CHAPTER-II

SYNTHESIS AND STRUCTURAL ELUCIDATION OF COBALT(II) AND NICKEL(II) COMPLEXES OF QBD, MQBD, QBO, MQBO, NQTC AND MNQTC.
2.1 Introduction and literature survey of cobalt(II) complexes

Complexes of cobalt have been continuously playing the role of an important aspect of the metal coordination chemistry due to their preparative accessibility, diversity and structural variability. The formations of stable cobalt complexes with ligands containing several monodentate, bidentate, tridentate, tetradeentate, pentadentate, hexadentate and heptadentate Schiff bases have been cited in literature. Brief reviews of several systems with some selected examples of these metal complexes are presented. An extensive review of cobalt complexes is found in literature. In a review, Cotton has surveyed the literature upto and inclusive of those published in 1994.

Cobalt(II) with d⁷ electronic configuration is known for four coordinate and six coordinate stereochemistry posing tetrahedral and octahedral geometry, respectively. The electronic spectra of cobalt(II) complexes in its different geometries are now quite well known and generalizations can readily be made with relatively simple ligands. It is well known that the electronic spectra of octahedral cobalt(II) complexes are less intense than those of tetrahedral ones. The different geometry of cobalt(II) complexes can be distinguished both spectroscopically and magnetically.

The discovery of cobalt complexes of macrocyclic ligands resembling that of Vitamin B₁₂ include aetoporphyrin, 1-(1-phenyl-3-p-chlorophenyl) pyrazolyl carboxaldehyde, Schiff bases with L-phenylalanine, L-leucines, L-histidine or L-tryptophan and aldehyde/ketone, 2,6-diaminopyridine and acetylacetone and dimethylglyoxime complex have led to the continued growth of the coordination chemistry of cobalt.

The complexes of cobalt(II) with the ligands from groups IA, IIA, IIIB, IVB, VB, and VIIB elements have been thoroughly reviewed. Cobalt(II) complexes
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with nitrogen, sulphur and/or oxygen donors are numerous. Some of the ligands reported in literature belonging to this system include:

