upon complexation compared with the vibration of free iodine [31] at 180 cm^{-1} is a real measure of the charge transfer quantity from donor to iodine.

Table 1
Far infrared spectra for I_3^- ion.

Compound[a]	Assignments[b]			Reference
	ν_{as}(I–I)	ν_s(I–I)	$\delta(I_3^-)$	
KI$_3$	149	103	69	[35]
[(TACPD)I]$^+$·I_3^-	132	109	60	[11]
[Ni(acac)$_2$]$_2$I$^+$·I_3^-	132	101	84	[13]
[(La(acac)$_3$)$_2$I]$^+$·I_3^-	138	104	76	Present work

[a] (TACPD), tetraazacyclopentadecane.
[b] ν, stretching; δ, bending.

The mid infrared spectra of [La(acac)$_3$] and [(La(acac)$_3$)$_2$I]$^+$·I_3^- are shown in Fig. 3 and tabulated with their band assignments in Table 2. The spectrum of [(La(acac)$_3$)$_2$I]$^+$·I_3^- shows almost the same characteristic bans for the free donor [La(acac)$_3$] but with some small changes of band positions and intensities. This is due to the complexation of the donor with iodine where changes in both electronic structure and symmetry of [La(acac)$_3$] are expected. However, it seems in our system that these changes are very limited and in particular for the υ(C=C) wavenumber values of the acac ring before and after complexation. This may infer that the donation from the acac comes mainly from the lone pair of its oxygens to the σ^*-molecular orbital of iodine in addition to from the π^* of the acac ring. Donation from π^* orbitals is expected to strengthen the C=C bond and hence increase of its bond vibration which is not over obvious in the case in [(La(acac)$_3$)$_2$I]$^+$·I_3^- spectrum. To clarify this point, vibrational normal coordinate analysis is needed along with bond force constant calculations for acac before and after complexation in the light that electronic and symmetry changes are expected between the two cases.

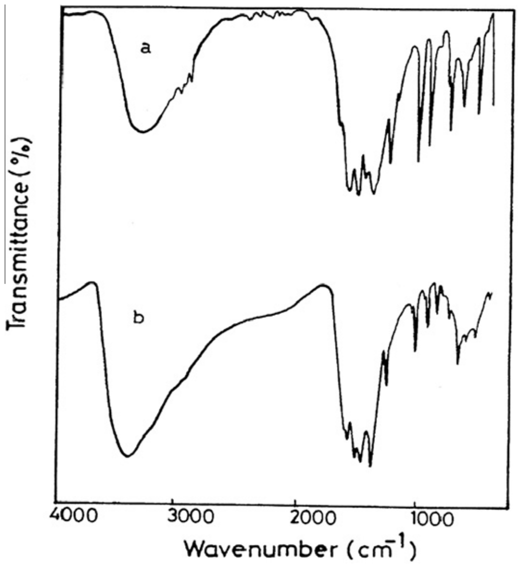

Fig. 3. Infrared spectra of (a) [La (acac)$_3$]·6H$_2$O and (b) [(La(acac)$_3$)$_2$I]$^+$·I_3^-·12H$_2$O.

Table 2
Infrared wavenumbers[a] (cm^{-1}) and tentative assignments for $La(acac)_3$ and $[(La(acac)_3)_2I]^+ \cdot I_3^- \cdot 12H_2O$.

$[La(acac)_3]$	$[(La(acac)_3)_2I]^+ \cdot I_3^-$	Assignments[b]
3299 br	3381 br	ν(O—H); H_2O
3063 sh	3187 sh	ν(C—H)
2995 w	3000 sh	
2919 w	2906 vw	
	2843 w	
1589 s	1640 sh	δ(H_2O)
1520 s	1577 s	ν(C=O)
1458 w	1517 s	ν(C=C)
1386 s	1464 s	δ(CH)
	1374 s	δ(CH_3)
1257 s	1262 s	ν(C—O),
1190 w	1050 w	ν(C—C)
1014 vs	1021 vs	
778 w	845 s	δ(CH); out of plane bend
757 vw	749 s	
649 vs	675 s	δ(CH_3); rock
609 w	608 w	
527 vs	531 w	ν(La—O)
453 w	–	
–	418	

