Discussion
Discussion

5.1. Absorption spectra of the complex ions, 

\[ \text{[Co(HEDTA)NO}_2\text{]}^- \quad \text{and} \quad \text{[Co(HEDTA)N}_3\text{]}^- \]

5.1.a. Ligand field bands

Cobalt(III) ion with Ar\(3d^6\) configuration forms low spin octahedral complexes and shows rather weak electronic transitions in the visible region which are assigned as \(d-d\) transitions\(^{20,21,104-107}\). Coordination complexes of cobalt(III) ion are, in general, diamagnetic, with the \(d\) electrons in paired configuration. According to the valence bond formalism two of the \(3d\) orbitals are involved in the formation of \(d^2sp^3\) hybrid orbitals which are utilized for bonding with the ligands and hence the six \(3d\) electrons have to get paired themselves in the remaining three \(3d\) orbitals.
In octahedral field, the ground state for the low spin complexes of cobalt(III) ion is $^1A_{1g}$ and it has the $t_{2g}^6$ electronic configuration. The configuration for the first excited state is $t_{2g}^5e_{g}^1$ and this leads to the following terms (Fig. 2):

$^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$

Accordingly, the following two spin-allowed and orbitally-forbidden d-d transitions are possible:

$^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$

Hence a typical absorption spectrum of a cobalt(III) complex is expected to show two typical ligand field bands in the visible or in the near ultraviolet region.
For instance, the spectrum of hexaaminecobalt(III) ion shows two such bands at 472 (ε = 55) and 338 nm (ε = 49). However, the actual positions of such bands depend on the strength of the ligand field. In addition to the spin-allowed transition, a series of spin-forbidden ligand field transitions such as $^1A_{lg} \longrightarrow ^3T_{lg}$ is expected to occur. However, the corresponding bands are not usually observed, since the bands are hidden in the more intense ligand field bands of lower energy.

Natarajan and Endicott$^{108}$, in their studies on cobalt(III) - EDTA complexes, have observed that the spectrum of ethylenediaminetetraacetatocobaltate(III) ion shows two ligand field bands at 380 (ε = 140) and 535 nm (ε = 270). The azido complex ion, [Co(HEDTA)$_3$N$_3$]$^{-}$ prepared for the first time, shows one less intense ligand field band at 575 nm (ε = 220) (Fig. 12) and the other ligand field transition is not observed as a separate band. Since the $N_3 \longrightarrow Co(III)$ charge-transfer band appears at a relatively low energy region, the second ligand field band is hidden in the tail of the intense charge-transfer band. Likewise, the band at 495 nm
(ε = 210) in the absorption spectrum of the nitro complex ion, [Co(HEDTA)NO₂]⁻ (Fig. 13), is assigned as the spin-allowed ligand field transition and the other, as in the case of the azido complex ion, is observed as a shoulder hidden in the tail of the more intense charge-transfer band.

5.1.b. **Charge-transfer bands**

Charge-transfer bands²⁵ are of high intensity and mostly seen in the ultraviolet region for cobalt(III)-ammine complexes. It has been reported that in the case of easily oxidizable cation or easily reducible ligand, the electron transfer of the lowest energy is from the cation to the ligand and in the case of easily reducible cation or easily oxidizable ligand, the transfer is from the ligand to the cation. It is also noted that the charge-transfer and ligand field bands are well separated in some complexes. For example the spectrum of hexaamminecobalt(III) ion shows one charge-transfer band at 200 (ε = 20,000) and two ligand field bands at 338 (ε = 49) and 472 nm (ε = 55). On the otherhand, the spectrum of monoazidopentaammine-cobalt(III) ion shows a charge-transfer band at 302 nm.
(ε = 8700) which extends towards the visible region and obscures one of the ligand field bands, resulting in only one ligand field band at 516 nm (ε = 280).

The absorption spectrum of ethylenediamine-tetraacetatocobaltate(III) ion shows an intense charge-transfer band at 225 nm (ε = 11,000). The absorption spectrum of the azido complex ion shows two intense charge-transfer bands at 220 (ε = 12,400) and 315 nm (ε = 5400) and that of the nitro complex ion also shows two such bands at 225 (ε = 20,100) and 345 nm (ε = 3400). The absorption spectral details for the complexes are given in Table-125.
**TABLE 125**

ULTRAVIOLET - VISIBLE ABSORPTION SPECTRAL DATA OF 
SOME COBALT(III) - EDTA COMPLEXES

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\lambda_{\text{max}}, \text{nm}$</th>
<th>$\epsilon, \text{m}^{-1} \text{ l} \text{ cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na[Co(HEDTA)$N_3$]</td>
<td>220</td>
<td>12400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>315</td>
<td>5400</td>
</tr>
<tr>
<td>Na[Co(HEDTA)$NO_2$]</td>
<td>575</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>20100</td>
</tr>
<tr>
<td>Na[Co(EDTA)]</td>
<td>345</td>
<td>3400</td>
</tr>
<tr>
<td></td>
<td>495</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>11000</td>
</tr>
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<td></td>
<td>380</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>535</td>
<td>270</td>
</tr>
</tbody>
</table>
5.2. **IR and NMR spectra**

