SECTION 4

COBALT (II) COMPLEXES
(a) Brief Review of Previous Work:

The effective electronic configuration of cobalt(II) ion is $3d^7$. It forms numerous complexes of various stereochemical types. The octahedral and tetrahedral structures are common, but there are a fair number of square ones as well as some of which are five-coordinate. Cobalt(II) ion in octahedral coordination may have either $t_2g^5 e_g^2$ in weaker field or $t_2g^6 e_g^1$ in stronger fields. Although octahedrally coordinated cobalt(II) complexes have usually three unpaid electrons, there are examples like $[\text{Co(NO}_2\text{)}_6]^4^-$, $[\text{Co(diarsine)}_2]^{2^+}$, and $[\text{Co(triarsine)}_2]^{2^+}$ where it has only one unpaired electron. For high spin octahedral complexes the magnetic moments range from 4.7 to 5.2 B.M., i.e., they have high orbital contributions, since the spin only moment for the three unpaired electrons is only 3.89 B.M. The high orbital contribution is explained by ligand field theory. Considerably less is known regarding magnetic and spectral properties of low-spin octahedral cobaltous complexes, since they are relatively rare and in the stronger ligand fields require to produce spin-pairing, there is appreciable mixing of metal and ligand orbitals which makes a simple L.F. theory treatment of their electronic structure somewhat inadequate. From energy level diagram of tetrahedral cobalt(II) complexes it follows that cobalt(II) complexes must have high-spin regardless of the strength of the ligand field. Like octahedral high-spin cobalt(II), the tetrahedral cobalt(II) ion
has a magnetic moment appreciably in areas of the spin-only value, again because of an orbital contribution which is well understood theoretically. Magnetic moments of tetrahedrally coordinated cobalt(II) ion range from 4.1 to 4.7 B.M. In this section various coordination numbers of cobalt(II) complexes studied by earlier workers are reported.

**Coordination Number 6 :-**

From the time of Werner, hexamine cobalt(II) complexes are well known. \([\text{Co(Py)}_2\text{Cl}_2]\) is known to be polymeric comprising of six-coordinate cobalt(II) ion\(^3\), whereas \([\text{Co(Py)}_2\text{Br}_2]\) and \([\text{Co(Py)}_2\text{I}_2]\) are tetrahedral\(^4\). Complexes like \([\text{Co(Py)}_2(\text{NCS})_2]\) and \([\text{Co(Py)}_2(\text{NCS})_2]\) form bridged octahedral structure\(^5\). Several octahedral complexes of Co(II) of the type \([\text{CoL}_4\text{X}_2]\), where \(L = \gamma\text{-picoline, } X = \text{Cl, Br, NCS}\) are known\(^6\). Lever, Lewis and Nyholm\(^7\) have reported polymeric complexes of both the types \([\text{LCoX}_2]_n\) and \([2\text{LCoX}_2]_n\) where the metal atom is octahedrally coordinated. A six-coordinate complex has also been reported\(^8\) with thiourea.

Cotton and Goodgame have reported\(^9\) complexes of composition \(\text{Co(Me}_3\text{PO})_2(\text{NO}_3)_2\) as six-coordinate involving bidentate nitrato coordination. Goodgame et al. have also reported\(^10\) octahedral cobalt nitrite complexes with amine ligands. Reedijk has studied\(^11\) complexes of methyl pyrazole with a number of divalent metal ions and calculated tetragonal distortion from ligand field spectra. Imidazoles as ligands have been extensively studied by D.M.L. Goodgame and Machado\(^12\). Pellacani and coworkers\(^13\) have reported octahedrally coordinated cobalt(II) complexes with \(\beta\)-ketoenolates and heterocyclic amines. Zacharias and his coworkers\(^14\) have synthesised some Co(II) complexes
taking triazine-1-oxide as the ligand and have suggested a distorted octahedral configuration for the complexes.

Six-coordinate Co(II) complexes of the composition $\text{CoX}_2(\text{oxime})_4$ have been synthesised by Yamada and his coworkers$^{15}$ where $X = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{NCS}, \text{OAc}$ and oxime = acetaldehydeoxime. Ramana Rao et al.$^{16}$ have reported octahedral Co(II) complexes of the type CoL$_2L'$ where LH = dibenzoylmethane and L' are the nitrogen donors. Tris-chelate complexes of 1,4,6-trimethylpyrimidine-2-thione with transition metal ions have been reported by Goodgame and Leach$^{17}$. Cobalt(II) halides form$^{18}$ both octahedral and tetrahedral complexes with 3-amino-5-methyl-isoxazole in the solid state and in solution. New cobalt(II) complexes with some quadidentate schiff bases derived from 2-hydroxy-1-naphthaldehyde and o-hydroxyacetophenone have been reported by Syamal et al.$^{19}$ The complexes have pseudo octahedral, square planar and pseudo tetrahedral structures.

Watton and his coworkers$^{20}$ have reported some six-coordinate Co(II) complexes with s-triazene ligand. Six-coordinate Co(II) complexes of the type $\text{CoX}_2(\text{oxime})_4$ and $\text{Co(NCS)}_2(\text{oxime})_2$ where $X = \text{Cl}, \text{Br}$, oxime = 2-thiophenealdehyde oxime have been prepared$^{21}$. Dash and Dash have reported$^{22}$ compounds of the type $[\text{Co(acac)}_2L_2]$ where Hacac = acetylacetone, L = imidazole, morpholine and their derivatives and suggested a trans pseudo octahedral configuration to the complexes. A tetragonally distorted octahedral structure has been assigned$^{23}$ to the Co(II) complexes of the composition $\text{CoL(H}_2\text{O})_2\text{Cl}_2$ where $L = \text{N-(2-aminoethyl)1,3-propanediamine}$. Both octahedral and tetrahedral Co(II) complexes of 4,6-dimethylpyridine-2-thione have been reported by Goodgame et al.$^{24}$ Cobalt(II) complexes of some o-hydroxycrotonophenones have been prepared$^{25}$ which possess a high-spin trans-octahedral configuration. Octahedral complexes of 2,4-dimercapto-s-triazolo
Oft-1,3,4-thiadiazole have been prepared. Magnetic and spectral properties of cyclic nitrogen bases of some Co(II) complexes of pyridine-2aldoxime and 6-methylpyridine-2aldoxime have been reported. Synthesis and structural characterisation of a paramagnetic octahedral cobalt-sulphur cluster has been reported. Octahedral complexes of the type CoLCl₂ have been isolated where L is a tetradeutate ligand, N,N'-bis-(acetoglucose)ethylenediamine.

**Coordination Number 5:**

Complexes of this coordination number are rare in comparison to hexa- and tetracoordinated complexes. Adamson reported the so-called [Co(CN)₆]⁴⁻ to be actually [Co(CN)₅]³⁻. Nyholm et al. have reported the compound [CoL₂·triarsine] to be penta-coordinated. A five-coordinate Co(II) chloride complex with N-methylated diethylene triamine have been prepared. Mukherjee et al. have reported some penta-coordinated lutidine adducts of Co(II) dithiophosphinate. Sacconi et al. have reported distorted trigonal bipyramidal Co(II) complexes of tris-(2-phenylphosphinoethyl)phosphine. Thompson and his coworkers have synthesised some 5-coordinate trigonal bipyramidal Co(II) complexes with tris-(2-benzimidazolylmethyl)amine.

Preti et al. have reported five-coordinate low-spin Co(II) complexes with benzeneeleninato ions ethylenediamine as ligands. Five-coordinate Co(II) complexes of macrocyclic ligands have been synthesised, the d-d electronic and e.s.r. spectra being consistent with a square pyramidal environment. Five-coordinated complexes of the composition CoL₃X₂ have been isolated where L = 2,6-dimethyl-4-pyrone, X = SCN, SeCN and the ligand is bonded via the O-atom. Penta-coordinated Co(II) complexes have been prepared using cycloserine as ligand. Drago and his coworkers have reported a series
of five-coordinated cobalt(II) triphosphine complexes and both
distorted trigonal bipyramidal and tetragonal pyramidal geometries
have been assigned to the complexes. Some new 2,6-bis-(diphenyl-
phosphinomethyl)pyridine (ppn) complexes of Co(II) have been prepa-
red and a five-coordinated high-spin Co(pnp)(NO₃)₂ are described.
Penta-coordinated Co(II) complexes with bis-[N-(2,6-diisopropylphenyl)-
salicylideneamine] have been synthesised.

Coordination Number 4:-

Tetrahedral isocyanate complexes of the type [Co(NCO)₄]²⁻
have been prepared and their magnetic, electronic and X-ray measure-
ments have been studied by Forster and Goodgame. Cotton and his
coworkers have made a thorough study of magnetic moment and electronic
spectra of the tetrahedral complexes Co(PR₃)₂X₂. Cotton and Goodgame
have also assigned a tetrahedral structure to the complexes
[Co(NCO)₄]²⁻ and [Co(N₃)₄]²⁻ on the basis of electronic spectra.

Gill and Nyholm have prepared tetrahedral tetrahalo complexes of
the type [Co(Hal)₄]²⁻ with Ph₃MeAs⁺, Et₄N⁺ and Me₄N⁺ ions etc.

Turco et al. have reported the formation of various complexes of
Co(II) with selenocyanate [Co(NCSe)₄]²⁻ and indicated a tetrahedral
structure. Marcotrigiano and his coworkers have synthesised some
tetrahedral complexes of the type CoX₄(Ln²⁺), where X = Cl, Br, I and
Ln²⁺ is diprotonated piperazine.

Cobalt(II) complexes of the composition CoX₂L₂ (X = Cl, Br,
I, NCS; L = 3- and 4-benzoylpyridine) have been prepared. Tetra-
halo complexes with N-benzoylphenylhydroxylamine and benzo-
hydroxamic acid have been reported. S-N chelating N,N'-ethylene-
bis-(amino-1-cyanopentanedithiocarboxylate) complexes of Co(II) has
been isolated. The chelate possesses a square planar geometry on
the basis of i.r., electronic, $^1$H NMR, mass spectra, conductance, magnetic moment, thermal and X-ray diffraction analysis. Fabretti et al. have prepared pseudotetrahedral complexes of composition Co$L_2X_2$ (X = Cl, Br, I, OAc; L = 2-amino-5-methyl-1,3,4-thiadiazole) and the ligand is bonded through the amine N-atom. $[\text{CoL}_2X_2]$ (X = Cl, Br, I) and $[\text{CoL}_4](\text{BF}_4)_2$ complexes have been prepared where L = N,N'-disubstituted imidazolidine-2-thiones. The ligand is bonded through S-atom and the complexes possess a tetrahedral stereochemistry around the metal atom.

Schiff bases derived from 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one and aromatic amines form tetrahedral cobalt(II) complexes. Cobalt(II) complexes of diacetyl-bis(dimethylhydrazone) have been synthesised and a tetrahedral structure has been assigned to them.
GRAPH 1  Methylene - bis -(1,1'-dicyano-2-phenyl-2'-methyl-ethylacrylate)  

GRAPH 2  N,N'-bis-(acetoacetanilide) ethylenediamine  

WAVE NUMBER (cm⁻¹)
Present Investigation:

(i) EXPERIMENTAL: In this section, several tetra-, penta- and hexa-coordinated complexes are reported with nitrogen, oxygen and sulphur donor ligands. They have been classified below into five categories.

(A) Cobalt(II) complexes with tetradentate ligands.

(B) Polymetallic cobalt(II) complexes with bi-bidentate and tridentate schiff bases.

(C) Cobalt(II) complexes with tri- and bidentate ligands.

(D) Mixed ligand cobalt(II) complexes.

(E) Anionic mixed ligand cobalt(II) complexes.

(A) Cobalt(II) complexes with tetradentate ligands

1. Cobalt(II) complexes with methylene-(1,1'-dicyano-2-phenyl-2'-methyl ethylacrylate):

(a) Preparation of the ligand: To a methanolic solution of ethyl-cyanooacetate (1.1 ml), benzoylacetone (1.6 g) and piperidine (4 ml) were added and refluxed for 4 hrs. The solution was then kept in refrigerator for 24 hrs. The yellow coloured needle-shaped crystals separated out which was then filtered off, dried and recrystallised from ethanol (95%). Melting point is 53°C. Calculated for C_{20}H_{20}O_{4}N_{2}, C, 68.18% H, 5.68% N, 7.95% found C, 67.85% H, 5.39% N, 7.64%. The purity of the compound was established by microanalysis, functional group analysis and i.r. spectral data. The structure of the compound is represented by the diagram 3. Graph 1.
(b) Preparation of the complexes:— Ethanol solution of the cobalt(II) salts were mixed with ethanol solution of the ligand (1:1 proportion) and the resulting solution refluxed for about 2 hrs. On cooling overnight, crystalline compounds of metal complexes separated out. These were filtered under suction, washed with ethanol followed by ether and dried in vacuo.

