Iron(II) reduction, protonation and iron(III) equilibria of some chlorocobalt(III)–
dioxime complexes

A Dayalan* & A Xavier
Department of Chemistry, Loyola College (Autonomous), Chennai 600 034, India
Email: a_dayalan_sgp@yahoo.com

Received 2 September 2003; revised 24 March 2004

Cobalt(III) complexes of the type [Co(dpgH)₂(s-py)Cl] where dpgH=diphenylethenedione dioxime, s-py= pyridine (py) or a substituted pyridine like nicotinic acid(nic-COOH), quinoline(Q) or 8-hydroxy quinoline(Q-OH) have been prepared and their iron(II) reductions have been studied at 300 nm under pseudo-first order conditions with an excess of the reductant in DMSO-H₂O (10% v/v) medium at 27±0.1°C and I=0.25 M (LiClO₄) in the [H⁺] range 0.01 - 0.1 M. An inverse acid dependence on the rate of reduction of the complexes indicates the oxime bridged inner-sphere reduction with equilibria involving H⁺. Hence, the second order rate constants and the rate coefficients have been determined considering the protonation equilibria at the oxime oxygen. A mixture of the complex and H⁻ shows an increase in absorption in the region 250-350 nm only; whereas, a mixture of the complex, H⁻ and iron(II) an intense absorption in another region also viz., 375-500 nm. The equilibrium constants for equilibria involving H⁻ and the cobalt(III) complexes and for equilibria involving H⁺, iron(III) and the cobalt(III) complexes have been evaluated by pH titrations and measuring the absorbance of the reaction mixtures in the region 375-500 nm, respectively.

IPC Code: Int. Cl.7 C01 G 51/00

Dimethylidionedioxime(dimethylgloxime) complexes of cobalt(III), generally known as cobaloximes, serve as models for the study of vitamin-B₁₂. Cobaloximes exhibit different or similar redox and other chemical behavior depending on the nature of the dioxime network and axial ligands. A recent report on the redox properties of cobalt(III)-dioximes, containing an aromatic ring in the dioxime, reveals that a powerful reducing metal ion like chromium(II) reduces the complexes by binding through equatorial oxime oxygen. Hence, it should be much more informative to study the chemical behavior of cobalt(III)-dioximes having greater aromatic substituents with less powerful reductant like iron(II). This report is a study of the iron(II) reduction, protonation and iron(III) equilibria of the complexes of the type [Co(dpgH)₂(s-py)Cl], where dpgH=diphenylethenedioxime, s-py = pyridine (py) or a substituted pyridine like nicotinic acid (nic-COOH), quinoline(Q) or 8-hydroxy quinoline (Q-OH).

Materials and Methods

E. Merck samples of benzil, hydroxylamine hydrochloride, cobalt(II) chloride, pyridine, nicotinic acid, quinoline and 8-hydroxyquinoline were used as such for the synthesis of complexes.

Preparation of diphenylethenedioxime, dpgH₂

About 42 g of benzil was ground into thin paste with ethanol and treated with an aqueous solution of hydroxylamine hydrochloride (36 g in 100 ml of water). The mixture was cooled to -5°C in an ice-salt bath and treated with 150 ml of 20% aqueous NaOH with constant stirring. The mixture was diluted with water to double its volume and filtered to remove the unreacted benzil. The filtrate was acidified with glacial acetic acid and allowed to stand for 50 min. The product formed as the precipitate was filtered and re-crystallised from aqueous ethanol.

Preparation of the complexes

Preparation of hydrogen dichlorobis(diphenylethenenedioxime)cobaltate(III): H⁺[Co(dpgH)₂Cl₂]

The dichlorocomplex was prepared by adopting the procedure reported for the preparation of dichlorocobaloxime. Cobalt(II) chloride (0.01 mol) was dissolved in 75 ml of acetone and diphenylethenedione-
dioxime (4.8 g, 0.02 mol) was added. The mixture was agitated for about 10 min and filtered to remove any undissolved material. The green coloured solution formed was allowed to stand overnight. Owing to its greater solubility in acetone, the complex remained in solution. This dichloro complex remaining in solution was frequently synthesized for preparing other complexes.

