

## **Synthesis and spectral studies of Co(III) complexes of salicylaldehyde N(4)-ring incorporated thiosemicarbazones: crystal structure of a sulfenato complex**

### **5.1. Introduction**

Cobalt compounds have been used for centuries to impart a rich blue color to glass, glazes, and ceramics. It is a hard, lustrous, silver-gray metal and is ferromagnetic. Cobalt-60, an artificial isotope, is an important  $\gamma$  ray source, and is extensively used as a tracer and a radiotherapeutic agent. Single compact sources of  $^{60}\text{Co}$  are readily available. Cobalt salts in small amounts are essential to many life forms, including humans. It is at the core of a vitamin called vitamin-B<sub>12</sub>. Cobalt was announced to be an element by Georg Brandt about 1739 (or possibly 1735). He had been trying to demonstrate that the blue color of glass was because of a new element, cobalt, rather than bismuth, an element often found in the same locations as cobalt.

Cobalt(III) complexes derived from symmetrical and unsymmetrical schiff bases have also attracted considerable attention in the past for their relevance as biologically active compounds [1, 2]. Many model complexes of cobalt in both +2 and +3 oxidation states have been prepared and investigated, which emphasis on the reactivity of the metal ions in the trans methylation reaction and reversible absorption of molecular oxygen [3, 4].

Controlled oxidation of thiols which are coordinated to cobalt(III) leads to coordinated, S-bonded sulfenic acids. Since the resultant sulfenato complexes are

considerably more stable than the corresponding free sulfenic acid ligands, these complexes provide a means of investigating the chemistry of sulfenic acids. The nucleophilicity of coordinated sulfur seems to be very important in governing the chemistry and reactivity of sulfur-containing complexes [5, 6, 7, 8], just as the nucleophilicity of noncoordinated sulfur molecules is crucial to the chemistry and reactivity of these species.

This chapter deals with the synthesis, structural and spectral characterization of Co(III) complexes with different N(4)-ring incorporated thiosemicarbazone ligands. The structure of one of the compounds has been solved by single crystal X-ray crystallography.

## 5.2. Experimental

### 5.2.1. Materials

The syntheses of ligands are discussed in Chapter 2. The Co(II) acetate tetrahydrate (BDH), sodium azide (Merck), potassium thiocyanate and heterocyclic bases, *viz*, 2,2'-bipyridine (Central drug house) and 1,10-phenanthroline (Ranbaxy fine chemicals) were of reagent grade and were used as such. The reagents used were of Analar grade and used without further purification.

### 5.2.2. Synthesis of the complexes

**[CoL<sup>2</sup>phenNCS]·0.5H<sub>2</sub>O (21):** The H<sub>2</sub>L<sup>2</sup> (0.5 mmol, 0.138 g) was dissolved in methanol, to which was added 1,10-phenanthroline (0.5 mmol, 0.099 g) in the solid form. The mixture was slightly warmed to ensure complete dissolution of the ligands. To the above mixture was added methanolic solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol, 0.124 g) with stirring. When a deep brown solution resulted, solid potassium thiocyanate (0.75 mmol, 0.728 g) was added. Stirring was continued for

about an hour. The product formed was filtered, washed with ethanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

**[CoL<sup>4</sup>bipyN<sub>3</sub>]·CH<sub>3</sub>OH (22):** Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol, 0.124 g) dissolved in methanol was added to hot methanolic solution of H<sub>2</sub>L<sup>4</sup> (0.5 mmol, 0.124 g) and 2,2'-bipyridine (0.5 mmol, 0.078 g) and stirred for 15 minutes. Solid sodium azide (0.75 mmol, 0.048 g) was then added to the resulting solution followed by a further stirring of 2-3 h. The brown colored complex formed was filtered, washed with ethanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

**[CoL<sup>4</sup>bipyNCS]·H<sub>2</sub>O (23):** To a solution of H<sub>2</sub>L<sup>4</sup> (0.5 mmol, 0.124 g) in methanol, 2,2'-bipyridine (0.5 mmol, 0.078 g) in the solid form was added. The mixture was slightly warmed to ensure complete dissolution of the ligands. Methanolic solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol, 0.124 g) was then added to the above mixture with stirring. To the resulting solution, solid potassium thiocyanate (0.75 mmol, 0.728 g) was added and stirring was continued for about an hour. A brown colored product formed was filtered, washed with ethanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

**[Co(L<sup>4</sup>O)phenN<sub>3</sub>] (24):** To a solution of H<sub>2</sub>L<sup>4</sup> (0.5 mmol, 0.124 g) and 1,10-phenanthroline (0.5 mmol, 0.099 g) in methanol, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol, 0.124 g) dissolved in methanol was added with stirring. To the resulting brown colored solution, solid sodium azide was added and further stirred for 3-4 h. The product was then concentrated on a water bath and cooled at room temperature, filtered and kept overnight. Brown shining crystals separated out, which was filtered, washed with ethanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

**[CoL<sup>4</sup>phenNCS]·1.5H<sub>2</sub>O (25):** Solutions of H<sub>2</sub>L<sup>4</sup> (0.5 mmol, 0.124 g) and 1,10-phenanthroline (0.5 mmol, 0.099 g) in methanol were mixed and to this was added methanolic solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol, 0.124 g) with stirring. The

stirring was continued for about 20 minutes. When a deep brown solution resulted, solid potassium thiocyanate (0.75 mmol, 0.728 g) was added. Stirring was continued for about an hour. A brown colored complex formed was filtered, washed with ethanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

### 5.2.3. Physical measurements

Details regarding physical measurements are presented in Chapter 3.