2. Cobalt(II) complexes with N,N'-bis-(acetoacetanilide)ethylenediamine
(a) Preparation of the ligand:— To an ethanol solution of acetoacetanilide (1.7 g), ethylenediamine (0.6 ml) was added and the reaction mixture was refluxed over a waterbath for $\frac{1}{2}$ hr. when a white precipitate of the compound separated out. It was then filtered, washed with ethanol, dried and recrystallised from ethanol (95%). Melting point is 209°C. The percentage of elemental analysis of the ligand molecule is as follows: C, 71.42 H, 6.92 N, 14.80 for $C_{22}H_{28}N_4O_2$ found C, 71.06 H, 6.58 N, 14.52.

Elemental analysis and i.r. spectral data indicate the structure of the ligand as represented in diagram 4. Graph 2.
GRAPH 3  N, N'-bis-(benzoin) 1,2-diamino propane
(b) **Preparation of the complexes:** Cobalt(II) salts in ethanol were added separately to the ligand solution in dioxane in 1:1 molar ratio and heating under reflux for about 2 hrs. On keeping overnight, the crystalline complexes separated out. These were then filtered off, washed with dioxane followed by ether, and dried in **vacuo**.

3. **Cobalt(II) complex with N,N'-bis(benzoin)1,2-diaminopropane**

(a) **Preparation of the ligand:** To an ethanolic solution of benzoin (2.12 g), 1,2-diaminopropane (0.7 ml) and anhydrous sodium acetate (4 g) were added and the reaction mixture refluxed for 2 hrs. The hot solution was then poured into a beaker containing ice-cold water slowly with constant stirring when a brown precipitate separated out. It was allowed to stand overnight and then filtered, washed with water, dried and recrystallised from ethanol (95%). Melting point is 125°C. Yield is 65%. Calculated for C$_{31}$H$_{28}$N$_2$O$_2$, C, 80.86%, H, 6.08%, N, 6.08%; found C, 80.57%, H, 5.95%, N, 5.90%.

Elemental analysis and i.r. spectral data indicate the structure of the compound as represented below by the diagram 5. Graph 3.

(b) **Preparation of the complexes:** An ethanolic solution of the schiff base was allowed to react with cobalt(II) chloride in ethanol under reflux in 1:1 ratio for 1 hr. On cooling, the pH of the solution was raised to around 7 by adding conc.$\text{NH}_4\text{OH}$
GRAPH 4  N, N’-bis-(benzoin) m — phenylenediamine
drop by drop, when metal chelate separated out. It was then filtered, washed with ethanol and ether and dried in vacuo.

Analytical, m.p., conductance, magnetic susceptibility, molecular weight and i.r. spectral data are given in Table 1 and electronic spectral data in Table 2.

(B) Polymetallic cobalt(II) complexes with bi-bidentate and tridentate schiff bases

1. Cobalt(II) complexes with bi-bidentate schiff base

N,N'-bis-(benzoin)m-phenylenediamine

(a) Preparation of the ligand - To an ethanolic solution of benzoin (4.2 g), m-phenylenediamine (1.0 g) and anhydrous sodium acetate (5 g) were added and the mixture refluxed over a waterbath for 2 hrs. The hot solution was then poured into ice-cold water with constant stirring when orange-red precipitate separated out. It was then left overnight and then filtered, washed with water, dried and recrystallised from ethanol (95%). Melting point is 131°C. Yield is 65%. Calculated for C_{38}H_{28}O_{2}N_{2}, C, 82.25%, H, 5.64%, N, 5.64% found C, 81.70% H, 5.60% N, 5.61%.

Elemental analysis and i.r. spectral data indicated structure as represented in diagram 6. Graph 4.

(b) Preparation of the complex - Ethanolic solution of cobalt(II) chloride was reacted with an ethanolic solution of the schiff base
Table 1. Analysis, m.p., conductance, magnetic susceptibility, molecular weight and i.r. spectral data

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<th>Compound</th>
<th>M.P. °C</th>
<th>Colour</th>
<th>% Cobalt Found (Reqd)</th>
<th>% Nitrogen Found (Reqd)</th>
<th>ΔM mgs cm² mole⁻¹</th>
<th>Σ eff. B.M.</th>
<th>Mol. wt. Found (Reqd)</th>
<th>γ(C=O)</th>
<th>γ(C=N)</th>
<th>γ(C=O)</th>
<th>γ(C=O)</th>
<th>γ(C=N)</th>
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<td>4.9</td>
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<td>4.7</td>
<td>5.0</td>
<td>568 (561)</td>
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<td>631 (636)</td>
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L = Methylene-bis-(1,1'-dicyano-2-phenyl-2'-methyl-ethylacrylate), L' = N,N'-bis-(acetoacetanilide)-ethylenediamine, L" H₂ = N,N'-bis-(benzoind)1,2-diaminopropane.
Table 2. Electronic spectral data of the complexes

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<th>$\gamma_1$ cm(^{-1})</th>
<th>$\gamma_2$ cm(^{-1})</th>
<th>$\gamma_3$ cm(^{-1})</th>
<th>10D(_q) cm(^{-1})</th>
<th>$\beta_{35}$</th>
<th>$D_q$</th>
<th>$B$</th>
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<td>CoLC(_1)(_2)</td>
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<td>780</td>
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<td>19400</td>
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<td>713</td>
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<td>839</td>
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<td>761</td>
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<td>16520</td>
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<td>781</td>
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<td>8700</td>
<td>806</td>
<td>2.12</td>
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</table>
GRAPH.5 Schiff base derived from benzoin with 2-amino-2-methyl-1-propanol

GRAPH.6 Schiff base derived from benzoin with 1-amino-2-propanol
in 1:1 ratio followed by the dropwise addition of ammonia, when
the metal chelate separated out. It was then filtered, washed with
ethanol followed by ether and dried in vacuo.

2.(i) Cobalt(II) complex with tridentate Schiff base derived from
benzoin with 2-amino-2-methyl-1-propanol \( [\text{BnAMPH}_2] \):

(a) Preparation of the ligand:– Benzoin (2.12 g) in ethanol was
mixed with 2-amino-2-methyl-1-propanol and refluxed over a waterbath
for 2 hrs. On cooling, light yellowish-white coloured Schiff base
separated out. It was then filtered, washed with ethanol, dried
and recrystallized from ethanol (95%). M.P. is 130°C. Yield is
70%. Calculated for \( \text{C}_{18}\text{H}_{21}\text{O}_2\text{N} \), C, 76.32 %; H, 7.42 %; N, 4.94 %;
found C, 75.47 %; H, 7.38 %; N, 4.91 %. Graph 5.

2.(ii) Cobalt(II) complex with tridentate Schiff base derived from
benzoin with 1-amino-2-propanol \( [\text{BnAPH}_2] \):

(a) Preparation of the ligand:– An ethanolic solution of benzoin
(2.12 g) was mixed with 1-amino-2-propanol (0.75 ml) and the mixture
was refluxed over a waterbath for 1-\( \frac{1}{2} \) hrs. On cooling, yellowish-white
crystalline compound of the Schiff base separated out. It
was then filtered, washed with ethanol, dried and recrystallized
from ethanol (95%). M.P. is 120°C. Yield is 80%. Calculated for
\( \text{C}_{17}\text{H}_{19}\text{O}_2\text{N} \), C, 75.83 %; H, 7.06 %; N, 5.2 %; found C, 74.26 %; H, 6.95 %
N, 5.18 %. Graph 6.

Elemental analysis and i.r. spectral data indicate the
formulae of the compounds as given in diagrams 7 and 8 respectively.
(b) Preparation of the complexes: -- Ethanolic solution of cobalt(II) chloride was reacted separately with an ethanolic solution of the schiff bases and the mixture refluxed for 1-1\(\frac{1}{2}\) hrs over a waterbath. It was then allowed to cool and pH of the solution was raised to around 7 by adding conc. NH\(_4\)OH drop by drop when the metal chelates separated out. These were then filtered, washed with ethanol, ether and dried in vacuo.

3. Cobalt(II) complex with tridentate schiff base derived from benzoin with o-aminophenol [BnOAPH\(_2\) ]:

(a) Preparation of the ligand: -- A mixture of o-aminophenol (1.1 g) and anhydrous sodium acetate (4 g) were added to an ethanolic solution of benzoin (2.12 g) and refluxed for 1-1\(\frac{1}{2}\) hrs. over a waterbath. Then the hot solution was poured into a beaker containing ice-cold water when a brown precipitate of the schiff base separated out. It was then filtered, washed with water, dried and recrystallised from ethanol (95%). M.P. is 128\(^\circ\) C. Yield is 50%. Calculated for C\(_{20}\)H\(_{17}\)O\(_2\)N, C, 79.20 %, H, 5.61 %, N, 4.62 %. Found C, 78.60 %, H, 5.58 %, N, 4.60 %.

Elemental analysis and i.r. spectral data indicate the structure of the compound as represented in diagram 9.
(b) **Preparation of the complexes** :- Ethanoic solution of the cobalt(II) chloride was reacted with an ethanoic solution of the schiff base in 1:1 ratio followed by the dropwise addition of NH$_3$ when the metal chelate separated out. It was then filtered, washed with ethanol, ether and dried in vacuo.

Elemental analysis, m.p., conductance, magnetic susceptibility, i.r. and electronic spectral data are given in Table 3.

(C) **Cobalt(II) complexes with tridentate and bidentate ligands** : 

1. (i) **Cobalt(II) complex with benzoin semicarbazone [BnS]** :

(a) **Preparation of the ligand** :- To an ethanoic solution of benzoin (2.12 g), semicarbazide (0.75 g) and anhydrous sodium acetate (4 g) were added and the reaction mixture refluxed for 2 hrs. over a water-bath. The hot solution was poured into ice-cold water slowly with constant stirring when a yellow-coloured compound of the semicarbazone separated out. It was then filtered, washed with water, dried and recrystallised from ethanol (95 %). M.P. is 206(d). Calculated for C$_{15}$H$_{15}$O$_2$N$_3$, C, 66.91 % H, 5.57 % N, 15.61 %, found C, 66.54 % H, 5.26 % N, 14.77 %. Graph 7.

(ii) **Cobalt(II) complex with benzoin thiosemicarbazone [BnTS]** :

(a) **Preparation of the ligand** :- To an ethanoic solution of benzoin (2.12 g), thiosemicarbazide (0.91 g) and anhydrous sodium acetate (4 g) were added and the reaction mixture refluxed for 2 hrs. over
Table 3. Analysis, melting point, conductance, magnetic susceptibility, i.r. and electronic spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>Colour</th>
<th>Found (% C)</th>
<th>% Cobalt</th>
<th>Found (% N)</th>
<th>% Nitrogen</th>
<th>(\Delta_{M})</th>
<th>(\nu_{\text{C=N}}) (cm(^{-1}))</th>
<th>(\nu_{\text{C=O}}) (cm(^{-1}))</th>
<th>(\nu_{\text{CO-N}}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LH}_2)</td>
<td>131</td>
<td>Orange red</td>
<td>5.61 (5.64)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{L'}\text{H}_2)</td>
<td>130</td>
<td>Yellowish</td>
<td>4.91 (4.94)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{L''H}_2)</td>
<td>120</td>
<td>-</td>
<td>5.18 (5.20)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{L'''H}_2)</td>
<td>128</td>
<td>Brown</td>
<td>4.60 (4.62)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Co}_2\text{L}_2\cdot\text{H}_2\cdot\text{O})</td>
<td>250</td>
<td>Pink</td>
<td>9.87 (8.96)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.6</td>
<td>2.80 (2.94)</td>
<td>2.59 (3.63)</td>
<td>2.45 (3.51)</td>
</tr>
<tr>
<td>(\text{Co}_2\text{L}_2\cdot\text{H}_2\cdot\text{O})</td>
<td>250</td>
<td>Black</td>
<td>15.48 (15.66)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.69</td>
<td>2.50 (2.60)</td>
<td>2.50 (3.60)</td>
<td>2.45 (3.50)</td>
</tr>
<tr>
<td>(\text{Co}_2\text{L}_2\cdot\text{H}_2\cdot\text{O})</td>
<td>250</td>
<td>Violet</td>
<td>16.12 (16.77)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.81</td>
<td>2.00 (2.75)</td>
<td>2.00 (3.75)</td>
<td>2.45 (3.50)</td>
</tr>
<tr>
<td>(\text{Co}_2\text{L}_2\cdot\text{H}_2\cdot\text{O})</td>
<td>250</td>
<td>Pink</td>
<td>14.60 (14.80)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.48</td>
<td>2.90 (2.90)</td>
<td>2.90 (2.90)</td>
<td>2.45 (3.50)</td>
</tr>
<tr>
<td>(\text{Co}_2\text{L}_2\cdot\text{H}_2\cdot\text{O})</td>
<td>250</td>
<td>Pink</td>
<td>14.60 (14.80)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.48</td>
<td>2.90 (2.90)</td>
<td>2.90 (2.90)</td>
<td>2.45 (3.50)</td>
</tr>
</tbody>
</table>

* = alcoholic, ** = phenolic.

