Spectrophotometric Determination of Cobalt(II) & Stepwise Formation Constants of Its Complex with 3-(o-Acetophenyl)-1-methyltriazene N-oxide

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3-(o-Acetophenyl)-1-methyltriazene N-oxide acts as a highly sensitive spectrophotometric reagent for cobalt (II). Co(II) forms a greenish-yellow complex with the reagent in 50% (v/v) ethanol-water mixture in the pH range 6.8-10.0. The complex is extractable with chloroform. The absorbance values for the complex remain unchanged for a few days indicating its stability. Spectral data show the formation of only 1 : 2 complex with $\lambda_{\text{max}}$ value at 430 nm. However, in this work all the measurements have been carried out at 460 nm where the reagent's absorption is negligible. The optimum range, molar-absorptivity and the photometric sensitivity have been found to be 0.56-3.0 p.p.m., $1.7 \times 10^4$ and 0.0034 $\mu g/cm^2$ respectively at 460 nm. The composition of the complex has been also verified from the value of $n$ obtained by graphical differentiation of $\phi$, the degree of complex formation. The stability constants for the complex have been determined by the methods of Harvey and Manning, Leden and Yatsimirskii. A number of common ions do not interfere with the determination of cobalt(II). The relative standard deviation for several determinations is ± 0.25%.

A number of reagents have been used for the spectrophotometric determination of cobalt. $\alpha$-Nitroso-$\beta$-naphthol and nitroso-R-salt are reported to give highly sensitive colour reactions with the metal ions. The former forms a tris-complex which requires prolonged digestion before extraction into chloroform layer for measurement and the latter absorbs strongly near the $\lambda_{\text{max}}$ of its complex which also needs digestion.

The reagent 3-(o-acetophenyl)-1-methyltriazene N-oxide which has so far been utilised in the preparative work is also found to be a sensitive spectrophotometric reagent for Co(II) avoiding solvent extraction. Since the reagent is sparingly soluble in water, the solvent chosen for this study is 50% (v/v) ethanol-water mixture. At lower ethanol concentrations the complex precipitates after several hours. The complex formation in 50% (v/v) ethanol is instantaneous and the complex is fairly stable over a considerable length of time within pH range 6.8-10. The complex is also extractable with chloroform from aqueous phase within the same pH range with no appreciable shift in the $\lambda_{\text{max}}$ value.

The stepwise formation constants $k_1$ and $k_2$ of the complexes CoL$_1^+$ and CoL$_2$ respectively have been evaluated following the graphical extrapolation methods of Leden and Yatsimirskii. Earlier, Bag and Chakrabarty have utilised these methods for the determination of stability constants from spectrophotometric data. In the present paper the general equations for computation of formation constants have been derived in brief and the method of graphical extrapolation technique is demonstrated in the system under investigation. The overall formation constant of the cobalt complex has also been evaluated by Harvey-Manning method.

Materials and Methods

3-(o-Acetophenyl)-1-methyltriazene N-oxide was prepared following the literature method. The reagent solution (0.05%, w/v) was prepared in absolute ethanol. A stock solution of Co$^{2+}$ was prepared from AR grade CoCl$_2$. 6H$_2$O and standardised. Solution of diverse ions were prepared from AR grade chemicals. Spectrophotometric measurements were carried out using a Hilger Uvispek spectrophotometer with matched 1 cm glass cells. The pH values were adjusted with a Cambridge bench model pH meter.

Absorbance curve — To 2.0 ml (0.025 mg/ml) of Co$^{2+}$ solution were added 1.0 ml of (0.05%) reagent solution in ethanol and 10.0 ml of water. After suitable adjustment of the pH, volume of the resultant solution was made upto 25 ml with ethanol so that the final solution contained 50% (v/v) alcohol. The pH of the solution was recorded after measuring the absorbance in the wavelength region 400-600 nm of the complex against a reagent blank. The absorption maxima was found at 430 nm. However, all the measurements were made at 460 nm since the reagent has insignificant absorption under identical conditions at 460 nm.

