Chapter 5

SYNTHESSES AND CHARACTERIZATION OF COBALT(II) COMPLEXES OF ACYLHYDRAZONES

5.1 Introduction

Cobalt exhibits two important oxidation states as +2 and +3 and salts of Co(II) are more stable, as they are not easily oxidised to Co(III) state. However, in basic solutions, oxidation of Co$^{2+}$ to Co$^{3+}$ takes place relatively easily. It is usually found that when both oxidation states of an element are subjected to complex formation, the overall formation constant is greater for the higher oxidation state and thus complexation makes it difficult to be reduced. Thus, Co(III) is stabilised by complexation and Co(II) forms relatively few complexes, which are not as stable as the corresponding complexes of Co(III). However, high spin six coordinate, high/low spin five coordinate and four coordinate complexes of Co(II) are widely reported [1-3].

Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [4-7]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities. There has been a
growing interest in the chemistry and biochemistry of cobalt because of its implication in many biological redox processes [8,9].

We now report the synthesis and characterization of Co(II) complexes of tridentate acylhydrazones.

5.2. Experimental

5.2.1. Materials

All the chemicals and solvents used for the syntheses were of analytical grade. Quinoline-2-carbaldehyde (Aldrich), benzhydrazide (Aldrich), nicotinic hydrazide (Aldrich), cobalt(II) acetate tetrahydrate (BDH), cobalt(II) bromide, potassium thiocyanate (Merck) and sodium azide (Reidel-De Haen) were used as received.

5.2.2. Syntheses of ligands

Preparation of the ligands was done as described previously in Chapter 2.

5.2.3. Syntheses of cobalt(II) complexes

5.2.3a. Synthesis of [Co(Qb)_2] (7)

HQb·1.5H_2O (0.606 g, 2 mmol) was dissolved in methanol (20 ml) by stirring and to this solution, cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) in methanol (20 ml) was added and refluxed the solution for 2 hours. Then the solution was cooled at room temperature. The dark brown crystalline precipitate of 7 obtained was washed with methanol followed by ether and then dried over P_4O_10 in vacuo. Yield: 78.9%. λ_m (DMF): 7 ohm^{-1} cm^2 mol^{-1}. μ (B.M.): 4.84. Elemental Anal. Found (calcd.) (%): C, 67.14 (67.22); H, 4.08 (3.98); N, 13.50 (13.83) for [Co(Qb)_2].

5.2.3b. Synthesis of [Co(Qn)_2] (8)

HQn·1.5H_2O (0.606 g, 2 mmol) was dissolved in methanol (20 ml) by stirring and to this solution, cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) in methanol (20 ml) was added and refluxed the solution for 4 hours. The dark brown precipitate of 8 obtained was washed with methanol followed by ether and
then dried over \(\text{P}_4\text{O}_{10}\) in vacuo. Yield: 74.5\%. \(\lambda_m\) (DMF): \(9\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}\). \(\mu\) (B.M.): 4.89. Elemental Anal. Found (calcd.) (%): C, 63.49 (63.06); H, 3.99 (3.64); N, 18.36 (18.38) for \([\text{Co(Qn)}_2]\).

### 5.2.3c. Synthesis of \([\text{Co(Qn)}\text{Br}]\cdot\text{H}_2\text{O}\) (9)

HQn·1.5H₂O (0.303 g, 1 mmol) was dissolved in methanol (20 ml) by stirring and to this solution, cobalt(II) bromide (0.218 g, 1 mmol) in methanol (20 ml) was added and refluxed the solution for 4 hours. The brown precipitate of 9 obtained was washed with methanol followed by ether and then dried over \(\text{P}_4\text{O}_{10}\) in vacuo. Yield: 34.9\%. \(\lambda_m\) (DMF): \(13\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}\). \(\mu\) (B.M.): 4.92. Elemental Anal. Found (calcd.) (%): C, 44.59 (44.47); H, 2.85 (3.03); N, 12.50 (12.97) for \([\text{Co(Qn)}\text{Br}]\cdot\text{H}_2\text{O}\).