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

A General mechanism describing the formation of the triiodide complex is proposed as follows:

(1) Formation of the outer complex; $2\ [La(acac)_3] + I_2 \rightarrow [(La(acac)_3)_2] \cdot I_2$
(2) Formation of the inner-complex; $[(La(acac)_3)_2] \cdot I_2 \rightarrow [(La(acac)_3)_2 \cdot I]^+ \cdot I^-$
(3) Triiodide formation; $[(La(acac)_3)_2\ I]^+ \cdot I^- + I_2 \rightarrow [(La(acac)_3)_2I]^+ \cdot I_3^-$

The formation of the $[(La(acac)_3)_2I]^+ \cdot I_3^-$ reaction intermediate is analogous to those well known species formed in this reaction of iodine with many various donors [2,11,33]. It is of interest to see from the 1:1 $[La(acac)_3] \cdot I_2$ reaction ratio with the formation of triiodide ion product $[(La(acac)_3)_2I]^+ \cdot I_3^-$ that the 6 acac rings from the two $[La(acac)_3]$ unit, all together accommodate the positive iodine ion, I^+. In this case, it is expected that I^+ ion is centered somehow between the two $[La(acac)_3]$ units and ionically bonded to the $\cdot I_3^-$ ion.

3.2. Reaction of La $(acac)_3$ with DDQ

Fig. 4 shows the electronic absorption spectra of 1×10^{-4} mol L^{-1} solutions of $[La(acac)_3]$, DDQ and their $[La\ (acac)_3]$–DDQ mixture in CH_2Cl_2. New absorption bands which do not belong to any of the free reactants are observed in the spectrum of the reaction mixture at 407 and 309 nm and assigned to the CT-transition in the formed $[La(acac)_3]$–DDQ complex. The stochiometry of the reaction in the solvents $CHCl_3$, CH_2Cl_2 and CCl_4 is shown to be the same 1:1 $[La\ (acac)_3]$ to DDQ. This is based on the photometric titration curve shown in Fig. 5. Accordingly, the formed CT-complex is formulated as $[La\ (acac)_3(DDQ)]$. This conclusion was supported by the elemental analysis data of the solid complex. The infrared spectra of the free reactants $[La(acac)_3]$, DDQ and the CT-complex $[La(acac)_3(DDQ)]$ are shown in Fig. 6 and tabulated and assigned in Table 3. The spectrum of the CT-complex shows the main characteristic bands for both $[La(acac)_3]$ and DDQ with as expected, small changes in band wavenumber values and intensities. For example the ν(CN) vibration of the complexed DDQ occurs as a strong band at 2216 corresponds to 2201 and 2190 cm^{-1} for the free DDQ while the ν(C=O) occurs at 1768

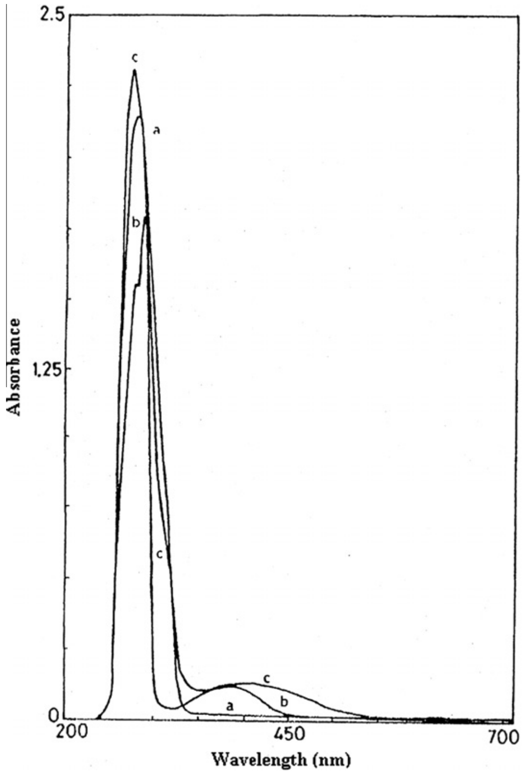

Fig. 4. Electronic absorption spectra of (a) $[La(acac)_3] = 1 \times 10^{-4}$ mol L^{-1}, (b) $[DDQ] = 1 \times 10^{-4}$ mol L^{-1}, (c) $[La(acac)_3]$–DDQ mixture; $[La(acac)_3] = [DDQ] = 1 \times 10^{-4}$ mol L^{-1}.