The infrared absorption spectrum of [Co(HEDTA)NO₂]⁻ ion (Fig. 7) shows three characteristic frequencies at 2850, 1730 and 1220 cm⁻¹ which are attributed to -COOH group. Three bands at 1405, 1340 and 833 cm⁻¹ are assigned to -NO₂ group and all these values are comparable to the reported values of Morris and Busch⁹⁴. The characteristic absorption bands and their assignments are given in Table-126. The band in the region 2050 cm⁻¹ is characteristic of the azide ion (Fig. 6). The presence of free carboxylic acid group in the azido complex was confirmed from NMR spectrum which shows a small peak at 8.3 δ (Fig. 9) integrating for one hydrogen. This peak slowly disappears, when recorded after shaking the solution with a drop of D₂O, indicating that the peak at 8.3 δ corresponds to carboxylic proton (Fig. 10-11). Similarly the nitro complex gives absorption for the carboxylic proton at 7.4 δ (Fig. 8).
<table>
<thead>
<tr>
<th>Absorption</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>2850 - 2900 (vw)</td>
<td>-OH</td>
</tr>
<tr>
<td>1730 (m)</td>
<td>-COOH</td>
</tr>
<tr>
<td>1640 (s)</td>
<td>-COOM</td>
</tr>
<tr>
<td>1220 (m)</td>
<td>-COOH</td>
</tr>
<tr>
<td>1405 (m)</td>
<td>-NO₂</td>
</tr>
<tr>
<td>1340 (m)</td>
<td></td>
</tr>
<tr>
<td>833 (m)</td>
<td></td>
</tr>
<tr>
<td>2050 (m)</td>
<td>-N₃</td>
</tr>
</tbody>
</table>

vw = very weak
m = medium
s = strong
The crystal structures of several EDTA complexes have been determined\textsuperscript{17-19,102}. The ultraviolet-visible absorption spectra of \([\text{Co(HEDTA)}N_3]^-\) and \([\text{Co(HEDTA)}\text{NO}_2]^-\) are similar to those of the other EDTA complexes. The structure is proposed to be octahedral with an uncoordinate carboxylic acid group and the sixth coordination is either \(N_3^-\) or \(\text{NO}_2^-\) ion (Fig. 1).

5.3. Acid dissociation constants of the complex ions,\[\text{[Co(HEDTA)}\text{NO}_2]^-\text{ and } \text{[Co(HEDTA)}N_3]^-\]

Many of coordination complexes of cobalt(III) ion are found to be so highly acidic that the acid dissociation constant in each complex can be measured directly. As reported by Schwarzenbach\textsuperscript{14} and later by Busch and Bailer\textsuperscript{13}, the hexadentate ethylenediamine-tetraacetate(enta) anion ligand, \((\text{EDTA})^4-\), forms a series of quinquedentate-chelate complexes with cobalt(III) ion in which one of the four carboxylate groups is free. The sixth coordination position of the cobalt(III) ion is occupied by another ligand.
which may be a neutral ligand or a simple anion (Fig. 1). The pK\textsubscript{a} value of the acid form of each of such complexes is ca.3 \textsuperscript{14,91,109}. It was stated that the pK\textsubscript{a} value is 'little affected' by the nature of the sixth ligand.

In the present investigation, we have determined the pK\textsubscript{a} values of the azido complex and the nitro complex. The values differ considerably from those reported by Schwarzenbach\textsuperscript{14} and Shimi and Higginson\textsuperscript{91} for the analogous chloro and bromo complexes. The pK\textsubscript{a} values of the azido and nitro complexes have been found to be 4.25 and 4.15 respectively. It thus appears that the pK\textsubscript{a} values of cobalt(III) complexes containing pentadentate ethylenediaminetetraacetato-cobaltate and NO\textsubscript{2}\textsuperscript{-} or N\textsubscript{3}\textsuperscript{-} as the sixth ligand are affected significantly by the nature of that ligand.

It is well known\textsuperscript{46,48,110-114} that the acid dissociation constant of a coordinated ligand in a metal complex is affected by factors such as solvent, the nature of the metal ions and the nature of other ligands.
Generally, the ionisation of a carboxylic acid group in a compound, if other factors are assumed to be absent, is increased by introducing electron-withdrawing substituents and decreased by electron-releasing substituents. In a complex ion like \([\text{Co(HEDTA)}\text{NO}_2]^−\), the presence of electron-withdrawing substituent, that is, nitro group, renders it more acidic and hence it is expected to show a pK\textsubscript{a} value less than that of its bromo analogue\textsuperscript{105,115}. In this connection, it is noteworthy that the azide ion can act as an electron-withdrawing as well as electron-releasing substituent.