\(\text{LH}_2\) = Schiff base, \(\text{L'}\text{H}_2\) = Schiff base derived from benzoin with 1-aminopropanol,
\(\text{L''H}_2\) = Schiff base derived from benzoin with 1-amino-2-propionol,
\(\text{L'''H}_2\) = Schiff base derived from benzoin with 1-aminopropanol,
\(\text{Co}_2\text{L}_2\cdot\text{H}_2\cdot\text{O}\) = phenylenediamine, \(\text{LH}_2\) = Schiff base derived from benzoin with 1-amino-2-propionol,
\(\text{L'\text{H}_2}\) = Schiff base derived from benzoin with 1-amino-2-propionol,
\(\text{L''\text{H}_2}\) = Schiff base derived from benzoin with 1-amino-2-propionol,
\(\text{L'''\text{H}_2}\) = Schiff base derived from benzoin with 1-amino-2-propionol,
a waterbath. The hot solution was poured into ice-cold water with stirring when a light yellow coloured compound separated out. It was then filtered, washed with water, dried and recrystallised from ethanol (95%). M.P. is 123°C. Calculated for C$_{15}$H$_{15}$OSN$_3$, C, 63.15%; H, 5.26%; N, 14.77% found C, 62.95%; H, 5.15%; N, 14.28%. Graph 8.

Elemental analysis and i.r. spectral data indicate the structure of the compounds as represented in diagrams 10 and 11 respectively.

Diagram 10

(b) Preparation of the complexes: Ethanolic solution of cobaltous chloride was reacted separately with the ligands in ethanol in 1:2 ratio and then conc. NH$_4$OH was added slowly dropwise until the metal chelates separated but. These were then filtered, washed with ethanol, ether and dried in vacuo.

2.(i) Cobalt(II) complex with benzoin phenylhydrazone:

(a) Preparation of the ligand: Phenylhydrazine (1.0 ml) in glacial acetic acid was added to ethanolic solution of benzoin (2.12 g) and heated under reflux for $\frac{1}{2}$ hr. On keeping overnight, yellow coloured compound of the hydrazone separated out. It was then filtered, washed with ethanol and dried on exposure to air and recrystallised from ethanol (95%). M.P. is 192°C. Graph 9.

(ii) Cobalt(II) complex with benzoin 2,4-dinitrophenylhydrazone:

(a) Preparation of the ligand: 2,4-dinitrophenylhydrazine (1.98 g)
in glacial acetic acid was added to ethanolic solution of benzoin (2.12 g) and refluxed for 1 hr. On keeping the reaction mixture overnight, yellow crystalline compound separated out. It was then filtered, washed in ethanol and dried on exposure to air and recrystallised from ethanol (95 %). M.P. is 198(d). Graph 10.

Elemental analysis and i.r. spectral data show the structure of these compounds as represented by the diagrams 12 and 13.

```
\begin{align*}
\text{Diagram 12} & \quad \text{Diagram 13}
\end{align*}
```

(b) Preparation of the complexes:— Ethanolic solution of metal chlorides were mixed with ethanolic solution of the ligands in 1:2 proportion, the resulting solution refluxed for 1 hr. On cooling overnight crystalline compounds separated out. These were filtered under suction, washed with ethanol and ether and dried in vacuo.

3. Cobalt(II) complex with the schiff base derived from benzoin with aniline:

(a) Preparation of the ligand:— To a methanolic solution of benzoin (2.12 g) and aniline (1 ml) was added anhydrous sodium acetate (4 g) and the mixture was refluxed for 1 hr. The hot solution was poured into ice-cold water when a yellow-coloured crystalline compound separated out. It was then filtered washed with water, dried and recrystallised from ethanol (95 %). M.P. is 130°C. Calculated for C_{20}H_{16}ON, C, 83.91 %, H, 5.59 %, N, 4.69 %. Found C, 82.64 %, H, 5.52 %, N, 4.84 %.
Elemental analysis and i.r. spectral data indicate the structure of the compound as represented by the diagram 14. Graph 11.

(b) Preparation of the complex :- Ethanolic solution of cobalt(II) chloride was treated with ethanolic solution of the schiff base in 1:2 molar ratio, followed by the dropwise addition of ammonia when metal chelate separated out. It was then filtered, washed with ethanol followed by ether and dried in vacuo.

4. Cobalt(II) complexes with dithioxamide :
(a) Preparation of the complexes :- Ethanolic solution of cobaltous chloride and thiocyanate were heated separately with dithioxamide (1:2 ratio) under reflux for about 1 hr and the resulting solution was concentrated by evaporation in air when crystalline compounds separated out. These were filtered under suction, washed with ethanol and ether and dried in vacuo.

5. Cobalt(II) complexes with ethyle-1-phenyl-2-cyanoacrylate :
(a) Preparation of the ligand :- Methanolic solution of benzaldehyde (2.12 ml) and cyanoacetic ester (2.26 ml) was treated with piperidine (2 ml) and the solution was warmed over a waterbath for 15 minutes. On cooling a yellow compound was separated out immediately. It was allowed to stand overnight, filtered and washed with methanol. On
crystallisation from ethanol (95 °/) yellow crystalline compound of the ligand separated out. M.P. is 58°C. Calculated for $C_{12}H_{11}O_{2}N$, C, 71.64 % H, 5.47 % N, 6.96 % found C, 71.28 % H, 5.30 % N, 6.52 %.

Elemental analysis and i.r. spectral data indicate the structure of the compound as represented by the diagram 15. Graph 12.

(b) Preparation of the complexes: A mixture of ethanolic solution of cobaltous salts and the ligand in ethanol was refluxed over a waterbath for 2 hrs. On cooling metal complexes separated out which were filtered, washed with ethanol followed by ether and dried in vacuo. Analytical, melting point, conductance and magnetic susceptibility data are given in Table 4 and i.r. spectral data in Table 5.

(D) Mixed ligand complexes of cobalt(II):

(a) Preparation of cobalt oxinate: To an aqueous solution of cobaltous chloride (2.36 g), sodium acetate (5 g) was added and warmed to 65-70°C. The ethanolic solution of oxine (3.0 g) was added to it when light brown amorphous cobalt oxinate separated out immediately. It was then filtered, washed with ethanol followed by ether and dried in vacuo. Graph 13.

(b) Preparation of mixed ligand complexes: To the ethanolic suspension of cobalt oxinate, nitrogen donor ligands were reacted in stoichiometric ratio separately and refluxed for 1-2 hrs. Then the compound were filtered off, washed with ethanol, ether and dried in vacuo.

Elemental analysis, melting point, conductance and magnetic moment data are given in Table 6.
### Table 4. Analysis, m.p., conductance and magnetic susceptibility data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. °C</th>
<th>Colour</th>
<th>% Cobalt Found (Reqd)</th>
<th>% Nitrogen Found (Reqd)</th>
<th>$\Delta M$ mohs cm², mole⁻¹</th>
<th>$\mu_{\text{eff.}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>206*</td>
<td>Yellow</td>
<td>-</td>
<td>14.77</td>
<td>12.0</td>
<td>4.9</td>
</tr>
<tr>
<td>L'H</td>
<td>123</td>
<td>— do-</td>
<td>-</td>
<td>14.28</td>
<td>10.5</td>
<td>5.1</td>
</tr>
<tr>
<td>L&quot;H</td>
<td>106</td>
<td>— do-</td>
<td>-</td>
<td>8.94</td>
<td>10.5</td>
<td>5.0</td>
</tr>
<tr>
<td>L'''H</td>
<td>234</td>
<td>— do-</td>
<td>-</td>
<td>14.42</td>
<td>10.5</td>
<td>5.0</td>
</tr>
<tr>
<td>L IVH</td>
<td>130</td>
<td>— do-</td>
<td>-</td>
<td>4.84</td>
<td>12.0</td>
<td>4.9</td>
</tr>
<tr>
<td>LV</td>
<td>190-200</td>
<td>White</td>
<td>-</td>
<td>22.94</td>
<td>12.0</td>
<td>4.9</td>
</tr>
<tr>
<td>LV'</td>
<td>58</td>
<td>Yellow</td>
<td>-</td>
<td>6.52</td>
<td>14.5</td>
<td>4.8</td>
</tr>
<tr>
<td>CoCl₂.2H₂O</td>
<td>&gt;250</td>
<td>Pink</td>
<td>14.52 (14.79)</td>
<td>10.38 (10.54)</td>
<td>12.0</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL'Cl₂.2H₂O</td>
<td>&gt;250</td>
<td>— do-</td>
<td>13.95 (14.22)</td>
<td>10.04 (10.13)</td>
<td>10.5</td>
<td>5.1</td>
</tr>
<tr>
<td>CoL&quot;₂.2H₂O</td>
<td>192</td>
<td>— do-</td>
<td>8.38 (8.45)</td>
<td>6.35 (6.38)</td>
<td>10.5</td>
<td>5.0</td>
</tr>
<tr>
<td>CoL'''₂.2H₂O</td>
<td>198*</td>
<td>— do-</td>
<td>6.68 (6.71)</td>
<td>12.64 (12.77)</td>
<td>12.0</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL IV₂.2H₂O</td>
<td>142</td>
<td>— do-</td>
<td>8.81 (8.86)</td>
<td>4.17 (4.21)</td>
<td>14.5</td>
<td>4.8</td>
</tr>
<tr>
<td>CoL₂Cl₂</td>
<td>237</td>
<td>Orange</td>
<td>15.36 (15.50)</td>
<td>7.16 (7.36)</td>
<td>10.5</td>
<td>4.8</td>
</tr>
<tr>
<td>CoL₂(SCN)₂</td>
<td>&gt;250</td>
<td>Violet</td>
<td>13.98 (14.19)</td>
<td>13.24 (13.48)</td>
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<td>4.9</td>
</tr>
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<td>CoL VI₂Cl₂</td>
<td>&gt;250</td>
<td>Pink</td>
<td>10.98 (11.07)</td>
<td>5.21 (5.26)</td>
<td>8.0</td>
<td>5.0</td>
</tr>
<tr>
<td>CoL VI₂ Br₂</td>
<td>&gt;250</td>
<td>Brown</td>
<td>9.38 (9.48)</td>
<td>4.47 (4.50)</td>
<td>4.6</td>
<td>5.1</td>
</tr>
<tr>
<td>CoL VI₂ (NO₃)₂</td>
<td>&gt;250</td>
<td>Chocolate-brown</td>
<td>10.00 (10.07)</td>
<td>9.52 (9.57)</td>
<td>11.0</td>
<td>5.1</td>
</tr>
<tr>
<td>CoL VI₂ (SCN)₂</td>
<td>&gt;250</td>
<td>Brown</td>
<td>10.17 (10.20)</td>
<td>9.64 (9.70)</td>
<td>9.5</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL VI₂ (SeCN)₂</td>
<td>&gt;250</td>
<td>— do-</td>
<td>8.71 (8.77)</td>
<td>8.25 (8.34)</td>
<td>7.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

LH = benzoinsemicarbazone, L'H = benzointhiosemicarbazone, L"H = benzoinphenylhydrazone, L'''H = benzoin-2,4-dinitrophenylhydrazone, L IVH = schiff base derived from benzoin with aniline, LV = dithioxamide, LV' = ethyle-1-phenyl-2-cyanoacrylate.

