5.1. Introduction

Cobalt is a ferromagnetic metal. Pure cobalt is not found in nature, but compounds of cobalt are common. Common oxidation states of cobalt include +2 and +3, although compounds with oxidation states ranging from -3 to +4 are also known. Co(II) complexes have a $d^7$ configuration and are very stable and difficult to oxidize. In contrast, in many cases during complexation, Co(II) is readily oxidized to Co(III) because the crystal field stabilization energy of Co(III) with a $d^6$ configuration is higher than Co(II) with a $d^7$ configuration. The synthesis and reactivity of cobalt complexes of Schiff base ligands have played an important role in the development of coordination chemistry [1].

Cobalt is an essential trace dietary mineral for all the animals, as the active centre of coenzymes called cobalamins, the most common example of which is vitamin B$_{12}$. Vitamin B$_{12}$ is an organometallic compound found in nature and is the only vitamin that contains a metal atom. The cobalt complexes of tetradeutate Schiff base ligands have been extensively used to
mimic cobalamin (B<sub>12</sub>) coenzymes [2,3], dioxygen carriers and oxygen activators [4,5]. Although less common than other metalloproteins, cobaltoproteins are known aside from B<sub>12</sub>. Cobaltocene is a structural analog to ferrocene where cobalt substitutes for iron. Cobaltocene is sensitive to oxidation much more than ferrocene. Cobalt carbonyl is a catalyst in carbylation reactions.

This chapter deals with the syntheses and characterization of Co(II/III) complexes of N<sup>4</sup>-phenylsemicarbazones including mixed ligand metal chelates incorporating heterocyclic bases and some pseudohalogens like azide and thiocyanate as coligands.

5.2. Experimental

5.2.1. Materials

Cobalt(II) acetate tetrahydrate (Nice Chemicals Pvt Ltd), 1,10-phenanthroline (Ranchem), 2,2′-bipyridine (Qualigens) and 4,4′-dimethyl 2,2′-bipyridine (Qualigens), potassium thiocyanate (Merck), 4-picoline (BDH) and sodium azide (Reidel-De Haen) were of Analar grade and were used as supplied and solvent used was methanol.

5.2.2. Syntheses of semicarbazones

Details regarding the syntheses of H<sub>2</sub>ASC·H<sub>2</sub>O and H<sub>2</sub>BSC are described in Chapter 2.

5.2.3. Syntheses of cobalt complexes of 2-hydroxy-4-methoxyacetophenone-N<sup>4</sup>-phenylsemicarbazone

5.2.3.1. [Co(HASC)]<sub>2</sub>·3H<sub>2</sub>O (15)

To a hot methanolic solution of H<sub>2</sub>ASC·H<sub>2</sub>O (0.317 g, 1 mmol), a solution of cobalt(II) acetate tetrahydrate (0.125 g, 0.5 mmol) in methanol was
Syntheses and spectral characterization of cobalt(II/III) complexes of N⁴-phenylsemicarbazones

added. The mixture was stirred for 4 h. and was kept overnight at room temperature. The brown colored compound formed was filtered, washed with methanol and ether. It was then dried over P₄O₁₀ in vacuo.

Elemental Anal. Found (Calcd.) (%): C: 54.26 (54.16); H: 5.90 (5.40); N: 11.39 (11.84)

5.2.3.2. [Co(ASC)phen(N₃)] (16)
A hot solution of H₂ASC·H₂O (0.317 g, 1 mmol) in methanol was mixed with methanolic solutions of 1 mmol each of cobalt(II) acetate tetrahydrate (0.249 g) and phenanthroline (0.198 g). The resulting mixture was stirred with sodium azide (0.065 g, 1 mmol) for 4 h. and was kept at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried in vacuo over P₄O₁₀.

Elemental Anal. Found (Calcd.) (%): C: 57.45 (57.24); H: 4.12 (4.12); N: 19.61 (19.07)

5.2.3.3. [Co(ASC)bipy(N₃)] (17)
Methanolic solutions of 1 mmol each of H₂ASC·H₂O (0.317 g), cobalt(II) acetate tetrahydrate (0.249 g) and 2,2'-bipyridine (0.156 g) were mixed and the resulting solution was stirred for 2 h. To this sodium azide (0.065 g, 1 mmol) was added and stirred for two more hours. The compound formed was filtered, washed with methanol followed by ether. It was then dried over P₄O₁₀ in vacuo.

Elemental Anal. Found (Calcd.) (%): C: 56.05 (56.22); H: 4.26 (4.36); N: 20.14 (20.17)
5.2.3.4. [Co(ASC)dmbipy(N\textsubscript{3})] (18)

This complex was prepared by stirring H\textsubscript{2}ASC-H\textsubscript{2}O (0.317 g, 1 mmol), cobalt(II) acetate tetrahydrate (0.249 g) and 4,4′-dimethyl 2,2′-bipyridine (0.184 g) in 1:1:1 ratio for 2 h. Then sodium azide (0.065 g) in methanolic medium was added in parts to the above mixture and continued stirring for another 2 h. and kept overnight at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 57.76 (57.73); H: 4.99 (4.67); N: 19.83 (19.24)

5.2.3.5. [Co(ASC)phen(NCS)]\cdot2H\textsubscript{2}O (19)

