Chapter-III

3.1 Introduction:

Cobalt is a bluish-white solid metal. It is malleable and ductile and ferromagnetic hence it is used in magnets. It is found naturally only in chemically combined form. The free element, produced by reductive smelting, is a hard, lustrous and silver-gray metal.

Cobalt-based blue pigments have been used since ancient times for jewelry and paints and to impart a distinctive blue tint to glass, but the color was later thought by alchemists to be due to the known metal bismuth. Miners had long used the name kobold ore (German for goblin ore) for some of the blue-pigment producing minerals; they were named because they were poor in known metals and gave poisonous arsenic-containing fumes upon smelting. In 1735, such ores were found to be reducible to a new metal (the first discovered since ancient times) and this was ultimately named for the kobold.

Now a days, some cobalt is produced specifically from various metallic-lusted ores, for example cobaltite (CoAsS), but the main sources of the element is a by-product of copper and nickel mining. The copper belt in the Democratic Republic of the Congo and Zambia yields most of the cobalt metal mined worldwide.

Cobalt is used in the preparation of magnetic, wear-resistant and high-strength alloys. Cobalt silicate and Co(II) aluminate (CoAl₂O₄, cobalt blue) give a distinctive deep blue color to glass, smelt, ceramics, inks, paints and varnishes. Cobalt occurs naturally as stable isotope, cobalt-59. Cobalt-60 is a commercially important radioisotope, used as a radioactive tracer and in the production of gamma rays.

Cobalt is one of the rare elements occurring on the earth's
surface. It is only a metal present[1] and essential constituents of fertile soil[2]. Cobalt is the active center of coenzymes called cobalamin or vitamin B₁₂, and is an essential trace element for all animals [3, 4]. Cobalt complexes of corrinoid ligands are known as cobalamines found in many organisms [5], including man. The human body contains 5 mg of cobalamines [6]; its deficiency causes the disease pernicious anemia [7]. Methyl cobalamin is used as cofactor as it is involved in the synthesis of acetic acid from CO₂ [8, 9]. Cobalt complexes with nitrogen donor ligands have been used to mimic biological systems such as vitamin B₁₂. They are also of interest in the contest of dioxygen activation [10]. Among polymer supported metal, chelates, Schiff base metal complexes are important in biological processes like catalysis etc. [11]. Co(II) complexes are found to have pronounced carcinostatic properties against a wide range of transplanted neoplasia [12, 13]. The binuclear Cu/Co compounds act as a functional model for cytochrome c-oxidase. The natural enzyme contains a copper atom coordinated to histidine residues and heme-Fe₃ in place of the Co, it catalyzes the four electron reduction of O₂ to water that derives adenosine triphosphate (ATP) formation, whereas the copper free cobalt complexes form an O₂ adduct [14].

The naturally occurring Co(II) substituted Bleomycin (CoBLM) is used as antitumor antibiotic and cause cleavage of double stranded DNA [15, 16]. Polydentate Co(II) complexes are capable of intercalation into the DNA strands and are capable of DNA cleavage under photochemical conditions [17]. Coboglin (CoHb) and cobalt myoglobin (CoMb) are the Co(II) substituent’s globins that binds O₂ reversibly and provide a paramagnetic probe of the electronic properties of the Co(II) and Co-O₂ linkage within the protein. In view of the above discussion, the synthesis and characterization of transition metal complexes of cobalt(II) are highly desirable.
Co(II) complexes of the general composition \([\text{Co}L_2X_2]\) (where \(X=\text{Cl}^-, \text{CH}_3\text{COO}^-, \text{NO}_3^-\)) have been reported in literature. All the complexes are of the high-spin type. The semicarbazone ligands bearing aliphatic substituents of benzyl methyl ketone and methyl-
-hexy ketone have been found to react\([18-19]\) with cobalt halides in
alkaline media in their enolic forms to yield neutral bis chelates of
the type \(\text{ML}_2\) which were found to have, six coordinate polymeric
species.

Co(II) complexes with different semicarbazones and
thiosemicarbazone have been synthesized by Chandra et al.\([20]\) and
characterized by physico chemical methods. Tunde et al.\([21]\) prepared
and studied properties of Co(II) complex of 2-pyridine carboxyldimale
thiosemicarbazone with an appropriate anion such as \(\text{Cl}^-, \text{NO}_3^-\) and
\(\text{CH}_3\text{COO}^-\) and characterized using elemental analysis, magnetic
measurements, EPR molar conductance and infrared spectra studies.
It is confirmed by trimetric analysis using standard solution of
thiosulphate that cobalt is in a tripositives state in all complexes.
Caovazuec et al.\([22]\) studied thiosemicarbazones of acetophenone,
aceton, formic acid, pyruvic acid, o-aminobenzaldehyde and their
complexes with cobalt. They found antitumour cytotoxicity correlated
with electronic parameter better than with the structural parameter.
Kumar \([23]\) synthesized cobalt (II) complexes of composition \(\text{CoL}_2\) with
thiosemicarbazone of butyrophenone or prohiphenone and
characterized by elemental analysis, magnetic moments, IR electronic
and ESR spectral studies. Cobalt complex was paramagnetic and had
square planar geometry. Chattopadhyay\([24]\) studied chelating
behaviour of biologically active ligand, pyridine-2-carboxyldimale-
dehyde-1-phenylthiosemicarbazone and pyridine 2-carboxyldimale
thiosemicarbazone (LH) towards Co(II) ion. The ligands act as tridentate
N-N-S donors, giving bis chelate complexes of Co(II) \((\text{A})_2\text{X.nH}_2\text{O}\) \((\text{A}=\text{L}
\text{or L}', \text{X}=\text{Cl}^-\text{CH}_3\text{COO}^-, \text{NO}_3^-)\). Bekheit et al.\([25]\) synthesized cobalt