* decomposition.
Table 5. Infrared spectral data (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(C=O)</th>
<th>$\nu$(C=O)</th>
<th>$\nu$(C≡N)</th>
<th>$\nu$(NH)</th>
<th>$\nu$(CO)</th>
<th>$\nu$(Co-O)</th>
<th>$\nu$(Co-Cl)</th>
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</thead>
<tbody>
<tr>
<td>LH</td>
<td>1200</td>
<td>1670</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L'H</td>
<td>1200</td>
<td>-</td>
<td>1085</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L''H</td>
<td>1210</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>L'''H</td>
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<td>-</td>
<td>3100, 3300</td>
<td>-</td>
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</tr>
<tr>
<td>L''''H</td>
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<td>-</td>
<td>3350</td>
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<tr>
<td>L''''''H</td>
<td>1210</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>L''''''''H</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L'''''''''H</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>-</td>
</tr>
<tr>
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<td>-</td>
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<td>220</td>
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<td>-</td>
<td>-</td>
<td>440</td>
<td>225</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CoL$^{'''}$Cl$_2$H$_2$O</td>
<td>1200</td>
<td>1070</td>
<td>-</td>
<td>340</td>
<td>260</td>
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</tr>
<tr>
<td>CoL$^{''''}$Cl$_2$H$_2$O</td>
<td>1590</td>
<td>-</td>
<td>-</td>
<td>450</td>
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<tr>
<td>CoL$^{'''''}$Cl$_2$H$_2$O</td>
<td>1590</td>
<td>-</td>
<td>3350</td>
<td>360</td>
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<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''}$Cl$_2$H$_2$O</td>
<td>1605</td>
<td>-</td>
<td>3350</td>
<td>350</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>CoL$^{'''''''}$Cl$_2$H$_2$O</td>
<td>1200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$H$_2$O</td>
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<td>1195</td>
<td>3200</td>
<td>350</td>
<td>260</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$S$_2$</td>
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<td>-</td>
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</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$Cl$_2$</td>
<td>-</td>
<td>1190</td>
<td>3200</td>
<td>340</td>
<td>255</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$Br$_2$</td>
<td>-</td>
<td>1595</td>
<td>2190</td>
<td>450</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$NO$_3$$_2$</td>
<td>-</td>
<td>1590</td>
<td>2185</td>
<td>440</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$(SCN)$_2$</td>
<td>-</td>
<td>1595</td>
<td>2190</td>
<td>450</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$(SeCN)$_2$</td>
<td>-</td>
<td>1590</td>
<td>2185</td>
<td>445</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoL$^{''''''''}$Cl$_2$(SeCN)$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
**Table 6. Analysis, m.p., conductance and magnetic moment data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Cobalt Found</th>
<th>% Cobalt Reqd</th>
<th>% Nitrogen Found</th>
<th>% Nitrogen Reqd</th>
<th>$\Delta_M$ mh$^\circ$s. cm$^2$-mole$^{-1}$</th>
<th>$\mu_{\text{eff.}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoL$_2$(Py)$_2$</td>
<td>11.59</td>
<td>11.66</td>
<td>10.97</td>
<td>11.09</td>
<td>12.0</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$(β-pic)$_2$</td>
<td>11.00</td>
<td>11.09</td>
<td>10.48</td>
<td>10.54</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>CoL$_2$(γ-pic)$_2$</td>
<td>10.97</td>
<td>11.09</td>
<td>10.52</td>
<td>10.54</td>
<td>8.5</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$Q$_2$</td>
<td>9.68</td>
<td>9.73</td>
<td>9.20</td>
<td>9.25</td>
<td>14.5</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$(pip)$_2$</td>
<td>11.35</td>
<td>11.39</td>
<td>10.73</td>
<td>10.83</td>
<td>15.0</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$(2,6-lut)$_2$</td>
<td>10.48</td>
<td>10.57</td>
<td>10.02</td>
<td>10.05</td>
<td>7.5</td>
<td>5.0</td>
</tr>
<tr>
<td>CoL$_2$(Quin)$_2$</td>
<td>9.27</td>
<td>9.30</td>
<td>8.76</td>
<td>8.84</td>
<td>12.5</td>
<td>4.8</td>
</tr>
<tr>
<td>CoL$_2$(4-AP)$_2$</td>
<td>10.94</td>
<td>11.01</td>
<td>10.38</td>
<td>10.48</td>
<td>9.0</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$(Mor)$_2$</td>
<td>11.26</td>
<td>11.30</td>
<td>10.63</td>
<td>10.75</td>
<td>11.0</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$oPhDA</td>
<td>12.88</td>
<td>12.94</td>
<td>12.27</td>
<td>12.31</td>
<td>10.5</td>
<td>4.9</td>
</tr>
<tr>
<td>CoL$_2$,1,10Phe</td>
<td>11.08</td>
<td>11.17</td>
<td>10.58</td>
<td>10.62</td>
<td>9.4</td>
<td>5.0</td>
</tr>
<tr>
<td>CoL$_2$,2',bipy</td>
<td>11.68</td>
<td>11.71</td>
<td>11.10</td>
<td>11.13</td>
<td>10.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

LH = oxine, Py = pyridine, β-pic = β-picoline, γ-pic = γ-picoline, Q = quinoline, Pip = piperidine, 2,6-lut = 2,6-lutidine, Quin = quinaldine, 4-AP = 4-aminopyridine, Mor = morpholine, o-PhDA = o-phenylenediamine, 1,10Phe = 1,10-phenanthroline, 2,2'-bipy = 2,2'-bipyridine.

(E) **Anionic mixed ligand complexes of cobalt(II):**

1.(a) **Preparation of bis-(monomethylammonium)tetrachlorocobaltate(II):**

Ethanolic solution of cobalt(II) chloride was treated with ethanolic solution of monomethylammonium chloride in 1:2 molar ratio. The blue crystalline compound of bis-(monomethylammonium)tetrachloro
cobaltate(II) appeared on warming the solution over a waterbath for 2 hrs. These compounds were then filtered, washed with ethanol and dried in vacuo.

(b) Preparation of mixed ligand complexes:— The mixed ligand complexes were prepared by adding stoichiometric proportion of the nitrogen and sulphur donor ligands (1:2 ratio) to methanolic solution of bis-(monomethylammonium)tetrachloro cobaltate(II) and heated under reflux for $\frac{1}{2}$ - 1 hr. On cooling, crystalline compounds separated out immediately which were then filtered, washed with ethanol, followed by ether and dried in vacuo.

2.(a) Preparation of the simple complex:— The simple complex [Co(Qn)$_2$Cl$_2$] was prepared by taking quinaldine and cobaltous chloride in 2:1 ratio in ethanolic medium. The blue complex thus appeared immediately was suction-filtered, washed with ethanol followed by ether and dried in vacuo.

(b) Preparation of tetrachloro complex:— Pure and dry chlorine gas was passed slowly to the ethanolic suspension of the above simple complex prepared till a clear solution was obtained with an exothermic reaction. The solution was kept overnight when crystalline complex separated out. It was then filtered, washed with ethanol and dried in vacuo.

(c) Preparation of mixed ligand complexes:— The mixed ligand complexes were prepared by adding requisite amount (1:2 ratio) of ligands separately to ethanolic suspension of bis-(quinaldinium)tetrachlorocobaltate(II) and refluxing for 2-3 hrs. Over a waterbath. On cooling crystalline compounds separated out which were then filtered, washed with ethanol followed by ether and dried in vacuo.

The analytical, m.p., conductance and magnetic moment data are given in Table 7.
Table 7. Analysis, m.p., conductance and magnetic susceptibility data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P.</th>
<th>Colour</th>
<th>%Cobalt Found (Reqd)</th>
<th>%Chlorine Found (Reqd)</th>
<th>%Nitrogen Found (Reqd)</th>
<th>ΔM</th>
<th>B.M.</th>
<th>μ_eff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[B]₂[CoCl₄(H₂O)₂]</td>
<td>&gt;250</td>
<td>Pink</td>
<td>19.47 (19.58)</td>
<td>46.80 (47.15)</td>
<td>9.25 (9.31)</td>
<td>240.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>[B]₂[CoCl₄OX]</td>
<td>&gt;250</td>
<td>-do-</td>
<td>14.52 (14.73)</td>
<td>35.41 (35.47)</td>
<td>10.37 (10.50)</td>
<td>220.0</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>[B][CoCl₃Qn]</td>
<td>185</td>
<td>Blue</td>
<td>17.16 (17.31)</td>
<td>31.18 (31.25)</td>
<td>8.18 (8.22)</td>
<td>120.0</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>[B][CoCl₃tu]</td>
<td>224</td>
<td>-do-</td>
<td>21.38 (21.63)</td>
<td>39.01 (39.06)</td>
<td>15.35 (15.42)</td>
<td>110.0</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>[B][CoCl₃P-dtc]</td>
<td>&gt;250</td>
<td>Olive-green</td>
<td>17.98 (18.10)</td>
<td>32.54 (32.69)</td>
<td>8.47 (8.55)</td>
<td>130.0</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>[B][CoCl₃M-dtc]</td>
<td>&gt;250</td>
<td>-do-</td>
<td>17.82 (17.99)</td>
<td>32.42 (32.49)</td>
<td>8.47 (8.55)</td>
<td>125.0</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>[QH]₂[CoCl₄(γ-pic)₂]</td>
<td>145</td>
<td>Pink</td>
<td>8.65 (8.72)</td>
<td>20.95 (21.01)</td>
<td>8.23 (8.29)</td>
<td>225.0</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>[QH]₂[CoCl₄(Py)₂]</td>
<td>172</td>
<td>-do-</td>
<td>8.82 (9.14)</td>
<td>21.59 (22.01)</td>
<td>8.21 (8.68)</td>
<td>230.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>[QH]₂[CoCl₄Phe]</td>
<td>&gt;250</td>
<td>Pink</td>
<td>8.72 (8.80)</td>
<td>21.13 (21.20)</td>
<td>8.28 (8.37)</td>
<td>230.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>[QH][CoCl₃Q]</td>
<td>224</td>
<td>Deep-blue</td>
<td>13.37 (13.44)</td>
<td>24.17 (24.26)</td>
<td>6.28 (6.38)</td>
<td>110.0</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>[QH][CoCl₃P-dtc]</td>
<td>265*</td>
<td>Deep-green</td>
<td>13.35 (13.47)</td>
<td>24.27 (24.32)</td>
<td>6.32 (6.40)</td>
<td>115.0</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>[QH][CoCl₃M-dtc]</td>
<td>&gt;250</td>
<td>Leafy-green</td>
<td>13.39 (13.41)</td>
<td>24.17 (24.21)</td>
<td>6.31 (6.37)</td>
<td>120.0</td>
<td>4.75</td>
<td></td>
</tr>
</tbody>
</table>

B = monomethylammonium cation, QH = quinaldinium cation, OX = oxine, tu = thiourea, Qn = quinaldine, Q = quinoline, Phe = 1,10-phenanthroline, γ-pic = γ-picoline, Py = pyridine, P-dtc = piperidyldithiocarbamate, M-dtc = morpholyldithiocarbamate.
(ii) DISCUSSION:

Divalent cobalt has $3d^7$ electronic structure and is unique in the sense that it is the only $d^7$ ion of common occurrence and forms various types of complex compounds. Cobalt(II) ion in octahedral coordination has the ground state $4T_1g(t_{2g})^5(e_g)^2$ or $2E_g(t_{2g})^6(e_g)^1$ depending upon the strength of the crystal field. Cobalt(II) forms tetrahedral complexes more readily than any other transition ion. This is expected to be so, because as pointed out by Pauling, as a rough rule the coordination number is twice the valency of the metal atom and that the coordination number increases with valency. Another factor which explains the ready formation of tetrahedral cobalt(II) complex is that, for a $d^7$ ion, the ligand field stabilisation energies disfavour the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other $d^n (1 \leq n \leq 9)$ configuration. Additionally, the electronic configuration ($e^4t^3_2$) of a tetrahedral cobalt(II) complexes is spherically symmetric and is expected to give rise to a stable tetrahedral structure. Because of small stability difference between octahedral and tetrahedral Co(II) complexes, there are several cases in which the two types with the same ligand are both known and may be in equilibrium. The ground state configuration in an octahedral ligand field is either $t_{2g}^5e_g^2$ in weaker fields or $t_{2g}^6e_g^1$ in stronger fields. It is seen that at a sufficiently high value of the octahedral field $2E$ state originating in the $2G$ state of the free ion will become the ground state. However, it can be estimated that rather high values of ligand field strength ($\Delta_0 > 15,000 \text{ cm}^{-1}$) will be required and thus low-spin cobalt(II) complexes can be expected only with ligands lying very far to the strong end.
of the stereochemical series. Moreover, because $t^6_{eg}e^1_g$ configuration should give rise to a large Jahn-Teller distortion, a truly octahedral complex may not be expected. The energy level diagram for tetrahedral cobalt(II) is qualitatively the same as for octahedral Cr(III) and from this it follows that tetrahedral Co(II) complexes must have high spin regardless of the strength of the ligand field.