In the present investigation pK\textsubscript{a} values of the nitro and azido complexes have been determined and found to be 4.15 and 4.25 respectively. This observation is different from that observed for \([\text{Co(HEDTA)}\text{Cl}]^−\) and \([\text{Co(HEDTA)}\text{Br}]^−\) ions and such a behaviour can be accounted for in terms of the specific influence exerted by the nitro/azido ligand on the protonation of the carboxylate group.

A hydrogen bond can be visualized\textsuperscript{116} as a proton, shared by two lone pairs of electrons and it is more localized than any other type of weak intermolecular
forces. As a result of hydrogen bonding, the covalent bond in the proton-donor group is weakened, but not broken, and also the properties of the proton-accepting group are changed. The behaviour of coordination complexes in aqueous solutions in general, and in particular their relative acidities are attributed to the extent to which the hydroxide ion in the aqueous solution is stabilised by hydrogen bonding.\(^{116}\)

It is observed \(^{117}\) that the \(pK_a\) value increases with the increase in the possibility of hydrogen bonding, as is evident from the \(pK_a\) values of water (16) and hydrogen sulphide (7). Hence it is predicted that the \(pK_a\) values of the nitro and azido complexes, which are supposed to be involving hydrogen bonding must be higher than those of the similar chloro and bromo complexes, in which hydrogen bonding is absent. In fact, our results of \(pK_a\) values, 4.15 and 4.25 for the nitro and azido complexes respectively when compared to ca.3 for both the chloro and bromo complexes, agree well with the prediction.

Since there are two kinds of hydrogen bonding, viz., intramolecular and intermolecular, it is of interest to verify what type of hydrogen bonding is present in the
nitro and azido complexes. Intramolecular hydrogen bonding is possible only when the hydrogen atom of the donor group and the acceptor site is between 1.4 and 2.5 Å and the angular orientation of the acceptor site does not deviate much from the bond-axis of the donor group. One of the useful methods of distinguishing intramolecular hydrogen bonding from intermolecular hydrogen bonding is to determine how $pK_a$ values change with the change of the ionic strength of the medium. Complexes containing intramolecular hydrogen bonding do not show much variation of $pK_a$ values while those complexes involving intermolecular hydrogen bonding do reflect much variation, since in intermolecular hydrogen bonding, with the increase of the ionic strength of the medium, preferential orientation of the solvent molecules will be more towards the dissolved complex salt and hence the complex ion is free to associate, leading to the increase of $pK_a$ value.

The $pK_a$ values of the nitro complex in aqueous solution, in 0.05 M sodium perchlorate solution and in 0.1 M sodium perchlorate solution are 4.15, 4.15 and 4.1 (Table 14) respectively and those of the azido
complex in the same set of solutions are 4.25, 4.3 and 4.3 (Table 1) respectively. In addition, it is observed that use of sodium chloride and sodium sulphate solutions in the place of sodium perchlorate solution do not produce any appreciable effect on the $pK_a$ values for both the nitro (Table 14) and azido (Table 1) complexes. These results support the presence of intramolecular hydrogen bonding in both the complexes. However, increase of temperature of the aqueous solution of both the nitro and azido complexes shows a small graded decrease in the $pK_a$ values (Table 1, 14) thus in conformity with the Le Chatlier principle. It is thus concluded that in the nitro and azido complexes, intramolecular hydrogen bonding is present between the hydrogen atom of the free carboxylic acid group of the pentadentate EDTA and the highly electronegative oxygen atom of the nitro ligand in the former complex, and in the latter complex, the acceptor site is the nitrogen atom of the azido ligand. The structures of the two complexes, viz., $[\text{Co(HEDTA)Cl}]^-$ and $[\text{Co(HEDTA)N}_3]^-$, are shown.
5.4. **Kinetics of the aquation of the complex ions,**

\[ [\text{Co(HEDTA)N}_3]^2- \text{ and } [\text{Co(HEDTA)NO}_2]^2- \]