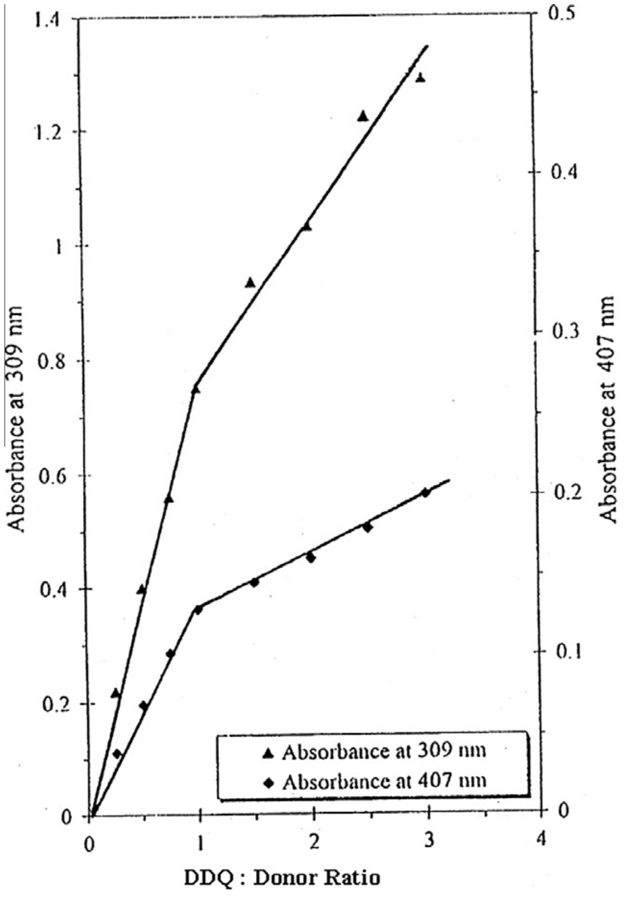

Fig. 5. Photometric titration curves for $[La(acac)_3]$–DDQ mixture.

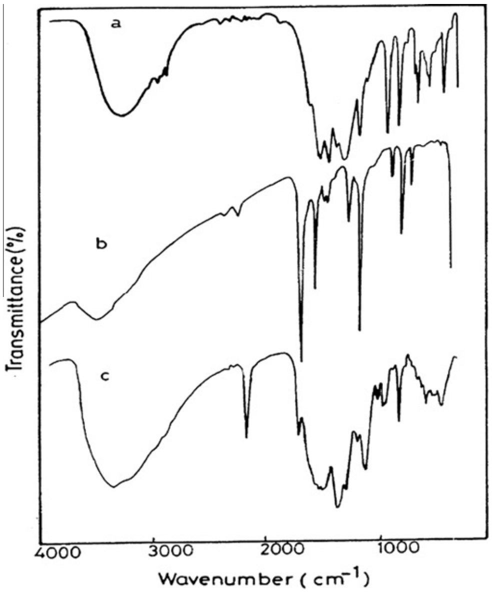

Fig. 6. Infrared spectra of (a) [La(acac)$_3$]·6H$_2$O, (b) DDQ, (c) [La(acac)$_3$(DDQ)]·6H$_2$O.

and 1760 cm^{-1} for the complexed and free DDQ, respectively. The decrease of both CN and C=O vibrations of DDQ upon complexation could be arise from donation from the acac rings to the π^*-molecular orbitals of DDQ lowering its bond order value and hence its bond vibrations. Again to clarify this conclusion, vibrational analysis and bond force constant calculations are needed. The observed small changes between the spectrum of the CT-complex and those of the reactants could also be resulted from the expected changes in both symmetry and electronic structures of both reactants upon complexation.