2,5-Dithiohexane and 3,6-dithiooctane, Bis(β-diketones), octamethyl pyrophosphonamide, 2- and 4-vinylpyridines, antipyrine, trimethylene-N-oxide, N,N,N,N-tetramethylethenediamine, propionamide, n-butyramide, 1,2-dimethoxyethane, 1,10-phenanthrolinecarboxamide, pyruvic acid, m-carboxyphenylhydrazine, morpholine, ethylene-di-morpholine, thiomorpholine-3-thione and thiazalidine-2-selenone, β-alanine, isobutyramide benzoxazole-2-thione, scuccinic acid, 4-methyl pyridine, napthalene-1-sulphonic acid, 2,2-dibenzimidazol, bis(2,6-acetylpyridinedihydrazone), quinoline-N-oxide, hydrazine, ethylenediamine, o-phenylenediamine, 5(3)-methyl pyrazole-3(5)-carboxyphenylhydrazone, 3,5-dimethyl-2'-pyrimidylpyrazole, 1-methylpyrazole-4,4-di mercaptopiperidine, N,N'-ethylene-bis-(3-carboxysalicylaldimine), 3,6-bis(1-pyrazolyl)pyridazine, 2,2-bis(2-pyridyl)-1,3-dioxaline, 1,4-bis(2'-hydroxy-3'-carboxy-5'-sulphonicphenylazo)benzene, monoacetylferrocene thiosemicarbazone, 3-(1-hydroxy-2-naphthyl)-5-(4-X-phenyl)pyrazoline, 2,2'-bis(2-imidazolyl)biphenyl, salicylaldehyde morpholine-N-thiohydrazone and 2-hydroxyacetophenone-N-thiohydrazone, 2,3-bishydrazinoquinoxaline, benzothi-azoles, benzilic and mendalicesters, 1-(2-carbamylethyl)-2-methylimidazole, 1-(2-carbamylethyl)-2-ethylimidazole, tropocoronand, N,N-bis(pyrazol-1-yl)(methyl)benzylamine, 1-aryl-4-arylisothiosemicarbazides, tris(2-biphenylphos-phinoethy)phosphine, 1,1-dicarboethoxy-2,2-ethylenedithiolate, isopropylmethylketone or isobutylmethylketonesemicarbazones and thiosemicarbazones, bis(Δ²-2-pyrimidinyl)-6,6'-dioximedi-hydrochloride, 1-[4-(2-phenyl)benzopyridineformyl]-4-phenyl-3-thio-
semicarbazide, 2-, 3-, and 4-cyanobenoates, Hydrazoniumformatehemihydrate, 2-hydroxyl-1-naphthyl)-5-(4-X-phenyl)-2-isoxazoline, N,N'-substituted dithiooxamides, 2-hydroxy-w-4-x-cinnamoylacetoephones, N,N'-b-s(2-tolyl)diaminoglyoxime(L1H2) and N,N'-bis(4-tolyl)diaminoglyoxime(L2H2), 1,8-di-(2'-hydroxyphenyl)-4,5-diphenyl-2,3,6,7-tetraoctan-1,3,5,6-tetraene, 5,5-di-methyl-cyclohexane-1,2,3-trionoe-2-arylhydrazones, quinolie-8-sulphonicacid, 5-(2-hydroxybenzylideneaminobenzopyrazole, N,N'-[(2-pyrolalylmethylene)amino]phenol, (N-[4-aminophenyl)sulfonyl]acetamide, N,N,N,N'-tetrakis(1-hydroxy-methyl-2-benzimidazolylmethyl)-1,2-ethanediamine, 1-N-(6-nitrobenzimidazole-1-carbonyl)-4-(A-naphthyl)-3-thiosemicarbazide, 1-(benzotriazole-1-acetyl)-4-(A-naphthyl)-3-thiosemicarbazide, 2,6-diacylpyridine-bis(N-benzylglycyl-hydrazone), 2-nitroso-2,3-dihydrophenalene-1,3-dione, butylmalonyl bis(4-phenylsemicarbazide), N-(2-thiophenecarbonyl)-N'-ferrocenecarbonylhydrazine and N-(4-methoxybenzyl)-N'-ferrocenecarbonylhydrazine, N,N'-bis(3,5-dibromosalicylidene)-1,2-diaminobenzene, 3,5-dimethylpyrazol-1-yl, 4-oxo-4H-1-benzopyran-3-carboxaldehyde-4-chlorobenzylhydrazone, 4-oxo-4H-1-benzopyran-3-carboxaldehyde-4-(methylbenzylhydrazone).

Recently, many workers have isolated and characterized several new cobalt(II) complexes with a variety of ligands and this work is briefly presented in the following paragraphs.

The isolation and characterization of the perchlorate salt of the symmetric trimeric cation, [Co3O(CH3CO2)6(C6H5N)3] was reported. Gao et.al. reported Co(II) binuclear complexes, namely [Co2(DPHA)L4](ClO4)2, where L=diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane; DPHA=diphenic acid dianion. Panda et.al. reported the synthesis and characterization of series of
binuclear complexes of the type \([\text{Co(HDCTH)(H}_2\text{O})_2]_2\text{X}_2\), where HDCTH=schiff base derived from condensation of isonicotinicacidhydrazide and diacetylmonoxime; \(\text{X}=\text{Cl}^-, \text{Br}^-, \text{NO}_3^-\).