To a methanolic solution of H\textsubscript{2}ASC-H\textsubscript{2}O (0.317 g, 1 mmol), solutions of 1,10-phenanthroline (0.198 g, 1 mmol) and cobalt(II) acetate tetrahydrate (0.249 g, 1 mol) in methanol were added with constant stirring and the resulting solution was stirred for 4 h. Then a solution of potassium thiocyanate (0.097 g, 1 mmol) in methanol was added to the above mixture and continued stirring for another 1 h. and allowed to cool at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 54.73 (55.24); H: 3.91 (4.32); N: 13.34 (13.33); S: 4.98 (5.09)

5.2.3.6. [Co(ASC)pic(N\textsubscript{3})] (20)

An equimolar mixture of H\textsubscript{2}ASC-H\textsubscript{2}O (0.317 g, 1 mmol), 4-picoline (0.198 g, 1 mmol) and cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) is stirred for 3 h. To this solution sodium azide (0.065 g, 1 mmol) in methanolic medium was added in drops and continued stirring for one more hour. The
compound formed was filtered, washed with methanol and ether. It was then dried over $P_4O_{10}$ in $\textit{vacuo}$.

Elemental Anal. Found (Calcd.) (%): C: 54.14 (53.77); H: 4.18 (4.51); N: 20.41 (19.95)

5.2.4. Syntheses of Co(II/III) complexes of 2-hydroxy-4-methoxybenzophenone-$N^4$-phenylsemicarbazone

5.2.4.1. $[\text{Co(HBSC)}_2] \ (21)$

To a hot methanolic solution of $\text{H}_2\text{BSC}$ (0.361 g, 1 mmol), a methanolic solution of cobalt(II) acetate tetrahydrate (0.125 g, 0.5 mmol) was added. The mixture was stirred for 4 h. and kept at room temperature. The brown colored compound formed was filtered, washed with methanol and ether. It was then dried over $P_4O_{10}$ in $\textit{vacuo}$.

Elemental Anal. Found (Calcd.) (%): C: 64.17 (64.70); H: 4.49 (4.65); N: 11.44 (10.78)

5.2.4.2. $[\text{Co(BSC)phen(N3)}] \cdot 2\text{H}_2\text{O} \ (22)$

To a hot solution of 1 mmol of $\text{H}_2\text{BSC}$ (0.361 g) in methanol, methanolic solutions of 1 mmol each of cobalt(II) acetate tetrahydrate (0.249 g) and phenanthroline (0.198 g) were added with constant stirring. The resulting mixture was stirred further with sodium azide (0.065 g, 1 mmol) for 4 h. and was allowed to cool at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over $P_4O_{10}$ in $\textit{vacuo}$.

Elemental Anal. Found (Calcd.) (%): C: 58.84 (58.58); H: 4.03 (4.32); N: 16.46 (16.56)
5.2.4.3. [Co(BSC)bipy(N\textsubscript{3})] (23)

Methanolic solutions of H\textsubscript{2}BSC (0.361 g, 1 mmol), cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) and 2,2\textquotesingle-bipyridine (0.156 g, 1 mmol) in the ratio 1:1:1 were mixed and stirred for 2 h. The resulting solution was stirred for 2 h. more with sodium azide (0.065 g). The compound formed was filtered, washed with methanol followed by ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 59.96 (60.39); H: 4.70 (4.09); N: 18.21 (18.18)

5.2.4.4. [Co(BSC)dmbipy(N\textsubscript{3})] (24)

This complex was synthesized by stirring 1:1:1:1 ratio of H\textsubscript{2}BSC (0.361 g), cobalt(II) acetate tetrahydrate (0.249 g), 4,4\textquotesingle-dimethyl 2,2\textquotesingle-bipyridine (0.184 g) and sodium azide (0.065 g) in methanolic medium for 4 h. and keeping overnight at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 59.82 (59.82); H: 4.89 (4.72); N: 16.91 (17.2)

5.2.4.5. [Co(HBSC)\textsubscript{2}(NCS)] (25)

Solutions of H\textsubscript{2}BSC (0.361 g, 1 mmol), potassium thiocyanate (0.097 g, 1 mmol), and cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) in methanol were mixed and stirred for 4 h. The resulting solution was allowed to cool at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.
Syntheses and spectral characterization of cobalt(II/III) complexes of N\textsuperscript{4}-phenylsemicarbazones

Elemental Anal. Found (Calcd.) (%): C: 61.67 (61.65); H: 4.27 (4.33); N: 11.58 (11.70); S: 3.23 (3.83)

5.2.4.6. [Co(BSC)phen(OAc)]·1.5H\textsubscript{2}O (26)

To a hot methanolic solution of H\textsubscript{2}BSC (0.361 g, 1 mmol), methanolic solutions of 1 mmol each of cobalt(II) acetate tetrahydrate (0.249 g) and phenanthroline (0.198 g) were added. The resulting mixture was refluxed for 4 h. and was allowed to cool at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 61.52 (61.41); H: 4.90 (4.56); N: 10.27 (10.23)

5.2.4.7. [Co(BSC)dmbipy(OAc)]·3H\textsubscript{2}O (27)

Methanolic solutions of H\textsubscript{2}BSC (0.361 g, 1 mmol), cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) and 4,4'-dimethyl-2,2'-bipyridine (0.184 g, 1 mmol) were mixed in 1:1:1 ratio and refluxed for 4 h. and kept overnight at room temperature. The compound formed was filtered, washed with methanol and ether. It was then dried over P\textsubscript{4}O\textsubscript{10} in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 58.78 (58.74); H: 5.73 (5.35); N: 10.29 (9.79)

5.2.4.8. [Co(BSC)pic]·3H\textsubscript{2}O (28)

This complex was prepared by stirring equimolar mixture of H\textsubscript{2}BSC (0.361 g, 1 mmol), 4-picoline (0.186 g, 1 mmol) and cobalt(II) acetate tetrahydrate (0.249 g, 1 mmol) in methanolic medium for 4 h. The compound formed was...
filtered, washed with methanol and ether. It was then dried over P$_4$O$_{10}$ in vacuo.