In this section, several tetra-, penta- and hexa-coordinated cobalt(II) complexes are reported with nitrogen, oxygen, sulphur and halogen ligands. They have been classified into five categories for ease of discussion.

(A) Cobalt(II) complexes with tetradentate ligands

For a metal ion to achieve higher coordination number, two conditions are to be satisfied: (i) effective size of the metal ion, and (ii) a high positive charge (resulting from high oxidation state) of central metal ion. As for ligands, chelates as a class dominate the area of higher coordination polyhedra in scope, in numbers, in kinetic and in thermodynamic stability. In fact the more compact the ligand and the smaller the bite, the more effective is the ligand in generating high coordination structure.

In order to prepare complexes of higher and rare coordination number, new polydentate ligands have been synthesised and their complexing behaviour with divalent metal ions is studied. Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with polydentate ligands have been reported earlier$^{58-68}$. 

1. Cobalt(II) complexes with methylene-bis-(1,1'-dicyano-2-phenyl-2'-methyl ethylacrylate):

The four cobalt(II) complexes reported in the present investigation have the composition \([\text{CoL}_2X_2]\) where \(L = \text{methylene-bis-}(1,1'-\text{dicyano-2-phenyl-2'-methyl ethylacrylate})\) and \(X = \text{Cl, Br, NO}_3, \text{ClO}_4\). The complexes are green, brown or yellowish grey in colour, have high melting points and low conductance values (Table 1) in acetone medium indicating non-electrolytic nature of the complexes. The complexes have high \(\mu_{\text{eff.}}\) values suggesting spin-free octahedral stereochemistries.

The i.r. spectra of the ligand and the complexes are quite informative. The appearance of the band at 1720 cm\(^{-1}\) in the ligand is attributable to \(\gamma(\text{C}=\text{O})\) vibration. On complexation, this frequency is shifted down to lower frequency region 1700 cm\(^{-1}\) indicating the coordination of the ligand through esteric carbonyl oxygen atom (Diagram 17). The weak band observed at 2230 cm\(^{-1}\) in the ligand corresponds to \(\gamma(\text{C}≡\text{N})\) vibration. Decrease of this frequency to 15-20 cm\(^{-1}\) in case of metal complexes shows the cyano nitrogen bonding to the metal ion. Further, when both the cyano-nitrogen and esteric carbonyl oxygen atoms are bonded to the metal ions, \(\text{C}≡\text{C}\) may be polarised and \(\gamma(\text{C}≡\text{C})\) should be shifted to lower frequency region. The band observed around 1625 cm\(^{-1}\) in the ligand may be assigned to \(\gamma(\text{C}≡\text{C})\) vibration and polarisation of the bond was noticed in metal complexes. Further, the conclusive evidence of bonding of potential donor atoms have been obtained by the occurrence of \(\gamma(\text{Co-O})\) and \(\gamma(\text{Co-N})\) around 450 and around 360 cm\(^{-1}\) respectively. The free perchlorate ion has four fundamental vibrations, viz. \(\gamma_1, \gamma_2, \gamma_3\) and \(\gamma_4\). Isolated \(\text{ClO}_4^-\) ions indeed show only two absorptions in the infrared due to \(\gamma_3\) (at 1100 cm\(^{-1}\)) and \(\gamma_4\) (at \(\sim 620\) cm\(^{-1}\)). The Td
Graph 14: [CoL(cla\textsubscript{4})\textsubscript{2}]

L = methylene-bis-(1,1-dicyano-2-phenyl-2'-methyl ethylacrylate)

Graph 15: [CoL(cla\textsubscript{4})\textsubscript{2}]

L = N,N'-bis-(acetoacetanilide) ethylenediamine
symmetry of the free ClO$_4$ ion is lowered$^{72,73}$ to $C_{3v}$ and $C_{2v}$ symmetry upon monodentate and bidentate (chelating as well as bridging) coordination respectively. In case of perchlorate complex under report, two prominent bands are observed at 1100 cm$^{-1}$ and 1000 cm$^{-1}$ which support the coordination$^{9,74}$ of the perchlorate group to the Co(II) ion in conformity with conductance data. In case of nitrate complex, the absence of $\gamma_3$ band of ionic nitrate (D$_{3h}$) around 1360 cm$^{-1}$ and occurrence of two strong bands at 1470 cm$^{-1}$ ($\gamma_1$) and at 1250 cm$^{-1}$ ($\gamma_4$) suggests the monodentate coordination of nitrato group$^{9,75-78}$ and hence an octahedral structure for the complex in conformity with earlier observations corroborated by the conductance data. Graph 14.

In the electronic spectra of the complexes, absorption bands are observed around 20,200 ($\gamma_3$) (36), 18,500 ($\gamma_2$) (32) and 8900 ($\gamma_1$) (15) cm$^{-1}$ regions attributable to $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow ^4A_{2g}$ and $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ transitions respectively. The ligand field parameters, Racah parameter ($B$), naphalaxetic parameter ($\beta_{35}$), transition energy ratio ($\gamma_2/\gamma_1$), 10 $D_q$ and $D_q/B$ have been calculated using the equations derived from the matrices of Tanabe and Sugano. The electronic spectral band positions, high magnetic moment values and the values of spectral parameters suggest an spin-free octahedral or distorted-octahedral configuration for these cobalt(II) complexes$^{79,80}$. 
2. Cobalt(II) complexes with ONNO tetradeutate N,N'-bis-(acetoacetanilide)ethylenediamine:

The complexes reported in the present investigation are of the type \([\text{CoLX}_2]\) where \(L = \text{N,N'-bis-(acetoacetanilide)ethylene diamine}\) and \(X = \text{Cl, Br, NO}_3, \text{ClO}_4\). The complexes are green, pink and yellowish-pink in colour. All the four complexes are non-electrolytes, as evident from low \(\Lambda_M\) values and have \(\mu_{\text{eff}}\) values around 5.0 B.M. suggesting a spin-free octahedral configuration for the complexes.

The ligand can exist in two tautomeric forms, ketoamine(18) and ketoimine(19). Holm et al. studied\(^\text{81}\) the p.m.r. spectra of \(\text{N,N'-ethylenebis-(acetylacetoneimine)}\) and \(\text{N,N'-ethylene bis-(benzoylacetoneimine)}\) and concluded that they exist mostly (> 95 \%) in ketoamine form. The possibility of ketoimine form was ruled out on the basis of low value of \(\text{C=O}\) stretching frequency in the i.r.

![Diagram 18]

![Diagram 19]

spectra and the absence of signal for the \(\alpha\)-methylene protons in the p.m.r. spectra. The ligand, \(\text{N,N'-bis-(acetoacetanilide)ethylene diamine}\), exists almost exclusively in the ketoamine form\(^\text{82}\). The strong absorption appearing at 3300 cm\(^{-1}\) can be ascribed to \(\gamma(\text{NH})\) of ethylenediamine moiety. The shift of about 200 cm\(^{-1}\) from the free NH band indicates that the two NH groups are intramolecularly hydrogen bonded. The band at 1645 cm\(^{-1}\) in the free ligand can be
ascribed to \( \gamma(C=O) \) vibration. The shift of around 15 cm\(^{-1}\) from the amidic C=O of 1660 cm\(^{-1}\) is also in agreement with the moderate intramolecular hydrogen bonding in the compound. The band appearing at 1600 cm\(^{-1}\) may be assigned to \( \gamma(C=C) \) vibration. In metal complexes splitting of \( \gamma(NH) \) band occurs indicating the bonding of ketoamine N-atoms to the metal ions. The shifting of \( \gamma(C=O) \) vibration occurs towards lower frequency region, \( \sim 1630 \text{ cm}^{-1} \), indicative of amidic carbonyl oxygen coordination to the metal ions. Furthermore, the conclusive evidence of bonding is provided by the occurrence of \( \gamma(Co-O) \) and \( \gamma(Co-N) \) around 480-445 and \( \sim 520 \text{ cm}^{-1} \) respectively in the far i.r. spectra of the complexes\(^{71}\). In case of Co(II) perchlorate complex two sharp bands are observed in 1000-1100 cm\(^{-1}\) regions which indicates that the perchlorate group is a coordinated\(^{72-74}\) one in conformity with conductance data. Strong absorption bands are observed at 1460 and 1230 cm\(^{-1}\) in Co(II) nitrate complex, suggesting unidentate coordination\(^{9,24,75-78}\) of the nitrate group and hence an octahedral structure for the complex. Graph 15.

Cobalt(II) complexes in octahedral environment should have three spin-allowed d-d transitions\(^{83}\). The complexes under report exhibit electronic spectral bands around 20,000, 17500 and 8500 cm\(^{-1}\) attributable to \( 4T_{1g}(F) \rightarrow 4T_{1g}(P)(\gamma_3) \), \( 4A_{2g}(F)(\gamma_2) \) and \( 4T_{2g}(F)(\gamma_1) \) transitions respectively. The ligand field parameters such as Racah parameter (B), naphalauxetic parameter (\( \beta_{35} \)), transition energy ratio (\( \gamma_2/\gamma_1 \)), 10 D\(_q\) and D\(_q/B\) have been calculated using the equations derived from the matrices of Tanabe and Sugano. The electronic spectral band positions, magnetic moment values, and spectral parameters indicate an octahedral\(^{84}\) coordination for Co(II) complexes.
3. Cobalt(II) complex with tetradeptate Schiff base \(N,N'-\text{bis-(benzoin)}1,2\text{-diaminopropane} \):

Cobalt(II) complex under report has the composition \([\text{Co}L\text{\textsubscript{2}}\text{H}_{2}\text{O}]\) where \(L\) is the title ligand. The complex is deep reddish-brown in colour and non-electrolytic in nature as evident from low molar conductance value in dimethylformamide medium. Magnetic moment value of the Co(II) complex is 5.0 B.M., suggesting an octahedral environment.

The Schiff base can function as a tetradeptate ligand using two hydroxyl groups and two imine nitrogen atoms as potential bonding sites. Assignments have been made for the two principal bands i.e. \(\gamma(C-O)\) and \(\gamma(C=N)\) in the i.r. spectrum. The C-O vibration in alcohols usually occurs in the 1260-1000 cm\(^{-1}\) region and appears in the ligand at 1205 cm\(^{-1}\) and is shifted to 1190 cm\(^{-1}\) in Co(II) complex. A lowering of the C-O frequency in the complex indicates that the ligand is bonded to the metal through oxygen. The stretching vibration of unchibed -OH group appears as a strong absorption band in the 3600 cm\(^{-1}\) region. A shift of this band to lower frequency region is accepted as a criterion for the presence of hydrogen bonding. In the ligand under report \(\gamma(\text{OH})\) appears at 3390 cm\(^{-1}\) as a broad and medium strong band which may be due to strong intramolecular O-H...N hydrogen bonding. The absence of this band in the Co(II) complex indicates the deprotonation of the alcoholic groups and the consequent dibasic nature of the ligand molecule. In the spectrum of the ligand \(\gamma(C=N)\) appears at 1655 cm\(^{-1}\) which has been shifted down to lower frequency due to coordination of imine nitrogen atoms to the Co(II) ion. In the complex under report, the presence of coordinated water molecules is shown by a broad double hump around 3400 cm\(^{-1}\) and
and an additional peak around 840 cm\(^{-1}\). The conclusive evidence of bonding of the ligand molecule with the metal ions is provided by the bands at 450 and at 510 cm\(^{-1}\) attributable\(^{71}\) to \(\gamma\)(Co-O) and \(\gamma\)(Co-N) vibrations respectively.

The electronic spectra of the Co(II) complex exhibits bands at 8800 (9.5), 18,500 (24), 20,000 (29) and 25,500 cm\(^{-1}\). The position and intensities of the first three bands suggest some amount of tetragonal distortion and can be attributed\(^{82}\) to transitions \(4T_{1g}(F) \rightarrow 4T_{2g}(F), \rightarrow 4A_{2g}(F), \rightarrow 4T_{1g}(P)\) respectively. The fourth band most probably results from charge-transfer transitions. The ligand field parameters like \(B\) (806 cm\(^{-1}\)), \(\beta_{35}\) (8.4), \(\gamma_{2}/\gamma_{1}\) (2.13), \(10D_{q}\) (9700 cm\(^{-1}\)) and \(D_{q}/B\) (1.20) have been calculated using the equations of Tanabe and Sugano. The electronic spectral band positions, high magnetic moments and the values of spectral parameters indicate an octahedral geometry for the Co(II) complex.