Preparation of [Co(dpgh)₂(py)Cl], [Co(dpgh)₂(nicot-COOH)Cl], [Co(dpgh)₂(Q)Cl] and [Co(dpgh)₂(Q-OH)Cl]
The green coloured (0.01 M) solution of the dichloro complex viz., H[Co(dpgh)₂Cl₂], obtained above, was treated separately with 0.01M of pyridine, nicotinic acid, quinoline or 8-hydroxyquinoline as the case may be. The mixture was warmed and stirred on a water bath for about 30 min. The solutions turned into characteristic coloured solid products. They were then allowed to stand for an hour. The yellow, violet, blue and dark brown coloured complexes formed, respectively were filtered and washed with ethanol and diethyl ether.

Carbon, hydrogen and nitrogen were analysed using Perkin-Elmer Series-II, 2400 CHN analyzer (Table 1). Cobalt was estimated by Kitson method. A known weight of the complex was ignited and boiled with conc. nitric acid. The residue was extracted with dil. HNO₃ and mixed with 2.5 ml of 50% ammonium thiocyanate. The resulting solution was made up to a known volume using acetone and its absorbance was measured at 625 nm (εₘₐₓ = 1864 M⁻¹ cm⁻¹).

The electronic spectra of the complexes in different media (neutral, acidic and basic) were obtained using Hitachi UV-visible spectrophotometer. Solutions of required concentration of complex in DMSO-H₂O was used to record the spectrum in neutral medium; whereas, required volume of complex solution in DMSO-H₂O was mixed with a known volume of standard perchloric acid or sodium hydroxide to provide acidic or basic media.

The IR spectra of the complexes and ligand were obtained using Perkin Elmer IR spectrophotometer in KBr disc.

Preparation of iron(II) perchlorate
Iron(II) perchlorate was prepared by dissolving 99.9% pure iron powder (0.56 g) in 150 ml of 0.25 M perchloric acid in nitrogen atmosphere. The dissolution of iron was complete over a period of 12 h. The solution was preserved in an air tight flask. Fresh solutions were prepared frequently. The concentration of iron(II) in the solution was estimated by titrating it against standard potassium permanganate. Excess acid present in the solution was determined by titrating against standard alkali.

Preparation of iron(III) perchlorate:
Iron(II) perchlorate was oxidised using hydrogen peroxide (100 volumes, 30% w/v) in the 1:1 ratio. This mixture was allowed to stand for 15 min, it was then warmed to remove the excess hydrogen peroxide. Iron(III) present in the solution was estimated using ammonium thiocyanate as follows. To 2.5 ml of freshly prepared iron(II) solution, 2.5 ml of 0.01 M perchloric acid was added followed by the addition of 5 ml of 40% ammonium thiocyanate. The solution was then diluted to 25 ml with water and the absorbance was measured at 485 nm (εₘₐₓ = 1.11 x 10⁴ M⁻¹ cm⁻¹).

Iron(II) reduction of the complexes
The iron(II) reduction of all the complexes were followed using Hitachi UV-visible spectrophotometer. Solutions of required volumes of the complex in DMSO-H₂O, lithium perchlorate (to provide 0.25 M ionic strength) and perchloric acid (to give the desired acid strength) were thermally equilibrated at 27±0.1°C. The reaction was initiated by the addition of a known volume of iron(II) solution. The rate of the reduction of the complexes was followed by monitoring the decrease in absorption of the reaction mix-

<table>
<thead>
<tr>
<th>Complex</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Co (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(dpgh)₂(py)Cl]</td>
<td>60.22(60.79)</td>
<td>4.11(4.15)</td>
<td>10.48(10.74)</td>
<td>8.81(9.04)</td>
</tr>
<tr>
<td>[Co(dpgh)₂(nicot-COOH)Cl]</td>
<td>58.42(58.67)</td>
<td>3.91(3.88)</td>
<td>10.19(10.66)</td>
<td>8.29(8.46)</td>
</tr>
<tr>
<td>[Co(dpgh)₂(Q)Cl]</td>
<td>63.17(63.30)</td>
<td>4.05(4.13)</td>
<td>9.70(9.98)</td>
<td>8.14(8.40)</td>
</tr>
<tr>
<td>[Co(dpgh)₂(Q-OH)Cl]</td>
<td>61.32(61.89)</td>
<td>4.14(4.04)</td>
<td>9.54(9.75)</td>
<td>8.13(8.21)</td>
</tr>
</tbody>
</table>
ture at 300 nm characteristic of the complex. The pseudo-first order rate constants, \( k_{\text{obs}} \), were obtained from the slopes of the linear plots of \( \log A_t \) vs time.

The stoichiometry of the reaction was determined by estimating Fe(III) and Co(II) present in the product mixture. Iron(III) was estimated using thiocyanate and cobalt(II) as [CoCl\(_4\)]\(^2-\). The ratio of Fe(III) : Co(II) was found to be 1:1.