Cezar and Kriza\(^9\) have synthesized and characterized the metal complexes containing nitrogen and sulphur of the type \(\text{ML}_2\text{Cl}_2\), where \(\text{M}=\text{Co(II)}, \text{Ni(II)}\) and \(\text{Cu(II)}\) and \(\text{L}=\text{schiff base formed by condensation of 2-thiophenecarboxaldehyde and propylamine, N-[2-thienylmethylidene]-1-propanamine (TNAP), or ethylamine, N-[2-thienylmethylidene]ethanamine (TNAE)}\). Infrared and NMR spectra of the complexes confirmed the co-ordination of the central metal atom through nitrogen and sulphur atoms. Magnetic susceptibility data coupled with electronic and ESR spectra suggested a D\(_{4h}\) symmetry for the Co(II) complexes, distorted octahedral structure for Cu(II) and tetrahedral geometry for Ni(TNAP)_2Cl_2.

Arounaguiri et.al.\(^9\) reported the DNA binding and photocleavage characteristics of a series of mixed ligand complexes of the type \([\text{M(phen)}_2\text{LL}]^{n+}\) (where \(\text{M}=\text{Co(III)}, \text{Ni(II)}\) and \(\text{Ru(II)}\), \(\text{LL}=\text{1,10-phenanthroline, phenanthrolinedione, or dipyridophenazine and n}=3\) or 2). Various physico-chemical and biochemical techniques including UV/Visible, fluorescence, viscometric titration, thermal denaturation, and differential pulse voltametry have been employed to probe the details of DNA binding of these complexes.

Kamenicek\(^9\) synthesized new Co(II) and Ni(II) complexes with 1,2-ethanedithiol containing bi-(tri)-dentate N, P-ligands \{4,4'-bipyridine, 5-nitro-1,10-phenanthroline, 2,2'-biquinoline, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propare, 1,1,1-tris(diphenylphosphinomethyl)ethane\}. All compounds were characterized by elemental analyses, IR, UV-Vis spectroscopy, thermal analysis, magnetochemical and conductivity measurements.
Kriza et al.\textsuperscript{93} reported the complex compounds of ions with $d^6$, $d^7$, $d^8$ and $d^{10}$ electronic configuration with 3-N-dibenzofurylthiourea. The complexes are found to be of the type $[MLCl_2]$, where $M=\text{Co(II)}, \text{Ni(II)}, \text{Pd(II)}$ or $\text{Pt(II)}$. The thioamide acts as bidentate ligand using both sulfur and nitrogen atoms as donors. The bacteriostatic activity of the thioamide and the complexes were determined against selected bacteria.

Zhang et al.\textsuperscript{94} reported the synthesis and characterization of the ligand ODHIP, 3,4-dihydroxy-imidazo[4,5-f][1,10]phenanthroline and its cobalt(II) complex $[\text{Co(bpy)}_2(\text{ODHIP})]^{3+}$. Binding of this complex with calfthymus DNA has been investigated by spectroscopic methods and viscosity methods. The experimental results indicated that the complex bound to DNA by interaction. In Tris buffer, the complex could emit relatively weak luminescence. After binding to DNA, the notable enhancement was observed. However, when the $\text{Cu}^{2+}$ was further added, the luminescence decreased gradually and disappeared after the equimolar concentrations of $\text{Cu}^{2+}$ was added, which exhibited the “off-on-off” properties of molecular light switch.

Sastri et al.\textsuperscript{95} reported the synthesis, characterization and DNA binding properties of four new mixed-ligand complexes, namely $[\text{Co(phen)}_2(\text{qdppz})]^{3+}$, $[\text{Ni(phen)}_2(\text{qdppz})]^{2+}$, $[\text{Co(phen)}_2(\text{dicnq})]^{3+}$, and $[\text{Ni(phen)}_2(\text{dicnq})]^{2+}$ (phen=1,10-phenanthroline, qdppz=naptho[2,3-a]dipyrido[3,2-h:2'3'-f]phenazine-5,18-dione and dicnq=dicyanodipyridoquinoxaline), by FAB-MS, UV/Vis, IR, $^1\text{H}$ NMR, cyclic voltametry and magnetic susceptibility methods. Absorption and viscometric titration as well as thermal denaturation studies revealed that each of these octahedral complexes is an avid binder of CT DNA. The apparent binding constants for the dicnq and qdppz bearing complexes are in the order of $10^4$ and $> 10^6$ M$^{-1}$.\hspace{1cm}
respectively. Based on the data, an intercalative mode of DNA binding is suggested for these complexes. While both the investigated cobalt(III) complexes and also \([\text{Ni(phen)}_2(\text{qdppz})]^2+\) affected the photocleavage of DNA (super coiled pBR 322) upon irradiation by 360 nm light, the corresponding dicnq complex of nickel(II) was found to be ineffective under a similar set of experimental conditions.