Effect of pH and the reagent concentration — The colour intensity of the complex remained constant at least for 72 hr in the pH range 6.8-10.0. The minimum metal to ligand ratio to be maintained during complex formation to produce maximum colour intensity within the given pH range was found to be 1 : 8. Addition of more reagent (upto M:L = 1:50) did not produce any adverse effect on the colour system.

Beer's law range, optimum concentration range,
molar absorptivity and sensitivity — It was found that the Beer’s law is obeyed over the \([\text{Co}^{2+}]\) range 0.25–4.5 p.p.m. However, the optimum concentration range with the highest accuracy as evaluated from Ringbom’s\(^\text{16}\) curve was 0.56–3.0 p.p.m. The molar absorptivity of the complex as calculated from the Beer’s law data and the photometric sensitivity according to Sandell\(^\text{17}\) were found to be 1.7 \(\times\) 10\(^4\) and 0.0034 \(\mu\text{g/cm}^2\), respectively at 460 nm.

Composition of the complex — In both, the Job’s\(^\text{18}\) and mole-ratio\(^\text{19}\) methods equimolecular concentration (2.12 \(\times\) 10\(^{-4}\)M) of the reactants were employed for studying the composition of the complex. In either case complex in solution contains cobalt(II) and ligand in the ratio of 1:2.

To verify the composition of the complex we have evaluated \(\bar{n}\) by a graphical differentiation of \(\phi\), the degree of complex formation. \(\bar{n}\) may be defined as:

\[
\bar{n} = \text{Average number of donors bound to the metal atom}
\]

\[
\frac{\sum_1^n n \beta n [L]^n}{1 + \sum_1^n n \beta n [L]^n}
\]  

...(1)

This on differentiation and in combination with Eq.(1) simplifies\(^\text{10}\) to :

\[
\bar{n} = \frac{d \log \phi}{d \log [L]}
\]

The plot of the logarithm of degree of complex formation (\(\phi\)) versus the negative logarithm of the equilibrium free ligand concentration, \(pL\) is shown in Fig. 1. The gradient of the tangent to the curve at any point yields the value of \(\bar{n}\). The highest value of \(\bar{n}\) obtained in this way is 1.57, indicating the formation of CoL\(_2\) in solution.

Effect of diverse ions — Of the various anions and complexing agents, EDTA interferes seriously. Oxalate, tartrate acetate, borate, fluoride and thiocyanate could be tolerated at least in 200 fold excess, whereas citrate and phosphate could be tolerated up to 100 fold excess. Among the cations, \(\text{Zn}^{2+}, \text{Cd}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}\) have no effect on the determination even if present in 30 fold excess. \(\text{Cr}^{3+}, \text{VO}^{2+}, \text{UO}_2^{2+}, \text{Ce}^{4+}\) Mo\(_4^+\), V\(_6^+\), Cu\(_{2+}\), Al\(_{3+}\) however interfere with the determination. Interference due to 20 times excess of Fe\(^{3+}\) and Pb\(^{2+}\) could be prevented by the addition of \(\text{NH}_4\text{HF}_2\) and \(\text{NH}_4\text{OAc}\) respectively as masking agents. The above determinations were carried out with 1.0 p.p.m. of Co\(^{2+}\).