Elemental Anal. Found (Calcd.) (%): C: 57.21 (57.35); H: 5.21 (5.35); N: 10.21 (9.91)

**Caution!** Azide complexes of metals with organic ligands are potentially explosive. So they should be synthesized and handled with due caution.

### 5.3. Results and discussion

Out of the fourteen complexes of Co(II/III) complexes presented here, compounds 15 and 21 have been synthesized by refluxing methanolic solutions of the semicarbazones and cobalt acetate in 2:1 ratio and in all other compounds it is in 1:1 ratio. Some mixed ligand metal chelates incorporating heterocyclic bases and some pseudohalogenes like azide and thiocyanate as coligands are included in this group. All the complexes are brown in color and are soluble in solvents like DMSO, DMF and acetonitrile. In compounds 15, 21 and 25 cobalt is in +2 oxidation state and found to be paramagnetic. All other complexes synthesized are diamagnetic confirming the oxidation of Co(II) to Co(III) during syntheses. In compounds 15, 21 and 25 semicarbazones are in the amido form and in all others they are in the iminol form. The synthesized compounds are characterized by the following physico-chemical methods.

#### 5.3.1. Elemental analyses

Elemental (C, H, N, S) analyses of all samples were tabulated in Sections 5.2.3 and 5.2.4. The observed C, H, N, S values showed that all the
complexes are analytically pure and in consistent with the stochiometry of the formulae suggested.

5.3.2. Molar conductivity

For all the complexes the molar conductance values observed in 10^{-3} M DMF solutions are in the range 2-18 ohm^{-1} cm^{2} mol^{-1}. These low values indicate their non-conductive nature so that the pseudohalogen, azide and thiocyanate are present inside the coordination sphere and get coordinated with the metal ion [6].

5.3.3. Magnetic susceptibility

The magnetic moments of the complexes were calculated from the magnetic susceptibility measurements at room temperature. All complexes except 15, 21 and 28 are found to be diamagnetic which confirms the oxidation of Co(II) to Co(III) during synthesis as has been reported previously with N^4-substituted semicarbazones, showing that it has no unpaired electrons with a spin paired octahedral configuration [7].

The magnetic moment values are of great significance in a structural context in the case of Co(II) complexes. Magnetic moments of tetrahedral, octahedral and square planar complexes differ significantly and therefore structural type can be easily identified using magnetic data. The low spin square planar Co(II) complexes may have magnetic moment 2.9 B.M., arising from one unpaired electron plus an apparently large orbital contribution [8].

Both tetrahedral and high-spin octahedral Co(II) complexes possesses 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
Co(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 4.4-4.8 B.M. [9,10]. In octahedral Co(II) complexes, the ground state is $^4T_{1g}$ is orbitally degenerate and this causes large orbital contribution to the magnetic moment and exhibit $\mu_{\text{eff}}$ in the range 4.8-5.6 B.M. [11]. The observed magnetic moments for the octahedral complexes [Co(HASC)$_2$]-3H$_2$O (15) and [Co(HBSC)$_2$] (21) are 4.80 B.M. and 4.73 B.M. respectively. These values are larger than the spin only value of high spin Co(II) (3.87 B.M.; $\mu_{\text{SO}} = [4S(S+1)]^{1/2}; S=3/2$), but are close to that expected when the spin and orbital angular momenta exist independently (5.20 B.M.; $\mu_{\text{LS}} = [ L(L+1) + 4S(S+1) ]^{1/2}; L=3, S=3/2$). This suggests a contribution of the orbital angular momentum [12,13]. The compound [Co(BSC)pic]-3H$_2$O (28) exhibited a magnetic moment of 2.25 B.M., which is much lower than that expected of four coordinate Co(II) tetrahedral complexes (4.4-4.8 B.M.). This suggests a possible tendency towards a square planar geometry in this complex [14].

5.3.4. Infrared spectra

IR spectra of the semicarbazones and the complexes have been recorded as KBr pellets. The characteristic IR bands of the complexes show significant changes when compared with those of the free ligands and these changes in the characteristic vibrational frequencies of the ligands upon complexation provided evidence for the mode of their binding to the metal ion.