(38)
complex of 1-(2-naphthyl acetyl)-2-phenyl-3-thiosemicarbazide (H₃N
TSC), Co (HNTSC)-OAC and characterized on the basis of elemental
analysis, magnetic moment, molar conductance and spectral (IR, NMR
and visible) studies. El Asmy et al.[26] prepared and studied properties
of Co (SPTS)nH₂O [H₂SPTS=Succinyl-bis {1-phenylthiosemicarbazide}n=0, 2]. On the basis of spectral (IR, ¹H NMR) magnetic and
electronic studies a tetrahedral geometry has been assigned for the
complexes. Stoichiometry and stability constants of complexes have
been detected spectrophotometrically. Electrical properties of H₂SPTS
and its complexes with cobalt were investigated and their activation
energies calculated. Chatterjee et al.[27] reported schiff bases (HL),
derived by condensation of vanillin or 4-phenylthiosemicarbazide with
transition metals. All the compounds were characterized by IR diffuse
reflectance spectra, magnetic susceptibility measurements varying
current and thermal studies. On the basis of spectral studies an
octahedral geometry has been assigned for the complexes. Calculated
ligand field parameters were consistent with the proposed geometry.
Garg et al.[28] reported complexes with monoacetyl ferrocene
thiosemicarbazone (MAFTSC). Two bimetallic complexes of cobalt have
been prepared and characterized by elemental analysis, molar
conductance measurements, electronic, IR and ¹H NMR spectral
techniques. Conductance measurements in DMF indicated the
complex non electrolytic nature. Contrary to previous opinion
potentially bidentate thiosemicarbazone [NH₂(S)NNH.CRR₃] may also
act as unidentate ligands where R¹ and R³ is an aryl group. During
spectral characterization, differences between observed and possible
steric chemistry has been assigned to the complex.

Chandra et al.[29] synthesized CoL₂X₂, (L=H₂C (CH₃)₅ C(CH₃);
NNHC (E) NH₃ . (E=O, X=X=Cl, NO₃ , CH₃COO⁻) and characterized the
complexes by elemental analysis, molar conductance, magnetic
moments, IR, UV and ESR spectral studies. All the complexes have
magnetic moments corresponding to 3 unpaired electrons. The possible geometries of complexes were assigned by using electronic, IR and ESR data. Cristofoli et al. [30] suggest for a selective method for the flow injection spectrophotometric determination of Co(II) based on use of pyridoxal-4-phenyl thiosemicarbazone (PPT). The method suggests the fact that strong acidic medium used to prevent formation of most of the complexes of the reagents with other ions. Stapathy et al. [31] prepared [HDAMTH Co (H₂O)] X₄ (HDAMTH = diacetyl monoxime semicarbazone, X = Cl⁻, Br⁻, CH₃COO⁻, NO₃⁻ (ClO₄⁻). IR spectra of the complex suggests that ligand coordinates to the metal ion through its azomethine N, oxime O and S atoms. The H₂O molecules seem to be coordinated as evident from IR, thermal analysis of the complexes. Aggarwal et al. [32] prepared cobalt complexes of CoLₓX₄₋X₂O, where, L = 2-hydroxy-5-carboxy acetophenone semicarbazone. The complexes were characterized by IR spectra, magnetic and molar conductance measurements. Lu et al. [33] prepared (CoL) X nH₂O complex from the corresponding Co(II) salt (where HL = bicolinaldehyde semicarbazone N-oxide and X = ClO₄⁻, NO₃⁻, SCN⁻). All the complexes are diamagnetic. Balakrishna et al. [34] observed that the reaction of Co(II) salt with 3, 4-dimethoxybenzaldehyde thiosemicarbazone (LH) in a mixed alcoholic water or absolute alcohol yield Co (LH)ₙX₄₋X₂O (X = Cl⁻, Br⁻, I⁻, n = 1, 2).

Aggarwal et al. [35] prepared complex [Co(L)CH₂O]ⁿ⁺ where, (HL = gallactophene thiosemicarbazone, L = pyridine, 2-ethoxy, carbonyl aminopyridine -N-oxide) and characterized by TG/DTA and electronic spectral studies. These complexes were screened for antibacterial activities. Arvindakashan et al. [36] prepared CoL-O-5H₂O. (H₂L = 2 hydroxy-5-methylacetophenone thiosemicarbazone) and characterized by TG, DTG and DTA. Soliman et al. [37] prepared CoLCl (HL = o-hydroxy acetophenone semicarbazone) and characterized on the basis of spectrophotometric analysis, IR and magnetic moment data. Isolation
of solid complexes and physical measurements revealed the existence of mono and bis ligand complexes. Sonavane et al.[38] isolated Co(II) complexes in basic medium by coordination to phenyl pyruvate thiosemicarbazone (H₂PPVATSc) in its binegative thiolate forms. X-ray structure determination of the resulting meridional isomer was found to contain mutually cis sulphur, trans nitrogen and trans oxygen donor atoms, respectively. The two five membered rings formed by each ligand are puckered towards each other, resulting in a distortion from regular octahedron geometry around the Co(II) atom. The complex was found only a metal based one electron reversible reduction at-0.97V, while the parent ligands consisting of two irreversible reduction peaks at 0.75 and 1.05 V reduction of acycemethyl group.