The kinetic aspects of the formation of ethylenediaminetetraacetatocobaltate(III) ion from the chloro and bromo complexes, viz., \([\text{Co(HEDTA)Cl}]^-\), \([\text{Co(EDTA)Cl}]^{2-}\), \([\text{Co(HEDTA)Br}]^-\) and \([\text{Co(EDTA)Br}]^{2-}\), have been studied by Shimi and Higginson\(^{91}\) and Dyke and Higginson\(^{92,118}\). Identical first-order rate constant, in each case of the acid hydrolysis of the complexes, cited above, has been found. An interesting factor noticed in these hydrolysis reactions is that either the incoming group or the departing group will be one of the functional groups of the coordinated ethylenediaminetetraacetate anion depending on whether in the substitution reaction EDTA is converted from pentadentate to the hexadentate ligand or vice versa. Shimi and Higginson\(^{91}\) have reported that the rate of release of the bromide ion from the bromo complex, \([\text{Co(EDTA)Br}]^{2-}\), is virtually unchanged over the pH range 1-7, the first-order velocity constant being approximately
$4 \times 10^{-3} \text{ min}^{-1}$ at $25^\circ \text{C}$ in a medium of ionic strength 0.1 M. The interpretation, given, is that neither the carboxylate ion in the bromo complex, $[\text{Co(EDTA)Br}]^{2-}$ nor the free carboxylic acid group in its conjugate acid $[\text{Co(HEDTA)Br}]^{-}$, takes part in the rate-determining step. Dyke and Higginson\textsuperscript{92,118} have carried out experiments on the rate of formation of $[\text{Co(EDTA)}]^{-}$ ion from the chloro complex, $[\text{Co(HEDTA)Cl}]^{-}$, and its conjugate base and observed $1.92 \times 10^{-3} \text{ min}^{-1}$ as the first-order rate constant in the pH range 2–6 for the release of the chloride ion from the chloro complex, $[\text{Co(HEDTA)Cl}]^{-}$. The constancy of this value with the $pK_a$ value of $[\text{Co(HEDTA)Cl}]^{-}$ ($pK_a = \text{ca.} 3$) shows that both $[\text{Co(HEDTA)Cl}]^{-}$ and $[\text{Co(EDTA)Cl}]^{2-}$ release chloride ion at the same rate. In this connection, it is noted that a similar observation has been reported for the elimination of bromide ion from similar bromo complex ions. Dyke and Higginson\textsuperscript{92,118} have suggested an $S_N1$ mechanism for the formation of $[\text{Co(EDTA)}]^{-}$ ion from the chloro and bromo complex ions $[\text{Co(EDTA)Cl}]^{2-}$.
and \([\text{Co(EDTA)Br}]^{2-}\); and also found that the rate is nearly equal to that of the formation of \([\text{Co(EDTA)}]^-\) ion from their conjugate acids, \([\text{Co(HEDTA)Cl}]^-\) and \([\text{Co(HEDTA)Br}]^-\). It follows that the equation reaction of these conjugate acids also proceeds through an \(S_{N1}\) mechanism, involving a five-coordination transition state. The kinetic scheme is given below.
It is well known that increasing the size of the inert ligand about the central cobalt ion may not favour an $S_{N2}$ mechanism, because in the transition state, according to this mechanism, the coordination number of the cobalt ion increases from six to seven. An increase in the size of the ligand favours $S_{N1}$ mechanism because of the decrease in the coordination number of the cobalt ion in the transition state by one unit. Otherwise, a sterically-crowded and energetically - unfavourable transition state results, owing to the increase of the repulsive and distortion forces among the ligands. It is further noted that in an $S_{N1}$ mechanism, bond-breaking is more important than bond-making. In the mechanism, proposed above, the first and the fast step involves aquation of the bromo ligand and only in the second step, which is the rate-determining step, does the aquated complex undergo ring closure leading to the final product. A similar mechanism has been proposed for the conversion of $[\text{Co(EDTA)}x]^2^-$, ($x = \text{Cl or Br}$) to $[\text{Co(EDTA)}]^-$ ion.
Transition state
The preparation and characterization of some cobalt(III) complexes containing quinuedentate (PDTA)⁻ ion such as [Co(PDTA)Br]²⁻ and [Co(PDTA)Cl]²⁻ and their kinetics of aquation have been reported. Preliminary rate data indicate that the rate of the elimination reactions for these PDTA complexes is only slightly higher than that for EDTA complexes. Such an observation is in line with the above postulated mechanism, owing to the fact that the relative stabilities of the ground state cobalt ion with coordination number six and the transition state cobalt ion with coordination number five cannot be affected substantially by the difference in the structures of PDTA and EDTA ligands.