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of cobalt(II) complex has been studied. The complex is found to be fairly stable at room temperature. It starts losing water molecules, one at 100\(^{o}\)C and the other at 220\(^{o}\)C. The mass loss corresponding to the first endothermic peak and second exothermic are 3.10 \(\%\) and 6.05 \(\%\) respectively. Thereafter the complex loses its mass gradually with the rise of temperature and at 360\(^{o}\)C, a sharp exothermic peak is observed in the DTA curve which can be ascribed to the loss of a quarter of the ligand molecule. The sharp exothermic peak at 430\(^{o}\)C corresponds to the mass loss of 34.05 \(\%\) against the calculated value 34.23 \(\%\) indicating the loss of \(\frac{1}{3}\)rd of the ligand molecule. Thereafter, a mass loss of 82.50 \(\%\) is observed at 860\(^{o}\)C by the endothermic peak on DTA curve which corresponds to the formation of CoO. Graph 16.
The alcoholic C-O vibration appears at 1210 cm\(^{-1}\) in the ligand and shifted down to lower frequency region 1200 cm\(^{-1}\) indicating the coordination of the ligand with the metal ion through the alcoholic oxygen atoms. Compounds containing C=N group such as Schiff base, oximes, imminocarbonates, thiazole and guanidine etc. have \(\gamma(C=\text{N})\) in the 1690-1470 cm\(^{-1}\). In the ligand, this band appears at 1600 cm\(^{-1}\).
GRAPH.17  \[ \text{CO}_2 \text{L}_2 \text{4H}_2\text{O} \]

\[ \text{L} = \text{N, N'-bis-(benzoin) m-phenylenediamine} \]
On complexation shifting of this band occurs to lower frequency region 1590 cm\(^{-1}\), due to reduction of electron density in the azomethine link, as the imino nitrogen atoms coordinate\(^{85,86}\) to the metal ions. The band observed at 1560 cm\(^{-1}\) both in the ligand and the complex is assigned to ring breathing vibrations of the phenyl ring. The ligand shows sharp band of medium intensity at 1250 cm\(^{-1}\) attributable to \(\nu (C-N)\) mode which consistently shifts towards lower frequency side and appears near 1240 cm\(^{-1}\) with a reduced intensity in the metal complex. Further, the \(\sigma (O-H)\) appears at 1445 cm\(^{-1}\) and \(\gamma (O-H)\) at 3350 cm\(^{-1}\) as a relatively sharp band, lowered due to intramolecular hydrogen bonding in the ligand. In case of the complex, the presence of coordinated water is ascertained by the observation of broad double hump around 3450 cm\(^{-1}\) which is further confirmed\(^{87,88,94}\) by an additional peak at 625 cm\(^{-1}\) in the complex. However, the conclusive evidence of bonding of oxygen and nitrogen atoms have been provided by the occurrence\(^{71}\) of \(\gamma (Co-O)\) and \(\gamma (Co-N)\) at 450 cm\(^{-1}\) and 510 cm\(^{-1}\) respectively. Graph 17.

In the electronic spectrum of cobalt(II) complex, the absorption bands at 8,500 (10), 18,000 (25) and 19,500 (30) cm\(^{-1}\) have been observed attributable to \(4T_{1g} (F) \rightarrow 4T_{2g} (F), \rightarrow 4A_{2g} (F), \rightarrow 4T_{1g} (P)\) transitions respectively in conformity with an octahedral environment\(^{80}\) around the Co(II) ion. Sub-normal magnetic moment, spectral position, high melting point and sparing solubility in common organic solvents support the binuclear structure of the Co(II) complex as represented by the Diagram 20.

![Diagram 20]
2. Cobalt(II) complexes with tridentate schiff bases

Complexation behaviour of a number of tridentate dibasic ligands with a variety of metal (II and III) ions have been reported in recent years. These ligand force the metal ions to form poly-metallic complexes with uncommon structural and magnetic properties. Therefore it was thought worthwhile to synthesise two new tridentate biprotic schiff bases by reacting benzoin with 2-amino-2-methyl-1-propanol and 1-amino-2-propanol and the complexing ability of these two ligands with Co(II) ion has been studied.

Two cobalt(II) complexes under report in the present investigation have the compositions \( \text{Co}_2L_2\cdot4\text{H}_2\text{O} \) and \( \text{Co}_2L'\cdot4\text{H}_2\text{O} \) where \( L\text{H}_2 \) and \( L'\text{H}_2 \) are the tridentate biprotic schiff bases derived from benzoin with 2-amino-2-methyl-1-propanol and 1-amino-2-propanol respectively. The complexes are black and violet in colour, amorphous, high melting points and donot dissolve in common organic solvents but slightly soluble in dimethylformamide. Low conductance values in D.M.F. indicate the non-electrolytic nature of the complexes. The analytical data indicate a 1:1 (metal:ligand) stoichiometry and hence the schiff bases act as dibasic tridentate ligands. In the i.r. spectra of the ligands, a band of medium intensity around 2750 cm\(^{-1}\) may be assigned to intramolecularly hydrogen bonding (\( \nu \text{ O-H} \)). In the spectra of the complexes, absence of this band indicates the deprotonation of the alcoholic groups and the consequent dibasic behaviour of the schiff bases. The structure of the ligands show that the bridging must take place through any one of the alcoholic oxygen atom. The \( \nu \text{(C-O)} \) vibration appears at 1195 cm\(^{-1}\) in the ligand \([\text{BnAMPH}_2]\) and at 1220 cm\(^{-1}\) in \([\text{BnAPH}_2]\) and it undergoes a positive
LH₂ = Schiff base derived from benzoin with 2-amino-2-methyl-1-propanol

LH₂ = Schiff base derived from benzoin with 1-amino-2-propanol
shift of 10-20 cm\(^{-1}\) and this is due to the formation of the \(\text{M} \overset{\text{O}}{\text{O}} \text{M}\) bridge in conformity with earlier observation.\(^{99}\) In the spectra of the ligands, bands at 1670 cm\(^{-1}\) \([\text{BnAMPH}_2]\) and 1620 cm\(^{-1}\) \([\text{BnAPH}_2]\) can be assigned to \(\nu(C=N)\) vibration. In the metal complexes these bands are observed around 1620 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively. This lowering of \(\nu(C=N)\) frequency in the complexes in comparison to the free ligand values indicates coordination\(^{85,86}\) of azomethine group of the schiff bases through the nitrogen atom. The presence of coordinated water molecules is ascertained by the observation of a broad double hump around 3400 cm\(^{-1}\). This is further confirmed by an additional peak around 820 cm\(^{-1}\) in the complexes.\(^{87,88,94}\) However, the conclusive evidence regarding the bonding of the potential donor atoms of the schiff bases with the Co(II) ions have been provided by the bands ~450 and ~510 cm\(^{-1}\) attributable \(^{71}\) to \(\nu(\text{Co-O})\) and \(\nu(\text{Co-N})\) vibrations respectively. Graph 18 and 19.

The magnetic moments of the two Co(II) complexes lie in the range 2.80-2.85 B.M. Nyholm and Figgis have reported\(^{100}\) that low spin octahedral complexes possess magnetic moments in the range 1.8-2.9 B.M. Electronic spectra of the complexes exhibit bands at 8500(10), 18,000(25), 19,500(30) and 26000 cm\(^{-1}\) and at 8,200(8), 18,500(27), 19,700(35) and 26,300 cm\(^{-1}\) respectively. The positions and intensities of the first three bands in case of two complexes suggest some amount of tetragonal distortion and can be attributable to the transitions \(^{4T_{1g}}(F) \rightarrow ^{4T_{2g}}(F), \rightarrow ^{4A_{2g}}(F), \rightarrow ^{4T_{1g}}(P)\) respectively, for an approximately octahedral field around low-spin Co(II) ion. The band ~26,000 cm\(^{-1}\) most probably results from either intra-ligand or charge-transfer transitions.

Subnormal magnetic moments, spectral positions, high melting
points and sparing solubility in common organic solvents support binuclear structure of the Co(II) ion. So on the basis of above formulations, we propose a dimetallic structure with alcoholic oxygen bridge [Diagram 21].

[Diagram 21]

3. Cobalt(II) complex with the schiff base [BnOAPH₂] :

The cobalt(II) complex has the composition Co₂L₂·4H₂O where LH₂ = tridentate schiff base derived from benzoin with o-aminophenol. The complex is pink in colour, possess high melting point and insoluble in common organic solvents but sparingly soluble in dimethylformamide. Non-electrolytic nature of the complex is indicated by the low \( \Lambda_m \) value in dimethyl formamide. The complex shows a magnetic moment of 2.9 B.M. in conformity with earlier observation for polynuclear Co(II) complex.

In the i.r. spectrum of the ligand and the complex the principal bands like \( \gamma(C=O), \gamma(C-O), \gamma(O-H), \gamma(Co-O) \) and \( \gamma(Co-N) \) have been assigned. The structure of the ligand shows two types of OH groups, one phenolic and the other alcoholic. Hence bridging can take place either through phenolic oxygen or alcoholic oxygen atom. Harris et al. and Jonassen et al. have earlier suggested that the shift of the \( \gamma(C-O) \) band of the ligand (1520 cm\(^{-1}\)) to higher frequency region by 20 cm\(^{-1}\) on complexation indicates the formation
of phenolic oxygen bridge in dinuclear complexes. Here we observe an increase of C=O frequency by 30 cm\(^{-1}\) in the Co(II) complex which shows the presence of phenolic oxygen atom bridge. The \(\gamma(C=O)\) vibration (alcoholic) undergoes a negative shift of 10 cm\(^{-1}\) in the Co(II) complex. This lowering of frequency of C=O band indicates the coordination of alcoholic oxygen atom to the metal ion. In the ligand \(\gamma(C=N)\) appears at 1610 cm\(^{-1}\) and in the complex, shifting of this band to lower frequency region is observed at 1600 cm\(^{-1}\) and this may be ascribed due to reduction of electron density in the azomethine link as the imino nitrogen atom is bonded\(^{85,86}\) to the Co(II) ion. The band observed at 1550 cm\(^{-1}\) both in the ligand and in the metal complex is assigned to ring breathing vibration of the phenyl ring. The ligand shows a sharp band of medium intensity at 1250 cm\(^{-1}\) attributed to \(\gamma(C-N)\) vibration which consistently shifts towards lower frequency region and appears near 1240 cm\(^{-1}\) with a reduced intensity in the metal complex. Further \(\gamma(O-H)\) appears around 3400 cm\(^{-1}\) as a relatively sharp band and \(\sigma(O-H)\) at 1445 cm\(^{-1}\) indicative of the presence of intramolecularly hydrogen bonding in the ligand. In the complex the presence of coordinated water molecules is observed\(^{87,88}\) by the appearance of a broad double hump around 3450 cm\(^{-1}\) and an additional peak around 825 cm\(^{-1}\). The conclusive evidence of bonding of the ligand moiety to the Co(II) ion is provided by the occurrence\(^{71}\) of \(\gamma(C-O)\) and \(\gamma(C-O)\approx 450\) cm\(^{-1}\) and \(\approx 510\) cm\(^{-1}\) respectively in the far i.r. spectra of the metal complex.

In the electronic spectrum of Co(II) complex, the absorption bands at 8300(10), 18,200(26) and 19,700(32) cm\(^{-1}\) have been observed, assignable to \(4T_{1g}(F) \rightarrow 4T_{2g}(F)\), \(4A_{2g}(F)\) and \(4T_{1g}(P)\) transitions respectively in conformity with an octahedral environment.
Sub-normal magnetic moments, spectral positions, high m.p. and sparing solubility in common organic solvents support a binuclear structure of the Co(II) complex which can be represented by the following Diagram 22.

(C) Cobalt(II) complexes with tri- and bidentate ligands:

1. Cobalt(II) complexes with semicarbazone and thiosemicarbazone:

Semicarbazone and thiosemicarbazone of aldehydes and ketones have attracted special attention because of their potential antitubercular, antiprotozoal and antiviral activities. A metal chelate of thiosemicarbazone is also used in cancer treatment. In view of their significant biological activities, it is thought worthwhile to synthesise new semicarbazone and thiosemicarbazone of benzoin and their complexation behaviour with divalent metal ions have been studied.

Complexes reported in the present investigation are of the types [CoLClB₂] and [Co'LClB₂], where LH and L'H are benzoin-semicarbazone and benzoin-thiosemicarbazone respectively, B = H₂O. The two Co(II) complexes are pink in colour, have melting points above 250°C and low conductance values indicating the non-electrolytic nature of the complexes. Magnetic moment of Co(II) complexes show
GRAPH.20
[CoCl\textsubscript{2}H\textsubscript{2}O]  
LH = benzoin semicarbazone

GRAPH.21
[CoCl\textsubscript{2}H\textsubscript{2}O]  
LH = benzoin thiosemicarbazone
the presence of three unpaired electrons suggesting a high-spin octahedral configuration for these complexes.