Co(II) complexes [CoL (CH₃COO)] where [HL=1-salicyloyl-4-p-tolylthiosemicarbazide (STOTSc), 1-salicyloyl-4-p chlorophenylthiosemicarbazide (SPPTSc), 1-isonicotinoyl-4- chlorophenylthiosemicarbazide (INTOTSc), 4-benzoyl-4-p-tolylthiosemicarbazide (BTOTSc) and 1-benzoyl-4-p chlorophenyl-thiosemicarbazide (BCLTSc)] were prepared by Jirgi et al.[39]. The ratio of bonding and the possible structure of the complexes were discussed. Martinze et al.[40] have prepared 2-acetylpyridine N(4) and N(4) dicylohexyl thiosemicarbazone i.e. HAC₄DHeX and HAC₄DChcX, respectively and characterized by molar conductivities, magnetic susceptibility spectroscopic technique. For many of the complexes, loss of the N(2) H hydrogen occurs and the ligands coordinate to the metal centres as NNS mono anionic tridentate ligand e.g. [M (NNS)X]M=Co(II), Ni (II) NNS= Ac₄D HeX or Ac₄DC HeX and X=Cl or Br, [Co(NNS)₃] BF₄. Chattopadhyay et al.[41] have synthesized bis (pyridine-2-carbaldehyde thiosemicarbazone) and characterized by crystal structure analysis. Bindu et al.[42] have synthesized and studied the spectral studies of iron(III) and cobalt(II) complexes of N(4)-phenylthiosemicarbazone with heterocyclic bases.
These complexes were characterized by IR, electronic and ESR spectral studies. ESR spectra of the low spin Cobalt(II) complexes indicate the presence of unpaired electron in dz² orbital. Magnetic and spectroscopic data indicates a square planar structure for four coordinate cobalt (II) complexes. West et al.[43] have prepared Co(II) complexes with 2-aminoacetophenone thiosemi-carbazone and three N(4)-substituted thiosemicarbazones in EtOH solutions and characterized by physical and spectral methods. IR and electronic spectra of the thiosemicarbazones and their complexes, along with physical properties of the complexes were discussed. Labisbal et al.[44] have prepared the complexes of Co(II), Ni(II), Cu (II), Zn (II), Cd(II) and Pb (II) of isatin 3-hexamethyleneiminyldithiosemicarbazone [M (Ishexim)2] by electrochemical synthesis. The metal complexes were characterized using various techniques i.e. ¹H and ¹³C NMR, IR, UVVIS and mass spectra. Swearingen et al.[45] have prepared the complexes of cobalt (II), nickel (II), and copper (II) with two new bis(di-2-pyridyl ketone) dithiosemicarbazone in EtOH solution. These complexes were characterized by physical and spectral methods. The bis (di-2-pyridyl ketone) dithiosemicarbazones were prepared from dithiosemi-carbazides derived from piperazine and N, N'-dimethylenediamine. NMR, IR and electronic spectra of the dithiosemicarbazones and their complexes along with ESR spectra of the Cu(II) complexes were recorded. Singh et al.[46] prepared a new ligand, 1-(2-furanthiocarbo)-3-thiosemicarbazide (H₂ftsc) from thiosemicarbazide carboxy methyl-2-furandithioate and its complexes (Mn(ftsc)(H₂O)₂), [Pd(ftsc)].2H₂O, [M(Hftsc)(acac)₂] (M=Co³⁺ or Cr³⁺) which were characterized by elemental analysis, magnetic susceptibility, IR, electronic and N.M.R. spectral data. Hall et al.[47] have studied the cytotoxicity of copper and cobalt complexes of 2-furfural semicarbazone
and thiosemicarbazone. They also reported cytotoxicity against the growth of suspended leukemias and lymphomas as well as human lung. The copper and cobalt complexes functioned by multiple mechanisms to suppress synthetic steps in nucleic acid to reduce deoxynucleotide pools for incorporation into DNA. Wang et al.[48] have prepared and characterized metal complexes of new thiosemicarbazone derived from 3-acetylsalicylaldehyde (HL). The complexes have the general formula $\text{ML}_n \cdot n\text{H}_2\text{O}$ where $\text{M}^{2+} = \text{Co, Ni, Cu and Zn (n=0 and 2)}$. The ligand and its complexes have been studied for their possible antitumor activity against HL-60 human leukemia in vitro. Goran et al.[49] have synthesized three compounds $[\text{Co}^{2+}(\text{L})\text{(py)}]_2$, $[\text{Co}^{2+}(\text{py})\text{Cl}]_2$ EtOH and $[\text{Co}^{2+}(\text{L})\text{(py)}]_3$ (H$_2$L=salicylaldehyde S-methylthiosemicarbazone, py=pyridine). The crystal structure was determined by the single-crystal X-ray diffraction. The compounds were also characterized by elemental analysis, molar conductivity, magnetic susceptibility and electronic spectra. Jouad et al.[50] have synthesized the complexes (M(M$_5$FTSC)$_2X_2$), (M(M$_5$FTSC)X)$_3$ by the reaction of cobalt, nickel and copper salts with 5-methyl furfural thiosemicarbazone (M$_5$FTSC). The complexes were characterized by spectroscopic studies (infrared, NMR and electronic spectra). The crystal structure of the free ligand M$_5$FTSC and of the compound have been determined by X-ray diffraction methods. Swearingen et al.[51] have prepared the complexes of cobalt (II), nickel (II) and copper (II) of di-2-pyridalketone N(4)-methyl and N(4)-di methylthiosemicarbazone, and characterized by physical and spectral methods. Use of different ligand to metal chloride molar ratios in the preparation of the complexes has produce both mononuclear and polynuclear species for the three metal ions.
3.2 Present Work:

In the present work Co(II) complexes of the type [Co(L)₂X₂] were prepared where L is the newly synthesized ligands reported in Chapter 2nd i.e. acetoacetic ester semicarbazone (L₁), isopropyl ester semicarbazone (L₂), methyl ester of 4-hydroxy-6-methyl-2-oxo Pyran-2-carboxylic acid (L₃) and 4-formyl salicylate semicarbazone (L₄) and X is Cl, CH₃COO⁻ and NO₃⁻. All the newly synthesized complexes are characterized by elemental analysis, magnetic moment measurement, IR, electronic and EPR spectral studies.

3.3 Synthesis of Co(II) complexes:

All the complexes were prepared by the following method. A hot ethanolic solution of metal salt (0.05 mol) was mixed with hot ethanolic solution of the corresponding ligand (0.1 mol). The contents were refluxed for about two hours. On cooling, the coloured complex was separated out. The complex was filtered, washed with 50% ethanol and dried in a vacuum desicator over P₂O₅.

3.4 Characterization of the complexes:

3.4.1 Elemental Analysis:

The results are shown in Table 3.1.

3.4.2 IR Spectra of the Complexes:

As discussed earlier, the ligands display IR bands in the range 1570-1592 cm⁻¹ and 1672-1695 cm⁻¹ which are attributed to the ν(C= N) and ν(C=O) vibration. On complex formation the position of these bands is shifted to the lower side. This indicates that coordination takes places through the nitrogen atom of ν(C=N) and oxygen atom of
v(C=O) groups.

In addition, the ligand L³ display bands at 3150 cm⁻¹ due to phenolic oxygen and the position of this band is shifted towards ligand side on complexation.

IR spectra of the nitrato complexes (Fig. 3.1-3.3) show bands corresponding to the coordinated nitrate group. The coordinated nitrate group show absorption at 1405-1375 (v₁), 1225-1175 (v₂), 1005-990 (v₃) and 785 cm⁻¹ (v₄). The complexes under study show IR bands at 1380-1329 cm⁻¹ (v₁), 1245-1174 cm⁻¹ (v₂), 1036-976 cm⁻¹ (v₃) which indicates that the nitrate group attached in unidentate manner.

IR spectra of acetato complexes (Fig. 3.4-3.6) with ligands L¹, L², L⁴ show bands in the region 1490-1520 cm⁻¹ v(C=O) and 1270-1339 cm⁻¹ v(C=O). It indicate the unidentate nature. On the other hand acetato complex with ligand L³ shows bands correspondent to free acetate group.

IR spectra of chloro complexes (Fig. 3.7-3.10) with ligands L¹, L² and L⁴ show absorption bands in the region (295-315 cm⁻¹, v(M-Cl). It indicates that chloro group coordinates with metal ion. On the other hand in case of ligand L³ there is no band in the region 295-315 cm⁻¹ with corresponding metal chloride. It indicates that Cl⁻ is present outside the coordination sphere.

3.4.3 Magnetic moment

In an octahedral field the ground state is orbitally degenerated and would cause an orbital angular momentum contribution to the magnetic moments. The moment therefore would lie between the limit of \([4S (S+1)]^k = 3.88 \text{ B.M.}\) and \([4S (S+1) + L (L + 1)]^k = 5.2 \text{ B.M.}\).
depending upon the amount of (L) remaining associated with the ground state orbitally, triplet\(^2\). Experimental moments in literature usually lie in the range 4.7 to 5.2 B.M.\[33\]. For tetrahedral Co\(^{2+}\) complexes the ground state is orbitally singlet \(^5\)A\(_g\). Under the action of spin orbit coupling the higher lying \(\Upsilon_1\) and \(\Upsilon_2\) states are mixed in to the ground state so that the magnetic moment of such complexes is given by \(\mu_{\text{eff}} = 2 \left( 1 - \frac{4\Lambda}{10Dq} \right)[S(S+1)]^{\frac{3}{2}}\) B.M. All the complexes show magnetic moments in the range 4.75-4.95 B.M., indicating a spin quartet ground state which is obtained for four coordinate tetrahedral, five coordinate square pyramidal or trigonal bipyramidal and six coordinate octahedral. On the basis of electronic spectral studies the possible geometry of the complexes is evaluated. The results are shown in Table 3.2.

