

# Spectrophotometric and Thermal Studies of the Reaction of Iodine with Nickel(II) Acetylacetonate

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## ABSTRACT

The reaction of iodine (acceptor) and nickel(II) acetylacetonate (donor) was studied photometrically in different solvents such as chloroform, dichloromethane and carbon tetrachloride at room temperature. The results indicate the formation of a 1:1 charge-transfer complex in each solvent and the iodine complex is formulated as the triiodide species  $[\text{Ni}(\text{acac})_2]_2\text{I}_3^+ \cdot \text{I}_3^-$ , based on the characteristic electronic absorptions of the  $\text{I}_3^-$  ion at 361 and 285 nm, as well as on the far infrared absorption bands characteristic of the  $\text{I}_3^-$  ion with  $\text{C}_{2v}$  symmetry. These bands are observed at 132, 101 and 84  $\text{cm}^{-1}$  and are assigned to  $\nu_a(\text{I-I})$ ,  $\nu_s(\text{I-I})$  and  $\delta(\text{I}_3^-)$ , respectively. The values of the equilibrium constant (K), absorptivity ( $\epsilon$ ) and oscillator strength ( $f$ ) of the iodine complex are shown to be strongly dependent on the type of solvent used. The important role played by the solvent is suggested to be mainly due to the interaction of the ionic complex with the solvent. The proposed structure of the new solid triiodide charge-transfer complex reported in this study is further supported by thermal and mid-infrared measurements.

## KEYWORDS

Charge-transfer; iodine; nickel acetylacetonate; triiodide.

## 1. Introduction

The reactions between iodine and various donor bases have been studied by several authors.<sup>1-7</sup> However, electron donors like cyclic polyamine, polysulphur and mixed oxygen-nitrogen cyclic bases are known to form stable charge-transfer (CT) complexes with iodine.<sup>8-14</sup> Some of the iodine complexes show interesting physical properties such as electrical conductivity.<sup>6,7</sup>

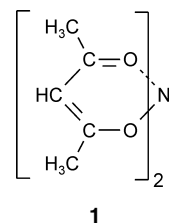
One interesting aspect of the chemistry of metal acetylacetonates  $[\text{M}(\text{acac})_n]$  concerns the pseudoaromatic  $\pi$ -electron delocalization in the  $\text{M}(\text{acac})_n$  rings.<sup>15</sup> The ability of  $\text{M}(\text{acac})_n$  compounds to form molecular complexes with  $\text{I}_2$ ,<sup>16-19</sup> is one property that has been taken as evidence for such delocalization.<sup>15</sup> It was proposed that these complexes are similar to those formed by aromatic hydrocarbons with  $\text{I}_2$  and that  $\text{M}(\text{acac})_n$  compounds behave as  $\pi$ -electron donors. That  $\text{I}_2$  interacts with  $\text{M}(\text{acac})_n$  compounds was demonstrated by measurements of the electronic spectra,<sup>16</sup> relative permittivities<sup>17</sup> and refractive index measurements<sup>18</sup> of solutions containing mixtures of the components.

In all previous studies<sup>16-19</sup> concerning the interaction of iodine with metal acetylacetonates, it has been found that the authors ignored the formation of  $\text{I}_3^-$  with its characteristic absorptions around 290 and 360 nm.

Remarkably, in their studies of the interaction of iodine with metal acetylacetonates, Kulevsky and Butamina<sup>19</sup> wrongly claimed that the 360 nm band was assigned to the blue-shifted  $\text{I}_2$  band, while the lower peak around 290 nm was attributed to intermolecular CT in  $\text{M}(\text{acac})_n \cdot \text{I}_2$ . In another study by Singh and Sahai,<sup>16</sup> the observation of a new absorption band around 360 nm was interpreted as a CT band of the  $\text{M}(\text{acac})_n \cdot \text{I}_2$  molecular complex.