Aqueous alkali of known strength was added gradually from the burette to 50 ml mixture of complex \( \{ 1 \times 10^{-3} \text{ M in 20\% DMSO-H}_2\text{O(v/v)}, 25 \text{ ml and aq. HClO}_4, 1.94 \times 10^{-3} \text{ M, 25 ml} \} \). The pH was measured using Control Dynamics digital pH meter for every 0.2 ml addition of alkali. These measurements were repeated by adding alkali to the blank in the absence of the complex.

The iron(III)-complex equilibrium was studied in 10\% DMSO-H\(_2\)O medium in the wavelength region 375-500 nm, where the iron(III)-complex mixture showed maximum absorption. Solutions of the complex DMSO-H\(_2\)O was mixed with varied concentrations of iron(III) perchlorate. The solutions were allowed to stand for 3-4 hr and their electronic spectra were recorded at the end.

**Results and Discussion**

The complexes were prepared by adopting the procedure reported for the preparation of hydrogen dichlorobis(dimethylglyoximato)cobaltate(III)\(^3\). Such complexes were found to be green in colour. The dichloro complexes prepared using the ligand synthesised, diphenylethanedionedioxide(dpgH\(_2\)), were also found to be green in colour similar to dimethylglyoxime complexes indicating the validity of the procedure adopted and the composition of the complex formed. Octahedral complexes of cobalt(III) with four equatorial nitrogen and two axial halogens are generally green in colour\(^3\). However, they change their green colour upon replacement of any one or both halogens by a non-halogen ligand.

**Electronic spectra**

All the cobalt(III)-dioxime complexes exhibit characteristic absorption in the UV-visible region as reported in the literature\(^9,13\). The absorption around 350-400 nm, which is much well defined for the complex containing 8-hydroxyquinoline, can be assigned to spin-allowed \( ^1\Delta_g \rightarrow ^3T_{1g} \) transition\(^9\).

The other spin-allowed \( ^1\Delta_g \rightarrow ^3T_{2g} \) band is masked by the charge transfer bands in the region 300-370 nm. The absorptions in this region are found to be sensitive to the nature of the axial ligands\(^12\).

The ligand, dpgH\(_2\) and its cobalt(III) complexes exhibit an intense peak around 250 nm which can be attributed to \( \pi-\pi^* \) intra ligand transition in benzenoid and pyridine rings and \( n-\pi^* \) and \( \pi-\pi^* \) transitions due to C=N group of the oximes\(^8\). The absorption in this region are found to be sensitive to pH of the medium. This may be due to the change in energy level of \( n-\pi^* \) transition due to protonation or deprotonation.

\[
[\text{Co(dpg)H}_2(B)Cl] \xrightleftharpoons{H_2O} [\text{Co(dpg)H}](dpgH)(B)Cl] + H_2O
\]

\[
\uparrow \text{OH}^- \quad \text{(low pH)}
\]

\[
[\text{Co(dpg)}](dpgH)(B)Cl] + H_2O
\]

\[
\text{(high pH)}
\]

**IR spectra**

A medium sharp peak around 1640 cm\(^{-1}\) confirms the presence of C=N group of the oxime in the ligand synthesised. Further, the absence of carbonyl stretching vibration around 1725 cm\(^{-1}\) indicates the complete condensation between carbonyl group and hydroxyl amine. The peak in the region 1440-1595 cm\(^{-1}\) is characteristic of C\(=\)C stretching of the aromatic ring. A sharp absorption around 3380 cm\(^{-1}\) suggests free O-H bond in the ligand.

The medium peak around 1640 cm\(^{-1}\) for C=N is being shifted to lesser frequency in the complexes confirming\(^11,15\) that the oxime nitrogen is bonded to cobalt(II). A broad peak around 3400-3550 cm\(^{-1}\) accounts for intramolecular hydrogen bonding. A strong band around 1220 cm\(^{-1}\) for N-O is being shifted to higher region 1220-1260 cm\(^{-1}\) for complexes\(^10\). The C-O stretching observed at 1700 cm\(^{-1}\), for the complex containing nicotinic acid, shows that the carboxyl group in the molecule is not involved in coordination and the metal is bound to nicotinic acid only through the pyridine nitrogen.