Table 3
Infrared wavenumbers[a] (cm^{-1}) and tentative assignments for [La(acac)$_3$], DDQ and [La(acac)$_3$(DDQ)].

La(acac)$_3$	DDQ	[La(acac)–(DDQ)]	Assignments[b]
3299 br	3430 m	3358 s, br	ν(O—H); H$_2$O
3063 sh	–	3187 w	ν(C—H)
2995 w	–	3000 w	
2919 w	–	2906 w	
	–	2812 w	
–	2201 m	2216 vs	ν_{as}(CN); DDQ
	2190 w		ν_s(CN); DDQ
	1760 vs	1768 ms	ν(C=O); DDQ
–	1634 ms	1625 w	ν(C=C); La(acac)$_3$ and DDQ
1589 s	1592 w	1594 w	
1520 s	–	1566 w	
1458 w	–	1442 vs	δ(CH$_3$)
1386 s	1374 m	1368 w	ν(C—C); DDQ and La(acac)$_3$
1257 s	1187 s	1260 ms	
1190 w	–	1195 vs	δ(CH$_3$); La(acac)$_3$
		1083 s	
		1041 s	
1014 vs		1000 w	
		992 w	CH deformation; La(acac)$_3$
917 vs		910 vs	
859 w			
778 w	748 m	752 w	ν(C—Cl); DDQ and CH in plane
757 vw	685 ms	703 w	Bend
645 vs	625 m	670 ms	ν(C—Cl); DDQ
609 w		593 w	CH out of plane bend
527 vs		543 ms	

[a] br, broad; m, medium; s, strong; v, very; w, weak.
[b] ν, streching; δ, bending.

It was of interest to calculate the values of both the formation constant, *K*, and the molar absorptivity, ε, for each of the formed complexes [(La(acac)$_3$)$_2$I]$^+$·I$_3^-$ and [La(acac)$_3$–(DDQ)]. The 1:1 modified Benesi–Hildebrand equation [34] was used in the calculations. Figs. 7 and 8 show these plots. The obtained data for the reactions in CHCl$_2$ are given in Table 4. The data reveals that both complexes [(La(acac)$_3$)$_2$I]$^+$·I$_3^-$ and [La(acac)$_3$(DDQ)] show high values of both the *K* and ε. The high values of *K* reflect the high stability of the formed CT-complex as a result of the expected high electron

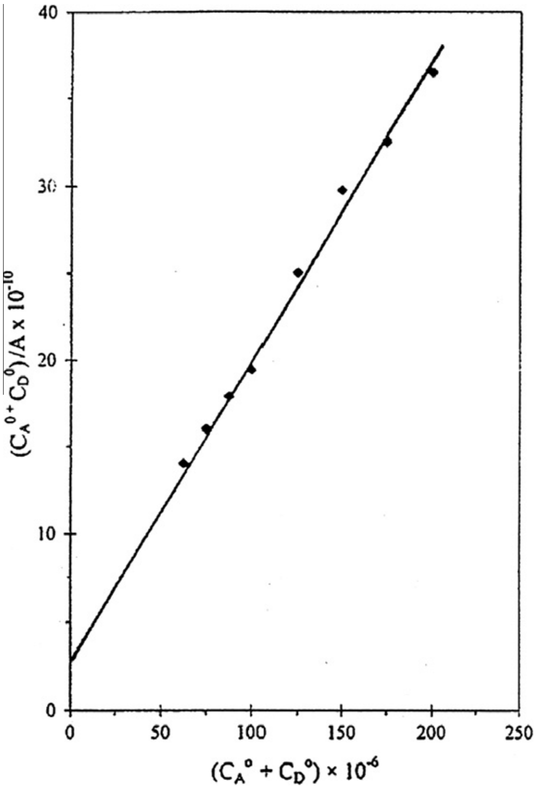

Fig. 7. The modified Benesi–Hildebrand plot for [La(acac)$_3$]–iodine reaction based on the absorption at λ = 290 nm.