The tentative assignments of the IR spectral bands of H$_2$ASC·H$_2$O and its cobalt(II/III) complexes useful for determining the ligand’s mode of coordination are listed in Table 5.1. The characteristic $\nu(\tilde{\nu}N$–H) and $\nu(C=O)$
observed at 3295 and 1692 cm\(^{-1}\) respectively for the free ligand, indicate the amido nature of the semicarbazone in the solid state [15]. In all the complexes synthesized except in 15, these bands disappeared, providing a strong evidence for the ligand coordination around cobalt(III) ion in its deprotonated enolate form [16]. Correspondingly a new band has appeared in the region 1528-1539 cm\(^{-1}\) which is due to the stretching frequency of the newly formed C=\(\text{N}\) group on enolization. But in compound 15 (Fig. 5.1), \(\nu(\text{N–H})\) and \(\nu(\text{C=O})\) bands do not disappear, but undergo some shift, indicating the amido form of the semicarbazone in the complex. The broad band around 3400 cm\(^{-1}\) observed in this complex indicates the presence of lattice water. The azomethine band observed at 1619 cm\(^{-1}\) in the spectrum of H\(_2\)ASC·H\(_2\)O is shifted to lower wavenumbers by 14-21 cm\(^{-1}\) in the case of complexes. This red shift indicates the participation of azomethine nitrogen in coordination. The \(\nu(\text{N–N})\) band is observed at 1020 cm\(^{-1}\) for H\(_2\)ASC·H\(_2\)O. The increase in frequency of this band in the case of complexes (1028-1099 cm\(^{-1}\)) again confirms the coordination of azomethine nitrogen. This increase in \(\nu(\text{N–N})\) value is due to the increase in double bond character, off-setting the loss of electron density via donation to the metal. Medium bands around 457-496 cm\(^{-1}\) corresponding to \(\nu(\text{Co–N})\) further support azomethine nitrogen coordination [17]. The spectra of the complexes do not exhibit the band at 3535 cm\(^{-1}\) due to the –OH stretching mode of phenolic group present in the semicarbazone, indicating deprotonation during coordination. Weak bands in the region 713-735 cm\(^{-1}\) indicate the presence of a Co–O bond resulting from coordination of the phenolic oxygen. Besides, the shifting of the band due to the Ar–O bond to lower frequencies indicates the weakening of the Ar–O bond due to coordination [18], the shift is being from 1270 cm\(^{-1}\) to 1235-1248 cm\(^{-1}\) region in the complexes.
Table 5.1. The important IR frequencies (cm\(^{-1}\)) of \(\text{H}_2\text{ASC} \cdot \text{H}_2\text{O}\) and Co(II/III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{C=O}))</th>
<th>(v(\text{C=N}))</th>
<th>(v(\text{C=N})^a)</th>
<th>(v(\text{N=N}))</th>
<th>(v(\text{C-O}))</th>
<th>(v(\text{Co-O}))</th>
<th>(v(\text{Co-N}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{ASC} \cdot \text{H}_2\text{O})</td>
<td>1692</td>
<td>1619</td>
<td>----</td>
<td>1020</td>
<td>1270</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>([\text{Co(HASC)}_2] \cdot 3\text{H}_2\text{O}) (15)</td>
<td>1661</td>
<td>1599</td>
<td>----</td>
<td>1028</td>
<td>1235</td>
<td>532</td>
<td>476</td>
</tr>
<tr>
<td>([\text{Co(ASC)}\text{phen(N}_3\text{)}]) (16)</td>
<td>----</td>
<td>1605</td>
<td>1532</td>
<td>1096</td>
<td>1248</td>
<td>534</td>
<td>496</td>
</tr>
<tr>
<td>([\text{Co(ASC)}\text{bipy(N}_3\text{)}]) (17)</td>
<td>----</td>
<td>1603</td>
<td>1528</td>
<td>1093</td>
<td>1239</td>
<td>536</td>
<td>490</td>
</tr>
<tr>
<td>([\text{Co(ASC)}\text{dmbipy(N}_3\text{)}]) (18)</td>
<td>----</td>
<td>1605</td>
<td>1532</td>
<td>1099</td>
<td>1245</td>
<td>535</td>
<td>494</td>
</tr>
<tr>
<td>([\text{Co(ASC)}\text{phen(NCS)}] \cdot 2\text{H}_2\text{O}) (19)</td>
<td>----</td>
<td>1598</td>
<td>1539</td>
<td>1090</td>
<td>1243</td>
<td>531</td>
<td>457</td>
</tr>
<tr>
<td>([\text{Co(ASC)}\text{pic(N}_3\text{)}]) (20)</td>
<td>----</td>
<td>1604</td>
<td>1530</td>
<td>1094</td>
<td>1242</td>
<td>529</td>
<td>492</td>
</tr>
</tbody>
</table>

\(^a\) Newly formed C=N
The most interesting part of the spectra of all the complexes 16-20 is the region above 2000 cm\(^{-1}\), where the absorptions due to pseudohalogens are observed.

The azido complexes 16, 17, 18 (Fig. 5.2-5.4) and 20 (Fig. 5.6) exhibited the antisymmetric \(\nu(\text{NNN})\) vibration as sharp bands at 2021, 2014, 2020 and 2016 respectively. The presence of terminal azido group in the coordination sphere is evident from these values. The slight lowering in values is assumed to be the result of its coordination with Co(III) ion [19]. The strong bands at 1349, 1374 and 1348 cm\(^{-1}\) are attributed to their \(\nu_s(\text{NNN})\) vibrations [20]. The \(\delta(\text{NNN})\) bands are observed at 588, 654 and 587 cm\(^{-1}\) for these complexes. The medium bands in the region 411-419 cm\(^{-1}\) are assigned to the \(\nu(\text{Co-Nazido})\) bands.