### 5.2.3d. Synthesis of \([\text{Co(Qn)}\text{SCN}]\) (10)

HQn·1.5H₂O (0.303 g, 1 mmol) was dissolved in methanol (20 ml) by stirring. To this solution, KSCN (0.097 g, 1 mmol) in methanol (10 ml) was added followed by cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) in methanol (20 ml) and refluxed the mixture for 4 hours. The compound 10 was obtained as brown precipitate. It was then washed with methanol followed by ether and then dried over \(\text{P}_4\text{O}_{10}\) in vacuo. Yield: 68.2\%. \(\lambda_m\) (DMF): \(25\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}\). \(\mu\) (B.M.): 4.76. Elemental Anal. Found (Calcd) %: C, 52.18 (52.05); H, 3.11 (2.83); N, 17.68 (17.85) for \([\text{Cu(Qn)}\text{SCN}]\).

### 5.2.3e. Synthesis of \([\text{Co(Qn)}\text{N}_3]\) (11)

HQn·1.5H₂O (0.303 g, 1 mmol) was dissolved in methanol (20 ml) by stirring. To this solution, NaN₃ (0.065 g, 1 mmol) in methanol (10 ml) and cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) in methanol (20 ml) were added and stirred the mixture for 2 hours. The brown precipitate of 11 was washed with methanol followed by ether and then dried over \(\text{P}_4\text{O}_{10}\) in vacuo. Yield: 58.4\%. \(\lambda_m\) (DMF): \(13\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}\). \(\mu\) (B.M.): 4.85. Elemental Anal. Found (Calcd) %: C, 51.01 (51.08); H, 3.04 (2.95); N, 26.41 (26.06) for \([\text{Co(Qn)}\text{N}_3]\).
Caution: Although not encountered in our experiments, azido complexes of metal ions with organic ligands are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

5.3. Results and discussion

The reaction of quinoline-2-carbaldehyde with hydrazide in 1:1 ratio in methanol gives the corresponding hydrazone. The complexes were prepared by the reaction of the ligand with the metal salts in methanol. Based on the elemental analyses, conductivity measurements and spectral investigations, the complexes were formulated.

Five cobalt(II) complexes of hydrazones were prepared and they are found to be brown in color. The molar conductivities of the complexes in DMF (10^{-3} M) solutions were measured at 298 K with a Systronic model 303 direct-reading conductivity bridge, which show that all the complexes are non-conducting in nature [10]. The magnetic moments of the complexes were calculated from the magnetic susceptibility measurements at room temperature. The effective magnetic moments for the complexes are found to be in the range 4.70-5.00 B.M., which are typical for a high spin cobalt(II) system [11].

5.3.1. Infrared spectra

The IR spectra of the hydrazones and their Co(II) complexes were recorded in the solid state as KBr discs. The bands of diagnostic importance are listed in Table 5.1.

The spectra of hydrazones exhibit a peak at 3193 and 3173 cm^{-1} for HQb·1.5H_{2}O and HQn·1.5H_{2}O, respectively and this band is assigned to the stretching frequency of the N–H group. Also, they exhibit a sharp band at \textit{ca.} 1655 cm^{-1}, which is attributable to the stretching mode of the C=O group. It is worthy mentioning that both of these bands are absent in the spectra of the complexes. This is due to the ability of hydrazones to exhibit keto-enol tautomerism. From the IR spectra of complexes, it is confirmed that the
hydrazones coordinate to the metal centre in the enolate form. In the complexes, a new band is observed at ca. 1330 cm\(^{-1}\) which is due to the \(\nu(C-O)\) band formed due to the enolization of the hydrazone moiety [12,13].

**Table 5.1.** IR spectral data of hydrazones and their Co(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(C=O)) cm(^{-1})</th>
<th>(\nu(NH)) cm(^{-1})</th>
<th>(\nu(C=N)) cm(^{-1})</th>
<th>(\nu(C=N)^a) cm(^{-1})</th>
<th>(\nu(C=O)) cm(^{-1})</th>
<th>(\nu(N-N)) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQb(\cdot)1.5H(_2)O</td>
<td>1655</td>
<td>3193</td>
<td>1593</td>
<td>----</td>
<td>1544</td>
<td>1580</td>
</tr>
<tr>
<td>[Co(Qb)(_2)] (7)</td>
<td>----</td>
<td>----</td>
<td>1544</td>
<td>1580</td>
<td>1330</td>
<td>1209</td>
</tr>
<tr>
<td>HQn(\cdot)1.5H(_2)O</td>
<td>1656</td>
<td>3173</td>
<td>1591</td>
<td>----</td>
<td>1546</td>
<td>1583</td>
</tr>
<tr>
<td>[Co(Qn)(_2)] (8)</td>
<td>----</td>
<td>----</td>
<td>1546</td>
<td>1583</td>
<td>1331</td>
<td>1201</td>
</tr>
<tr>
<td>[Co(Qn)Br](\cdot)H(_2)O (9)</td>
<td>----</td>
<td>----</td>
<td>1554</td>
<td>1590</td>
<td>1339</td>
<td>1199</td>
</tr>
<tr>
<td>[Co(Qn)SCN] (10)</td>
<td>----</td>
<td>----</td>
<td>1551</td>
<td>1589</td>
<td>1337</td>
<td>1198</td>
</tr>
<tr>
<td>[Co(Qn)N(_3)] (11)</td>
<td>----</td>
<td>----</td>
<td>1552</td>
<td>1589</td>
<td>1330</td>
<td>1199</td>
</tr>
</tbody>
</table>