In this paper an attempt has been made to investigate the new solid CT complex formed by the reaction of nickel(II) acetylacetonate **1** with iodine in three different solvents, using

both electronic and infrared absorption spectroscopy, and thermal measurements. This has enabled us to make an assessment of the correct nature and bonding of the resulting iodine complex.



## 2. Experimental

All the solvents used were purified employing standard methods, and iodine was obtained from BDH. The nickel(II) acetylacetonate was prepared using a known method.<sup>20</sup> A solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.25 mol) in 250 ml of water was added to a solution of acetylacetone (0.5 mol in 100 ml of methanol) with continuous stirring. A solution of 0.5 mol of sodium acetate in 150 ml of water was then added and the whole mixture was heated briefly on a hot plate, cooled to room temperature, and placed in the refrigerator for several hours. The solid green precipitate was filtered off on a Buchner funnel, washed with water several times, and then recrystallized using methanol and dried under vacuum. The solid  $[\text{Ni}(\text{acac})_2] \cdot \text{I}_2$  CT complex, with the general formula  $[\text{Ni}(\text{acac})_2]_2\text{I}_3^+ \cdot \text{I}_3^-$ , was isolated as a dark brown solid by the addition of an excess of saturated iodine solution (50 ml) to a saturated solution (10 ml) of  $[\text{Ni}(\text{acac})_2]$  in dichloromethane with constant stirring for about 10 min. The dark brown precipitate formed was filtered immediately and washed several times with minimum amounts of dichloromethane (3–5 ml) and dried under vacuum. The solid iodine complex was characterized by its elemental analysis, vibrational and electronic absorption bands and thermal analysis data, and it was identified as  $[\text{Ni}(\text{acac})_2]_2\text{I}_3^+ \cdot \text{I}_3^-$ ; analysis: C, 22.93% (23.51%);

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**Table 1** Fundamental wavenumbers of some triiodide compounds.

Compound	Wavenumber <sup>a</sup> /cm <sup>-1</sup>			Reference
	$\nu_1$	$\nu_2$	$\nu_3$	
KI <sub>3</sub>	111		143	22
CsI <sub>3</sub>	103	69	149	25
(CH <sub>3</sub> ) <sub>4</sub> NiI <sub>3</sub>	111	74	138	25, 26
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NiI <sub>3</sub>	104	72, 66	132	26
[(TACPD)]I <sup>+</sup> . I <sub>3</sub> <sup>-</sup>	109	60	132	13
[(HMTACTD)]I <sup>+</sup> . I <sub>3</sub> <sup>-</sup>	110	61	144	13
[Ni(acac) <sub>2</sub> ] <sub>2</sub> I <sup>+</sup> . I <sub>3</sub> <sup>-</sup>	101	84	132	Present work

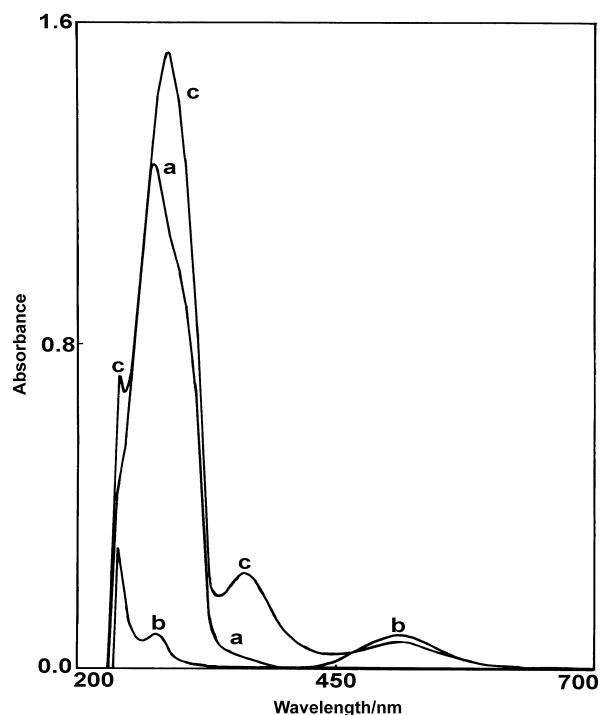
<sup>a</sup>  $\nu_1$ ,  $\nu_s$ (I-I);  $\nu_2$ ,  $\delta$ (I<sub>3</sub><sup>-</sup>);  $\nu_3$ ,  $\nu_a$ (I-I)

H, 2.95% (2.76%); Ni, 11.61% (11.50%); O, 12.82% (12.53%) and I, 50.02% (49.70%) (calculated values are shown in brackets).