### 5.2.4. X-ray crystallography

X-ray quality single crystals of the complex **24** were obtained from its solution in methanol by slow evaporation over a period of 10 days. Brown crystal of the compound **24** having approximate dimensions of 0.33 x 0.28 x 0.21 mm<sup>3</sup> was selected. The compound was diffracted by CrysAlis CCD, Oxford Diffraction Ltd, with graphite-monochromated Mo K $\alpha$  ( $\lambda=0.71073$  Å) radiation. The trial structure was solved using SHELXS-97 [9] and refinement was carried out by full-matrix least squares on  $F^2$  (SHELXL) [9]. The graphical tool used was DIAMOND (version 3.1d) [10], PLATON [11] and MERCURY. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed at calculated positions. The crystallographic data and structure refinement parameters for the complex **24** are given in Table 5.1.

**Table 5.1.** Crystal data and experimental parameters of compound **24**

Empirical formula	C <sub>24</sub> H <sub>22</sub> Co N <sub>8</sub> O <sub>2</sub> S
Formula weight	528.47
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions	a = 10.4512(12) Å b = 18.877(4) Å c = 11.9526(12) Å α = 90° β = 90.858(9)° γ = 90°
Volume	2357.8(6) Å <sup>3</sup>
Z	4
Density (calculated)	1.537 g/cm <sup>3</sup>
Absorption coefficient	0.857 mm <sup>-1</sup>
F(000)	1124
Crystal size	0.33 x 0.28 x 0.21 mm <sup>3</sup>
θ range for data collection	3.36 to 25.00°
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -14 ≤ l ≤ 14
Reflections collected	20583
Independent reflections	4100 [R(int) = 0.0555]
Refinement method	Full-matrix on F <sup>2</sup>
Data / restraints/parameters	4100 / 0 / 325
Goodness-of-fit on F <sup>2</sup>	1.070
Final R indices [I > 2σ(I)]	R1 = 0.0392, wR2 = 0.1110
R indices (all data)	R1 = 0.0483, wR2 = 0.1162
Largest diff. peak and hole	0.440 and -0.391 e Å <sup>-3</sup>

### 5.3. Results and discussion

The analytical data of the complexes are presented in Table 5.2. The Co(II) ion undergoes oxidation in the presence of methanol or chloroform unlike in ethanol [12]. All the complexes are brown in color. H<sub>2</sub>L<sup>2</sup> was found to give the products more easily, while compounds of H<sub>2</sub>L<sup>4</sup> gave crystalline products on keeping. The elemental analyses data are consistent with the general empirical formula [MLBX] for all the complexes except **24**, where X are coligands like N<sub>3</sub>

and NCS groups, and M is the cobalt metal atom, L is the doubly deprotonated thiosemicarbazone ligand and B are the heterocyclic bases *viz*, bipy and phen. Compounds **21–25** were prepared by a mathematical displacement of the acetate anion of the cobalt acetate by the addition of 0.75 mmol of the KSCN or NaN<sub>3</sub> to the reaction mixture of the principal ligand, cobalt acetate and heterocyclic base. In complex **24**, during the course of the synthetic reaction, the thiosemicarbazone may undergoes oxidation at the sulfur center whereby it is converted into sulfenate, and the transformed thiosemicarbazone is coordinated to cobalt as a dianionic tridentate ONS donor. The rate of oxidation of a coordinated thiol is relatively insensitive to the nature of the thiolate complex (thiolate chelate ring size or steric requirements, ancillary ligands, etc.). However, the rate of oxidation of a coordinated sulfur atom is very sensitive to the steric requirements of the sulfur atom, two coordinate sulfur being oxidized more than 10<sup>3</sup> times faster than three coordinate sulfur. Thus the sulfenato complex formed is stable. The oxidation at sulfur depends on the nucleophilicity of the sulfur atom and it is assumed that there is at least some  $\pi$ -back bonding character in the M–S bond. Since cobalt(III) has six t<sub>2g</sub> electrons, metal to sulfur  $\pi$ -bonding places more electron density on the sulfur atom coordinated to cobalt(III) and consequently causes this species to be the more effective nucleophile [13]. One molecule of 1,10-phenanthroline and one molecule of azide are also coordinated to cobalt(III). It is notable that azido coordination is unidentate and non-bridging where in most of the reported cases it is bridging [14].

**Caution!** Azide complexes of metals with organic ligands are potentially explosive and should be handled with care.

Table 5.2. Analytical data

Compound	Anal: Found (Calcd.) %		
	C	H	N
[CoL <sup>2</sup> phenNCS]·0.5H <sub>2</sub> O ( <b>21</b> )	55.99(55.76)	4.37(4.51)	14.58(14.45)
[CoL <sup>4</sup> bipyN <sub>3</sub> ]·CH <sub>3</sub> OH ( <b>22</b> )	51.67(51.49)	4.94(4.70)	20.91(20.89)
[CoL <sup>4</sup> bipyNCS]·H <sub>2</sub> O ( <b>23</b> )	51.17(51.30)	4.25(4.30)	15.81(15.61)
[Co(L <sup>4</sup> O)phenN <sub>3</sub> ] ( <b>24</b> )	53.50(52.94)	4.13(3.89)	20.85(20.58)
[CoL <sup>4</sup> phenNCS]·1.5H <sub>2</sub> O ( <b>25</b> )	52.24(52.53)	4.05(4.23)	15.57(14.98)

Magnetic susceptibility measurements at 293 K suggest that the compounds are diamagnetic indicating the oxidation of cobalt(II) to cobalt(III) and hence corresponds to  $d^6$  ion in a strong field.

### 5.3.1. Crystal structure of the compound [Co(L<sup>4</sup>O)phenN<sub>3</sub>]

The molecular structure of [Co(L<sup>4</sup>O)phenN<sub>3</sub>] (**24**) along with atom labeling scheme is shown in Figure 5.1 and selected bond lengths and bond angles are summarized in Table 5.3. Dark brown X-ray quality single crystals of the compound **24** were grown by slow evaporation of its solution in methanol. Earlier reports have shown that controlled oxidation of thiols which are coordinated to cobalt(III) gave sulfenato complexes [6, 15-17]. The salient structural characteristic of the compound is that the coordinated sulfur atom is bonded to one and only one, oxygen atom. This conclusively establishes that the isolated complex does indeed contain a coordinated sulfenic acid, and thus oxidation of the [CoL<sup>4</sup>phenN<sub>3</sub>] occurs without disruption of the primary coordination sphere of the cobalt center. The oxidized tridentate ligand provides one azomethine nitrogen, a sulfur from the sulfenato group and phenolic oxygen, while two nitrogens from the phenanthroline and terminal azide group complete the coordination geometry.