Trace quantities of Co(II) in several determinations have been estimated with a standard deviation\(^\text{20}\) of \(\pm 0.25\%\) only.

\[
[S\text{Calc.}] = \Sigma_1^n \sqrt{(X_i - \bar{X})^2/(n - 1)}
\]

Evaluation of metal ligand formation constants — Method of Leden\(^\text{19}\) — In this method the degree of formation (\(\phi\)) of a complex system is utilised for the evaluation of stepwise formation constants. The degree of formation is defined as the ratio of overall concentration of metal ion \(C_M\), to the equilibrium concentration of free metal ion \([M]\) :

\[
\phi = \frac{C_M}{[M]} = 1 + \sum_1^n \beta [L]^n
\]  

...(3)

In the present system where the ratio of cobalt to 3-(o-acetophenyl)-1-methyltriazene N-oxide is 1:2, \(\phi\) reduces to :

\[
\phi = 1 + k_1 [L] + k_1 k_2 [L]^2
\]  

...(4)

The coefficients \(k_1\), \(k_2\) of the variable [L] are obtained by constructing suitable auxiliary functions (\(\psi_1\), \(\psi_2\)) and extrapolations of these to zero value of the variable.

Thus ; \(\psi_1 = \frac{\phi - 1}{L} = k_1 + k_1 k_2 [L]\)

\[
\lim_{[L] \to 0} \psi_1 = k_1 = C_1
\]

\[
\lim_{[L] \to 0} \psi_2 = \frac{\psi_1 - 1}{L} = k_1 k_2 = C_2
\]

\[
[H_2]\text{O} \to 0 \quad [L] \to 0
\]

The intercepts \(C_1\) and \(C_2\) on the ordinate are thus numerically equal to \(k_1\) and \(k_1 k_2\), respectively.

Method of Yatsimirskii\(^\text{21,22}\) — The mean molar extinction coefficient \(\varepsilon\) of the species \(\text{ML}_N\) \((N \geq 0)\) and \(L\) which absorb strongly at a definite wavelength is given by Eq. 5.

\[
\varepsilon = \frac{A}{(C_M + [L])l}
\]  

...(5)
Where the terms have their usual meanings. In the present system $M:L = 1:2$, $l = 1$ cm, $e_0 = 0$ and $e_L = 0$ since the metal ions and the complexing agent showed no absorptions at 460 nm, the region where all absorbances were measured. The equation (5) then simplifies to Eq.

$$
e = \frac{e_1 k_1 [L] + e_2 k_1 k_2 [L]^2}{1 + k_1 [L] + k_1 k_2 [L]^2} \quad \ldots \ldots (6)$$

A series of $\varepsilon$ values were obtained from spectrophotometric absorbance data for a number of determinations and consequently a large number of equations of the type (6) were generated. These equations were then solved for coefficients $(\varepsilon, \beta)$ of the variable $[L]$ by the help of suitable auxiliary $(f_1, f_2)$ functions and extrapolation of these to zero value of the variable.

Introducing a new variable $Y$ where,

$$Y = \frac{l}{[L]} = \frac{i}{[L]} \quad \text{(for } l = 1 \text{ cm)}$$

and then considering Eq. (6) we get,

$$
\varepsilon = e_1 k_1 Y + e_2 k_1 k_2 \frac{Y}{Y^2 + k_1 Y + k_1 k_2} \\
\frac{\varepsilon - b_1}{Y} = \frac{e_1 - e_2}{k_2} = b_2 \quad \ldots \ldots (9)
$$

The intercept equations are solved for the coefficients $k_1$, $k_2$ when we get,

$$k_1 = \frac{a_1 b_1 - a_2 b_2}{b_2^2 + a_2 b_1 - a_1 b_2} \quad k_2 = \frac{a_1^2 + a_1 b_1}{a_2^2 + a_1 b_1 - a_2 b_2}$$

It is seen that knowing $k_1$, the molar extinction coefficient $e_1$ of the complex $ML_1^+$ may be computed while the corresponding value of $ML_2$ is equal to the intercept $b_1$.