The pseudohalide thiocyanate ion is a typical ambidentate ligand involving two different terminal donor atoms, the sulfur and nitrogen atoms. It is a very interesting anion for it may coordinate to a metal through the sulfur (thio) or through nitrogen (isothio) or through both of these atoms (bridging). Infrared spectroscopy is very useful in elucidation of the type of bonding exists. The various criteria proposed for determining the mode of bonding have been discussed by Nakamoto [21]. 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 \(\nu(\text{CN})\) well above 2100 cm\(^{-1}\). The \(\nu(\text{CS})\) band for S-bonded complexes are found in the 720-690 cm\(^{-1}\) region. The N-bonded complexes exhibit a single sharp \(\delta(\text{NCS})\) near 480 cm\(^{-1}\), where as the S-bonded complexes show several weak bands near 421 cm\(^{-1}\). However these frequencies are very sensitive to the overall structure of
the complexes, the nature of the central metal, nature of other ligands in the complex and steric consideration [22]. Here in the thiocyanato complex [Co(ASC)phen(NCS)]·2H2O (19) (Fig. 5.5) in the 2000-2100 cm⁻¹, expected for the $\nu$(CN) stretching of the thiocyanato group absorption, the occurrence of two sharp and strong bands at 2126 and 2065 cm⁻¹, indicates the presence of two different coordinated thiocyanato groups. Such a higher wavenumber of 2126 cm⁻¹ is probably due to the presence of bridging thiocyanato group. But in the absence of crystal structure, it is impossible to draw definite conclusions. A broad band due to the presence of lattice water in the complex is seen at 3420 cm⁻¹, which is also evident from the thermogravimetric analysis. The IR data are in conformity with the previous reports dealing with complexes having similar ligand systems [7].

![IR spectrum of [Co(HASC)₂]·3H₂O (15).](image)

**Fig. 5.1.** IR spectrum of [Co(HASC)₂]·3H₂O (15).
Fig. 5.2. IR spectrum of [Co(ASC)phen(N3)] (16).

Fig. 5.3. IR spectrum of [Co(ASC)bipy(N3)] (17).
Fig. 5.4. IR spectrum of \([\text{Co(ASC)dmbipy(N}_3\text{)}]\) (18).

Fig. 5.5. IR spectrum of \([\text{Co(ASC)phen(NCS)}\cdot 2\text{H}_2\text{O}]\) (19).
Syntheses and spectral characterization of cobalt(II/III) complexes of $N^\circ$-phenylsemicarbazones

IR spectra of cobalt complexes of the semicarbazone $H_2BSC$ showed similar dramatic changes as that of $H_2ASC\cdot H_2O$ for its complexes. The spectral assignments of the complexes are made, compared with that of the ligand and are tabulated in Table 5.2. The IR spectrum of $H_2BSC$ shows a strong band at 1662 cm$^{-1}$ attributed to $\nu$(CO) and medium bands at 3145 and 3249 cm$^{-1}$ assigned to $\nu$(2NH) and $\nu$(4NH) respectively. This suggests the amido form of semicarbazones in the solid state [23]. For the complexes $[Co(HBSC)_2]$ (21) and $[Co(HBSC)_2(NCS)]$ (25) these are shifted to lower frequencies indicating the ligand’s existence in the amido form itself (Figs. 5.7 and 5.11) and coordination of the carbonyl oxygen atom to the central metal ion. But in all other complexes 22-24 and 26-28, the bands due to the stretching vibrations of $\nu$(2NH) and $\nu$(CO) are disappeared, giving evidence for the existence of semicarbazones in the iminol form. As a result of enolization we can observe the appearance of bands in the 1520-1555 cm$^{-1}$ range due to the stretching vibrations of newly formed C=N.
bond (Figs. 5.8- 5.10 and 5.12- 5.14). This is further confirmed by the new bands in the 493-519 cm\(^{-1}\) range due to the \(\nu(\text{Co–O})\) stretching vibrations. The IR spectral band observed at 1631 cm\(^{-1}\) is assigned to the \(\nu(\text{C=N})\) mode. The peak of this azomethine group was found in the lower frequency in the spectra of complexes which is an evidence of the bonding of azomethine nitrogen to the central cobalt ion [24]. Correspondingly the characteristic band of the semicarbazone at 1059 cm\(^{-1}\) due to \(\nu(\text{N–N})\) stretch undergoes a shift to higher wavenumbers upon complexation due to diminished repulsion between the lone pairs of adjacent nitrogen atoms. Further proof for the azomethine coordination is the presence of new band in the range 442-474 cm\(^{-1}\) which is assignable for \(\nu(\text{Co–N})\) for the complexes.