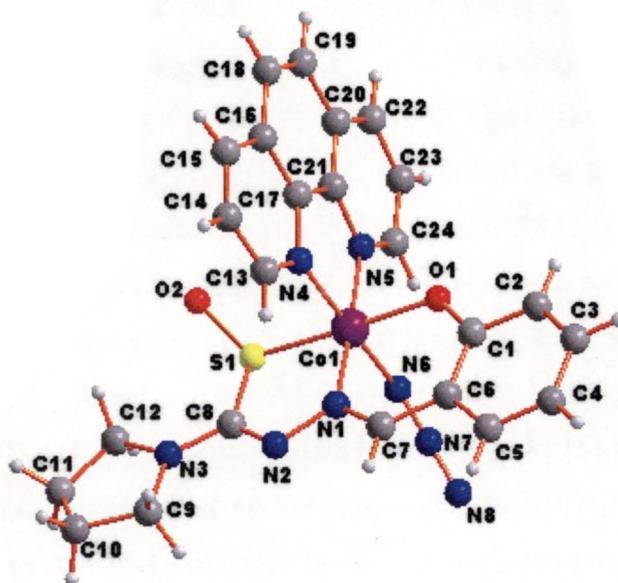


Figure 5.1. Structure and labeling diagram of the compound 24

The molecular structure of the compound was found to be distorted octahedral, fully expected from the known structures of the analogous thiolate [18], sulfenato [5] and sulfinato [14] complexes. The bond angles  $\text{N6-Co1-N4}$  [ $173.41(10)^\circ$ ] and  $\text{N5-Co1-N4}$  [ $83.56(10)^\circ$ ] define largest distortion of the geometry. Figure 5.1 shows that the  $\text{L}^4\text{O}$  ligand is functioning as an ONS donor ligand like the parent  $\text{H}_2\text{L}^4$  and it is coordinated in a meridional arrangement along with phen and terminal azido group. This coordination results in two five membered and one six membered rings in this complex. The bond angles indicate a distorted octahedral geometry in this complex. The azido group is coordinated to metal as a terminal ligand with a bond distance of  $1.942(3)$  Å ( $\text{Co1-N6}$ ). This value is comparable with that of bipyridine analog of thiosemicarbazone and phenanthroline analog of semicarbazone reported elsewhere [18, 19]. The sulfenato sulfur atom is three coordinated (the cobalt atom, the carbon atom of the chelate ring and the oxygen atom) in an approximately tetrahedral (counting the sulfur lone pair of electrons as occupying the fourth site) configuration.

The Co–S bond length in the compound [2.1952(8) Å] is significantly shorter than the analogous thiolate {[CoL<sup>4</sup>bipyN<sub>3</sub>]; 2.2126(7) Å [18] and [(en)<sub>2</sub>CoSCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>]<sup>2+</sup>; 2.226(2) Å [5]} and greater than the sulfinato [(en)<sub>2</sub>CoS(O)<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>]<sup>2+</sup>; 2.191(2) Å [5] cobalt complexes. The Co–S bond length is shorter compared to that for [(en)<sub>2</sub>CoS(O)CH<sub>2</sub>NH<sub>2</sub>]<sup>2+</sup>; 2.253(1) Å [5]. This means that the  $\pi$ -bonding in the cobalt(III) system increases the bond order of the cobalt-sulfur linkage. The S–O bond length in **24** [1.491(3) Å] is longer than the S–O bond lengths observed in sulfinato complex [(en)<sub>2</sub>CoS(O)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>]<sup>2+</sup>; 1.456(4)–1.476(4) Å [5] but shorter compared to sulfenato complex reported earlier [(en)<sub>2</sub>CoS(O)CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>]<sup>2+</sup> 1.552(3) Å [5]. The oxidation state three of cobalt is shown by its coordination bond lengths Co–S, Co–N<sub>(azomethine)</sub> and Co–O<sub>phenolic</sub> (Table 5.3) which are in the expected ranges of 2.201–2.230, 1.882–1.901, 1.866–1.9373 Å respectively. The coordination lengthens the oxidized thiosemicarbazone moiety's C8–S1 bond (1.811(3)°) and shortens C8–N2 bond (1.298(3) Å) compared to salicylaldehyde with a seven membered ring rather than five in the present case [salicylaldehyde 3-hexamethyleiminyl thiosemicarbazone C8–S1= 1.684(3) Å, C8–N2= 1.362(3) Å] [20]. Strong coordination of azomethine nitrogen is indicated by much shorter Co1–N1 (1.882(2) Å) bond length.

In the cobalt-thiol system discussed here, two oxidation reactions occur in the presence of air. The cobaltous ion is oxidized to the +3 state; the thiol is oxidized to sulfenate.

The azide anions which are nearly linear [N6–N7–N8=175.2(3)°] is coordinated with a N7–N6–Co1 angle of 122.2(2)°. The N–N bond lengths in the azide group are not equal. The longer N–N bonds involve the N atoms coordinated to the metal centre [N6–N7 = 1.204(3) Å, N7–N8 = 1.143(4) Å] and these values are comparable {1.199(7) and 1.163(7) Å respectively for

[CoLN<sub>3</sub>{o-(CH<sub>3</sub>C=O)C<sub>6</sub>H<sub>4</sub>O}] [21]; 1.196(3) and 1.151(3) Å respectively for [CoL<sup>4</sup>bipyN<sub>3</sub>] [18] and 1.214(6) and 1.147(7) Å for [CoLphenN<sub>3</sub>] [19]} to the corresponding values in other Co(III) azido complexes.