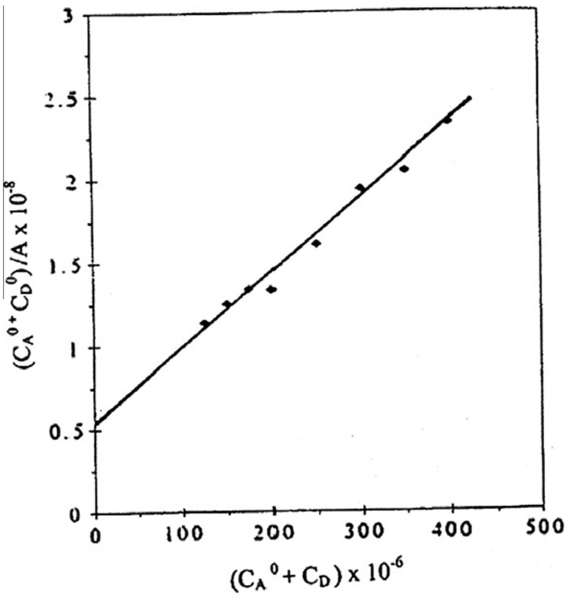

Fig. 8. The modified Benese–Hildebrand plot for [La(acac)$_3$]–DDQ reaction based on the absorption at 407 nm.

Table 4
Spectorophotometric results of the formed CT-complexes $[(La(acac)_3)_2I]^+{\cdot}I_3^-$ and $[La(acac)_3(DDQ]$ in CH_2Cl_2.

Complex	K ($l\ mol^{-1}$)	λ max (nm)	ε ($l\ mol^{-1}\ cm^{-1}$)
$[(La(acac)_3)_2I]^+{\cdot}I_3^-$	7.32×10^4	362	0.62×10^4
		290	1.15×10^4
$[La(acac)_3(DDQ)]$	1.85×10^4	407	0.341×10^4

donation from the $[La(acac)_3]$ while the high value of ε agree quite well with the formation of CT-complexes which are known to have high absorpativity values [11]. The values of K and ε for both complexes show variation as the solvent is changed from CH_2Cl_2 to $CHCl_3$ or CCl_4, but no clear relationship with solvent properties can be obtained. The value of K for $[(La(acac)_3)_2I]^+{\cdot}I_3^-$ is about four times higher than that of $[La(acac)_3(DDQ)]$. It might be difficult to discuss such a variation in the light that the iodine is a σ-acceptor while DDQ is a π-acceptor. The molecular sizes of both acceptors are also different reflecting a higher steric hindrance in case of DDQ and hence, an expected decrease in its formation constant value compared with that of iodine.

In conclusion, The formation of $[(La(acac)_3)_2I]^+{\cdot}I_3^-$ is analogous to a number of other complexes [2,11] such as [(TACTD)] $I^+{\cdot}I_3^-$ and $[((TACTDD)]I^+{\cdot}I_3^-$; (TACTD), 1,4,8,11-tetraazacyclotetradecane and (TACTDD). 1,4,8,11-tetraazacyclotetradecane-5,7-dione. The $[La(acac)_3]$: I_2 ratio is 1:1. Here, two donor molecules of $[La(acac)_3]$ are required for the formation and stabilization of the $I^+{\cdot}I_3$ unit. This might indicate that $[La(acac)_3]$ acts as a relatively weaker donar compared with other donors such as amines, TACTD and TACTDD where one donor molecule is able to stabilize the trioidide product. On the other hand, $[La(acac)_3]$ reacts with the donor DDQ with the same stoichiometry of 1:1 forming the CT-complex $[La(acac)_3(DDQ)]$. Here, the steric hindrance could play an important role in decreasing the complex stability compared with that of iodine complex. This is evident from that the formation constant of the iodine complex $[(La(acac)_3)_2I]^+{\cdot}I_3^-$ is almost four times higher than that of the corresponding complex $[La(acac)_3(DDQ)]$.