The i.r. spectra of the ligands and the metal chelates are quite illustrative. The ligands can function as tridentate chelates with the hydroxy oxygen, carbonyl oxygen or thiocarbonyl sulphur and the imino nitrogen atoms as the potential bonding sites. \( \gamma(C=S) \) in the free ligand occurs at 1085 cm\(^{-1} \) which shifts in the complexes to slightly lower frequency indicating bonding through the thiocarbonyl sulphur atom. The appearance of a sharp peak at 1670 cm\(^{-1} \) in the free ligand is attributable to a \( \gamma(C=O) \) vibration. In the complexes, this band has been shifted to lower frequency (i.e. \( \sim 1660 \) cm\(^{-1} \)) which indirectly supports the bonding of carboxyl oxygen atom to Co(II) ion. \( \gamma(C=N) \) observed at 1590 cm\(^{-1} \) in the free ligand decreases by 15 cm\(^{-1} \) in the complexes and this implies the coordination of the imino nitrogen atom of the azomethine link to the metal ions. In the ligands, the appearance of a band at 1200 cm\(^{-1} \) due to \( \gamma(C=O) \) has shifted down to \( \sim 1190 \) cm\(^{-1} \) in the Co(II) complexes. In case of the two Co(II) complexes a broad hump is observed at \( \sim 3450 \) cm\(^{-1} \) indicating the presence of coordinated water. However, evidence of the mode of bonding is obtained by the occurrence of bands \( \sim 220 \) cm\(^{-1} \), \( \sim 260 \) cm\(^{-1} \), \( \sim 350 \) cm\(^{-1} \) and \( \sim 450 \) cm\(^{-1} \) which correspond to \( \gamma(C-O) \), \( \gamma(C-S) \), \( \gamma(C-N) \) and \( \gamma(C-O) \) respectively.

Two absorption bands were observed in the visible electronic spectra of the Co(II) complexes at 20,000(28) and 8,500(15) cm\(^{-1} \) regions, assignable to \( 4T_{1g}(F) \rightarrow 4T_{1g}(P) \) and \( 4T_{2g}(F) \) transitions respectively, the other transition being unobserved due to its nearness and closeness due to the \( 4T_{1g}(P) \) transition.

The metal chelates are represented by the following Diagrams 23 and 24. Graph 20 and 21.
2. Cobalt(II) complexes with chelating hydrazones:

Study of literature reveals that various hydrazones possess strong bactericidal, herbicidal, insecticidal and fungicidal properties. Katyal and Dutta have studied the analytical application of hydrazones. A few hydrazones have also been used for the detection and determination of metal ions gravimetrically. Keeping these observations in view, we have synthesised phenylhydrazone and 2,4-dinitrophenylhydrazones of benzoin and studied their complexing ability with divalent metal ions.

The two pink coloured cobalt(II) complexes have the composition [CoL₂B₂] and [CoL'₂B₂], where LH and L'H are hydrazones derived from benzoin with phenyl hydrazine and 2,4-dinitrophenylhydrazine respectively. The complexes have low molar conductances in acetone medium indicating non-electrolytic nature. The magnetic moment values show the presence of three unpaired electrons.

The ligand molecules possess two potential donor sites namely, the hydroxylic oxygen and the hydrazinic nitrogen atoms. In the ligands $\gamma(C=\text{N})$ appears at 1600 cm$^{-1}$ (in case of phenylhydrazone) and at 1615 cm$^{-1}$ (in case of 2,4-dinitrophenylhydrazine). In the Co(II) complexes a decrease of 10-15 cm$^{-1}$ indicates the bonding of hydrazinic nitrogen atom to the metal ions. The appearance of the band at 1210 cm$^{-1}$ in the ligands can be attributed to $\gamma(C=\text{O})$ vibration. This band has been shifted down to lower frequencies.
(\sim 1200 \text{ cm}^{-1}) \text{ in the chelates showing the coordination of hydroxylic oxygen atom to metal ions. The ligands as well as metal chelates have two absorption bands \sim 3350 \text{ cm}^{-1} \text{ region assignable to } \tilde{\gamma}(N-H) \text{ in the } 1500-1600 \text{ cm}^{-1} \text{ region assignable to } \sigma(N-H) \text{ vibration which shows the non-coordination of secondary amino group with the Co(II) ions. In the Co(II) complexes the presence of coordinated water is confirmed}^{87,88} \text{ by the observation of a broad double hump around 3450 cm}^{-1}. \text{ However, the conclusive evidence of bonding of oxygen and nitrogen atoms have been provided by the occurrence}^{71} \text{ of } \tilde{\gamma}(Co-O) \text{ and } \tilde{\gamma}(Co-N) \text{ around 450 and around 360 cm}^{-1} \text{ regions respectively in the complexes.}

Absorption bands appear at 6000(15) and 20,500(19) \text{ cm}^{-1} \text{ assignable}^{80} \text{ to } 4_{1g}(F) \rightarrow 4_{2g}(F), \rightarrow 4_{1g}(P) \text{ transitions respectively. Three transitions are expected for Co(II) complexes of } O_h \text{ symmetry. The } 4_{1g}(F) \rightarrow 4_{2g}(F) \text{ transition involving a two-electron process gives rise to a weak band on the high frequency side of the } 4_{1g}(P) \text{ band. The low intensity combined with closeness to } 4_{1g}(P) \text{ transition renders it unobservable in the present case.}

The complex compounds can be represented by the following Diagrams 25 and 26.

[Diagram 25]  [Diagram 26]
3. Cobalt(II) complex with the schiff base [BnAH] :

The pink coloured cobalt(II) complex is of the type 
\[ \text{[CoL}_2\text{B}_2] \], where LH = schiff's base derived from benzoin with aniline, 
B = H,0. The complex has fairly low melting point and low conductance value indicating non-electrolytic nature of the complex. Magnetic moment value is 4.85 B.M. showing the presence of three unpaired electrons.

The schiff base can function as a bidentate ligand with the hydroxy oxygen and imino nitrogen atom as the principal bonding sites. The \( \gamma(\text{C-O}) \) vibration in the ligand appears at 1210 cm\(^{-1}\). The decrease of this frequency by 10 cm\(^{-1}\) in the metal chelate shows the bonding of hydroxylic oxygen atom to the Co(II) ion. Coordination of the azomethine nitrogen atom to the metal ion is probably indicated by the shift of \( \gamma(\text{C=N}) \) frequency towards the lower side. In the i.r. spectrum of the schiff base, strong band due to \( \gamma(\text{C=N}) \) appears at 1600 cm\(^{-1}\) whereas in the complex this band is observed at 1590 cm\(^{-1}\). In case of Co(II) complex a broad hump is observed at 3450 cm\(^{-1}\) followed by another peak at 820 cm\(^{-1}\), indicative of the presence of coordinated water\(^{87,88}\).

Cobalt(II) complex exhibits two bands at 21,000(26) and 9,000(10) cm\(^{-1}\) attributable\(^{80}\) to \( ^4T_{1g}(F) \rightarrow ^4T_{1g}(P), \rightarrow ^4T_{2g}(F) \) transitions respectively. Molar absorptivity values, position of absorption bands and magnetic moment value indicate a high-spin octahedral configuration for the Co(II) complex.

4. Cobalt(II) complexes with dithioxamide :

Among the ligands having > C = O group as the donor site, the amides and lactams are particularly interesting since these molecules possess also an amine group, which potentially may act as
a donor to the metal ion. However, with transition metal ions thus for only compounds have been isolated that contain oxygen coordinated lactams and amides. This was concluded from i.r. spectra (shift to lower frequencies of the C=O stretching vibration). In our attempt to study complexes with ligands containing both sulphur and nitrogen as the bonding sites, we now report complexes of dithiooxamidewith several divalent metal ions.

Cobalt(II) complexes reported in the present investigation have the composition \([\text{CoL}_2X_2]\), where \(L = \text{dithiooxamide}, X = \text{Cl, SCN}\). Co(II) complexes are deep violet in colour, have fairly low melting points, are soluble in acetone in which medium the \(\Delta M\) values are very low indicating non-electrolytic nature of the complexes. Magnetic moment measurement indicates Co(II) complexes to be paramagnetic, \(\mu_{\text{eff}}\) values suggest a possible octahedral environment around the metal ions.

I.R. spectra of dithiooxamide and its cobalt complexes have been studied in detail. Usually thiocarbonyl absorption occurs in the 1020-1250 cm\(^{-1}\) region but the carbon is also linked to nitrogen, several other bands appear in the 1560-700 cm\(^{-1}\) region due to coupling of C=S and C-N absorption bands. In the present case dithiooxamide has prominent bands in the 3200-3100, 1500-1600, 1205 and 700-800 cm\(^{-1}\) region. In the Co(II) complexes there are several bands in the 3300-3100 cm\(^{-1}\) region due to modification and splitting of \(\gamma(\text{N-H})\) indicating coordination through the nitrogen of the \(-\text{NH}_2\) group. Also the band at 1205 cm\(^{-1}\) attributable to \(\gamma(\text{C=S})\) appear at lower frequency region in complexes suggesting coordination through the sulphur atom of the thiocarbonyl group. Further, the two sharp bands at 1600 and 1580 cm\(^{-1}\) region go to higher frequency region in the complexes. Bonding through sulphur and nitrogen has been substantiated by observation of
\( \gamma(\text{Co-N}) \) and \( \gamma(\text{Co-S}) \) at around 350 and around 260 cm\(^{-1} \) regions respectively in the low frequency i.r. spectra of the complexes.

In the case of thiocyanato complex, observation of \( \gamma(\text{C=N}) \) at 2090 cm\(^{-1} \) indicates terminal N-bonding of the thiocyanato group.

In the U.V. spectra of the ligand and complexes, two bands appear in the 215 and 312 nm region presumably due to \( \pi \rightarrow \pi^* \) and \( n \rightarrow \sigma^* \) transitions in the C=S group usually occurring in the 250-320 nm region. In addition, there may be bands due to \( n \rightarrow \pi^* \) transition of the thiocarbonyl group. Since the two bands obtained are broad, it might have been due to all these three possible transitions. Two absorption bands are noticed around 550(16) and around 1210(12) nm regions attributable to \( ^5T_{2g}(F) \rightarrow ^4T_{1g}(F), ^4T_{1g}(P) \rightarrow ^4T_{2g}(F) \) transitions respectively. Magnetic moment values of around 4.8 B.M. indicate a possible octahedral configuration for these complexes.

5. Ethyle-1-phenyl-2-cyanoacrylate complexes of cobalt(II):

Cobalt(II) complexes are brown to chocolate brown in colour and are of the general composition \([\text{CoL}_2X_2]\), where \( L = \text{ethyl-1-phenyl-2-cyanoacrylate}, X = \text{Cl, Br, NO}_3, \text{SCN, SeCN} \). The conductance measurements in acetone medium indicate that all the complexes are non-electrolytic in nature. All the Co(II) complexes exhibit normal magnetic moments 4.9 - 5.1 B.M.

The appearance of the band at 1605 cm\(^{-1} \) in the ligand is attributable to \( \gamma(\text{C=O}) \) vibration. On complexation, this frequency shifts down to lower frequency region around 1595 cm\(^{-1} \) indicating coordination of the ligand through esteric carbonyl oxygen atom. The weak band observed at 2200 cm\(^{-1} \) in the ligand corresponds to \( \gamma(\text{C=N}) \) vibration. Decrease of this frequency to 10-15 cm\(^{-1} \) in case of the complexes shows the cyano nitrogen bonding to metal ions.
Further, when both the cyano-nitrogen and esteric carbonyl oxygen atoms are bonded to Co(II) ions, C=C may be polarised and $\gamma(\text{C}=\text{C})$ should be shifted to lower frequency region. In case of nitrate complex, the i.r. bands are observed at 1475 and 1260 cm$^{-1}$ suggesting$^9,75,76$ the unidentate coordination of the nitrate group and hence an octahedral structure for the complex. The thiocyanate and selenocyanate anions can coordinate through both the N- and S- or Se- end and thus function as ambidentate ligands. The CoL$_2$(SCN)$_2$ and CoL$_2$(SeCN)$_2$ complexes exhibit C=N stretching frequencies around 2040 cm$^{-1}$ indicating the formation$^{112,113}$ of terminal N-bonded pseudohalides. However, conclusive evidence of bonding is provided by the occurrence$^7$ of $\gamma$(Co-O) and $\gamma$(Co-N) around 450 and around 510 cm$^{-1}$ respectively.