**Table 5.3.** Selected bond lengths (Å) and bond angles (°) for **24**

Bond lengths (Å)			
Co1–N1	1.882(2)	S1–C8	1.811(3)
Co1–O1	1.9373(19)	O1–C1	1.298(3)
Co1–N6	1.942(3)	N1–C7	1.292(3)
Co1–N5	1.947(2)	N1–N2	1.397(3)
Co1–N4	1.948(2)	N2–C8	1.298(3)
Co1–S1	2.1952(8)	N3–C8	1.331(3)
S1–O2	1.491(3)	N6–N7	1.204(3)
N7–N8	1.143(4)		
Bond angles (°)			
N1–Co1–N6	91.30(10)	N5–Co1–S1	90.62(7)
O1–Co1–N6	92.05(11)	N4–Co1–S1	89.14(8)
N1–Co1–N5	177.51(9)	C8–S1–Co1	93.54(9)
O1–Co–N5	86.02(9)	C1–O1–Co1	125.64(17)
N6–Co1–N5	90.81(10)	C7–N1–N2	113.9(2)
N1–Co1–N4	94.25(9)	C7–N1–Co1	124.55(18)
O1–Co1–N4	90.98(10)	N2–N1–Co1	121.51(16)
N6–Co1–N4	173.41(10)	C8–N2–N1	113.6(2)
N5–Co1–N4	83.56(10)	N7–N6–Co1	122.2(2)
N1–Co1–S1	88.15(7)	N8–N7–N6	175.2(3)
O1–Co1–S1	176.60(6)	N2–N1–Co1	121.51(16)
Co1–S1–O2	113.19(12)	C8–S1–O2	106.39(15)

The molecules of **24** are packed in an ‘offset’ manner within the unit cell (Figure 5.2). The assemblage of molecules in the respective manner within the unit cell is resulted by the diverse  $\pi$ – $\pi$  stacking, CH and hydrogen bonding (Figure 5.3) interactions depicted in Table 5.4.

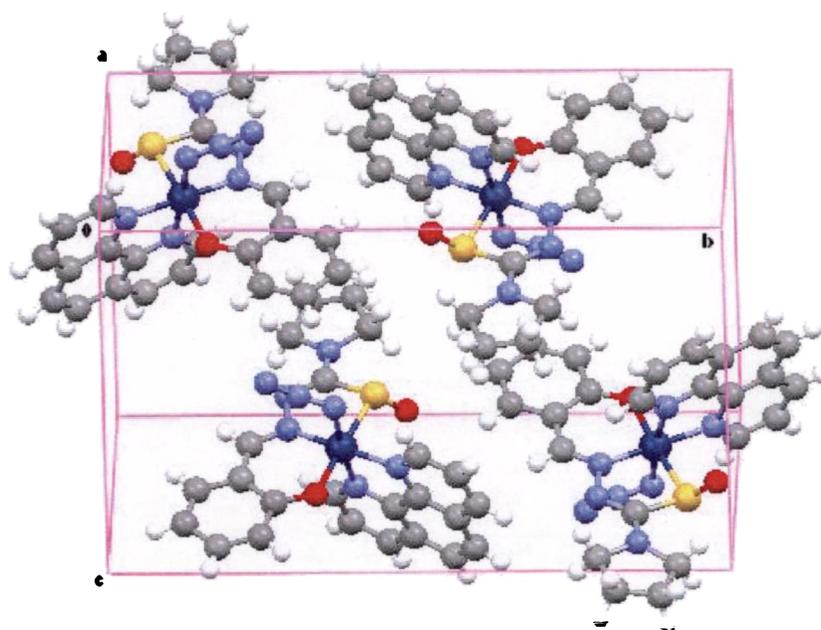


Figure 5.2. Unit cell packing diagram of the compound 24

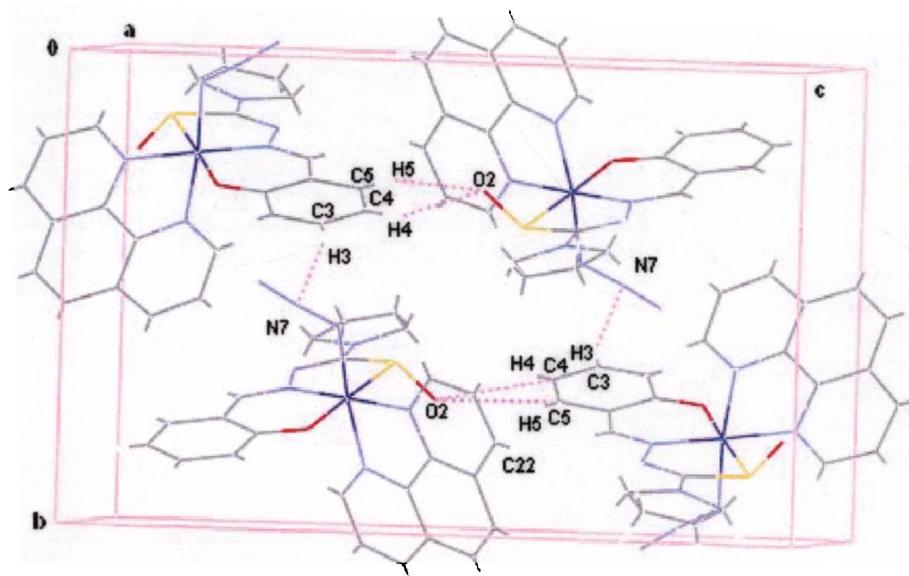


Figure 5.3. Hydrogen bonding interactions for the compound 24

**Table 5.4.** Interaction parameters of the compound 24 **$\pi$ - $\pi$  interactions**

Cg(I)-Res(1)···Cg(J)	Cg-Cg (Å)	$\alpha^\circ$	$\beta^\circ$
Cg(1) [1] -> Cg(5) <sup>a</sup>	3.8169	84.04	28.65
Cg(3) [1] -> Cg(7) <sup>b</sup>	3.9326	13.16	16.04
Cg(7) [1] -> Cg(3) <sup>c</sup>	3.9326	13.16	18.45