* Newly formed C=N bond.

The azomethine band, \(\nu(C=N)\), is observed at around 1590 cm\(^{-1}\) in the spectra of the hydrazones, but this band is shifted to lower wavenumber in the case of the complexes. This red shift indicates the participation of azomethine nitrogen in coordination. The \(\nu(N-N)\) band is observed at 1184 cm\(^{-1}\) for HQb\(\cdot\)1.5H\(_2\)O and 1195 cm\(^{-1}\) for HQn\(\cdot\)1.5H\(_2\)O. The increase in frequency of this band in the spectra of the complexes again confirms the coordination of hydrazone through azomethine nitrogen. The increase in \(\nu(N-N)\) value in the spectra of complexes is due to the increase in its double bond character, off-setting the loss of electron density via donation to the metal.

In the spectra of complexes, a new band is observed at ca. 1580 cm\(^{-1}\) which is due to the stretching frequency of the newly formed C=N group on enolization. The sharp medium intensity band at 985-954 cm\(^{-1}\) is assigned to the pyridine ring breathing mode of vibration [13,14]. The sharp medium bands within the 920-620
cm\(^{-1}\) range can be assigned to the various out-of-plane deformations of the aromatic C–H groups. IR spectrum of [Co(Qb)\(_2\)] (7) is shown in Fig. 5.1.

A thiocyanate ion is a typical ambidentate ligand involving two different terminal donor atoms; the sulfur atom and the nitrogen atom. The SCN group may coordinate to a metal through the nitrogen or sulfur or both sulfur and nitrogen. Thiocyanate coordination is known to occur in thiocyanate M-SCN, isothiocyanate M-NCS and binuclear M-SCN-M (bridging) forms. The mode of coordination can be determined from the vibrational modes. The CN stretching frequencies are generally lower in N–bonded complexes (near and below 2050 cm\(^{-1}\)) than in S-bonded complexes (near 2100 cm\(^{-1}\)) and the bridging [M-NCS-M'] complexes exhibits \(\nu\)(CN) well above 2100 cm\(^{-1}\). The \(\nu\)(CS) band for S-bonded complexes are found in the 720-690 cm\(^{-1}\) region. The N-bonded complexes exhibit a
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A single sharp $\delta$(NCS) band near 480 cm$^{-1}$, whereas the S-bonded complexes show several weak bands near 421 cm$^{-1}$ [15].

The complex [Co(Qn)SCN] (10) (Fig. 5.2) exhibits strong and sharp bands at 2091, 723 cm$^{-1}$ and several bands of low intensity near 421 cm$^{-1}$ which can be attributed to $\nu$(CN), $\nu$(CS) and $\delta$(NCS) respectively. These values are typical for S-bonded thiocyanato complexes.

![Fig. 5.2. IR spectrum of [Co(Qn)SCN] (10).](image)

The azido compound, [Co(Qn)N$_3$] (11), exhibited the antisymmetric $\nu$(NNN) vibration as a sharp band observed at 2058 cm$^{-1}$. Another band at 1319 cm$^{-1}$ is assigned to $\nu$(NNN) of the coordinated azido group [16]. The broad bands observed at 636 and 432 cm$^{-1}$ in the spectrum of the complex are assigned to $\delta$(NNN) and $\nu$(Co–N$_{azido}$) bands (Fig. 5.3).
5.3.2. Electronic spectra

The observed values of magnetic moments for cobalt(II) complexes are generally diagnostic of the coordination geometry about the metal ion. The low-spin square-planar cobalt(II) complexes may be 2.9 B.M., arising from one unpaired electron plus an apparently large orbital contribution [17].