3.4.4 Electronic Spectra:

For the interpretation of the visible spectral data, it will be assumed that the weak crystal-field is a good approximation for the complexes containing metal ions with an oxidation of +2 i.e. Co(II). Based upon the fact that the gaseous metal ions has the ground state \(^4\)F and the higher state having the same spin multiplicity of \(^4\)F, the splitting of these in weak octahedral and tetrahedral crystal field occurs. Thus in octahedral complexes three spectral bands corresponding to the following transitions are expected.

\[\Upsilon_{1s} \ (4F) \rightarrow \ Upsilon_{2e} \ (4F) \ v_1\]

\[\Upsilon_{1s} \ (4F) \rightarrow \ Upsilon_{4a} \ (4F) \ v_2\]

\[\Upsilon_{1s} \ (4F) \rightarrow \ Upsilon_{1e} \ (4F) \ v_3\]

\[46\]
These bands are observed in the range of 9600-11000 ($v_1$), 14400-15600 ($v_2$) and 18800-19800 ($v_3$) cm$^{-1}$ respectively. The energy difference of $v_2-v_1$ is exactly equal to 10Dq. Unfortunately $v_2$ transition is usually very weak and rarely observed. These are Laporte forbidden transitions and the extinction coefficient lie between 1-20 Mmole$^{-1}$ cm$^{-1}$. However, the energy level in octahedral having different configuration can be represented as:

$$t_{2g}^{6}eg^{1} \quad ^{3}E - 18Dq + 7B + 4C - 60B^{2} / 10Dq$$

$$t_{2g}^{5}eg^{2} \quad ^{4}T_{1} 7.5B - 3Dq - 1/2 (225B^{2} + 100Dq^{2} + 180 DqB)$$

$$t_{2g}^{4}eg^{5} \quad ^{4}T_{2} + 2Dq$$

$$^{4}T_{1} 7.5B - 3Dq + 1/2 (225B^{2} + 100Dq^{2} + 180 DqB)$$

$$t_{2g}^{3}eg^{4} \quad ^{4}A_{2} + 12Dq$$

Tetrahedral Co(II) complexes also, show three bands corresponding to the following spin-allowed transitions[54].

$$^{4}A_{2} \rightarrow ^{4}T_{3} (F) v_{1}$$

$$^{4}A_{2} \rightarrow ^{4}T_{1} (F) v_{2}$$

$$^{4}A_{2} \rightarrow ^{4}T_{1} (F) v_{3}$$

The bands are generally found around 5500, 14800 and 19000 cm$^{-1}$ respectively. Thus in both the tetrahedral and octahedral fields, Co(II) will absorb around 14800 and 19000 cm$^{-1}$ regions and so these two geometries cannot be differentiated by these absorptions. However, in tetrahedral case, a third band is expected to appears in the near IR region (~5500 cm$^{-1}$) which might not be present in octahedral complexes. So the appearance of this band is the characteristic feature.
to distinguish between tetrahedral and octahedral complexes.

If the metal is five-coordinated then either the complex has square pyramidal or trigonal bipyramidal geometry. If the complex has trigonal bipyramidal geometry both high and low spin complexes are known. In high spin trigonal bipyramidal complex $^4\text{I}$ term splits, in $D_{3h}$ symmetry. The transition from ground state $^4\text{A}_2$ term generally occur both in the near infrared and in the visible region[55]. The possible transitions in increasing order of energy are as follows:

\begin{align*}
^4\text{A}_2 (F) & \rightarrow ^4\text{E}^* (F), \text{ near } 5870 \text{ cm}^{-1} \\
^4\text{A}_2 (F) & \rightarrow ^4\text{E}^* (F), \text{ near } 12500 \text{ cm}^{-1} \\
^4\text{A}_2 (F) & \rightarrow ^4\text{A}_2^* (P), \text{ near } 15000 - 16100 \text{ cm}^{-1} \\
^4\text{A}_2 (F) & \rightarrow ^4\text{E}^* (P), \text{ near } 21000 \text{ cm}^{-1}
\end{align*}

For low spin trigonal pyramidal the ground configuration $e^3e^3$ derives from $^2\text{G}$. The early theory predicted[56] that one fairly low energy transition probably in the near IR and a grouping of closely spaced high energy transitions in the visible region (to components of $^2\text{G}$, $^2\text{H}$ and $^2\text{F}$) were expected.

Similarly, high spin and low spin square pyramidal complexes are known. The ground state configuration of low spin complex in order of increasing energy, is generally taken to be $(dxy, (b_3), (b_2)^2$ $(dxz, dyz (e)^4$ $(dz^2 (a_1))^1$. Hence in these strong field complexes the two energy transitions should be observed i.e. at 10350 and 23300 cm$^{-1}$, which may be assigned to the following transitions $^2\text{A}_1 \rightarrow ^2\text{B}_1$ and $^4\text{A}_1 \rightarrow ^4\text{E}_1$ respectively.

Square planar complexes of cobalt(II) can be distinguished from
tetrahedral complexes both spectroscopically and magnetically. Low spin square planar complexes exhibit a narrow band or a complex multiplet in a region 8300-11000 cm\(^{-1}\) and a second stronger and broader band near 20000 cm\(^{-1}\). The narrow nature of the near infrared band suggests that the transition involves non-bonding rather than the antibonding orbitals. The order of energy level was deduced with considering the order as \(d_z^2 < d_{xy}, D_{xy} < d_{yz}, d_{x^2 - y^2}\). In strong field the ground state of low spin orbital in a square environment is probably \(^3A_{1g}\) with the configuration \(4b_{2g}^1 2a_{ig}^1\). The narrow band near 2000 cm\(^{-1}\) can be assigned as a transition from the lower field orbitals to the \(a_{ig}(d_z^2)\) orbital. The visible band is probably a transition from these orbitals to the empty \(b_{ig}(d_{x^2 - y^2})\) anti-bonding orbital[57].