Equivalent position code: a= x, y, z; b= 1/2+x, 1/2-y, -1/2+z; c= -1/2+x, 1/2-y, -1/2+z  
 Cg(1)= Co1, S1, C8, N1, N2; Cg(3)= N3, C9, C10, C11, C12; Cg(5)= N4, C13, C14, C15, C16, C17; Cg(7)= C1, C2, C3, C4, C5, C6

**CH- $\pi$  interactions**

X-H(I)···Cg(J)	H...Cg (Å)	X-H...Cg (°)	X...Cg (Å)
Y-X (I)···Cg(J)			
C13-H13 [1] -> Cg(1) <sup>a</sup>	2.69	144	3.4857
N7-N8 [1] -> Cg(4) <sup>a</sup>	2.69	139	3.4420

Equivalent position code: a= x, y, -z  
 Cg(4)= Co1, O1, N1, C1, C6, C7

**H-bonding**

D-H...A	D...H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
C3-H3...N7 <sup>a</sup>	0.930	2.620(2)	3.476(4)	153.21(21)
C5-H5...O2 <sup>b</sup>	0.930	2.498(3)	3.148(4)	127.15(18)
C4-H4...O2 <sup>b</sup>	0.930	2.640(3)	3.208(4)	120.02(21)

D= donor, A= acceptor,  $\alpha$  = Dihedral angle between planes I and J (°)

$\beta$  = Angle Cg(I)->Cg(J) or Cg(I)->Me vector and normal to plane I (°)

Equivalent position code: a= x-1/2, -y+1/2, +z+1/2; b= -x+1/2+1, y+1/2, -z+1/2

### 5.3.2. IR spectra

Assignments of selected characteristic IR bands ( $4000\text{--}200\text{ cm}^{-1}$ ) for the free ligands ( $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^4$ ) and its cobalt(III) complexes, compiled in Table 5.5, indicate the bonding sites of the primary ligand molecule when complexed with the cobalt(III) ion. A medium band at  $3050\text{ cm}^{-1}$  ( $\text{H}_2\text{L}^2$ ) and  $3072\text{ cm}^{-1}$  ( $\text{H}_2\text{L}^4$ ) in the free ligands due to the  $\nu(^2\text{NH})$  vibration disappeared in the spectra of complexes providing strong evidence for ligand coordination around the Co(III) ion in its deprotonated form.

IR spectra of  $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^4$  show broad bands at  $3315$  and  $3232\text{ cm}^{-1}$ , respectively, due to intermolecular hydrogen bonded phenolic  $-\text{OH}$  groups. These bands disappeared in the spectra of the complexes. It is further corroborated with the downward shift of  $60\text{--}80\text{ cm}^{-1}$  for  $\nu(\text{CO})$  as well as an appearance of a band at  $510\text{--}565\text{ cm}^{-1}$  region due to a  $\nu(\text{Co}\text{--}\text{O})$  band in the spectra of complexes resulting from coordination of phenolic oxygen [18]. Absence of any bands in the  $2800\text{--}2550\text{ cm}^{-1}$  region points towards the lack of  $-\text{SH}$  stretching frequencies in the molecule. It reveals the presence of only the thione tautomer in the solid state. Compounds **21**, **22**, **23** and **25** show broad IR bands at  $\sim 3400\text{ cm}^{-1}$ , which are due to the  $\text{O}\text{--}\text{H}$  stretching modes of uncoordinated water molecules.

The infrared spectrum of compound **24** exhibits an intense band which is not present in the spectra of corresponding thiolate complexes. This band is therefore assigned as arising from the expected sulfur–oxygen stretch of the S–bonded sulfenato moiety. The frequency observed for this band is  $997\text{ cm}^{-1}$  is in agreement with the frequencies reported earlier

$\{[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{SCN})_2,$			$986\text{ cm}^{-1}$	[18];
$[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{NO}_3)_2,$	$993$	$\text{cm}^{-1}$		[18];
$[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{NO}_3)(\text{ClO}_4),$	$998$	$\text{cm}^{-1}$		[18];

$[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]I_2$ ,  $953\text{ cm}^{-1}$  [16]} for the S-bonded sulfenato moiety.

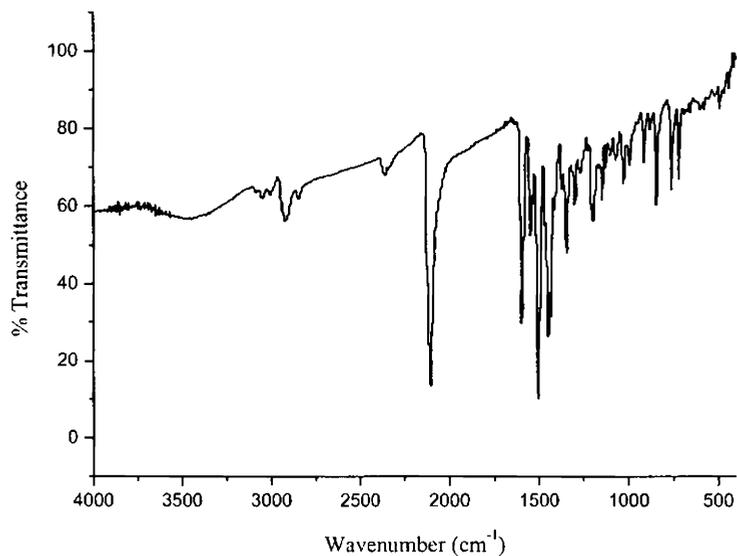
Negative shift of bands assigned to  $\nu(C=N_{azo})$  of the free ligands at  $\sim 1615\text{ cm}^{-1}$  to  $1592\text{--}1597\text{ cm}^{-1}$  in its complexes, is consistent with coordination of azomethine nitrogen to the central cobalt(III) ion; the bands at  $460\text{--}473\text{ cm}^{-1}$  in the complexes are then assigned to  $\nu(Co-N)$  [18, 22-26]. The  $\nu(N-N)$  of the thiosemicarbazone is found at  $\sim 1035\text{ cm}^{-1}$  region. The increase in frequency of this band in the spectra of complexes is due to the increase in bond strength, again confirmed the coordination *via* the azomethine nitrogen.