Prasad and Mathur\(^\text{96}\) reported the synthesis and characterization of twenty membered tetraazamacrocyclic ligand 2,12-dimethyl-3,13-di-n-propyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene(L) and its metal complexes of the type \([\text{MLX}_2]X\) (where \(\text{M}=\text{Cr(III)}\) or \(\text{Fe(III)}\); \(X=\text{NO}_3^\text{−}\)) \([\text{CoLNO}_3]^2\), \([\text{NiL(NO}_3^\text{−})_2]\), \([\text{CuL}]^2\), \([\text{ZnLCl}_2]\) by 2+2 cyclocondensation of 2,3-hexanedione with 1,6-diaminohexane in the presence of metal ions as templates.

The crystal structures of two face-to-face diporphyrin compounds based upon the ligand \((1,8\text{-bis}(5-(2,8,13,17\text{-tetraethyl-3,7,12,18-tetramethyl-porphyrinyl}))\text{anthracene)}\) (DPA), i.e. \(\text{H}_4(\text{DPA})\) and \((\text{DPA})\text{Co}_2\) were reported by Drouin et.al.\(^\text{97}\). The structural data were compared to that of other bimetallic DPA systems, and diporphyrinic cobalt complexes. In addition, the luminescence properties of \([\text{(OEP)Co}]\) \((\text{OEP}=2,3,7,8,12,13,17,18\text{-octaethylporphyrin})\), \([\text{H}_2(\text{DPA})\text{Co}]\), \([\text{H}_2(\text{DPA})(\text{CoIm})\text{O}_2]\), \([(\text{DPA})\text{Co}_2]\), \([(\text{DPA})\text{Co(Im)}\text{O}_2]\), where \(\text{Im}\) is 1-t-butyl-5-phenylimidazole, were studied. Contrary to previous literature reports, the Co(II) species were found to be weakly luminescent, where fluorescence detected for both the mono- and diporphyrinic systems was assigned to emissions arising from the lowest \(1^1\text{Q(ππ*)}\) states, while phosphorescence was detected at 77 K only for the monoporphyrin species, \((\text{OEP})\text{Co}\). On the other hand, the Co(III) complexes were not luminescent.
Rafat et al.\(^9\) reported the synthesis of 16 membered macrocyclic complex by the reaction of \([M(ppn)_2X_2]\) (where \(M=\text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}\) and \(ppn=1,3\)-diaminopropane) with formaldehyde and ethylenediamine in methanol. The complexes were characterized by using elemental analysis, IR, EPR, electronic spectral data, magnetic moments and conductance measurements. The Cu(II), Ni(II) and Co(II) complexes are coordinated axially with both pendant groups of the hexadentate macrocycle. These pendant donors are attached to the macrocycle by a carbon chain. The electrical conductivities of the Cu(II) and Ni(II) chelates indicated them to be 1:2 electrolytes whilst those of Co(III) is a 1:3 electrolyte in DMSO. Spectroscopic evidence suggests that the metal ion is in an octahedral environment in all the complexes.

Donkova et al.\(^10\) investigated the inclusion of 3d-impurities Mn(II), Co(II), Ni(II) and Cu(II) in a crystalline precipitate of ZnC\(_2\)O\(_4\).2H\(_2\)O. This study is a part of the systematic one deal with the mechanism of inclusion of 3d-ions in sparingly soluble oxalate systems. The experiments were carried out in bi- and multi-component systems at two different mediums, one with deficiency of oxalate ions, and another with excess.