### Table 1 — Determination of Metal-Ligand Formation Constants by Leden’s Method

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>[Metal complexed] (moles/litre) \times 10^6</th>
<th>[Free metal] (moles/litre) \times 10^6</th>
<th>[Total ligand] (moles/litre) \times 10^6</th>
<th>[Free ligand] (moles/litre) \times 10^6</th>
<th>Degree of complex formation $\phi = CM/M$</th>
<th>$\psi_1 \times 10^{-4}$</th>
<th>$\psi_2 \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.090</td>
<td>0.3087</td>
<td>1.8131</td>
<td>0.8480</td>
<td>0.2306</td>
<td>1.170</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.110</td>
<td>0.6792</td>
<td>1.4408</td>
<td>1.6960</td>
<td>0.3376</td>
<td>1.471</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.136</td>
<td>0.8397</td>
<td>1.2903</td>
<td>2.1200</td>
<td>0.4410</td>
<td>1.647</td>
<td>1.461</td>
<td>0.3198</td>
</tr>
<tr>
<td>0.161</td>
<td>0.9940</td>
<td>1.1260</td>
<td>2.5440</td>
<td>0.5560</td>
<td>1.882</td>
<td>1.586</td>
<td>0.4784</td>
</tr>
<tr>
<td>0.205</td>
<td>1.2660</td>
<td>0.8540</td>
<td>3.3920</td>
<td>0.8600</td>
<td>2.482</td>
<td>1.724</td>
<td>0.4698</td>
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<tr>
<td>0.244</td>
<td>1.5070</td>
<td>0.6130</td>
<td>4.2400</td>
<td>1.2260</td>
<td>3.492</td>
<td>2.004</td>
<td>0.5580</td>
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<tr>
<td>0.265</td>
<td>1.6710</td>
<td>0.4490</td>
<td>5.0880</td>
<td>1.7460</td>
<td>4.722</td>
<td>2.131</td>
<td>0.4645</td>
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<tr>
<td>0.282</td>
<td>1.7410</td>
<td>0.3790</td>
<td>5.5100</td>
<td>2.0300</td>
<td>5.421</td>
<td>2.263</td>
<td>0.4656</td>
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<tr>
<td>0.293</td>
<td>1.8090</td>
<td>0.3110</td>
<td>5.9360</td>
<td>2.3180</td>
<td>6.816</td>
<td>2.509</td>
<td>0.5131</td>
</tr>
<tr>
<td>0.296</td>
<td>1.8280</td>
<td>0.2920</td>
<td>6.7850</td>
<td>3.1280</td>
<td>7.269</td>
<td>—</td>
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</table>

### Table 2 — Determination of Metal-Ligand Formation Constants by Yatsimirskii’s Method

| [Metal] = [reagent] = 2.12 \times 10^{-4}M; [metal] : [reagent] = 1 : 2; metal taken = 2.50 ml of 2.12 \times 10^{-4}M final volume = 25 ml absorbance for metal conc. 6.792 \times 10^{-4}M = 1.10, wavelength for measurement = 460 nm |