The presence of the azide group in the coordination sphere is evidenced from the very strong and sharp absorption peak at  $\sim 2020\text{ cm}^{-1}$ . The azido group is bound to cobalt as a terminal one is indicated by a strong absorption at  $2030\text{ cm}^{-1}$  characteristic of a terminal azido group [21, 26]. The slight lowering in values is assumed to the result of its coordination to the metal [27]. In the thiocyanato complexes, the very strong band observed at  $\sim 2090\text{ cm}^{-1}$  corresponds to  $\nu(C=N)$  of NCS [21]. Bands at  $\sim 714\text{ cm}^{-1}$  is assigned to  $\delta(NCS)$ . These facts indicate that thiocyanate group is N-coordinated to Co(III) [18], since the characteristic bands formed due to sulfur coordination are observed at  $\sim 2150\text{ cm}^{-1}$  [27].

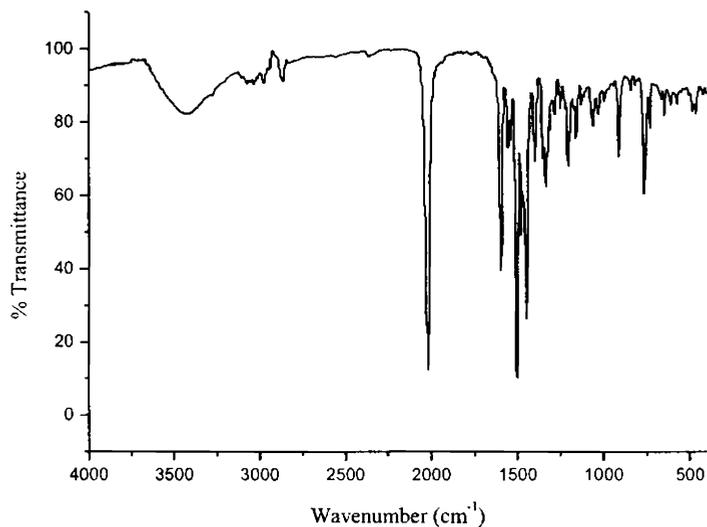
In the uncomplexed thiosemicarbazones, strong bands at  $1324, 861\text{ cm}^{-1}$  ( $H_2L^2$ ) and  $1338, 839\text{ cm}^{-1}$  ( $H_2L^4$ ) due to thioamide stretching and bending vibrations, respectively, are shifted to lower frequencies in the ranges  $1270\text{--}1290$  and  $750\text{--}800\text{ cm}^{-1}$ . This negative shift of the  $\nu(C=S)$  band in the complexes are indicated by the coordination *via* the thiolato sulfur atom. In all the Co(III) complexes, another strong band is found in the range  $1530\text{--}1550\text{ cm}^{-1}$ , which may be due to the newly formed  $\nu(C=^2N)$  bond as a result of enolization. Strong bands observed in the  $340\text{--}353\text{ cm}^{-1}$  region have been assigned to the

$\nu(\text{Co-S})$  band [23]. The IR spectra of the complexes display bands characteristics of coordinated heterocyclic bases [18].

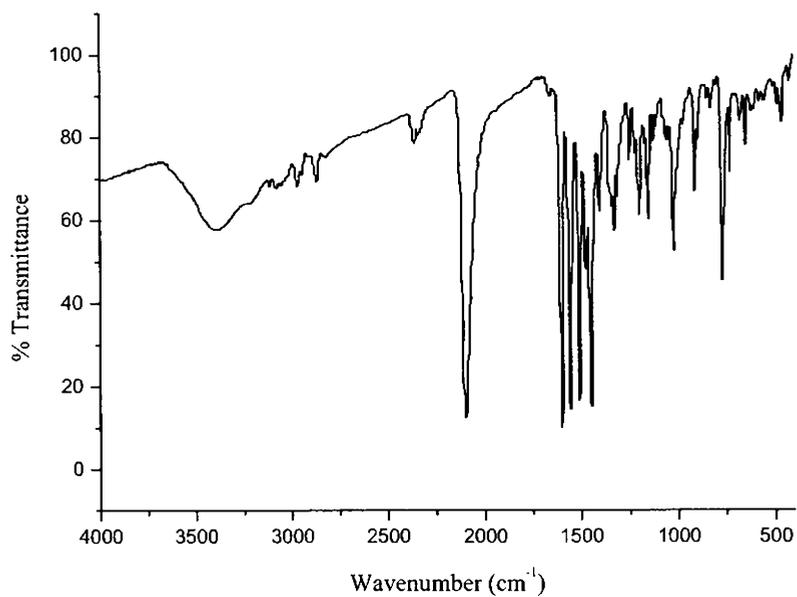
IR spectra of the complexes **21–24** are presented in Figures 5.4-5.7.