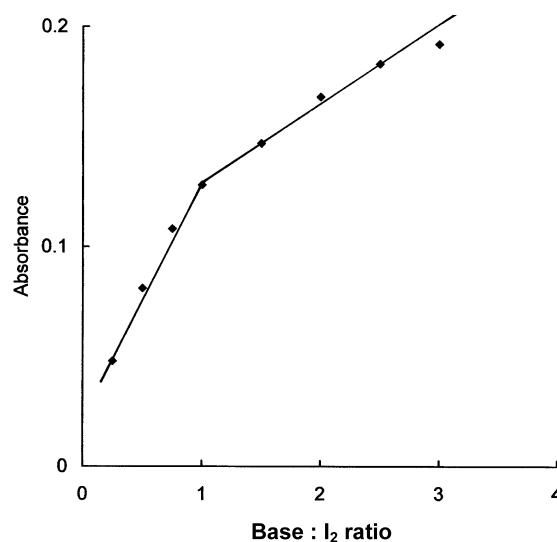
The electronic spectra of the donor [Ni(acac)<sub>2</sub>], iodine and the CT complex in different solvents (chloroform, dichloromethane and carbon tetrachloride) were recorded in the region 200–700 nm using a Shimadzu model 1601PC UV spectrophotometer with quartz cells of 1-cm path length. The mid-infrared spectra of the donor [Ni(acac)<sub>2</sub>] and the iodine complex were recorded in KBr discs using a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer, while the far infrared spectra for the same compounds were recorded in Nujol mulls dispersed on polyethylene windows in the region 300–50 cm<sup>-1</sup> using a Mattson Infinity series FT-IR spectrophotometer. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under a nitrogen atmosphere, using Shimadzu model TG-50H and DTA-50 detectors. Photometric titrations were performed<sup>21</sup> in all solvents at 25°C, under the conditions that the solutions employed for the measurements were prepared from stock solutions by pipetting the calculated volumes into 10 ml volumetric flasks. The concentration of the [Ni(acac)<sub>2</sub>] in the reaction mixture was kept fixed at  $0.5 \times 10^{-4}$  M, while the concentration of iodine was varied over the range of  $0.125 \times 10^{-4}$  M to  $1.5 \times 10^{-4}$  M. These concentrations produce base:I<sub>2</sub> ratios extending through the range from 1:0.25 to 1:3. The absorbances of the iodine complex formed were measured in each case and plotted as a function of the base:iodine ratio, as will be seen in the results section. All stock solutions were freshly made on the day of measurement.