Shimi and Higginson have studied the following rate processes:

\[
[\text{Co(HEDETA)H}_2\text{O}] \rightarrow [\text{Co(EDTA)}]^- + \text{H}_3\text{O}^+
\]

\[
[\text{Co(EDTA)OH}]^{2-} \rightarrow [\text{Co(EDTA)}]^- + \text{OH}^-
\]

\[
[\text{Co(ELTA)H}_2\text{O}]^- \rightarrow [\text{Co(EDTA)}]^- + \text{H}_2\text{O}
\]
The first reaction follows $S_N^1$ mechanism, involving three steps, viz., elimination of water ligand, ionisation of carboxylic acid group and cyclisation. But Dyke and Higginson\textsuperscript{92,118} have argued that there is no compelling reason to accept these three steps and no reason to overlook a transition state in which these three steps may be merged into one step. Another possibility involves elimination of water and hydrogen ion as hydronium ion.
Regarding the elimination of the hydroxide ion from [Co(EDTA)OH]^{2-}, a mechanism similar to that of water from [Co(EDTA)H_2O]^{-} is not expected because in the rate-determining step there exists electrostatic repulsion between the free carboxylate ion and the incipiently formed hydroxide ion \(^{92,118,121}\). Hence a mechanism similar to the mechanism already proposed for the elimination of bromide ion from [Co(EDTA)Br]^{2-} ion has been suggested.

The kinetic aspects of the new complex ion, [Co(HEDTA)N_3]^{-} and the nitro complex ion, [Co(HEDTA)NO_2]^{-} show a different behaviour compared to the other known bromo and chloro complex ions, [Co(EDTA)Br]^{2-} and [Co(EDTA)Cl]^{2-}, and their corresponding conjugate acids. The rates of acid hydrolysis reactions of the nitro and azido complex ions are pH dependent in contrast to those of the chloro and bromo complex ions which are pH independent. For the nitro complex ion at 54.8°C in a medium of ionic strength 0.35 M the values of \( k \times 10^{3} \) min\(^{-1}\) at pH 0.16, 0.95, 1.23, 2.0, 2.5 and 2.6 are 16.08, 11.58, 11.09, 7.83, 7.71 and 5.63 (Table 54) respectively and
similarly for the azido complex ion at 59.5°C in a medium of ionic strength 0.35 M, when pH is 1.52, the value of \( k \times 10^3 \, \text{min}^{-1} \) is found to be 15.11; at 2.35 it is 6.14 and at 3.2 it is 2.59 (Table 47). When the pH is above 3 and 3.5 in the case of the nitro and azido complexes respectively, the change in absorbance is found to be too low, practically becoming negligible, (Fig. 87) indicating that the rate of these aquation reactions is strongly acid dependent and hence these reactions are better referred to as acid-catalysed acid hydrolysis such reactions have been studied by Staples\textsuperscript{59}, Haim and Wilmarth\textsuperscript{58} and Lambert and Mason\textsuperscript{119}.

In the present investigation, we have used the azide ion as the sixth ligand which is more easily oxidizable than the bromo and chloro ligands. So the absence of the rate-limiting step leading to the aquated product is visualised.

Staples and Tobe\textsuperscript{120} have studied the kinetics of both the acid and base hydrolysis reactions of some azidobis(ethylenediamine)cobalt(III) complexes such as
Fig. 87 Formation of $[\text{Co(EDTA)}]^{-}$ ion from $[\text{Co(HEDTA)N}_3]^-$ ion at pH $> 3.5$. Temp. = 50°C. $0, 0' = 0$ min; $1, 1' = 60$ min.
[Co(en)$_2$Cl N$_3$]$^+$ and observed that the chloro ligand is replaced far more easily than the azido ligand. In the base hydrolysis reactions of these complexes, it was observed$^{120}$ that the azido ligand seems to behave as an electron-withdrawing agent like the nitro ligand but to a smaller extent. The azido complex exhibits a second mode of action in its reaction with water, in which it behaves as an electron-releasing group. These two types of behaviour of the azide ion is expected because it can act both as an electron-withdrawing and an electron-releasing agent, depending upon the requirement of the reaction by virtue of the following two canonical structures of the azide ion.

\[
\begin{array}{c}
\vdots & \vdots & \vdots \\
-\dot{N} = N \Rightarrow N : \\
& \downarrow \\
\odot & \vdots & \vdots \\
-\dot{N} - N \equiv N
\end{array}
\]
Based on the measurements of the $pK_a$ values, the presence of intramolecular hydrogen bonding in both the nitro and azido complexes has already been suggested (p.176). All these experimental findings have led us to propose the following kinetic steps for the acid-catalysed acid hydrolysis of both the azido and nitro complex ions.
The first step is the protonation of the azido or nitro ligand, which is in pre-equilibrium. The occurrence of such a step has been reported in some acid-catalysed acid hydrolysis reactions of cobalt(III) complexes. Haim and Wilmarth have suggested that in the absence of added thiocyanate ions, the acid-catalysed aquation of monoazidopentacyanocobaltate(III) ion can be adequately described in terms of the following scheme:

\[
[\text{Co(CN)}_5\text{N}_3\text{]}^{3-} + \text{H}^+ \rightleftharpoons [\text{Co(CN)}_5\text{N}_3\text{H}]^{2-} \quad \text{(Pre-equilibrium)}
\]