<table>
<thead>
<tr>
<th>[Total ligand] (moles/litre) \times 10^6</th>
<th>Absorbance</th>
<th>[Free ligand] (moles/litre) \times 10^6</th>
<th>Mean molar Extinction coefficient $g \times 10^3$</th>
<th>($f_1 \times 10^{-14}$)</th>
<th>($f_2 \times 10^{-14}$)</th>
<th>($Y = 10^{-4}$)</th>
<th>$g \times 10^4$</th>
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<tbody>
<tr>
<td>1.696</td>
<td>0.110</td>
<td>0.3376</td>
<td>0.0518</td>
<td>0.1537</td>
<td>0.1075</td>
<td>2.962</td>
<td>-4.188</td>
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<tr>
<td>2.120</td>
<td>0.136</td>
<td>0.4410</td>
<td>0.0641</td>
<td>0.1445</td>
<td>-0.1009</td>
<td>2.268</td>
<td>-4.939</td>
</tr>
<tr>
<td>2.544</td>
<td>0.161</td>
<td>0.5560</td>
<td>0.0759</td>
<td>0.1366</td>
<td>-0.0960</td>
<td>1.799</td>
<td>-5.615</td>
</tr>
<tr>
<td>3.392</td>
<td>0.205</td>
<td>0.6600</td>
<td>0.0957</td>
<td>0.1125</td>
<td>-0.0800</td>
<td>1.162</td>
<td>-6.817</td>
</tr>
<tr>
<td>4.240</td>
<td>0.244</td>
<td>1.2260</td>
<td>0.1510</td>
<td>0.0956</td>
<td>-0.0769</td>
<td>0.8156</td>
<td>-9.917</td>
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<tr>
<td>5.088</td>
<td>0.265</td>
<td>1.7460</td>
<td>0.1250</td>
<td>0.0716</td>
<td>-0.0678</td>
<td>0.5728</td>
<td>-8.904</td>
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<tr>
<td>5.512</td>
<td>0.282</td>
<td>2.0300</td>
<td>0.1330</td>
<td>0.0655</td>
<td>-0.0613</td>
<td>0.4926</td>
<td>-8.730</td>
</tr>
<tr>
<td>5.936</td>
<td>0.293</td>
<td>2.3180</td>
<td>0.1382</td>
<td>0.0596</td>
<td>-0.0562</td>
<td>0.4314</td>
<td>-8.762</td>
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</table>
The overall stability constant has also been calculated using Harvey–Manning method.14

Results and Discussion

The values of all the secondary concentration variables $\varepsilon$, $\phi$ [L] and [M] and that of the different functions, $\psi_1$, $\psi_2$, $f_1$, $f_2$ and $g$ employed for the evaluation of stepwise formation constants $k_1$ and $k_2$ of the complexes CoL$^+$ and CoL$_2$, respectively, have been calculated from mole-ratio and Beer’s law data and are presented in Tables 1 and 2. The plots of the functions $\psi_1$, $\psi_2$ or $f_2$ vs [L] and that of $g$ against $Y$ (figures omitted to avoid duplication of data) gave linear relationships. On the other hand $f_1$ vs [L] and $g$ vs $Y$ plots are curved in nature. A few experimental points, particularly near [L] = 0 are scattered from the usual graph. It might be due to low absorbance values as [L] tends to zero and inherent experimental error that might be introduced in recording these data. However, it was observed that no significant error was introduced in plotting the best lines and in measuring their intercepts on extrapolation. The values of different intercepts and that of $e_1$ and $e_2$ obtained are given below:

$$a_1 = 0.19 \times 10^{10} \quad c_1 = 1.320 \times 10^5$$
$$a_2 = -0.11 \times 10^{15} \quad c_2 = 0.465 \times 10^{10}$$
$$b_1 = 0.18 \times 10^6 \quad e_1 = 1.110 \times 10^4$$
$$b_2 = -0.093 \quad e_2 = 1.800 \times 10^4$$

The values of metal ligand formation constants obtained by Leden, Yatsimirskii and Harvey–Manning’s methods (Table 3) are comparable to each other. The small differences between log $k_1$ and log $k_2$ values indicate that CoL$^+$ and CoL$_2$ are formed in solution simultaneously. The value of molar extinction coefficient obtained from Beer’s law shows a close resemblance with the value ($e_2$ = $1.80 \times 10^4$) obtained by Yatsimirskii’s method.

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References


<table>
<thead>
<tr>
<th>Method</th>
<th>log $K_1$</th>
<th>log $K_2$</th>
<th>log $\beta_2$</th>
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<tr>
<td>Leden’s</td>
<td>1.80</td>
<td>5.12</td>
<td>9.67</td>
</tr>
<tr>
<td>Yatsimirskii’s</td>
<td>5.21</td>
<td>4.55</td>
<td>10.04</td>
</tr>
<tr>
<td>Harvey and Manning’s</td>
<td>---</td>
<td>4.83</td>
<td>9.80</td>
</tr>
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</table>

The error limit is ± 0.1.