The electronic spectra of the complexes (Table 3.2) under study display three well defined bands in the range 9707-10897 cm\(^{-1}\), 13350-14886 cm\(^{-1}\) and 18075-19950 cm\(^{-1}\) corresponding to \(^4T_{2g}\) \((^1F) \rightarrow \ ^4T_{2g}\) \((^4F)\) \(v_1\), \(^4T_{1g}\) \((^1F) \rightarrow \ ^4A_{2g}\) \((^1F)\) \(v_2\) and \(^4T_{1g}\) \((^1F) \rightarrow \ ^4A_{1g}\) \((^1F)\) \(v_3\) transitions characteristic of octahedral geometry[58-59] (Fig. 3.11-3.15).

### 3.4.5 EPR Spectra:

The \(^4F\) state of d\(^{1}\) system in an octahedral crystal field is split into three states. Since these states are connected by spin-orbit coupling, the spin lattice-relaxation times are short, making EPR measurements possible only at very low temperature. In an octahedral or near octahedral symmetry, the spin orbit coupling splits into the twelve low-lying spin states, leaving a doublet state lowest in energy. This Kramer's doublet is split by the magnetic field and the only transitions observed in EPR are between these two states, since they are the only ones populated at the low temperature required to observe
the EPR. Transitions in this Kramer’s doublet can be represented by spin Hamiltonian solved.

\[ \mu = \beta \left[ g_x S_x + g_y S_y + g_z S_z \right] + A_x S_x \pm A_y S_y + A_z S_z \]

For \( S = \frac{1}{2} \) and nuclear spin \( I = \frac{7}{2} \) all the results of \( d^7 \) in near octahedral fields have been interpreted with this Hamiltonian.

Low[60] has considered the case of \( d^7 \) in an octahedral field. The spin-orbit coupling split into the twelve spin states of the three orbital ground states in two states of energy (15/4) \( A \), four states of energy 3/2 and six states of energy (9/4). For \( d^7 \), is negative, so the doublet state is the ground state. The \( G \) and \( A \) parameters may be given by following expression:

\[ G = 1 + 5/3 \times (2.0023) = 4.34372 \]

\[ A = P \left[ -5/3K + 1 + 2/63 \right] \]

Inclusion of covalent bonding and configuration interaction with the ‘P states of \( d^7 \) tend to reduce both \( G \) and \( A \) in magnitude, whereas inclusion of second order terms in solving the \( T_{2g} \) state to increase \( G \) and \( A \). Low and Rubin[61] estimate the reduction in the orbital contribution to \( g \) from covalent effects to be 0.89 for Co (II) in both MgO and CaO.

Abragam and Pryce[62] have discussed the theory of \( d^7 \) in an octahedral field with small tetragonal and trigonal distortions. They found that the values of \( g \) for transition between the two states of Kramer’s doublet was very sensitive to distortions in crystal field and were able to account for observed values readily in terms of the theory.

In tetrahedral and cubic symmetry, the crystal field levels are
inverted, giving a single orbital state lowest. For d⁷ in an octahedral field the 4F state also has the single orbital state lowest, so we would expect that d⁷ configuration in a tetrahedral or cubic field to behave in a similar fashion and fit the spin Hamiltonian, solved for:

\[ \mu = g_e \beta \mu_B S_x^2 + g_e \beta \mu_B [S_x^2 H_x + S_y^2 H_y + D(S_x^2 - 5/4) + E(S_y^2 - S_z^2) + A S_z + B S_x S_y] \]

For most examples S=3/2, the tetrahedral symmetry is not distorted so that D=E=0 and no find structure is reported. The S=3/2 character of spin state is revealed in these cases by the fact that the equation \[ \mu_B S_x^2 (S_x^2 H_x + S_y^2 H_y + S_z^2 H_z - 1/5) + |S(S+1) - 1| S.H_z \], must be added to spin Hamiltonian to explain EPR results on d⁷ in tetrahedral and cubic field[63].

The EPR spectra of the complexes under study were recorded polycrystalline sample at Liquid nitrogen temperature, because the rapid spin lattice relaxation of Co(II) broadens the lines at higher temperature. g-Values [Fig. 3.16-3.18] are represented in Table 3.3. The large deviation of the g-values from the ion value (g=2.0023) is due to the large angular momentum contribution. These results correspond with the magnetic susceptibilities and electronic spectra as discussed earlier.

3.4.6 Ligand field parameters:

Various ligand field parameters viz. Dq, B, β and LFSE have been calculated and reported in Table 3.3. Dq values were evaluated by using Orgel diagram[64]. Nephlexautic parameters β has been evaluated by using the equation.

\[ \beta = B_{\text{complex}} / B_{\text{free ion}} \]
where $B_{\text{free ion}}$ for Co(II) is 1120 cm$^{-1}$. The values of $\beta$ lines in the range 0.52-0.61 indicating appreciable covalent character in the complexes.