\[
[\text{Co(CN)}_5\text{N}_3\text{H}]^{2-} + \text{H}_2\text{O} \rightleftharpoons [\text{Co(CN)}_5\text{H}_2\text{O}]^{2-} + \text{N}_3\text{H}
\]

\[\text{slow}\]
The first step is rapidly reversible and the second one determines the rate of the reaction. Lambert and Mason have carried out studies on the acid-catalysed acid hydrolysis reactions of trans-\([\text{Co(Ni)}_2(\text{NO}_2)_2]^+\) as a function of acid concentration in perchloric acid, hydrochloric acid, hydrobromic acid, sulphuric acid and nitric acid at 25°C and observed that the results are consistent with the protonation of the nitro ligand as the pre-equilibrium step, followed by the attack of water on the protonated complex as the rate-determining step. The equations describing these steps are shown:
\[ \text{enCoNO}_2^+ + \text{H}^+ \rightleftharpoons \text{enCoNO}_2^{2+} \] (Pre-equilibrium)

\[ \text{enCoNO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{enCoNO}_2 + \text{H}_2\text{O} \] (Slow)
For the aquation of the nitro complex at 55°C, for the change of the ionic strength of the medium from 0.15 M to 0.6 M with the consecutive increments of 0.05 unit, $k \times 10^2$, min$^{-1}$ values are found to be 1.08, 1.16, 1.02, 1.06, 1.10, 1.04, 1.07, 1.13, 1.12 and 1.16 (Table 43) respectively and similarly for the azido complex at the same temperature, for a similar change of the ionic strength of the medium from 0.15 M to 0.4 M, $k \times 10^2$, min$^{-1}$ values are 2.79, 2.90, 2.68, 2.84, 2.87 and 2.79 (Table 32) respectively. Since the change in the ionic strength of the medium does not reflect any appreciable effect on the rate, it is inferred that the rate-determining step does not involve either oppositely charged ions or ions of the same charge as the reactant species. In addition, it is to be noted that there exists a linear relationship between the rate constant and the hydrogen ion concentration, as is evident from the linear curve obtained by plotting log $k$ versus pH (Fig. 59, 66) and in consistent with the following equation:

$$k_1 = k_0 + k_H [H^+]$$
where

\[ k_1 = \text{first-order rate constant} \]

\[ [H^+] = \text{concentration of } H^+ \text{ ions and} \]

\[ k_o \text{ and } k_H \text{ are constants.} \]

The second step in the mechanism involves ionisation of the free carboxylic acid group of (EDTA)^- ion and in this step it is expected that the equilibrium is shifted more towards the reactant side, since the hydrolysis is carried out in a solution of high hydrogen ion concentration.

The third step is the aquation step and the fourth and the last one involves cyclisation. One of these two steps is the rate-determining one. Since the aquation step involves an anion and a neutral molecule and the cyclisation step involves only one reactant species, neither step should show any appreciable change with the change of the ionic strength of the medium and, in fact, experimentally it is proved to be so.
The activation parameters for the aquation of the chloro complex have been reported by Dyke and Higginson. The entropy of activation was found to be -6.137 eu in the temperature range 35 to 50°C and it is independent of pH. However, for the azido complex, it is observed that -54.59, -15.25, -5.18, -2.25 and +9.10 eu as entropy of activation at pH 2.35, 1.20, 1.04, 0.99 and 0.66 (Table 89) respectively. Similarly the values of entropy of activation for the nitro complex are found to be -21.9, -15.95, -5.90, -4.06 and +7.45 eu at pH 1.43, 1.27, 1.13, 0.68 and 0.52 (Table 123) in the temperature range 49 to 59°C respectively.

The thermodynamic data for aquation at different pH show that the entropy of activation is not constant within the temperature range 49 to 59°C. Hence the applicability of the compensation law for the present system has been checked by plotting $\Delta H^\#$ versus $\Delta S^\#$ (Fig. 88,89). There is a linear relationship with a positive slope. This implies that there is an isokinetic relationship between the two quantities, $\Delta H^\#$ and $\Delta S^\#$. This establishes that the mechanism of aquation does not undergo a change within the pH range considered. The
Fig. 88  $\Delta H^\#$ versus $\Delta S^\#$

Acid hydrolysis of $[\text{Co(HEDTA)NO}_2]^{-}$ ion at different pH
Fig. 89  $\Delta H^\#$ versus $\Delta S^\#$

Acid hydrolysis of $[\text{Co(HEDTA)}N_3]^-$ ion at different pH
equation for isokinetic relationship may be written

in the following form:

\[ \Delta H^\# = \Delta H_0^\# + \beta \Delta S^\# \]

where,

\[ \Delta H_0^\# \] is the intercept and the slope of

the relationship is \( \beta \)