### 3. Results and Discussion

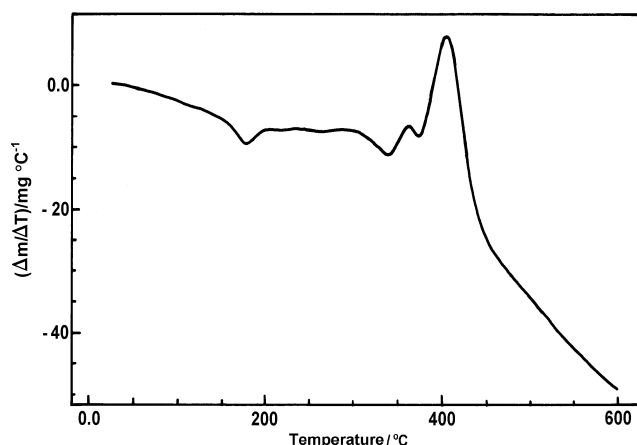
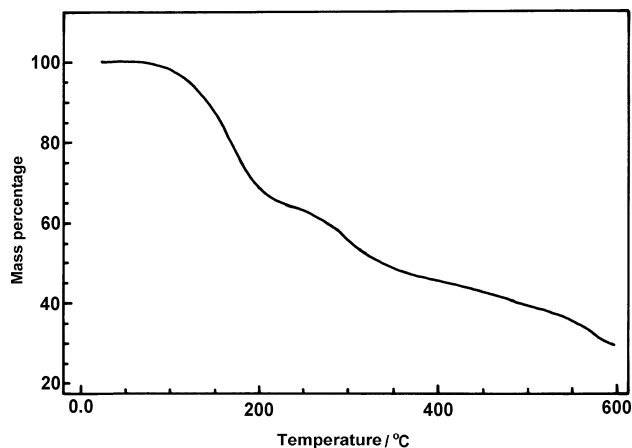
The electronic absorption spectra of the 1:1 [Ni(acac)<sub>2</sub>]-I<sub>2</sub> complex, [Ni(acac)<sub>2</sub>] ( $10^{-4}$  M) and iodine ( $10^{-4}$  M) in chloroform are shown in Fig. 1. The absorption spectra indicate that the [Ni(acac)<sub>2</sub>]-I<sub>2</sub> complex formed has real absorptions at 361 and 285 nm. Neither free iodine nor [Ni(acac)<sub>2</sub>] show these two absorption bands. A photometric titration curve in chloroform based on the band at 361 nm was obtained and is given in Fig. 2. The [Ni(acac)<sub>2</sub>]-I<sub>2</sub> equivalence point shown in this curve clearly indicates that the [Ni(acac)<sub>2</sub>]:I<sub>2</sub> ratio is 1:1. Such a ratio was also obtained for the reactions in carbon tetrachloride and dichloromethane, under the same conditions. The formation of the 1:1 complex was supported by both elemental analysis and thermal measurements. However, the appearance of the two absorption bands around 361 and 285 nm is well known<sup>22–24</sup> to be characteristic of the formation of the triiodide ion (I<sub>3</sub><sup>-</sup>). This was also supported by the far infrared spectrum of the iodine complex (Table 1). This spectrum shows the characteristic bands of the triiodide ion at 132, 101 and 84 cm<sup>-1</sup>, which are assigned to  $\nu_a$ (I-I),  $\nu_s$ (I-I) and  $\delta$ (I<sub>3</sub><sup>-</sup>), respectively. These three absorptions do not exist in the spectrum of the donor. However, the I<sub>3</sub><sup>-</sup> ion may be



**Figure 1** Electronic absorption spectra of (a) [Ni(acac)<sub>2</sub>] ( $1.0 \times 10^{-4}$  M), (b) I<sub>2</sub> ( $1.0 \times 10^{-4}$  M) and (c) [Ni(acac)<sub>2</sub>]-I<sub>2</sub> mixture [Ni(acac)<sub>2</sub>] =  $1.0 \times 10^{-4}$  M and [I<sub>2</sub>] =  $1.0 \times 10^{-4}$  M.



**Figure 2** Photometric titration curve for the [Ni(acac)<sub>2</sub>]-I<sub>2</sub> system in chloroform at 361 nm.

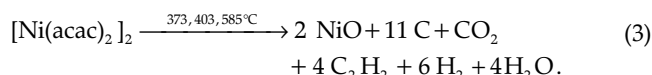
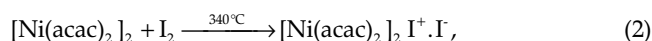
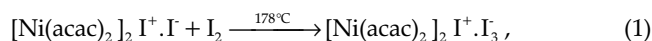
Figure 3 DTA diagram of  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ .Figure 4 TGA diagram of  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ .**Table 2** Maximum temperature,  $T_{\text{max}}$ , and percentage mass loss values of the decomposition stages for the  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$  complex.