Both tetrahedral and high-spin octahedral cobalt(II) complexes possess three unpaired electrons but may be distinguished by the magnitude of the deviation of $\mu_{\text{eff}}$ from the spin-only value. The magnetic moment of tetrahedral cobalt(II) complexes with an orbitally non-degenerate ground term is increased above the spin only value via contribution from higher orbitally degenerate terms and occurs in the range 4.2–4.7 B.M.; octahedral cobalt(II) complexes, however, maintain a large contribution due to $^4T_g$ ground term and exhibit $\mu_{\text{eff}}$ in the range 4.8–5.6 B.M. [18].

Fig. 5.3. IR spectrum of [Co(Qn)N₃] (11).
The magnetic moments of the complexes reported herein are in the range $4.70-5.00\text{ B.M.}$ showing the presence of three unpaired electrons with a high-spin octahedral configuration. These values are larger than the spin only value of high-spin cobalt(II) ($3.87\text{ B.M.; }\mu_{SO} = \left[4S(S+1)\right]^{1/2}; S = 3/2$). The values are close to the value expected when the spin and orbital angular momenta exist independently ($5.20\text{ B.M.; }\mu_{LS} = \left[L(L+1) + 4S(S+1)\right]^{1/2}; L = 3, S = 3/2$). This indicates a contribution of the orbital angular momentum [1,11].

The $d^7$ system, with the ground state term $^4F$, is split into three states in an octahedral crystal field. So, in an octahedral geometry, Co$^{2+}$ complexes usually show three bands corresponding to the spin allowed transitions $^4T_{2g}(F) \leftarrow ^4T_{1g}(F) (\nu_1)$, $^4A_{2g}(F) \leftarrow ^4T_{1g}(F) (\nu_2)$ and $^4T_{1g}(P) \leftarrow ^4T_{1g}(F) (\nu_3)$ transitions. Electronic spectra of all the cobalt(II) complexes in DMF showed three bands in the region 11510-12730, 14940-16230 and 17820-18970 cm$^{-1}$, which may be assigned to the $\nu_1$, $\nu_2$ and $\nu_3$ of octahedral Co(II) system [19-21].

The electronic absorption spectra of the hydrazones and their cobalt(II) complexes were recorded both in acetonitrile and DMF within the region 45000-11000 cm$^{-1}$.

The intense broad band observed for the complexes in the region 24530-26100 cm$^{-1}$ is assigned to the intramolecular charge transfer transitions involving the whole molecule [19-23]. Electronic spectra of the hydrazones and their metal complexes, within the region 45000-20000 cm$^{-1}$, are shown in Figs. 5.4 and 5.5. The $d-d$ bands observed for [Co(Qn)$_2$] (8) and [Co(Qb)SCN] (10) are shown in Fig. 5.6.

The bands in the region 32000-44000 cm$^{-1}$ are assigned to $\pi-\pi^*$ transitions within the ligand moiety. The spectra show bands in the range 27000-32000 cm$^{-1}$, assignable to $n-\pi^*$ transitions of the azomethine and amide functions. These intraligand bands are slightly shifted on complexation. Electronic spectral data of the hydrazones and their cobalt(II) complexes are given in Table 5.2.
Fig. 5.4. Electronic spectra of HQb·1.5H₂O and [Co(Qb)₂] (7), recorded in acetonitrile.

Fig. 5.5. Electronic spectra of HQn·1.5H₂O and its Co(II) complexes, recorded in acetonitrile.
Table 5.2. Electronic spectral data of the hydrazones and their cobalt(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance $\lambda_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQb·1.5H$_2$O</td>
<td>43790, 41640, 35860, 32580, 31690, 30430, 29130</td>
</tr>
<tr>
<td>[Co(Qb)$_2$] (7)</td>
<td>36530, 33360, 31050, 24760, 17890, 15650, 12730</td>
</tr>
<tr>
<td>HQn·1.5H$_2$O</td>
<td>43920, 41490, 35840, 32580, 31750, 30440, 29150</td>
</tr>
<tr>
<td>[Co(Qn)$_2$] (8)</td>
<td>37060, 32900, 24530, 17860, 15170, 12130</td>
</tr>
<tr>
<td>[Co(Qb)Br]·H$_2$O (9)</td>
<td>37430, 32640, 24740, 18840, 16170, 11630</td>
</tr>
<tr>
<td>[Co(Qb)SCN] (10)</td>
<td>37390, 32850, 24880, 17820, 16230, 11510</td>
</tr>
<tr>
<td>[Co(Qb)N$_3$] (11)</td>
<td>40560, 33800, 26030, 18970, 14940, 11790</td>
</tr>
</tbody>
</table>