If we assume that cyclisation is the rate-
determining step, then it is reasonable to expect a
value of entropy of activation around \(-6\) eu (Table 127)
as in the case of \([\text{Co(HEDTA)Cl}]^-\) ion. For the two
complex ions investigated presently, a more negative
value of entropy of activation is observed. In
addition, it is to be noted that the rate constant for
the aquation of \([\text{Co(HEDTA)Cl}]^-\) and \([\text{Co(HEDTA)Br}]^-\) ions
is \(1 \text{ to } 4 \times 10^{-3}, \text{ min}^{-1}\) at \(25^\circ\text{C}\). However, the nitro
and azido complexes do not undergo any significant
aquation reaction at 25°C. The rate is reasonably fast only at around 50°C and at a pH less than three. Hence the cyclisation step does not seem to be the rate-determining step. It is, therefore, postulated that the aquation step determines the rate of the reaction as shown in the following scheme:

\[
[\text{Co(HEDTA)}N_3]^− + H^+ \underset{\text{pH} < 3}{\overset{\text{Pre-equilibrium}}{\leftrightarrow}} [\text{Co(HEDTA)}N_3H]^{+} \\
[\text{Co(HEDTA)}N_3H] \overset{\text{slow}}{\rightarrow} [\text{Co(EDTA)}N_3H]^− + H^+ \\
[\text{Co(EDTA)}N_3H]^− + H_2O \underset{\text{slow}}{\rightarrow} [\text{Co(EDTA)}H_2O]^− + N_3H \\
[\text{Co(EDTA)}H_2O]^− \rightarrow [\text{Co(EDTA)}]^− + H_2O
\]
TABLE-127

THERMODYNAMIC PARAMETERS FOR THE AQUATION REACTIONS

<table>
<thead>
<tr>
<th>Complex ion</th>
<th>$k \times 10^3$, min$^{-1}$</th>
<th>$\Delta E^#$, cal</th>
<th>$\Delta S^#$, e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$35^\circ C$</td>
<td>$40^\circ C$</td>
<td>$50^\circ C$</td>
</tr>
<tr>
<td>$[\text{Co(HEDTA)Cl}]^-$</td>
<td>0.58</td>
<td>1.115</td>
<td>3.57</td>
</tr>
<tr>
<td>$[\text{Co(HEDTA)N}_3]^-$</td>
<td>4.277</td>
<td>5.264</td>
<td>6.147</td>
</tr>
<tr>
<td>$[\text{Co(HEDTA)NO}_2^-]$</td>
<td>1.56</td>
<td>2.67</td>
<td>3.73</td>
</tr>
</tbody>
</table>
5.5. **Photochemical pathways of monoazidoethylene-diaminetetraacetatocobaltate(III) ion**

The irradiation of coordination complexes in the region of absorption bands, in general, leads to a variety of photochemical reactions, such as ligand labilization, ligand isomerization and reduction of the central metal ion. It is known that irradiation at LMCT bands leads predominantly to redox decomposition reaction while that at ligand field bands gives the photoaquated product. In general, charge-transfer excitation leads to redox decomposition while ligand field excitation to photoaquation and the occurrence of both reactions simply reflects the degree of overlap of the two kinds of irradiation.

With very few exceptions, cobalt(III) complexes show two kinds of photoreactions and their behaviour is determined by a complicated balance of a variety of chemical and spectroscopic analyses. The generalisations are:
(i) In all the ammine complexes, the irradiation in the region of LMCT bands, leads to oxidation reduction decomposition reactions.

(ii) The quantum-yields are generally higher for those complexes containing more easily oxidizable ligands.

(iii) The easier the oxidation of the ligands, the more does the reaction tend towards photo-redox process.

(iv) In the region of the charge-transfer bands, the quantum-yield is essentially independent of wavelength in spite of the fact that, in most cases, it varies with the wavelength.

(v) The quantum-yields of photoaquation are found to be not accurate enough for comparison.

(vi) The possibility of relating the quantum-yield of the photoaquation reactions to the intrinsic properties of the complexes is limited
(vii) However, it is noteworthy that the occurrence of a photoaquation reaction is not generally limited to the type of excitation performed.