Decomposition	$T_{\text{max}}/^\circ\text{C}$	Lost species	% Mass loss	
			Found	Calc.
First stage	178	$\text{I}_2$	25.0	24.85
Second stage	340	$\text{I}_2$	25.0	24.85
Third stage	373, 403, 583	$\text{CO}_2 + 4\text{C}_2\text{H}_2 + 6\text{H}_2 + 4\text{H}_2\text{O}$	20.97	22.74
Total loss			70.97	72.44
Residue			29.03	27.56

linear ( $D_{3h}$ ) or non linear ( $C_{2v}$ ). Group theoretical analysis indicates that  $\text{I}_3^-$  with  $C_{2v}$  symmetry displays three vibrations,  $\nu_s(\text{I-I})$  ( $a_1$ ),  $\nu_a(\text{I-I})$  ( $b_2$ ) and  $\delta(\text{I}_3^-)$  ( $a_1$ ); all are infrared-active in agreement<sup>13,22,25,26</sup> with the observed three infrared bands for  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ , as shown in Table 1. Accordingly, the iodine complex formed is formulated as  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ . The conversion of iodine molecules into polyiodide ions is well known in the literature. The formation of  $\text{I}_3^-$  ions was previously reported by Nour *et al.*,<sup>2,11,13</sup> in the reaction of iodine with hexamethylene-tetramine, phenazine, acridine and polyamines.

To confirm the proposed formula and structure of the new  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$  complex, thermogravimetric (TG) and differential thermal analysis (DTA) were carried out for this complex under nitrogen flow. DTA thermograms and TGA curves are shown in Figs 3 and 4, respectively. Table 2 gives the maximum temperature values,  $T_{\text{max}}$ , together with the corresponding mass loss for each step of the decomposition reaction of this complex. The data obtained strongly support the structure proposed for the complex under investigation as follows. The thermal decomposition of the  $[\text{Ni}(\text{acac})_2]_2\text{I}_2$  CT complex in inert atmosphere proceeds with three main degradation steps (Figs 3 and 4). The first stage of degradation at 178°C is accompanied by a mass loss of 25.0%, corresponding to the loss of an iodine molecule. Theoretically, the loss of an iodine molecule corresponds to a mass loss of 24.85%. The second decomposition stage occurs at the maximum temperature of 340°C. The mass loss in this step is 25.0%, due to the loss of the second iodine molecule, in agreement with the theoretical mass loss of 24.85%. The third decomposition stage occurs at three different maximum temperatures of 373, 403 and 583°C. The mass loss associated with these stages is 20.97%, corresponding to the loss of  $\text{CO}_2 + 4\text{C}_2\text{H}_2 + 6\text{H}_2 + 4\text{H}_2\text{O}$ , as will be described by the mechanism of the decomposition. The final thermal products obtained at 583°C are  $2\text{NiO} + 11\text{C}$ . Accordingly, the mechanism for the thermal decomposition

of the complex,  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ , is as follows.



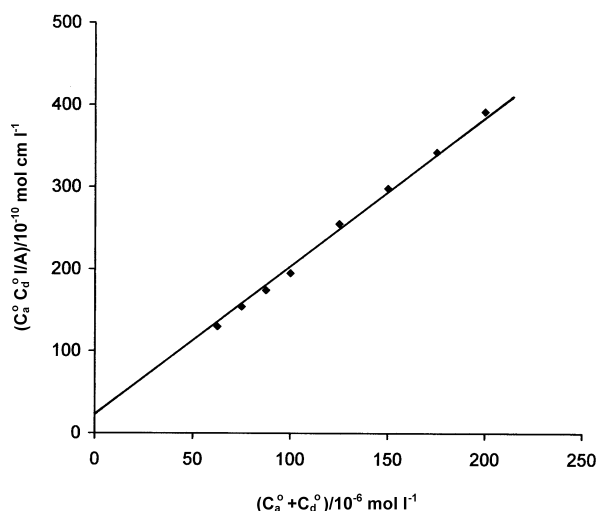
The infrared spectra of  $[\text{Ni}(\text{acac})_2]$  and the CT complex,  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$ , and their band assignments are reported in Table 3. As expected, the bands characteristic of the  $[\text{Ni}(\text{acac})_2]$  unit in  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$  are observed with small changes in