Ghosh et al.\(^11\) prepared the complex \{Co\(_2\)(ptcH)\(_2\)(4,4'-bpy)(H\(_2\)O)\(_4\)\}.2H\(_2\)O\} by the reaction of pyridine-2,4,6-tricarboxylic acid (ptcH\(_3\)) with Co(NO\(_3\))\(_2\).6H\(_2\)O in presence of 4,4'-bipyridine (4,4'-bpy) in water at room temperature. The solid-state structure reveals that the compound is a dimeric Co(II) complex assembled to a 3D architecture via an intricate intra- and inter-molecular hydrogen-bonding interactions involving water molecules and carboxylate oxygens of the ligand ptcH\(^2\)-.
2.2 Introduction and literature survey of nickel(II) complexes

Nickel(II) forms a large number of complexes encompassing coordination numbers 4, 5 and 6 and all the main structural types, namely, octahedral, trigonal bipyramidal, square pyramidal, tetrahedral and square planar. Moreover it is characteristic of nickel(II) complexes that complicated equilibria which are generally temperature dependent and sometimes concentration dependent often exist between these structural types.

The main coordination number of nickel(II) is six. Magnetically octahedral nickel(II) complexes have simple behaviour. These complexes have been assigned octahedral geometry on the basis of analytical data, spectral, thermal and magnetic studies. Alper and Zompa have reported a tetragonally distorted octahedral nickel(II) complex. Slightly distorted octahedral nickel(II) complexes with different donor atoms have been reported by many workers. Green and orange coloured octahedral nickel(II) complexes have been synthesized by Riggle et al. A number of square pyramidal complexes and trigonal bipyramidal nickel(II) have been reported rarely.

There are few reports on the mono and binuclear square bipyramidal nickel(II) complexes. In binuclear complexes it is found that one nickel(II) is of square planar and the other nickel(II) is of square pyramidal geometry.

When small substituents are present, planar or nearly planar complexes are formed. However in some cases there are marked distortions even from the highest symmetry possible given inherent shapes of the ligands. There are many studies reported on square planar nickel(II) with diamagnetic character. Distorted square planar nickel(II) has been reported by Rong Cao et al. Some polymeric
nickel(II) complexes with nickel(II) in square planar environments have also been reported.\textsuperscript{123-124}

For vast majority of four coordinate nickel(II) complexes planar geometry is preferred. They are invariably diamagnetic and frequently red, yellow or brown. For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. A few tetrahedral nickel(II) complexes have been studied\textsuperscript{125,126}. Stereochemistry and stability of nearly regular and distorted tetrahedral nickel(II) complexes have been studied by Mokhlesur et al.\textsuperscript{127}

Nickel(II) complexes with 7-R-substituted-2,4-dimethyl-6,7-benzol-1,5-diazepines, R=H, Me, Cl, NO$_2$ were characterised and assigned tetrahedral geometry for all the complexes.\textsuperscript{48} Synthesis, structure and properties of discrete mononuclear nickel(II) selenolate complexes were reported\textsuperscript{128}. The nickel(II) complex [NiLCl$_2$] (L=4,7-phenanthroline) was prepared and tetrahedral structure was proposed based on elemental analysis, magnetic moment, vibrational and electronic spectra.\textsuperscript{129}