In the case of free phenyl semicarbazone the sharp band at 3316 cm\(^{-1}\) is due to the O–H stretching mode of phenolic oxygen. This band is found to be absent in all the complexes, indicating deprotonation of phenolic –OH and its coordination to the central metal ion [25]. Thus in complexes 22, 23, 24, 26, 27 and 28 semicarbazone acts as dideprotonated tridentate ligands, whereas in compounds 21 and 25 it acts as monodeprotonated tridentate one. In complexes 22, 26, 27 and 28 broad bands are seen \(ca.\) 3380 due to the presence of lattice water which is further confirmed from their thermogravimetric analyses.
### Table 5.2. The important IR frequencies (cm\(^{-1}\)) of H\(_2\)BSC and Co(II/III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{C}=\text{O}))</th>
<th>(\nu(\text{C}=\text{N}))</th>
<th>(\nu(\text{C}=\text{N})^a)</th>
<th>(\nu(\text{N}=\text{N}))</th>
<th>(\nu(\text{C}=\text{O}))</th>
<th>(\nu(\text{C}=\text{O}))</th>
<th>(\nu(\text{Co}=\text{O}))</th>
<th>(\nu(\text{Co}=\text{N}))</th>
</tr>
</thead>
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<tr>
<td>H(_2)BSC</td>
<td>1662</td>
<td>1631</td>
<td>----</td>
<td>1059</td>
<td>1294</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td><a href="21">Co(HBSC)(_2)</a></td>
<td>1647</td>
<td>1605</td>
<td>----</td>
<td>1064</td>
<td>1238</td>
<td>497</td>
<td>449</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)phen(N(_3))] \cdot 2\text{H}_2\text{O} (22)</td>
<td>----</td>
<td>1606</td>
<td>1521</td>
<td>1071</td>
<td>1280</td>
<td>508</td>
<td>443</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)bipy(N(_3))] (23)</td>
<td>----</td>
<td>1604</td>
<td>1555</td>
<td>1076</td>
<td>1259</td>
<td>524</td>
<td>444</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)dmbipy(N(_3))] (24)</td>
<td>----</td>
<td>1606</td>
<td>1532</td>
<td>1092</td>
<td>1250</td>
<td>497</td>
<td>458</td>
<td>----</td>
</tr>
<tr>
<td>[Co(HBSC)(_2)(NCS)] (25)</td>
<td>1650</td>
<td>1605</td>
<td>----</td>
<td>1112</td>
<td>1254</td>
<td>519</td>
<td>442</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)phen(OAc)] \cdot 1.5 \text{H}_2\text{O} (26)</td>
<td>----</td>
<td>1605</td>
<td>1520</td>
<td>1107</td>
<td>1240</td>
<td>515</td>
<td>474</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)dmbipy(OAc)] \cdot 3\text{H}_2\text{O} (27)</td>
<td>----</td>
<td>1599</td>
<td>1543</td>
<td>1100</td>
<td>1259</td>
<td>497</td>
<td>451</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)pic] \cdot 3\text{H}_2\text{O} (28)</td>
<td>----</td>
<td>1607</td>
<td>1529</td>
<td>1105</td>
<td>1256</td>
<td>493</td>
<td>463</td>
<td>----</td>
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</tbody>
</table>

\(^a\) Newly formed C=N
The most peculiar feature for IR spectra of azido and thiocyanato complexes are observed in the region 2000-2100 cm\(^{-1}\). In azido complexes 22, 23 and 24 the strong and sharp bands observed at 2021, 2033 and 2035 cm\(^{-1}\) are assigned to the antisymmetric stretching modes and the bands at 1353, 1358 and 1349 cm\(^{-1}\) are due to symmetric stretching modes of azido group. The deformation modes of the azido ligand are observed as weak bands at 699, 696 and 700 cm\(^{-1}\) respectively for these compounds [26]. The presence of a single strong band at 2065 cm\(^{-1}\) is due to \(\nu(CN)\) band of thiocyanato group. The \(\nu(CS)\) of the NCS ligand at 744 cm\(^{-1}\) indicates the coordination through nitrogen atom of the terminal NCS ligand [27], the bending vibration of the NCS group is observed near 484 cm\(^{-1}\). The intensity and band position indicate the coordination of the thiocyanate through the nitrogen atom of the NCS ligand.

The free acetate ion CH\(_3\)COO\(^{-}\) exhibits asymmetric and symmetric vibrations at 1578 and 1414 cm\(^{-1}\) respectively. It is reported that if it is covalently bonded to a metal as a unidentate ligand, the \(\nu_{as}\) and \(\nu_{s}\) are shifted to higher and lower frequencies respectively [21].

The very intense peak \textit{ca.} 1600 cm\(^{-1}\) present in acetato complexes 26 and 27 are possibly due to the combination of \(\nu(C=\text{N})\) and \(\nu_{as}(\text{CH}_{3}\text{COO})\) stretching frequencies. Also these complexes displayed bands at 1363 and 1349 cm\(^{-1}\) may be due to the \(\nu_{s}\) stretch of the acetate ion [28]. The difference between these two frequencies is of \(\sim 250\) cm\(^{-1}\), which is greater than that for uncoordinated acetate ion by \(\sim 143\) cm\(^{-1}\) and that for bidentate acetate ion by \(\sim 217\) cm\(^{-1}\). It is strongly supported that both acetate ions are coordinated to the metal ion in a unidentate fashion [21,29]. Coordination of bases are indicated by the
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presence of weak bands in the 410- 485 cm$^{-1}$ region. The heterocyclic breathing are observed in the 740-1450 cm$^{-1}$ region.

![Fig. 5.7. IR spectrum of $[\text{Co(HBSC)}_2]$ (21).](image)

![Fig. 5.8. IR spectrum of $[\text{Co(BSC)phen(N}_3\text{)}] \cdot 2\text{H}_2\text{O}$ (22).](image)
Fig. 5.9. IR spectrum of [Co(BSC)bipy(N3)] (23).

Fig. 5.10. IR spectrum of [Co(BSC)dmbipy(N3)] (24).
Syntheses and spectral characterization of cobalt(II/III) complexes of $N^\delta$-phenylsemicarbazones

Fig. 5.11. IR spectrum of [Co(HBSC)$_2$(NCS)] (25).

Fig. 5.12. IR spectrum of [Co(BSC)phen(OAc)]·1.5H$_2$O (26).
Fig. 5.13. IR spectrum of [Co(BSC)dmbipy(OAc)]·3H₂O (27).

Fig. 5.14. IR spectrum of [Co(BSC)pic]·3H₂O (28).
5.3.5. Electronic spectra

The UV spectra of the semicarbazone \( \text{H}_2\text{ASC} \) and its complexes were recorded in acetonitrile and the spectral data are presented in Table 5.3. The semicarbazone \( \text{H}_2\text{ASC} \) shows bands in the range 31780–41750 cm\(^{-1}\) due to intraligand transitions. Upon complexation these bands are slightly shifted to the 30780–44250 cm\(^{-1}\) region. For all the complexes a broad band having two peaks is observed in the 25450-27000 cm\(^{-1}\) region which is assigned to the intramolecular charge transfer transitions combined with \( \nu_2 ; (^1T_{2g} \leftarrow ^1A_{1g}) \) [30,31]. The broadness is explained as the combination of O → Co and N → Co charge transfer bands (Fig 5.15).