Electronic spectra of Co(II) complexes show$^80$ three absorption bands around 8,700, around 18,500 and around 19,500 cm$^{-1}$ regions assignable to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F), \rightarrow ^4A_{2g}(F), \rightarrow ^4T_{1g}(P)$ transitions respectively. Band positions and extinction coefficient values indicate a high-spin octahedral stereochemistry for the complexes corroborated by the magnetic moment values.

(D) Mixed ligand complexes of cobalt(II):

The mixed ligand complexes reported here are of the type [CoL$_2$L$'$] and [CoL$_2$L$''$] where LH = oxine, L$'$ = pyridine, $\beta$-picoline, $\gamma$-picoline, quinoline, piperidine, 2,6-lutidine, 4-aminopyridine, quinaldine, morpholine, L$''$ = o-phenylenediamine, 1,10-phenantholine and 2,2'-bipyridine. The complexes show low conductance values in acetone medium indicating non-electrolytic nature of the complexes.

I.R. spectra of the ligand, cobalt oxinate and mixed ligand complexes are informative. The i.r. active bands at 1500 cm$^{-1}$,
1280 cm\(^{-1}\) and 900 cm\(^{-1}\) can be assignable to the phenolic OH deformation modes coupled with C-O stretching modes (\(\gamma_{\text{CO}} + \gamma_{\text{OH}}\)) and to the out of plane deformation vibration (\(\sigma_{\text{OH}}\)) respectively. The absence of these bands in case of cobalt oxinate indicates that the proton of the hydroxyl group is replaced by the Co(II) ion. The bands found at 1450 cm\(^{-1}\), 1260 cm\(^{-1}\), 1095 cm\(^{-1}\) and 1060 cm\(^{-1}\) in the spectra of both heterocyclic ligands and mixed ligand complexes are characteristic\(^{114}\) of substituted pyridine ring vibration. A medium broad band appears at around 3450 cm\(^{-1}\) region in case of cobalt oxinate assignable\(^{87}\) to \(\gamma(\text{O-H})\) of coordinated water molecules present and its conspicuous absence in the mixed ligand complexes support the coordination of nitrogen donor ligands to the metal ions. Graph 22 and 23

The Co(II) complexes in dimethylformamide give rise to two absorption bands with maxima around 8.6 and 19.7 kK regions which can be assigned\(^{80}\) to \(4_{\text{T}_{1g}}(F) \rightarrow 4_{\text{T}_{2g}}(F), \rightarrow 4_{\text{T}_{1g}}(P)\) transitions. These absorption bands along with magnetic moment values indicate a high-spin octahedral configuration for cobalt(II) complexes.

(E) Anionic mixed ligand complexes of cobalt(II):

1. Anionic mixed ligand complexes of cobalt(II) with nitrogen and sulphur donor ligands:

A large number of tetrahalo and tetrapseudohalo anionic complexes of divalent metal ions of the type \([L]_2[MX_4]\) where \(L = \text{tetraalkylammonium cation}\) have been reported\(^{43-48}\) earlier\(^{115,116}\). Study of literature reveals that little effort has been made in this field to change the stereochemistry of these anionic complexes. It is found interesting to synthesise complexes of unusual coordination number particularly coordination number five through complexation of these

Basing upon analysis and conductance data the complexes have the compositions $[B_2][CoCl_4L_2^2]$, $[B_2][CoCl_4L']^2$ and $[B][CoCl_3L'']^2$, where $B = \text{monomethylammonium cation}$, $L = H_2O$, $L' = \text{oxine}$, $L'' = \text{quinaldine, thiourea, piperidylidithiocarbamate, morpholyldithiocarbamate}$. The complexes are pink, blue and olive green in colour. The complexes of the third type are 1:1 electrolytes and the rest are 2:1 electrolytes in acetone medium as evident from their $\Lambda_M$ values. Magnetic moment data of aquo and oxine adducts are 5.0 and 5.1 B.M. respectively, normally expected for octahedral complexes. $\mu_{\text{eff}}$ values of quinaldine and thiourea adducts are found out to be 4.7 and 4.6 B.M. respectively in accordance with tetrahedral stereochemistry. P-dtc, and M-dtc adducts of Co(II) complexes exhibit magnetic moment values in between tetrahedral and octahedral which are in consistent with the pentacoordination of the central metal atom.

Absorption bands are observed in the complexes at 930(vs), 985(s), 1265(vs), 1410(s), 1480(s) and 3150(s) cm$^{-1}$ characteristic of the bands due to monomethylammonium cation. Most of the absorption bands due to free nitrogen donor ligands have been modified in the anionic mixed ligand complexes indicating their bonding to the metal ions. Dithiocarbamate can act as an uninegative bidentate or monodentate ligand. The former exhibits $\gamma(C=S)$ near 1000 cm$^{-1}$ as a single band whereas the latter shows a doublet in the same region. Also bidentate dithiocarbamate moiety exhibits the band $\gamma(C-N)$ above 1420 cm$^{-1}$ whereas in case of monodentate dithiocarbamate, it is observed below 1420 cm$^{-1}$. In the present case, piperidylidithiocarbamate and morpholyldithiocarbamate exhibit $\gamma(C-N)$ band around 1435 cm$^{-1}$ and a singlet at around 1015 cm$^{-1}$ due to $\gamma(C=S)$ indicating the coordination...
of these ligands to the metal ions through both the sulphur atoms in conformity with earlier observations\textsuperscript{119}. The $\nu$(C=O) and $\nu$(C=N) of the oxine nucleus in the complexes appear at 1205 cm\textsuperscript{-1} and 1580 cm\textsuperscript{-1} respectively indicating the coordination of oxine moiety to the metal ions through both the hydroxyl oxygen and endocyclic nitrogen atom. In case of aquo adduct a broad double hump is observed at 3450 cm\textsuperscript{-1} which indicates the presence of water molecules in the complex. Irving and coworkers have argued that the band at 730 cm\textsuperscript{-1} (thiourea) was mainly due to C=S stretching and this shifts consistently to lower frequency region forming metal-sulphur bond. In case of thiourea adduct, a sharp band appears at 715 cm\textsuperscript{-1} which indicates the coordination of thiourea moiety to the Co(II) ion through sulphur atom.

In the electronic spectra of Co(II) complexes with quinoline and thiourea adducts, two bands are observed around 15.5 (1400) and around 8.5 (220) kK regions attributable to $^{4}A_{2} \rightarrow ^{4}T_{1g}(P)$ and $^{4}A_{2} \rightarrow ^{4}T_{1g}(F)$ transitions respectively, the other transition is not observed probably because of its very weak intensity due to orbital selection rule. The high extinction coefficient value of $^{4}A_{2} \rightarrow ^{4}T_{1g}(P)$ and low magnetic moment values support a tetrahedral stereochemistry for the complexes. Two bands are noticed for aquo and oxine adducts of the complexes around 18.5 (35) and around 8.0 (25) kK regions attributable to $^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)$ and $^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)$ transitions respectively. The intensity of $^{4}T_{1g}(P)$ band and high magnetic moment of the complexes suggest a spin-free octahedral configuration. Only one absorption band is observed around 19.2 kK region for P-dtc and M-dtc adducts, the other bands probably being outside the range of spectrophotometer used. Intensity of this band is nearer to that of an octahedral complex, but analysis, conductance and comparatively low magnetic moment value suggest those complexes
to be presumably penta-coordinated in conformity with earlier observation.

2. Some anionic mixed ligand complexes of cobalt(II):

On the basis of analysis and conductance data, the complexes have the compositions \([\text{QH}]_2[\text{CoCl}_4\text{L}_2], [\text{QH}]_2[\text{CoCl}_4\text{L}'],\) and \([\text{QH}][\text{CoCl}_3\text{L}''\text{]}\) where \(\text{QH} = \text{quinaldinium cation, L = Pyridine, } \gamma\text{-picoline, L'} = \text{oxine, } 1,10\text{-phenanthroline, L}'' = \text{quinoline, piperidyldithiocarbamate and morpholyldithiocarbamate.} \) The magnetic moments of cobalt(II) complexes of first and second categories are around 4.9 B.M. suggestive of an octahedral configuration, the quinoline adduct in the third category exhibits \(\mu_{\text{eff}}\) value 4.4 B.M. consistent of tetrahedral environment and the rest two \(P\)-dtc and \(M\)-dtc adducts show the \(\mu_{\text{eff}}\) values around 4.7 B.M. which may be ascribed to penta-coordinated square pyramidal or trigonal bipyramidal geometry around the Co(II) ion. Conductance data indicate that the complexes of the third category are 1:1 electrolytes and rest are 2:1 electrolytes.

When chlorine gas is passed into the suspension of the simple complex of the type \(\text{CoQ}_2\text{Cl}_2\) in ethanol, three possible reactions may take place: (i) oxidation of bivalent cobalt to a higher oxidation state (ii) substitution in the quinaldine ring and (iii) solvolysis of the halogen and consequent addition of the hydrogen halide to the ligand forming quaternary halide. In the present case, definitely halogenation has resulted in the formation of quinaldinium chloride which subsequently reacts with cobalt(II) chloride forming anionic tetrachloro cobaltate(II). This complex further accepts nitrogen and sulphur donor ligands giving rise to complexes of higher coordination numbers five or six.

I.R. spectra indicate the \(\gamma(\text{N-H})\) and \(\sigma(\text{N-H})\) frequencies
GRAPH.24

$[Qd.H]_2 [CoCl_4 (pyridine)_2 ]$
around 3300 and around 1590 cm\(^{-1}\) respectively of quinaldinium cation in conformity with above formulations. Hence it is clear that the anionic complexes are formed involving \([\text{QH}]^+\) cation formed due to solvolytic reaction mechanism. Most of the absorption bands due to free nitrogen and sulphur donor ligands have been modified in the mixed ligand complexes indicating their coordination to the Co(II) ion. In addition, \(\gamma(\text{C=S})\) and \(\gamma(\text{C-O})\) bands have been observed at 1240 cm\(^{-1}\) and 1205 cm\(^{-1}\) for the thiocarbamate and oxine complexes. In case of oxine complex, \(\gamma(\text{O-H})\) has disappeared indicating coordination of the oxine moiety to the metal ion. Evidence for the coordination of the bases has been further substantiated by the occurrence of bands around 320 cm\(^{-1}\) assignable\(^{71}\) to \(\gamma(\text{Co-N})\) and the bands around 450 cm\(^{-1}\), around 260 cm\(^{-1}\) and around 220 cm\(^{-1}\) attributable to \(\gamma(\text{Co-O})\), \(\gamma(\text{Co-S})\) and \(\gamma(\text{Co-Cl})\) vibrations respectively. Graph 24.

In octahedral cobalt(II) complexes, three transitions\(^{80}\) namely \(4_{1g}(F) \rightarrow 4_{2g}(F), \rightarrow 4_{2g}(F), \rightarrow 4_{1g}(P)\) are possible out of which absorption bands due to first and third transitions are generally observed. The \(\gamma_1\) is generally broad and is a set of multiple bands and may be mixed with spin-forbidden transition. In the present case, bands due to \(\gamma_1\) and \(\gamma_3\) are observed in the region around 9,500 and around 21,000 cm\(^{-1}\) respectively. The \(\gamma_2\) band is very weak but is observed in the region 18,000 cm\(^{-1}\). In case of quinoline adduct, two absorption bands are observed at 15,000 (1350) and at 9,000 (250) cm\(^{-1}\) attributable to \(4_{2g}(P), \rightarrow 4_{1g}(F)\) transitions respectively. The high extinction coefficient value of \(4_{1g}(P)\) transition and low magnetic moment value support a tetrahedral configuration for the complex. In case of P-dtc and M-dtc adducts one absorption band is noticed around 19,200 cm\(^{-1}\) region. Intensity of this band is nearer to that of an octahedral complex but from
analysis, conductance and comparatively low magnetic moment values suggest these two complexes to be presumably five-coordinated in conformity with earlier observation\textsuperscript{33}. 
REFERENCES

30. A.W. Adamson, J. Am. Chem. Soc. 73, 5710 (1951)
31. R.S. Nyholm and G.A. Barclay, Chem. and Ind. 378 (1953)
34. L. Sacconi, S. Midollini and C.A. Ghilardi, Inorg. Chem. 16(9), 2377 (1977)
103. G. Dogmagk, R. Behenisch, F. Mierzsch and H. Schmidt, Naturwissenschaften, 33, 315 (1946)
106. J.A. Crim and H.G. Petering, Cancer Res. 27, 1278 (1967)
111. M. Katyal and Y. Dutta, Talenta, 22, 151 (1975)