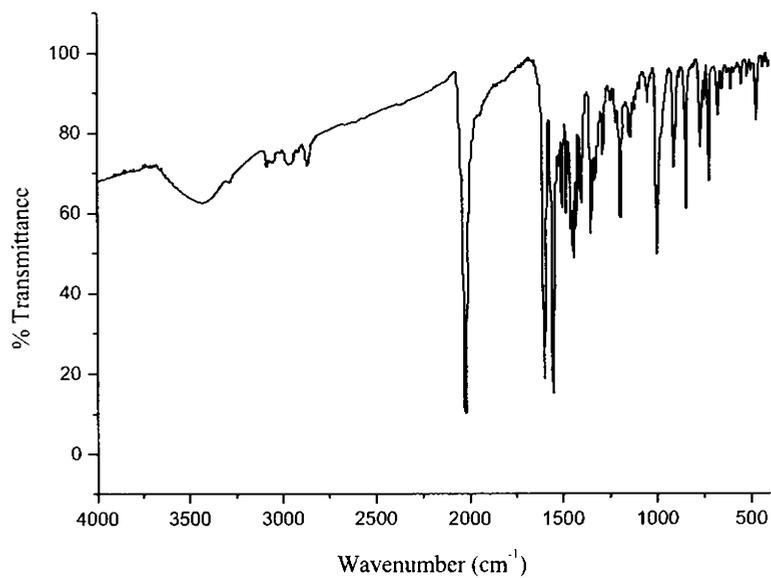
**Figure 5.4.** IR spectrum of the compound  $[\text{CoL}^2\text{phenNCS}] \cdot 0.5\text{H}_2\text{O}$  (**21**)



**Figure 5.5.** IR spectrum of the compound  $[\text{CoL}^4\text{bipyN}_3] \cdot \text{CH}_3\text{OH}$  (**22**)



**Figure 5.6.** IR spectrum of the compound  $[\text{CoL}^4\text{bipyNCS}] \cdot \text{H}_2\text{O}$  (23)



**Figure 5.7.** IR spectrum of the compound  $[\text{Co}(\text{L}^4\text{O})\text{phenN}_3]$  (24)

Table 5.5. Selected IR bands ( $\text{cm}^{-1}$ ) with tentative assignments of the ligands and its Co(III) complexes

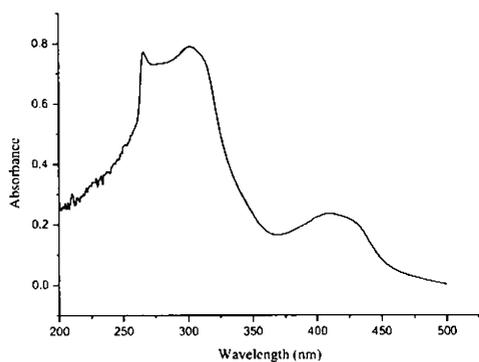
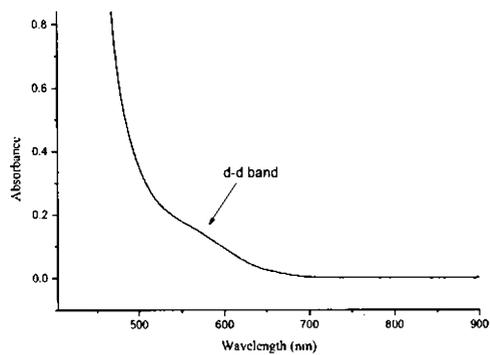
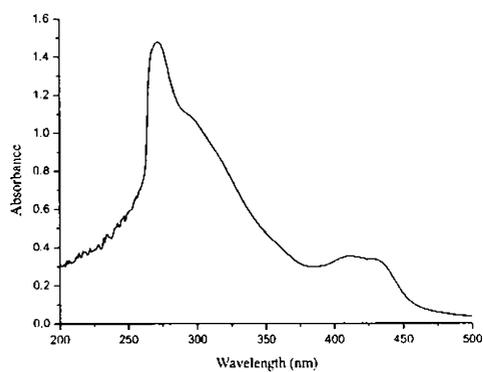
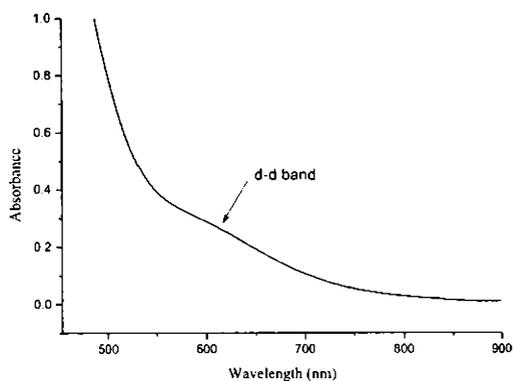
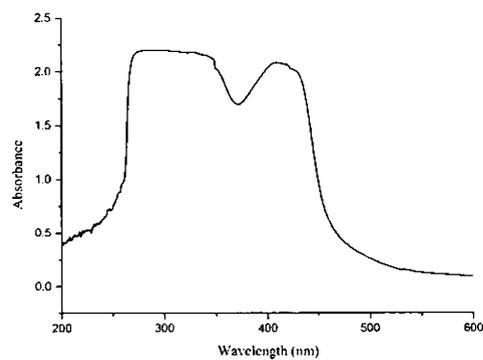
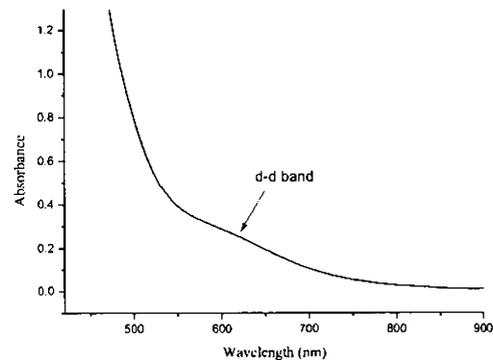
Compound	$\nu(\text{C}=\text{N}_{\text{azo}})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu^{\delta}[(\text{C}=\text{S})/(\text{C}-\text{S})]$	$\nu(\text{C}-\text{O})$	$\nu(\text{Co}-\text{N})$	$\nu(\text{Co}-\text{O})$	$\nu(\text{N}_3)/\text{NCS}$	Bands due to heterocyclic bases
$\text{H}_2\text{L}^2$	1612	----	1037	1324, 861	1271	----	----	----	----
$[\text{CoL}^2\text{-phenNCS}] \cdot 0.5\text{H}_2\text{O}$ (21)	1592	1548	1068	1278, 798	1189	479	566	2104, 710	1432, 831
$\text{H}_2\text{L}^4$	1622	----	1034	1338, 839	1288	----	----	----	----
$[\text{CoL}^4\text{-bipyN}_3]\text{-CH}_3\text{OH}$ (22)	1592	1548	1057	1283, 754	1200	462	567	2010	1443, 892
$[\text{CoL}^4\text{-bipyNCS}] \cdot \text{H}_2\text{O}$ (23)	1598	1549	1048	1270, 768	1199	454	543	2094, 723	1446, 892
$[\text{Co}(\text{L}^4\text{O})\text{phenN}_3]$ (24)	1597	1553	1053	1277, 760	1206	468	539	2022	1437, 831
$[\text{CoL}^4\text{-phenNCS}] \cdot 1.5\text{H}_2\text{O}$ (25)	1597	1542	1052	1287, 754	1206	473	572	2098, 714	1443, 842