![Fig. 5.15. UV spectra of \( \text{H}_2\text{ASC} \) and its Co(II/III) complexes.](image)

The electronic spectra in the visible region were recorded in DMF for all the complexes. The electronic spectra of spin paired trivalent cobalt complexes of approximate \( O_h \) symmetry have the following assignments of \( d-d \)
bands: two spin allowed transitions at relatively low energies; $^{1}T_{1g} \leftrightarrow ^{1}A_{1g}$ and $^{1}T_{2g} \leftrightarrow ^{1}A_{1g}$. We have assigned for the complexes 16, 17 and 20, these two spin allowed transitions, to be the bands in the 19420-20540 cm$^{-1}$ region ($\nu_1$; $^{1}T_{1g} \leftrightarrow ^{1}A_{1g}$) (Figs. 5.17.2.-5.17.4) and 25450-25930 cm$^{-1}$ region ($\nu_2$; $^{1}T_{2g} \leftrightarrow ^{1}A_{1g}$), found along with the charge transfer transitions. The band assigned to $\nu_2$ is a combination band between it and charge transfer bands. There are two additional spin-forbidden transitions $^{3}T_{1g} \leftrightarrow ^{1}A_{1g}$ and $^{3}T_{2g} \leftrightarrow ^{1}A_{1g}$ at higher energies and these are usually complicated by the overlap of intraligand and charge transfer transitions. $^{3}T_{2g} \leftrightarrow ^{1}A_{1g}$ is the most difficult to assign because this weak spin forbidden band is always at the onset of other high energy intense bands [32,33].

Table 5.3. Electronic spectral assignments (cm$^{-1}$) of H$_2$ASC and Co(II/III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intraligand transitions</th>
<th>LMCT</th>
<th>d-d</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ASC</td>
<td>31780, 34540, 35600 (sh), 41750</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[Co(HASC)$_2$]·3H$_2$O (15)</td>
<td>31750, 36500, 40850 (sh), 42530</td>
<td>25930, 27000</td>
<td>18850</td>
</tr>
<tr>
<td>[Co(ASC)phen(N$_3$)] (16)</td>
<td>31100, 37080, 44140</td>
<td>25550, 26630</td>
<td>20360</td>
</tr>
<tr>
<td>[Co(ASC)bipy(N$_3$)] (17)</td>
<td>32400, 33470, 36970, 40310</td>
<td>25450, 26520</td>
<td>20540</td>
</tr>
<tr>
<td>[Co(ASC)dmbipy(N$_3$)] (18)</td>
<td>30780, 32720, 37130, 40370</td>
<td>25450, 26690</td>
<td>----</td>
</tr>
<tr>
<td>[Co(ASC)phen(NCS)]·2H$_2$O (19)</td>
<td>31320, 37000, 44250</td>
<td>25770,26790</td>
<td>----</td>
</tr>
<tr>
<td>[Co(ASC)pic(N$_3$)] (20)</td>
<td>31250, 36990, 42210</td>
<td>25530,26700</td>
<td>19420</td>
</tr>
</tbody>
</table>

From the magnetic susceptibility measurements it is assumed that the compounds [Co(HASC)$_2$]·3H$_2$O (15) and [Co(HBSC)$_2$] (21) have high spin octahedral configuration with cobalt in the +2 oxidation state. For a $d^7$ 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 $^4T_{2g}(F) \leftrightarrow ^4T_{1g}(F) (v_1), ^4A_{2g}(F) \leftrightarrow ^4T_{1g}(F) (v_2)$ and $^4T_{1g}(P) \leftrightarrow ^4T_{1g}(F) (v_3)$ transitions. The band observed at
18850, 18660 cm\(^{-1}\) respectively for compounds 15 and 21 (Figs. 5.17.1 & 5.17.5) can be assigned to \(^4T_{1g}(P) \leftarrow ^4T_{1g} (F) (\nu_3)\) transitions. The other two bands are not well defined [34].

Fig. 5.17.1. [Co(HASC)\(_2\)]

Fig. 5.17.2. [Co(ASC)phen(N\(_3\))]

Fig. 5.17.3. [Co(ASC)bipy(N\(_3\))]

Fig. 5.17.4. [Co(ASC)pic(N\(_3\))]

Fig. 5.17. Visible spectra of Co(II/III) complexes of H\(_2\)ASC.
For the low spin Co(III) complexes of H₂BSC (22-27) the bands observed in the 30170-43600 cm⁻¹ region are intraligand transitions of the metal free ligand, suffered some shift due to complexation. For the free ligand these bands are in the 31330-41680 cm⁻¹ region. The charge transfer transitions are occurred as a broad band in the range 25780-26740 cm⁻¹. For the compounds 23 and 24 additional peaks seen at 24920 and 25030 cm⁻¹ can be attributed to the $\nu_2 (^1T_{2g} \leftrightarrow ^1A_{1g})$. Since $^1T_{2g} \leftrightarrow ^1A_{1g}$ transition occurs at ca.25000 cm⁻¹ for octahedral geometry, the bands assigned to charge transfer can be considered as a combination of LMCT and $\nu_2$ (Fig. 5.16). The bands in the region 20820-21550 cm⁻¹ are assigned to ($\nu_1; ^1T_{1g} \leftrightarrow ^1A_{1g}$) transitions (Figs. 5.17.6.-5.17.10.). For compounds 18, 19 and 22 we couldn’t locate the $d$-$d$ bands.