**Table 3** Infrared wavenumbers<sup>a</sup> ( $\text{cm}^{-1}$ ) and tentative assignments for  $[\text{Ni}(\text{acac})_2]$  base and  $[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$  complex.

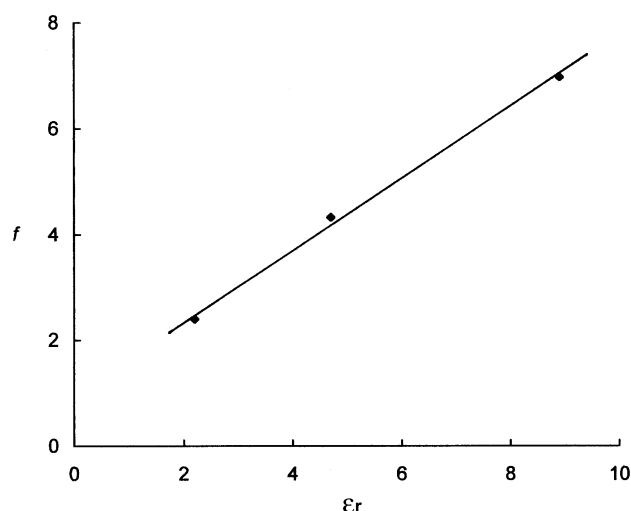
$[\text{Ni}(\text{acac})_2]$	$[\text{Ni}(\text{acac})_2]_2\text{I}^+ \cdot \text{I}_3^-$	Assignment <sup>b</sup>
1592 vs	1575 s	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$
1515 vs	1519 vs	$\nu(\text{C}=\text{O}) + \delta(\text{CH})$
1446 sh	1423 mw	
1392 vs	1378 vs	$\delta(\text{CH}_3)$
1363 sh	–	$\delta(\text{CH}_3)$
1196 mw	1190 w	$\delta(\text{CH})$ in-plane bend
1018 vs	1018 vs	$\delta(\text{CH}_3)$ rock
926 vs	930 s	$\nu(\text{C}-\text{CH}_3) + \nu(\text{C}-\text{O})$
765 vs	787 s	$\delta(\text{CH})$ out-of-plane bend
666 ms	680 w	Ring def. + $\nu(\text{M}-\text{O})$
–	644 w	$\delta(\text{C}-\text{CH}_3)$ bend + $\nu(\text{M}-\text{O})$
581 vs	585 vs	Ring def. + $\nu(\text{M}-\text{O})$
450 vw	460 ms	$\nu(\text{M}-\text{O})$
420 vs	424 vs	Ring def.

<sup>a</sup> m, medium; s, strong; sh, shoulder; v, very; w, weak.

<sup>b</sup>  $\nu$ , stretching;  $\delta$ , bending.



**Figure 5** Modified Benesi-Hildebrand plot for the  $[\text{Ni}(\text{acac})_2]\text{-I}_2$  reaction;  $C_a^0$ ,  $C_d^0$ ,  $A$  and  $l$  are the acceptor concentration, donor concentration, absorbance and path length, respectively.



**Figure 6** Plot of the oscillator strength of  $[\text{Ni}(\text{acac})_2]\text{I}^+\text{.I}_3^-$  versus the relative permittivity of the solvent.

**Table 4** Spectrophotometric results of  $[\text{Ni}(\text{acac})_2]\text{-I}_2$  complex in different solvents, and the relative permittivities of the solvents.