References

[1] M. Mizuno, J. Tanaka, I. Harada, J. Phys. Chem. 85 (1981) 1789.
[2] E.M. Nour, S.Y. Alqaradawi, A. Mostafa, E. Shams, H.S. Bazzi, J. Mol. Struct. 980 (2010) 218.
[3] S.Y. AlQaradawi, H.S. Bazzi, A. Mostafa, E.M. Nour, Spectrochim. Acta 71A (2008) 1594.
[4] S.Y. AlQaradawi, E.M. Nour, Spectrochim. Acta A 62 (2005) 578.
[5] S.Y. AlQaradawi, E.M. Nour, J. Mol. Struct. 794 (2006) 251.
[6] E.M. Nour, L.H. Chen, J. laane, J. Phys. Chem. 90 (1986) 2841.
[7] E.M. Nour, Spectrochim. Acta 56A (2000) 167.
[8] L.L. Rodina, V.A. Ryzhakov, Heterouycles 40 (1995) 1035.
[9] E.M. Nour, L.A. Shahada, L.A. Al-Kaabi, Bull. Soc. Chim. Fr. 6 (1989) 727.
[10] E.M. Nour, A.S. Barkat, A. Amer, A. Ebrahim, Spectrosc. Lett. 32 (1999) 155.
[11] E.M. Nour, L. Shahada, Spectrochim. Acta A 45 (1989) 1033;
E.M. Nour, L. Shahada, Spectrochim. Acta 44A (1988) 1277.
[12] E.M. Nour, L.H. Chen, J. Laane, J. Raman Spectrosc. 17 (1986) 467.
[13] E.M. Nour, S.M. Teleb, M.A.F. Elmosallamy, M.S. Refat, S. Afr. J. Chem. 56 (2003) 10.
[14] Kh.A. Hassan, Spectorchim. Acta 60A (2004) 3059.
[15] R. Foster, Organic Charge-Transfer Complexes, Academic Press Inc., New York, 1969.
[16] P.J. Trotter, P.A. White, Appl. Spectrosc. 32 (1978) 323.
[17] F. Gutmann, C. Johnson, H. Keyzer, J. Molnar, Charge-Transfer Complexes in Biochemical Systems, Marcel Dekker Inc., 1997.
[18] M.C. Grossel, S.C. Weston, Chem. Mater. 8 (1996) 977.
[19] J.M. Masnovi, J.K. Kochi, E.F. Hilinski, P.M. Retzepis, J. Am. Chem. Soc. 108 (1986) 1126.
[20] K.Y. Rajpure, C.H. Bhosale, Chem. Mater. Chem. Phys. 64 (2000) 70.
[21] S. Licht, Solar Energy Mater. Solar Cells 38 (1995) 305.
[22] K. Ito, K. Saito, Heterocycles 38 (1994) 2691.
[23] P.R. Singh, R. Sahai, Aust. J. Chem. 23 (1970) 269.
[24] N. Kulevsky, K.N. Butamina, Spectrochim. Acta A 46 (1990) 79.
[25] R. Sahai, V. Singh, R. Verma, J. Ind. Chem. Soc. 58 (1981) 670;
V. Singh, R. Sahai, J. Macromol. Sci. Chem. A22 (1985) 33.
[26] L. Andrews, E.S. Prochaska, A. Loewenschuss, Inorg. Chem. 19 (1980) 463.
[27] W. Kiefer, H.J. Brenstien, Chem. Phys. Lett. 16 (1972) 5.
[28] T. Moeller, W.F. Ulrich, J. Inorg. Nucl. Chem. 2 (1956) 164;
J.G. Stites, C.N. McCarty, L.L. Quill, J. Am. Chem. Soc. 70 (1948) 3142.
[29] L. Shahada, A. Mostafa, E.M. Nour, H.S. Bazzi, J. Mol. Struct. 933 (2009) 1.
[30] D.A. Skoog, F.J. Holler, T.A. Niemen, Principles of Instrumental Analysis, fifth ed., Saunders College Publishing, New York, 1992 (Chapter 14).
[31] A. Anderson, T.S. Sun, Chem. Phys. Lett. 6 (1970) 11.
[32] W. Gabes, R. Elst, J. Mol. Struct. 21 (1974) 1.
[33] G.A. Bowmaker, R.J. Knappstein, J. Chem. Soc. Dalton Trans. (1977) 1928.
[34] R. Abu-Eittah, A. El-Kourashy, J. Phys. Chem. 76 (1972) 2405.
[35] A.G. Maki, R. Forneris, Spectrochim. Acta A 23 (1967) 867.