**Fig. 5.16. UV spectra of H₂BSC and its Co(II/III) complexes.**
**Table 5.4. Electronic spectral assignments of H₂BSC and its Co(II/III) complexes (λ<sub>max</sub> cm⁻¹)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intraligand transitions</th>
<th>LMCT</th>
<th>d-d</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂BSC</td>
<td>31330, 33820, 35030, 41680</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[Co(HBSC)&lt;sub&gt;2&lt;/sub&gt;] (21)</td>
<td>31170, 33760, 41600</td>
<td>26740</td>
<td>18660</td>
</tr>
<tr>
<td>[Co(BSC)phen(N₃)]·2H₂O (22)</td>
<td>36980, 43620</td>
<td>25780</td>
<td>----</td>
</tr>
<tr>
<td>[Co(BSC)bipy(N₃)] (23)</td>
<td>30170, 32470, 33710, 40400</td>
<td>24920, 25960</td>
<td>20820</td>
</tr>
<tr>
<td>[Co(BSC)dmbipy(N₃)]·H₂O (24)</td>
<td>32520, 34030, 40070</td>
<td>25030, 25960</td>
<td>20880</td>
</tr>
<tr>
<td>[Co(HBSC)&lt;sub&gt;2&lt;/sub&gt;NCS] (25)</td>
<td>30540 (sh), 36760 (sh), 43600</td>
<td>25920</td>
<td>21000</td>
</tr>
<tr>
<td>[Co(BSC)phenOAc]·1.5H₂O (26)</td>
<td>30670, 32500, 38480</td>
<td>25990</td>
<td>21550</td>
</tr>
<tr>
<td>[Co(BSC)dmbipy(OAc)]·3H₂O (27)</td>
<td>30580 (sh), 33700 (sh), 37230</td>
<td>25990</td>
<td>20900</td>
</tr>
<tr>
<td>[Co(BSC)pic]·3H₂O (28)</td>
<td>30420 (sh), 37680, 43340</td>
<td>26150</td>
<td>20330, 16000 (w)</td>
</tr>
</tbody>
</table>

sh=shoulder  w=weak

The compound 28 is probably square planar as evidenced from its μ<sub>eff</sub> (2.25 B.M) value. The band observed at ca. 20330 cm⁻¹ may be assigned to <sup>2</sup><sub>A₁g</sub> ←<sup>2</sup><sub>B₂g</sub> transition. The band due to <sup>2</sup><sub>E₉</sub> ←<sup>2</sup><sub>B₂g</sub> transition is not well resolved (Fig. 5.17.11.) [35].
Chapter 5

Fig. 5.17.5. [Co(HBSC)_2]

Fig. 5.17.6. [Co(BSC)bipy(N_3)]

Fig. 5.17.7. [Co(BSC)dmbipy(N_3)]

Fig. 5.17.8. [Co(HBSC)_2(NCS)]
5.3.6. Thermogravimetric analyses

Thermogravimetric analyses of complexes 15, 26, 27 and 28 have been done and mass losses observed below 180 °C indicate the water molecules present in these complexes are outside the coordination sphere [36]. Thermal behavior
of azido complexes have not been studied since they are potentially explosive. The thermograms of complexes 27 and 28 are presented in Figs. 5.18 and 5.19.

Fig. 5.18. Thermogram of [Co(BSC)dmbipy(OAc)]·3H2O (27).

The thermogram of the complex 27 shows two well defined mass losses. The first mass loss of 7% below 90 °C (calcd. 7.5%) corresponds to the removal of three molecules of water. This suggests that water molecules are present outside the coordination sphere [35]. The second mass loss of 26.8% (calcd. 27.7%) ca. 250 °C is due to the decomposition of heterocyclic base, dimethylbipyridine. Weight losses due to the decomposition of ligand was found over 250 °C and degradation was found to be completed at 1000 °C.
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Fig. 5.19. Thermogram of \([\text{Co(BSC)}\text{pic}] \cdot 3\text{H}_2\text{O} \) (28).

Thermogravimetric analysis shows that complex 28 undergoes three step degradation in the temperature range of 74-175 °C having a total mass loss of 9.5% (calcd. 10%) corresponding to three molecules of water. The second weight loss of 17.2% (calcd. 18%) is due to the removal of the base, picoline and it occurs in 200-260 °C range and above 260 °C degradation of the ligand takes place.

In the light of the above physical methods discussed we have suggested octahedral geometry for all the complexes except compound 28 which is assumed to be square planar. The semicarbazones undergo double deprotonation to form dianions in all the complexes except 15 and 21 and act as tridentate ONO donors occupying the three positions of the octahedron. In compounds 15 and 21 the semicarbazones are in the amido form. In the case of complexes having the general formula \([\text{CoLBX}]\), (B-Base and X-anion) base acts as a bidentate ligand and occupies the fourth and fifth positions. The azido, thiocyanato or acetato group occupies the sixth position as unidentate ligands in the octahedral geometry. The proposed structures of some compounds are presented here.
\[\text{[Co(HBSC)\_2]} \ (21)\]

\[\text{[Co(ASC)bipy(N\_3)]} \ (17)\]

\[\text{[Co(BSC)pic\_3\_H\_2O} \ (28)\]
References


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