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 \([\text{Ni(acac)}_2]I^+I_3^-\), based on the characteristic electronic absorptions of the \(I^-\) ion at 361 and 285 nm, as well as on the far infrared absorption bands characteristic of the \(I^-\) ion with \(C_2v\) symmetry. These bands are observed at 132, 101 and 84 cm\(^{-1}\) and are assigned to \(\nu_3(I-I), \nu_2(I-I)\) and \(\delta(I-I)\), respectively. The values of the equilibrium constant (K), absorptivity (\(\varepsilon\)) 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.\(^{1,2}\) However, electron donors like cyclic polyamine, polysulphur and mixed oxygen-nitrogen cyclic bases are known to form stable charge-transfer (CT) complexes with iodine.\(^{3-14}\) Some of the iodine complexes show interesting physical properties such as electrical conductivity.\(^{5,7}\)

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

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

Remarkably, in their studies of the interaction of iodine with metal acetylacetonates, Kulevsky and Butamina\(^{19}\) wrongly claimed that the 360 nm band was assigned to the blue-shifted \(I^-\) band, while the lower peak around 290 nm was attributed to intermolecular CT in \(\text{M(acac)}_n\). In another study by Singh and Sahai,\(^{18}\) the observation of a new absorption band around 360 nm was interpreted as a CT band of the \(\text{M(acac)}_n\). 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.\(^{20}\) A solution of \(\text{NiCl}_2\cdot6\text{H}_2\text{O} (0.25 \text{ mol})\) 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(acac)}_2\]I\(^2\)) CT complex, with the general formula \([\text{Ni(acac)}_2]I^+I_3^-\), 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 [Ni(acac)] 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 \([\text{Ni(acac)}_2]I^+I_3^-\); analysis: C, 22.93% (22.51%).
The electronic spectra of the donor [Ni(acac)₂], 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)₂] 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⁻¹ 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 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)₂] in the reaction mixture was kept fixed at 0.5 × 10⁻⁴ M, while the concentration of iodine was varied over the range of 0.125 × 10⁻⁴ M to 1.5 × 10⁻⁴ M. These concentrations produce base:I₂ 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)₂]-I₂ complex, [Ni(acac)₂] (10⁻⁴ M) and iodine (10⁻⁴ M) in chloroform are shown in Fig. 1. The absorption spectra indicate that the [Ni(acac)₂]-I₂ complex formed has real absorptions at 361 and 285 nm. Neither free iodine nor [Ni(acac)₂] 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)₂]-I₂ equivalence point shown in this curve clearly indicates that the [Ni(acac)₂]:I₂ 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 known⁵⁻¹⁰ to be characteristic of the formation of the triiodide ion (I₃⁻). 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⁻¹, which are assigned to v₁(I-I), v₂(I-I) and δ(I-I), respectively. These three absorptions do not exist in the spectrum of the donor. However, the I₃⁻ ion may be

<table>
<thead>
<tr>
<th>Compound</th>
<th>v₁/cm⁻¹</th>
<th>v₂/cm⁻¹</th>
<th>v₃/cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI₃</td>
<td>111</td>
<td>143</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>CsI₃</td>
<td>103</td>
<td>69</td>
<td>149</td>
<td>25</td>
</tr>
<tr>
<td>(CH₃)₂NI₃</td>
<td>111</td>
<td>74</td>
<td>138</td>
<td>25, 26</td>
</tr>
<tr>
<td>(C₂H₅)₂NI₃</td>
<td>104</td>
<td>72, 66</td>
<td>132</td>
<td>26</td>
</tr>
<tr>
<td>[TACPD][I⁺·I₃⁻]</td>
<td>109</td>
<td>60</td>
<td>132</td>
<td>13</td>
</tr>
<tr>
<td>[HMTACTD][I⁺·I₃⁻]</td>
<td>110</td>
<td>61</td>
<td>144</td>
<td>13</td>
</tr>
<tr>
<td>[Ni(acac)₂][I⁺·I₃⁻]</td>
<td>101</td>
<td>84</td>
<td>132</td>
<td>Present work</td>
</tr>
</tbody>
</table>

* v₁, v₁(I-I); v₂, δ(I-I); v₃, v₃(I-I)
linear (D∞h) or non linear (C2v). Group theoretical analysis indicates that I3– with C2v symmetry displays three vibrations, \(\gamma(I-I)\) (a 1), \(\alpha(I-I)\) (b 2) and \((I_3–)\) (a 1); all are infrared-active in agreement with the observed three infrared bands for \([\text{Ni(acac)}_2]_2I^+\). The conversion of iodine molecules into polyiodide ions is well known in the literature. The formation of I3– ions was previously reported by Nour et al., in the reaction of iodine with hexamethylene-tetramine, phenazine, acridine and polyamines.