When hexaamminecobalt(III) ion was irradiated in an aqueous solution with 254 nm light, corresponding to the tail of the LMCT band, Endicott and Hoffmann\(^{128}\) observed the redox decomposition reaction, resulting in the formation of Co\(^{2+}\) ion. During this reaction, hydrogen ions are consumed as per zero order kinetics. The quantum-yield of Co\(^{2+}\) ion is approximately 0.7 according to Endicott and Hoffmann\(^{128}\) and 0.16 according to Manfrin et al.\(^{129}\) and is found to be independent of the hydrogen ion concentration of the solution and the intensity of the light used. It is noteworthy that the photoredox reaction is accelerated by halides as well as easily oxidizable organic substances and inhibited by hydrogenperoxide. Simultaneous occurrence of both photoredox decomposition and photoaquation reactions is not known with clear evidence but
it was suggested by Manfrin et al.\textsuperscript{129} that if at all such a reaction occurs, its quantum-yield must be at least 5 times less than that of the photoredox process.

When the same complex ion i.e. $[\text{Co(NH}_3\text{)}_6]^{3+}$ was irradiated at 365 and 472 nm, the complex ion does not show any appreciable quantity of photoredox product. However, it undergoes a photoreaction in which the release of ammonia was observed, with the quantum yield of $5.4 \times 10^{-3}$ at 365 nm and $5.2 \times 10^{-4}$ at 472 nm and the rate of release of ammonia was estimated to be fifty times higher than the rate of photoredox decomposition process. The former quantum-yield corresponds to the excitation of ligand field band due to the transition $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ and the latter due to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition.

Adamson\textsuperscript{130,131} has reported that irradiation of aqueous solutions of monoazidopenta-amminecobalt(III), in the regions of both the charge-transfer and ligand field bands results only in the photoredox decomposition reaction. The quantum-yield was found to be 0.44 at 370 nm and 0.11 at 550 nm and
it depends on the nature of the solvent also. It is to be noted here that the nature of the final products depends on the pH of the solution. In the acid medium, Co$^{2+}$ species and nitrogen were formed whereas in neutral or basic medium, Co$^{2+}$ and azide species were obtained without the evolution of nitrogen. It is also to be noted that the free azide ion undergoes photodecomposition when its aqueous solution is subjected to irradiation at 250 nm. At this wavelength, the absorption coefficient of the azide ion is much lower than that of the complex.

The photochemical behaviour of the complex ions of the type $[\text{Co(HEDTA)}X]^-$ where $X = \text{Cl or Br or NO}_2$ has been studied. The only thermal reaction observed is the aquation of the azido group. Irradiation of these complexes in 0.1 M aqueous perchloric acid results in both the oxidation-reduction reaction and ligand labilization reaction.

\[ \phi \text{ Co}^{2+} \rightarrow \text{ Co}^{2+} + X^- + \text{CO}_2 + R \]

\[ \phi \text{ X}^- \rightarrow [\text{Co(HEDTA)H}_2\text{O}]^- + X^- \]
The newly prepared azido complex was subjected to irradiation using a light of wavelength 254 and 365 nm. The formation of $\text{Co}^{2+}$ ions and carbon dioxide were noted. The quantum-yields of the formation of $\text{Co}^{2+}$ ion at 254 and 365 nm were found to be 0.0438 and 0.0067 respectively. However, it is to be noted that irradiation of the azido complex in 0.1 M aqueous perchloric acid using visible light does not produce any appreciable quantity of $\text{Co}^{2+}$ ions (Fig. 90). Thus these results are in good agreement with the statement that irradiation in the region of LMCT bands leads to oxidation-reduction decomposition reaction with relatively high quantum-yields. For comparison, the quantum yields of $\text{Co}^{2+}$ ions, produced as a result of irradiation of $[\text{Co(HEDTA)}X]^{-}$ complexes at various wavelengths are summarized $^{135}$ in Table-128.

In flash photolysis experiments on both the nitro and azido complexes, no transients were observed in 95% acetonitrile and methanol. In addition, irradiation was done in the visible region for different duration of time (5, 10 and 15 min) and no significant change in absorption has been noted (Fig. 90).
Fig. 90 Ultraviolet – visible spectra of the complex after irradiation in the visible region at different intervals of time.
TABLE-128

PRODUCT YIELDS FROM IRRADIATION OF [Co(HEDTA)X]^- COMPLEXES

<table>
<thead>
<tr>
<th>X</th>
<th>Irradiation Wavelength, nm</th>
<th>$\phi_{\text{Co(II)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>254</td>
<td>0.17</td>
</tr>
<tr>
<td>Cl</td>
<td>254</td>
<td>0.18</td>
</tr>
<tr>
<td>Br</td>
<td>254</td>
<td>0.14</td>
</tr>
<tr>
<td>N$_3$</td>
<td>254</td>
<td>0.0438</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>400</td>
<td>0.004</td>
</tr>
<tr>
<td>Cl</td>
<td>400</td>
<td>0.030</td>
</tr>
<tr>
<td>Br</td>
<td>350</td>
<td>0.035</td>
</tr>
<tr>
<td>N$_3$</td>
<td>365</td>
<td>0.0067</td>
</tr>
</tbody>
</table>