**Iron(II) reduction and protonation equilibria of the cobalt(III) complexes**

The kinetics of iron(II) reduction of all the cobalt(III) dioxime complexes were studied in 10\% DMSO - H\(_2\)O (v/v) by monitoring the decrease in absorbance at 300 nm under pseudo-first order conditions with 40 fold excess of the reductant over the complex. All the reduction reactions were studied as a function of hydrogen ion concentration in the range.
0.01-0.10 M. A linear dependence of the pseudo-first order rate constant on Fe(II) was observed. The rate law for the reaction with an excess of iron(II) is of the form, Rate = k[complex], where k is pseudo-order rate constant with respect to the complex.

Plot of log A vs. s is linear confirming the first order dependence of rate with respect to the complexes. The pseudo-first order rate constants were evaluated from the slopes. Iron(II) reduction of cobalt(III) complexes is generally found to be second order. Hence, the second order rate constants were obtained by dividing the pseudo-first order rate constants by the concentration of iron(II) used. The values have been found to be in the range 0.434-0.495 M⁻¹ s⁻¹ at [H⁺] = 0.01 M and 0.130-0.145 M⁻¹ s⁻¹ at [H⁺] = 0.10 M (Table 2). The magnitude of the decrease in second-order rate constants with [H⁺] is much large and hence could not be attributed to medium effect. Medium effect will decrease the rate only about 10-20%. This behaviour is similar to that reported by earlier workers.

The second order rate constants thus calculated are considerably higher to be attributed to inner-sphere electron-transfer reaction, possible by bridging through the oxime with an acid-base dissociation equilibria involving the hydrogen bonded proton in the oxime. The outer-sphere electron-transfer reactions generally exhibit lesser rate constants. For example, the outer-sphere reduction⁹ of [Co(NH₃)₃H₂O]⁺ by [Ru(NH₃)₆]²⁺ has a rate constant of 0.04 M⁻¹ s⁻¹. Hence, the inner-sphere reaction of the cobalt(III) complexes can be represented as follows:

\[
[\text{Co(dpqH)(dpqH)_{2}}(B)Cl]^{+} + \text{H}^{+} \rightarrow [\text{Co(dpqH)(dpqFe)(B)Cl}]^{+} + \text{H}^{+} + \text{Co}^{2+} + \text{Fe}^{3+} + \text{Free ligands}
\]

This type of oxime bridged iron(II) and Cr(II) reductions of cobaloximes were recently reported in literature. Cobalt(II) is labile, hence, the complex dissociates when an electron is transferred from iron(II) to cobalt(III) accounting for the decrease in absorbance in the UV-region. The UV absorption around 300 nm was attributed to ligand to metal reduction, viz., oxime to cobalt(III) charge transfer transition (LMCT). In acid medium, the complexes will be in the protonated form. Hence, the ionisation constants \( K_{a1} \) and \( K_{a2} \) for the protonated form of the complexes may be defined as follows:

\[
\begin{align*}
\text{[Co(dpqH)(dpqH)_{2}}(B)Cl]^{+} + \text{H}_{2}\text{O} & \rightarrow \text{AH}^{2+} + \text{Cl}^{-} \\
\text{[Co(dpqH)(dpqH)_{2}}(nic-COOH)Cl]^{+} + \text{H}_{2}\text{O} & \rightarrow \text{AH} + \text{nic-COOH}
\end{align*}
\]

The values of \( K_{a1} \) and \( K_{a2} \) were determined by the method of Irving and Rossotti by titrating the solutions of complexes against standard alkali (Table 3). The end point for complexes like [Co(dpqH)(py)Cl] and [Co(dpqH)_{2}(nic-COOH)Cl] could be attributed \( K_{a1} \) due to their neutralisation in the protonated form. Complexes like [Co(dpqH)_{2}(nic-COOH)Cl] and [Co(dpqH)_{2}(Q-OH)Cl] exhibit two neutralisation points due to the neutralisation of the protonated complex and the acidic proton in nicotinic acid and 8-hydroxy quinoline which can be related to \( K_{a1} \) and \( K_{a2} \), respectively. Based on the above protonation equilibria, the iron(II) reduction of the complexes can be formulated as follows:

<table>
<thead>
<tr>
<th>Complex</th>
<th>M⁻¹ s⁻¹</th>
<th>M⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{Co(dpqH)(py)Cl}]</td>
<td>0.01</td>
<td>0.025</td>
</tr>
<tr>
<td>[\text{Co(dpqH)(nic-COOH)Cl}]</td>
<td>0.043</td>
<td>0.261</td>
</tr>
<tr>
<td>[\text{Co(dpqH)(nic-COOH)Cl}]</td>
<td>0.043</td>
<td>0.261</td>
</tr>
<tr>
<td>[\text{Co(dpqH)(Q-OH)Cl}]</td>
<td>0.044</td>
<td>0.297</td>
</tr>
</tbody>
</table>