5.3.3. Cyclic voltammetry

Cyclic voltammograms of the hydrazones and their Co(II) complexes were recorded on a CHI 608D electrochemical analyzer with a three electrode compartment consisting of a platinum disc working electrode, platinum wire counter electrode and Ag/Ag$^+$ reference electrode. The solutions of complexes in DMF have been used to study the electrochemical properties using TBAP (tetrabutylammonium phosphate) as the supporting electrolyte. The voltammogram is run between the potentials of $+2000$ and $-2000$ mV at a scan speed of 100 mV/s.

The electrochemical behavior of metal complexes with N, O - donor ligands has been studied in order to monitor spectral and structural changes accompanying electron transfer [24].
A comparative study of the cyclic voltammetric behavior of the hydrazones with their metal complexes could provide information on whether the redox reaction of the metal complexes is metal centered or ligand centered. The potentials of both the metal centered oxidation and reduction reflect the influence of the electronic nature of the ligand.

The cobalt(II)/cobalt(I) redox process is influenced by coordination number, stereochemistry and the hard/soft character of the ligand donor atoms [25,26]. The cyclic voltammetric data for the hydrazones and their Co(II) complexes are listed in Table 5.3. Representative cyclic voltammograms are shown in Figs. 5.7 and 5.8.

Patterson and Holm have shown that softer ligands tend to produce more positive $E^0$ values, while hard acids give rise to negative $E^0$ value. The observed values for the complexes of hydrazone indicate considerable “hard acid” character comparable to ligand like ethylene diamine, $(E^0, -350 \text{ mV})$ which is likely to be due to the pyridyl and azomethine nitrogen donors and solvent coordination [27].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pc}$ / mV ($I_{pc}$ / µA)</th>
<th>$E_{pa}$ / mV ($I_{pa}$ / µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HqB·1.5H$_2$O</td>
<td>-220 (0.91)</td>
<td>520 (3.48)</td>
</tr>
<tr>
<td>[Co(Qb)$_2$] (7)</td>
<td>-430 (0.41)</td>
<td>800 (0.84)</td>
</tr>
<tr>
<td></td>
<td>280 (0.22)</td>
<td>-70 (0.12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-380 (0.34)</td>
</tr>
<tr>
<td>HqN·1.5H$_2$O</td>
<td>-280 (1.83)</td>
<td>830 (13.8)</td>
</tr>
<tr>
<td>[Co(Qn)$_2$] (8)</td>
<td>-330 (0.55)</td>
<td>810 (0.66)</td>
</tr>
<tr>
<td></td>
<td>260 (0.43)</td>
<td>-100 (0.05)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-530 (0.26)</td>
</tr>
<tr>
<td>[Co(Qb)Br]·H$_2$O (9)</td>
<td>-280 (1.48)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 (1.31)</td>
<td></td>
</tr>
<tr>
<td>[Co(Qb)SCN] (10)</td>
<td>-790 (0.42)</td>
<td>490 (0.11)</td>
</tr>
<tr>
<td></td>
<td>240 (0.31)</td>
<td>-670 (0.65)</td>
</tr>
<tr>
<td></td>
<td>690 (0.21)</td>
<td></td>
</tr>
<tr>
<td>[Co(Qb)N$_3$] (11)</td>
<td>-300 (1.72)</td>
<td>940 (5.66)</td>
</tr>
<tr>
<td></td>
<td>380 (1.06)</td>
<td>670 (0.73)</td>
</tr>
<tr>
<td></td>
<td>970 (5.07)</td>
<td>-60 (1.23)</td>
</tr>
</tbody>
</table>
Absence of peaks for some complexes may result from kinetic complications during electron transfer, uncompensated solution resistance etc.

The drop of the voltammetric currents in the case of complexes compared to the corresponding ligand can be attributed to diffusion of the metal complex bound to the large ligand moiety. Additional peaks are observed for the complexes 9, 10 and 11, which may be due to the presence of coligands, which are also susceptible to redox processes.

![Fig. 5.7. Cyclic voltammograms of (a) HQb·1.5 H₂O and (b) [Co(Qb)₂] (7).](image1)

![Fig. 5.8. Cyclic voltammograms of (c) HQn·1.5 H₂O and (d) [Co(Qb)N₃] (11).](image2)
Chapter 5

References


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