Solvent	$K/10^4 \text{ l mol}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$	$f$	$\epsilon_r$
$\text{CCl}_4$	15.50	368	0.645	2.40	2.2
$\text{CHCl}_3$	7.32	361	0.591	4.33	4.7
$\text{CH}_2\text{Cl}_2$	10.00	363	1.000	6.97	8.9

intensity and frequency.

It was of interest to observe that the solvent has a pronounced effect on the spectral intensities of the  $[\text{Ni}(\text{acac})_2]\text{I}^+\text{.I}_3^-$  complex. To study this solvent effect in a quantitative manner, it was necessary to calculate the values of the equilibrium constant,  $K$ , the absorptivity,  $\epsilon$ , and the oscillator strength,  $f$ , of the iodine complex in each solvent. The modified 1:1 Benesi-Hildebrand equation,<sup>27</sup>

$$\frac{C_a^0 C_d^0 l}{A} = \frac{1}{K\epsilon} + \frac{C_a^0 + C_d^0}{\epsilon} \quad (4)$$

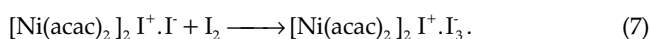
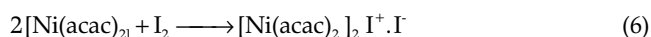
was used in the calculations, where  $C_a^0$  and  $C_d^0$  are the initial concentrations of the acceptor ( $\text{I}_2$ ) and the donor  $[\text{Ni}(\text{acac})_2]$ , respectively,  $A$  is the absorbance of the strong band around 361 nm, and  $l$  is the cell path length. Straight lines were obtained on plotting  $C_a^0 C_d^0 l / A$  against  $C_a^0 + C_d^0$  for each solvent (Fig. 5). In these plots the slope and the intercept,<sup>27</sup> for each case, should equal  $1/\epsilon$  and  $1/K\epsilon$ , respectively. The values of  $\epsilon$ ,  $K$  and  $f$  obtained for the complex, along with the relative permittivities of the solvents used, are given in Table 4. The oscillator strength  $f$  was obtained from the approximate formula<sup>28</sup>

$$f = (4.319 \times 10^{-9}) \epsilon_{\text{max}} \nu_{1/2} \quad (5)$$

where  $\nu_{1/2}$  is the band width at half-intensity in  $\text{cm}^{-1}$ . The data given in Table 4 reveal several facts. First,  $[\text{Ni}(\text{acac})_2]\text{I}^+\text{.I}_3^-$  shows high values of both the equilibrium constant ( $K$ ) and the absorptivity ( $\epsilon$ ). The high value of  $K$  reflects the high stability of the iodine complex, as a result of the expected strong donation of the  $[\text{Ni}(\text{acac})_2]$ , while the high value of  $\epsilon$  agrees quite well with the existence of the triiodide ion,  $\text{I}_3^-$ , which is known to have a high absorptivity value.<sup>22-24</sup> The value of the oscillator strength,  $f$ , increases with increase of the relative permittivity,  $\epsilon_r$ , of the solvent. Figure 6 shows the linear relationship obtained between  $f$  and  $\epsilon_r$ . The formation constant ( $K$ ) for  $[\text{Ni}(\text{acac})_2]\text{I}^+\text{.I}_3^-$  shows

some variation as the solvent is changed (Table 4), but no clear relation with solvent properties can be observed.

A general mechanism is proposed for the formation of  $[\text{Ni}(\text{acac})_2]\text{I}^+\text{.I}_3^-$  as follows:



The formation of the  $[\text{Ni}(\text{acac})_2]\text{I}^+ \cdot \text{I}$  reaction intermediate is analogous to that of the well-known species  $[(\text{base})\text{I}]^+ \cdot \text{I}$  formed in the reaction of iodine with many donors.<sup>8,11</sup> It has a characteristic<sup>1</sup> absorption around 250 nm (see Fig. 1). We conclude that the results reported here clearly indicate that the structure of the new complex formed in the reaction of iodine with  $[\text{Ni}(\text{acac})_2]$  is the triiodide complex  $[\text{Ni}(\text{acac})_2]_2 \text{I}^+ \cdot \text{I}_3^-$ .