### 5.3.3. Electronic spectra

The electronic spectral assignments of the ligands and their complexes are given in Table 5.6. Both the thiosemicarbazones and their cobalt(III) complexes show a ring  $\pi \rightarrow \pi^*$  band in the range 35500–36500  $\text{cm}^{-1}$  and an  $n \rightarrow \pi^*$  band in the range 29500–34000  $\text{cm}^{-1}$  (involving transitions within the thiosemicarbazone moiety mainly, C(7)=N(1), C(8)–S groups), is of reduced intensity in the spectra of the complexes [28]. In the case of complexes having ONS donor ligands, the shift of two ligand to metal charge transfer bands are found in the 24500–28000 and 23000–24000  $\text{cm}^{-1}$  ranges. The higher energy band is assigned to S→Cu(II) transitions.

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 energy,  ${}^1T_{1g} \leftarrow {}^1A_{1g}$ ,  ${}^1T_{2g} \leftarrow {}^1A_{1g}$ . There are additional spin-forbidden transitions  ${}^3T_{1g} \leftarrow {}^1A_{1g}$  and  ${}^3T_{2g} \leftarrow {}^1A_{1g}$  at higher energies and these are usually complicated by the overlap of intraligand and charge transfer transitions [18]. In all the complexes, only one broad band is observed for the  $d-d$  band.

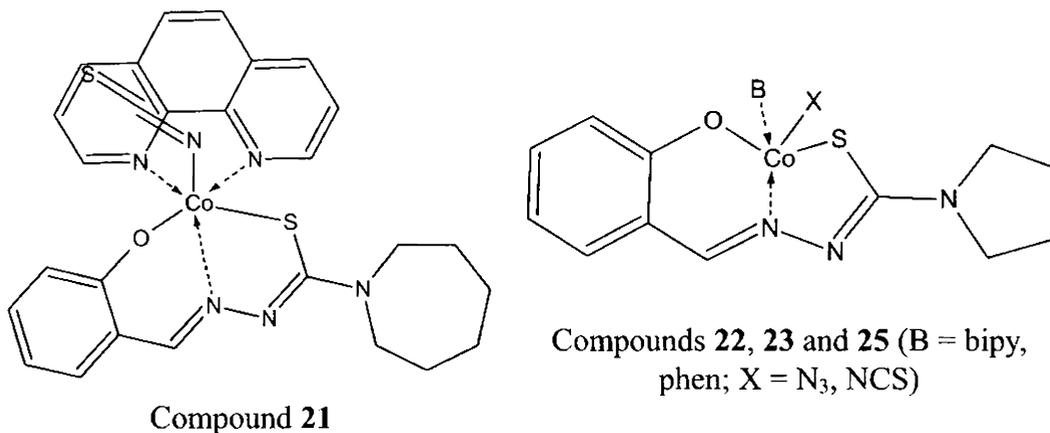
Representative spectra of the complexes **23**, **24** and **25** are presented in Figure 5.8.

 $[\text{CoL}^4\text{bipyNCS}]\cdot\text{H}_2\text{O}$  (23) $[\text{CoL}^4\text{bipyNCS}]\cdot\text{H}_2\text{O}$  (23) $[\text{Co}(\text{L}^4\text{O})\text{phenN}_3]$  (24) $[\text{Co}(\text{L}^4\text{O})\text{phenN}_3]$  (24) $[\text{CoL}^4\text{phenNCS}]\cdot 1.5\text{H}_2\text{O}$  (25) $[\text{CoL}^4\text{phenNCS}]\cdot 1.5\text{H}_2\text{O}$  (25)**Figure 5.8.** Electronic spectra of complexes 23, 24 and 25

**Table 5.6.** Electronic spectral assignments ( $\text{cm}^{-1}$ ) of the ligands and its Co(III) complexes

Compound	$\pi - \pi^*$	$n - \pi^*$	LMCT	d - d
$\text{H}_2\text{L}^2$	36110	29500	----	----
$[\text{CoL}^2\text{phenNCS}] \cdot 0.5\text{H}_2\text{O}$ ( <b>21</b> )	36010	30250	26190	17360
$\text{H}_2\text{L}^4$	36490	30210	----	----
$[\text{CoL}^4\text{bipyN}_3] \cdot \text{CH}_3\text{OH}$ ( <b>22</b> )	35620	30940	23510, 25880	16390
$[\text{CoL}^4\text{bipyNCS}] \cdot \text{H}_2\text{O}$ ( <b>23</b> )	36310	33220	23360, 24510	17250
$[\text{Co}(\text{L}^4\text{O})\text{phenN}_3]$ ( <b>24</b> )	36110	33780	23040, 24880	17510
$[\text{CoL}^4\text{phenNCS}] \cdot 1.5\text{H}_2\text{O}$ ( <b>25</b> )	36100	30480	23250, 24690	16180

Based on the elemental analyses and spectral studies following tentative structures were assigned for the complexes (Figure 5.9).

**Figure 5.9.** Tentative structures of the complexes

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