Nickel(II) complexes with nitrogen, sulphur and/or oxygen donors are numerous. Some of the ligands recently reported in the literature belonging to this system include: Famotidine\textsuperscript{130}, active aldehyde derivatives of thiamine\textsuperscript{131}, xanthosine, inosine, and guanosine\textsuperscript{132}, cytosinium\textsuperscript{133}, 4-amino-2,6-dimethyl-5-oxo-2,3,4,5-tetrahydro-1,2,4-triazine\textsuperscript{134}, 2,3-di(4-methylphenlamine)-5,6-bis(hydroxylimino)pyrazine and 2,3-diphenylamine-5,6-bis(hydroxyimino)pyrazine\textsuperscript{135}, bis(hydrazine)-malonates and succinates\textsuperscript{136}, vic-dioxime ligands\textsuperscript{137}, aminoacid schiff base\textsuperscript{138}, phenylbutazone\textsuperscript{139}, 4-methoxybenzoylhazrazide and salicylaldehyde, o-hydroxyacetophenone or diacetylmonoxime\textsuperscript{140}, pyridene-2-aldehydesalicyldiazine\textsuperscript{141}, 2,2'-bipyridyl\textsuperscript{142}, 5,6-diphenyl-3-(2'-hydroxyphenyl)-1,2,4-triazine\textsuperscript{143}, 1-acetyl-5-aryl-3-(substituted thienyl)-2-pyrazolines\textsuperscript{144}, pyrole-2-carboxaldehyde schiff bases of s-alkyl
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ester of dithiocarboxylic acid\textsuperscript{145}, bis-isopropylxanthate\textsuperscript{146}, 2,4-bipyridyl\textsuperscript{147}, 5,5-dimethylcyclohexane-1,2,3-trione-2-arylhydrazone\textsuperscript{71}, 1,2,3,5,6,7,8,8a-octahydro-3-oxo-N,1-diphenyl-5-(phenylmethylene)-2-naphthalene\textsuperscript{72}, 2-, 3-, 4-cyanobenzoates\textsuperscript{64}, 2,2-bipyridylamine and thioacids\textsuperscript{148}, dibenzotetrazatetradentate macrocyclic ligand\textsuperscript{149}, N-substituted N\textsuperscript{1}-ethoxycarbonylthiourea\textsuperscript{150}, benzoylethydrozones\textsuperscript{151}, tetrazamacrocycles\textsuperscript{152}, N-morpholine or N,N-diethyl, N\textsuperscript{1}-mono substituted benzoylethydroreas\textsuperscript{153}, nitronylnitroxidecarboxylicacid\textsuperscript{154}, 2,5-dihydroxy-p-benzoquinone\textsuperscript{155}, 5-sulphosalicylicacididiethylenetriamine\textsuperscript{156}, N-aroyle-N\textsuperscript{1}-thiobenzohydrazide\textsuperscript{157}, pyrrolidine-dithiocarbamate\textsuperscript{158}, 2-aminoethylidemethylphosphine\textsuperscript{159}, 2-phenyl-1,2,3-triazole-4-carboxaldehyde-2-aminophenol\textsuperscript{160}, 3-(2-hydroxy-5-chlorobenzylideneamino)-5-methylisoxazole\textsuperscript{161} and 1,2-bis-(hydroxyalkyl)phosphinoethane\textsuperscript{162}, bis-[4,5-disulfanyl-1,3-dithiol-2-onato]\textsuperscript{163}, bis[pendantacetate]macrocyle-1,4,7,10-tetrazacyclododecane-1,7-diaceticacid\textsuperscript{164}, tetrazamacrocycle with N-carboxymethyl groups as pendant arms\textsuperscript{165}, heterodetopic cryptand\textsuperscript{166}, 1-ethyl-1,4-dihydro-4-oxo(1,3)dioxole(4,5)-cinnoline-3-carboxylicacid\textsuperscript{167}, 1-(2\textsuperscript{1}-pyridyl)benzothiazole-2-thione\textsuperscript{168}, isatinisonicotinylethydrozone\textsuperscript{169}, Isothipendyl\textsuperscript{170}.

Raman et.al.\textsuperscript{171} have synthesized neutral tetradentate N\textsubscript{2}O\textsubscript{2} complexes of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) using a schiff base, formed by the condensation of o-phenylenediamine with acetoacetanilide in alcohol medium. IR and UV-Vis spectra suggested that all the complexes are square planar except Mn(II) and VO(II) chelates, which are of octahedral and square pyramidal geometry, respectively. The neutral and monomeric nature of the complexes was confirmed by their magnetic susceptibility data and low conductance values.