To confirm the proposed formula and structure of the new \([\text{Ni(acac)}_2]_2I^+\) 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 \([\text{Ni(acac)}_2]_2\) 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 2NiO + 11C. Accordingly, the mechanism for the thermal decomposition of the complex, \([\text{Ni(acac)}_2]_2I^+\), is as follows.

\[
[\text{Ni(acac)}_2]_2I^+ + I_2 \xrightarrow{178°C} [\text{Ni(acac)}_2]_2I^+I,
\]

\[
[\text{Ni(acac)}_2]_2I^+ + I_2 \xrightarrow{340°C} [\text{Ni(acac)}_2]_2I^+I,
\]

\[
[\text{Ni(acac)}_2]_2 \xrightarrow{373, 403, 583°C} 2\text{NiO} + 11\text{C} + \text{CO}_2 + 4\text{C}_2\text{H}_2 + 6\text{H}_2 + 4\text{H}_2\text{O}.
\]

The infrared spectra of \([\text{Ni(acac)}_2]\) and the CT complex, \([\text{Ni(acac)}_2]_2I^+\), and their band assignments are reported in Table 3. As expected, the bands characteristic of the \([\text{Ni(acac)}_2]\) unit in \([\text{Ni(acac)}_2]_2I^+\) are observed with small changes in

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**Table 2** Maximum temperature, \(T_{\text{max}}\), and percentage mass loss values of the decomposition stages for the \([\text{Ni(acac)}_2]_2I^+\) complex.

<table>
<thead>
<tr>
<th>Decomposition</th>
<th>(T_{\text{max}}/°C)</th>
<th>Lost species</th>
<th>% Mass loss</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>First stage</td>
<td>178</td>
<td>I₂</td>
<td>25.0</td>
<td>24.85</td>
<td></td>
</tr>
<tr>
<td>Second stage</td>
<td>340</td>
<td>I₂</td>
<td>25.0</td>
<td>24.85</td>
<td></td>
</tr>
<tr>
<td>Third stage</td>
<td>373, 403, 583</td>
<td>(\text{CO}_2 + 4\text{C}_2\text{H}_2 + 6\text{H}_2 + 4\text{H}_2\text{O})</td>
<td>20.97</td>
<td>22.74</td>
<td></td>
</tr>
<tr>
<td>Total loss</td>
<td></td>
<td></td>
<td></td>
<td>70.97</td>
<td></td>
</tr>
<tr>
<td>Residue</td>
<td></td>
<td></td>
<td></td>
<td>29.03</td>
<td></td>
</tr>
</tbody>
</table>

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**Table 3** Infrared wavenumbers (cm⁻¹) and tentative assignments for \([\text{Ni(acac)}_2]\) base and \([\text{Ni(acac)}_2]_2I^+\) complex.

| \([\text{Ni(acac)}_2]\) | \([\text{Ni(acac)}_2]_2I^+\) | Assignment*
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1592 vs</td>
<td>1575 s</td>
<td>v(C=C) + v(C=O)</td>
</tr>
<tr>
<td>1515 vs</td>
<td>1519 vs</td>
<td>v(C=O) + δ(CH)</td>
</tr>
<tr>
<td>1466 sh</td>
<td>1423 mw</td>
<td>δ(CH₃)</td>
</tr>
<tr>
<td>1392 vs</td>
<td>1378 vs</td>
<td>δ(CH₃)</td>
</tr>
<tr>
<td>1363 sh</td>
<td>–</td>
<td>δ(CH₃)</td>
</tr>
<tr>
<td>1196 mw</td>
<td>1190 w</td>
<td>δ(CH₃) in-plane bend</td>
</tr>
<tr>
<td>1018 vs</td>
<td>1018 vs</td>
<td>δ(CH₃) rock</td>
</tr>
<tr>
<td>926 vs</td>
<td>930 s</td>
<td>v(C-CH₃) + v(C=O)</td>
</tr>
<tr>
<td>765 vs</td>
<td>787 s</td>
<td>δ(CH) out-of-plane bend</td>
</tr>
<tr>
<td>666 ms</td>
<td>680 w</td>
<td>Ring def + v(M-O)</td>
</tr>
<tr>
<td>581 vs</td>
<td>585 vs</td>
<td>v(M-O)</td>
</tr>
<tr>
<td>450 vw</td>
<td>460 ms</td>
<td>Ring def.</td>
</tr>
<tr>
<td>420 vs</td>
<td>424 vs</td>
<td>Ring def.</td>
</tr>
</tbody>
</table>

*a* m, medium; s, strong; sh, shoulder; v, very; w, weak.

*b* v, stretching; δ, bending.
The oscillator strength, $f$, obtained for the complex, along with the relative permittivities of the solvent. Table 4 reveals several facts. First, $[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-$ 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 $[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-$, as follows:

$$2[\text{Ni(acac)}_2]^{2+}\text{I}^-\rightarrow[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-.$$  
(6)

$$[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-\text{I}^+\rightarrow[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-\cdot\text{I}^-.$$  
(7)

The formation of the $[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-$ 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. It has a characteristic 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 $[\text{Ni(acac)}_2]$ is the triiodide complex $[\text{Ni(acac)}_2]^{2+}\cdot\text{I}^-\cdot\text{I}_3^-$. 

References