## References

- M. Mizuno, J. Tanaka and I. Harada, *J. Phys. Chem.*, 1981, **85**, 1789.
- E.M. Nour, L.H. Chen and J. Laane, *J. Raman Spectrosc.*, 1986, **17**, 467.
- M. Tamres and J. Yarwood, *Spectroscopy and Structure of Molecular Complexes* (J. Yarwood, ed.), Plenum Press, London and New York, 1973, pp. 217–301.
- E. Mulazzi, I. Pollini, L. Piseri and R. Tubino, *Phys. Rev. B*, 1981, **24**, 3555.
- E.M. Nour, L.H. Chen and J. Laane, *J. Phys. Chem.*, 1986, **90**, 2841.
- P.J. Trotter and P.A. White, *Appl. Spectrosc.*, 1978, **32**, 323.
- I. Ikemoto, M. Sakairi, T. Tsutsumi, H. Kuroda, I. Harada, M. Tasumi, H. Shirakawa and S. Ikeda, *Chem. Lett.*, 1979, 1189.
- E.M. Nour, *Spectrochim. Acta*, 1991, **47A**, 743.
- E.M. Nour, L.A. Shahada and S.S. Alkaabi, *Bull. Soc. Chim. France*, 1989(6), 727.
- E.M. Nour, *Spectrochim. Acta*, 2000, **56A**, 167.
- E.M. Nour and L.A. Shahada, *Spectrochim. Acta*, 1988, **44A**, 1277.

- 12 E.M. Nour, L.A. Shahada and S.S. Alkaabi, *Acta Chim. Hung.*, 1990, **127**, 297.
- 13 E.M. Nour and L.A. Shahada, *Spectrochim Acta*, 1989, **45A**, 1033.
- 14 E.M. Nour, L.A. Shahada, S.A. Sadeek and S.M. Teleb, *Spectrochim. Acta*, 1995, **51A**, 471.
- 15 D.W. Thompson, *Struct. Bonding*, 1971, **9**, 27.
- 16 P.R. Singh and R. Sahai, *Aust. J. Chem.*, 1970, **23**, 269.
- 17 R. Sahai and V.N. Badoni, *Ind. J. Chem.*, 1978, **16A**, 1060; V. Singh and R. Sahai, *J. Macromol. Sci., Chem.*, 1985, **A22**, 33.
- 18 R. Sahai, V. Singh and R. Verma, *J. Ind. Chem. Soc.*, 1980, **57**, 493; R. Sahai, V. Singh and R. Verma, *J. Ind. Chem. Soc.*, 1981, **58**, 670.
- 19 N. Kulevsky and K.N. Butamina, *Spectrochim. Acta*, 1990, **46A**, 79.
- 20 R.G. Charles and M.A. Pawlikowski, *J. Phys. Chem.*, 1958, **62**, 440.
- 21 D.A. Skoog and D.M. West, *Principles of Instrumental Analysis*, 3rd edn., Saunders College Publishing, New York, NY, 1985, pp. 182–224.
- 22 W. Kiefer and H.J. Bernstein, *Chem. Phys. Lett.*, 1972, **16**, 5.
- 23 L. Andrews, E.S. Prochaska and A. Loewenschuss, *Inorg. Chem.*, 1980, **19**, 463.
- 24 K. Kaya, N. Mikami, Y. Udagawa and M. Ito, *Chem. Phys. Lett.*, 1972, **16**, 151.
- 25 A.G. Maki and R. Forneris, *Spectrochim. Acta*, 1967, **23A**, 867.
- 26 F.W. Parrett and N.J. Taylor, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2458.
- 27 R. Abu-Eittah and F. Al-Sugeir, *Can. J. Chem.*, 1976, **54**, 3705.
- 28 H. Tsubomura and R.P. Lang, *J. Am. Chem. Soc.*, 1961, **83**, 2085.