Table 2—Second order rate constants \( k (M^{1} s^{-1}) \) for the iron(II) reduction of the cobalt(III) complexes as a function of [H⁺] at 27 ± 0.1°C. Complex = 1.0 x 10⁻³M; [Fe(II)] = 4.0 x 10⁻⁷M Solvent = 10% DMSO-H₂O(v/v), Temp = 27±0.1°C; I = 0.25 M LiClO₄.
Table 3—Acid dissociation constants (K_a1 & K_a2) and the rate coefficients (k_1 and k_2) for the iron(II) reduction of cobalt(III)-dioxine complexes in 10% DMSO-H_2O (v/v) at 27 ± 0.1°C

<table>
<thead>
<tr>
<th>Complexes</th>
<th>K_a1 × 10^4</th>
<th>K_a2 × 10^4</th>
<th>k_1 M⁻¹ s⁻¹</th>
<th>k_2 M⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(dpgh)₂(py)Cl]</td>
<td>1.88</td>
<td>-</td>
<td>0.115</td>
<td>23.138</td>
</tr>
<tr>
<td>[Co(dpgh)₂(nic-COOH)Cl]</td>
<td>2.12</td>
<td>3.46</td>
<td>0.109</td>
<td>22.804</td>
</tr>
<tr>
<td>[Co(dpgh)₂(QCl)]</td>
<td>3.51</td>
<td>-</td>
<td>0.102</td>
<td>11.649</td>
</tr>
<tr>
<td>[Co(dpgh)₂(Q-OH)Cl]</td>
<td>1.55</td>
<td>0.25</td>
<td>0.112</td>
<td>30.278</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{[Co(dpgh)₂(B)Cl] + H}_2\text{O} & \xrightarrow{K_b} \text{AH} \\
\text{[Co(dpgh)(dpgh)₂(B)Cl]⁺ + H}_2\text{O} & \xrightarrow{k_1} \text{AH}_2^+ \\
\text{[Co(dpgh)(dpgh)₂(B)Cl]⁺ + Fe}^{2+} & \xrightarrow{k_2} \text{Co}^{2+} + \text{Fe}^{3+} + \text{Free ligands} \\
\text{[Co(dpgh)₂(B)Cl] + Fe}^{2+} & \xrightarrow{k_2} \text{AH} \\
\end{align*}
\]

Hence, the rate expression may be written as

\[
\text{Rate} = k_1 [\text{AH}_2^+][\text{Fe}^{2+}] + k_2 [\text{AH}][\text{Fe}^{2+}]
\]

Therefore, the second rate constant, \(k_2\) may be related as follows,

\[
k_2 = \frac{k_1 [H^+] + k_2 K_{a_1}}{K_{a_1} + [H^+]} = \frac{k_1 K_{a_1}}{K_{a_1} + [H^+]}
\]

where, \(K_{a_1} = 1/K_{a_1}\) and \(k_1\) and \(k_2\) are the second order rate coefficients for the reductions of protonated(AH⁺) and unprotonated(AH) forms of the complexes, respectively. However, in highly acidic medium the complexes would be present mostly in the protonated and un-protonated forms.

The plot of \(k\) versus \([H^+]\) would produce a nonlinear curve. The parameters \(k_1\) and \(k_2\) satisfying the above nonlinear equation were calculated by least squares method of best fit using a suitable program.

The observed \([H^+]\) dependence of \(k\) and the values of \(k_1\) and \(k_2\) indicates that the protonated form is reduced at a slower rate than the unprotonated form. It may also be noted that the magnitude of the rate coefficients \(k_1\) and \(k_2\) follows the order \(k_1 < k_2\) for all the complexes, with \(k_2\) values being more sensitive to \([H^+]\) variation accounting for protonation equilibria.