3.5 Result and Discussion:

On the basis of the elemental analysis (Table 3.1) the complexes have the composition M$\{L_2\}$X$_2$ (where X=Cl, NO$_3^-$ and CH$_3$COO$^-$. Molar conductance (Table 3.1) of the complexes with ligand $L^1$, $L^2$, $L^3$ and $L^4$ indicates the following nature:

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Metal Salts</th>
<th>Nature of complex</th>
<th>Composition</th>
</tr>
</thead>
</table>
| $L^1$, $L^2$, $L^4$ | CoCl$_2$·6H$_2$O  
               | Co(CH$_3$COO)$_2$·4H$_2$O  
               | Non-electrolyte   | [Co( L)$_2$X$_2$] |
| $L^2$  | CoCl$_2$·6H$_2$O  
               | Co(CH$_3$COO)$_2$·4H$_2$O  
               | 1:2 electrolyte   | [Co( L)$_3$X$_2$] |

Ligands $L^1$, $L^2$ and $L^4$ act in a bidentate manner coordinating through N and O atom. On the other hand $L^3$ acts as tridentate coordinating through N and two O atoms.

3.6 Proposed structure of the complexes:

On the basis of elemental analysis, magnetic moment, molar conductance, IR, electronic and EPR spectral studies an octahedral geometry has been assigned for the complexes with ligand $L^1$, $L^2$, $L^3$ and $L^4$ as follows:
$X = \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}$

Cobalt(II) complexes of acetoacetate ester semicarbazone

$X = \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}$

Cobalt (II) complexes of isopropyl ester semicarbazone

(53)
Cobalt(II) complexes of Methyl ester of 4-hydroxy-6-methyl-2-oxo-Pyran-3-carboxylic acid semicarbazone