Complex iron(III) – equilibria

The absorbance in the region 375 – 500 nm for the complexes increases with increase in Fe(III), suggesting an adduct formation with the complex. Such mode of binding of iron, Fe(III), to the co-ordinated oxime has been reported in literature. Espenson and co-workers have reported the formation constants for the binding on the oxime by Fe(III) on the basis of an intense absorption at 500 nm. Dash et al. observed a new band at 450 nm due to the reversible complexation of Fe(III) with [Co(dpgh)(im)]⁺. Hence, the adduct formation with the complexes arises due to the replacement of \(H^+\) by Fe(III) at the oxime region.

\[
\text{[Co(dpgh)₂(B)Cl] + Fe}^{3+} \xrightarrow{C_x} \text{[Co(dpgh)(dpgh)Fe(B)Cl]⁺ + H}^+
\]

Therefore, the equilibrium constant for the above equilibria may be defined as

\[
K = \frac{[C_x - \text{Fe(III)}][H^+]}{[C_x][\text{Fe(III)}]}
\]

The quantitative treatment requires the consideration of two additional equilibria:

(i) The acid ionisation of the hydrated iron(III)

\[
[\text{Fe(H}_2\text{O)}_₆]^{3+} \leftrightarrow [\text{Fe(H}_2\text{O)}₃(\text{OH})]^{2+} + \text{H}^+
\]
The equilibrium constant $K_{eq,	ext{Fe(III)}}$ for the above reaction has been found to be $1.65 \times 10^{-1} \text{M}^{-1}$.

(ii) The protonation at the oxime oxygen of the complex

$$\text{[Co(dpghH)_{2}(B)Cl]} + \text{H}_{2}\text{O} \rightleftharpoons \text{[Co(dpghH)(dpghH)_{2}(B)Cl]} + \text{H}_{2}\text{O}$$

The equilibrium absorbance values of $\varepsilon_{\text{H}_{2}\text{O}}$ for the cobaloxime over a range of concentrations of iron(III) with $[\text{H}^+]$ varying from 0.004 to 0.025 M were determined spectrophotometrically in the range 375-450 nm (Table 4). If $[\text{Fe(III)}]_0$ is used to represent $[\text{Fe}^{III}]+[\text{Fe(H}_{2}\text{O})_6(\text{OH})^{2+}]$, the equation relating these quantities is

$$\varepsilon_{\text{CS-Fe(III)}} = \varepsilon_{\text{O}} - \frac{(\varepsilon_{\text{II}} - \varepsilon_{\text{O}})K[\text{Fe(III)}]}{P + K[\text{Fe(III)}]}$$

where $P = [\text{K}_{\text{H}^+}] [\text{K}_{\text{H}^+] + 1]$, $[\text{Fe(III)}]_0 = [\text{Fe(III)}]_0 + [\text{Fe(III)}]_{\text{calc}} - [\text{CS}]$ and $\varepsilon_{\text{II}}$ is the molar absorptivity of the adduct. Excellent linear fittings were observed when $(\varepsilon_{\text{CS-Fe(III)}} - \varepsilon_{\text{O}})^{-1}$ was plotted against $P/[\text{Fe(III)}]_0$. The equilibrium constants were calculated from the slopes and the intercepts of the linear plot. The values of $K_x \times 10^{12}$ are 8.20, 16.76, 7.35 and 12.18 for $[\text{Co(dpghH)_{2}(py)Cl}]$, $[\text{Co(dpghH)_{2}(nic-COOH)Cl}]$, $[\text{Co(dpghH)_{2}(Q)Cl}]$ and $[\text{Co(dpghH)_{2}(Q-\text{OH})Cl}]$ respectively in 10% DMSO- H$_2$O (v/v), $I = 0.25$ M LiClO$_4$ at 27.2±0.1°C.

The values of equilibrium constants thus ($K$) determined for the cobalt(III) complexes of diphenylethenedionedioxide show that they exhibit a greater tendency for adduct formation with Fe(III) than cobaloximes. For example, Backac and Espenson reported rather lesser equilibrium constants for the reaction:

$$[\text{XCo(dpghH)_{2}(H}_{2}\text{O})]^{n+} + \text{Fe}^{III} \rightleftharpoons [\text{XCo(dpghH)_{2}(dpghFe)(H}_{2}\text{O})]^{n-1+} + \text{H}^+$$

as 16.2 for $X = \text{CH}_3$ and 2.5 for $X = \text{H}_2$O. The lesser value of equilibrium constant for diaquo-cobaloxime ($X = \text{H}_2$O) has been attributed to its cationic nature. But, relatively greater equilibrium constants, observed in the present study, for the Fe(III)-cobalt(III) complexes can be attributed to their neutral nature.

Acknowledgement

The authors are thankful to Rev. Fr. Dr. Francis M. Peter, Secretary & Rev. Fr. Dr. V. Joseph Xavier, Principal, Loyola College, Chennai-34 and to Dr. A. B. Mandal, Deputy Director, CLRI, Chennai-20 for facilities provided.

References