Cobalt(II) complexes of 4-Formyl methyl salicylate semicarbazone

(54)
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Complex</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>M. Point (°C)</th>
<th>Molar conductance</th>
<th>Elemental Analysis found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1.</td>
<td>[Co (L)₂ Cl₂] CoC₁₄H₂₈N₆O₈Cl₂</td>
<td>Pink</td>
<td>65</td>
<td>210</td>
<td>502.93</td>
<td>33.10 (33.40)</td>
</tr>
<tr>
<td>2.</td>
<td>[Co (L)₂ NO₃₂] CoC₁₄H₂₈N₆O₁₂</td>
<td>Pink</td>
<td>62</td>
<td>225</td>
<td>554.93</td>
<td>30.10 (30.27)</td>
</tr>
<tr>
<td>3.</td>
<td>[Co (L)₂ CH₃COO₂] CoC₁₈H₁₇N₆O₁₈</td>
<td>Light Pink</td>
<td>60</td>
<td>238</td>
<td>550.93</td>
<td>39.10 (39.20)</td>
</tr>
<tr>
<td>4.</td>
<td>[Co (L)₂ Cl₂] CoC₁₂H₂₆N₆O₈Cl₂</td>
<td>Pink</td>
<td>70</td>
<td>205</td>
<td>447.93</td>
<td>32.00 (32.14)</td>
</tr>
<tr>
<td>5.</td>
<td>[Co (L)₂ (NO₃)₂] CoC₁₂H₂₆N₆O₁₂</td>
<td>Light Pink</td>
<td>65</td>
<td>285</td>
<td>500.93</td>
<td>28.58 (28.74)</td>
</tr>
<tr>
<td>6.</td>
<td>[Co (L)₂ (CH₃COO)₂] CoC₁₆H₃₂N₆O₈</td>
<td>Light Pink</td>
<td>70</td>
<td>240</td>
<td>494.93</td>
<td>38.80 (38.79)</td>
</tr>
<tr>
<td>7.</td>
<td>[Co (L)₂] Cl₂ CoC₁₈H₂₆N₆O₁₂Cl₂</td>
<td>Pink</td>
<td>70</td>
<td>205</td>
<td>613.93</td>
<td>35.00 (35.18)</td>
</tr>
<tr>
<td>8.</td>
<td>[Co (L)₂ (NO₃)₃] CoC₁₈H₂₆N₆O₁₂</td>
<td>Light Pink</td>
<td>68</td>
<td>290</td>
<td>666.93</td>
<td>32.33 (32.38)</td>
</tr>
<tr>
<td>9.</td>
<td>[Co (L)₂] (CH₃COO)₂ CoH₂₂N₆O₁₈</td>
<td>Pink</td>
<td>65</td>
<td>210</td>
<td>660.93</td>
<td>39.54 (39.94)</td>
</tr>
<tr>
<td>10.</td>
<td>[Co (L)₃] Cl₂</td>
<td>Pink</td>
<td>60</td>
<td>199</td>
<td>603.93</td>
<td>39.63 (39.73)</td>
</tr>
<tr>
<td>11.</td>
<td>[Co (L)₃ (CH₃COO)₃] CoC₂₀H₂₂N₆O₉</td>
<td>Pink</td>
<td>60</td>
<td>206</td>
<td>656.93</td>
<td>36.45 (36.53)</td>
</tr>
<tr>
<td>12.</td>
<td>[Co (L)₃ (NO₃)₃] CoC₂₀H₂₂N₆O₁₄</td>
<td>Light Pink</td>
<td>63</td>
<td>222</td>
<td>650.93</td>
<td>44.20 (44.24)</td>
</tr>
</tbody>
</table>
Table 3.2: Magnetic moments and electronic spectral data of Co(II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu_{eff}$ BM</th>
<th>$v_1$ (cm$^{-1}$)</th>
<th>$v_2$ (cm$^{-1}$)</th>
<th>$v_3$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(L$^1$)$_2$Cl$_2$]</td>
<td>4.75</td>
<td>9750</td>
<td>13350</td>
<td>18400</td>
</tr>
<tr>
<td>[Co(L$^1$)$_2$(NO$_3$)$_2$]</td>
<td>4.92</td>
<td>10210</td>
<td>13387</td>
<td>18900</td>
</tr>
<tr>
<td>[Co(L$^1$)$_2$(CH$_3$COO)$_2$]</td>
<td>4.87</td>
<td>10223</td>
<td>14541</td>
<td>18885</td>
</tr>
<tr>
<td>[Co(L$^2$)$_2$Cl$_2$]</td>
<td>4.80</td>
<td>9918</td>
<td>14096</td>
<td>18925</td>
</tr>
<tr>
<td>[Co(L$^2$)$_2$(NO$_3$)$_2$]</td>
<td>4.95</td>
<td>9652</td>
<td>14055</td>
<td>19825</td>
</tr>
<tr>
<td>[Co(L$^2$)$_2$(CH$_3$COO)$_2$]</td>
<td>4.90</td>
<td>10197</td>
<td>14386</td>
<td>19885</td>
</tr>
<tr>
<td>[Co(L$^3$)][Cl$_2$]</td>
<td>4.92</td>
<td>10986</td>
<td>14015</td>
<td>18075</td>
</tr>
<tr>
<td>[Co(L$^3$)$_2$(NO$_3$)$_2$]</td>
<td>4.89</td>
<td>9881</td>
<td>14075</td>
<td>19950</td>
</tr>
<tr>
<td>[Co(L$^3$)$_2$(CH$_3$COO)$_2$]</td>
<td>4.80</td>
<td>9972</td>
<td>14019</td>
<td>19150</td>
</tr>
<tr>
<td>[Co(L$^4$)$_2$(Cl)$_2$]</td>
<td>4.95</td>
<td>9862</td>
<td>13915</td>
<td>18815</td>
</tr>
<tr>
<td>[Co(L$^4$)$_2$(NO$_3$)$_2$]</td>
<td>4.86</td>
<td>9905</td>
<td>13912</td>
<td>19900</td>
</tr>
<tr>
<td>[Co(L$^4$)$_2$(CH$_3$COO)$_2$]</td>
<td>4.87</td>
<td>9707</td>
<td>13992</td>
<td>18995</td>
</tr>
</tbody>
</table>
### Table 3.3: Ligand field parameters and ESR Spectral Data of Co (II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ligands field parameters</th>
<th>LFSE KJ/mol</th>
<th>ESR spectral data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dq (cm(^{-1}))</td>
<td>B (cm(^{-1}))</td>
<td>(\beta)</td>
</tr>
<tr>
<td>[Co(L)(_2)]Cl(_2)</td>
<td>975</td>
<td>617</td>
<td>0.53</td>
</tr>
<tr>
<td><a href="NO(_3)">Co(L)(_2)</a>(_2)</td>
<td>1021</td>
<td>708</td>
<td>0.61</td>
</tr>
<tr>
<td><a href="CH(_3)COO">Co(L)(_2)</a>(_2)</td>
<td>1082</td>
<td>679</td>
<td>0.58</td>
</tr>
<tr>
<td>[Co(L)(_2)]Cl(_2)</td>
<td>1071</td>
<td>644</td>
<td>0.55</td>
</tr>
<tr>
<td><a href="NO(_3)">Co(L)(_2)</a>(_2)</td>
<td>1012</td>
<td>605</td>
<td>0.52</td>
</tr>
<tr>
<td><a href="CH(_3)COO">Co(L)(_2)</a>(_2)</td>
<td>1119</td>
<td>668</td>
<td>0.57</td>
</tr>
<tr>
<td>[Co(L)(_2)]Cl(_2)</td>
<td>1108</td>
<td>680</td>
<td>0.58</td>
</tr>
<tr>
<td><a href="NO(_3)">Co(L)(_2)</a>(_2)</td>
<td>1033</td>
<td>617</td>
<td>0.53</td>
</tr>
<tr>
<td><a href="CH(_3)COO">Co(L)(_2)</a>(_2)</td>
<td>1017</td>
<td>606</td>
<td>0.52</td>
</tr>
<tr>
<td>[Co(L)(_2)]Cl(_2)</td>
<td>1036</td>
<td>680</td>
<td>0.58</td>
</tr>
<tr>
<td><a href="NO(_3)">Co (L')(_2)</a>(_2)</td>
<td>1040</td>
<td>703</td>
<td>0.60</td>
</tr>
<tr>
<td><a href="CH(_3)COO">Co (L')(_2)</a>(_2)</td>
<td>972</td>
<td>606</td>
<td>0.52</td>
</tr>
</tbody>
</table>
REFERENCES


38. P. Sonawane, A.S. Kumbhar, S.B. Padhye and R.J. Butcher, 