A series of neutral Ni(II) and Cu(II) complexes of tetraazatetraenemacrocyclic ligands with monomeric and dimeric species were synthesized and their redox,
structural and spectroscopic properties were studied by Grochala et al. The X-ray results showed planar geometry for the monomeric tetraazamacrocyclic complexes and interesting ‘organic-zeolite-like’ structures of the dimers. The dimeric nickel complexes had flexible cavities between the two single ligands linked with aliphatic chains suitable for accommodating small-sized guests. For the dimeric compounds the metal oxidation \([\text{M(II)/M(III)}]\) take place independently on each centre except one binuclear nickel complex, where the cooperativity of the metal centers was observed. Methyl substituents give rise to irreversibility of the oxidation process of the complexes studied. Pasorek et al. reported six novel binuclear Ni(II) dithiocarbamates with aromatic or nonaromatic monothiols as bridging ligands of the composition\([\text{Ni(\(\mu\)-HL)\(\text{hmtdc}\)})_2\] (HL=thiophenol, 4-methylthiophenol, 2-thionaphthol, thiosalicylicacid, 1-hexanethiol, 1-butanethiol; hmi=C\(_6\)H\(_{12}\); dtc=S\(_2\)CN). These compounds have been studied by employing elemental analysis, IR, electron spectroscopy, magnetochemical, conductivity measurements and thermal analysis. The used methods indicated that the complexes are diamagnetic, non-electrolytes with two square planar NiS\(_4\) chromophores.

Choudhury et al. synthesized and characterized the pyrazine bridged polymeric complex \([\text{Ni(pyz)(H}_{2}\text{O}_{4})(\text{NO}_3)_2\cdot 2\text{H}_2\text{O})_n\]. The complex was characterized by employing elemental analysis, IR, UV-Vis spectra and a single crystal X-ray diffraction study. The coordination around the Ni centre was perfectly octahedral. The Ni(H\(_2\)O\(_4\)) coordination planes were bridged by pyrazine ligands forming an infinite chain structure. Two nitrate anions and two water molecules were exist in the lattice and are linked by intermolecular hydrogen bonds to the coordinated water molecules.
Xiao-Zeng Li et al.\textsuperscript{175} prepared a trinuclear complex of the type $[\text{Cu(NiL)}_2(\text{NCS})_2]$ by the reaction of new macrocyclic oxamido complex ligand NiL, Cu(ClO)$_2$.6H$_2$O and KNCS, where L is doubly deprotonated form of dimethyl-5,6,7,8,15,16-hexahydro-15-methyl-6,7-dioxodibenzo[1,4,8,11]tetraazacyclotetradecine-13,18-dicarboxylate. Excess Cu(ClO)$_2$.6H$_2$O is necessary for the formation of the title compound. The structure of the title complex was further characterized by X-ray single crystal analysis. Cu(II) and each Ni(II) is bridged by the oxamido group from the corresponding macrocyclic ligand. The coordination geometry around each Ni(II) ion is slightly distorted square planar with N$_4$ donor set, and the Cu(II) ion has a distorted octahedral coordination geometry of O$_4$N$_2$ donor set.

Nickel(II) and copper(II) complexes of 2-cyano-2-(hydroxyimino)acetic acid have been prepared and characterized by Malek\textsuperscript{176}. Molecular structures of the compounds in the solid state were proposed. The bidentate ligand chelates the copper and nickel ions through the oxime nitrogen and the carboxyl oxygen atoms to form a trans bis-complexes. However, two sodium ions are bonded to the deprotonated oximic as well as carboxylic groups. Equilibrium geometries, atomic charges, harmonic vibrational frequencies with potential energy distribution (PED), infrared and Raman intensities were calculated for all compounds studies here by using the hybrid functional of DFT(B3LYP) with 6-311++G(d,p) and LanL2DZ basis sets, for sodium and transition metal ions complexes, respectively. The computed properties are compared to the experimental values.

The above literature survey indicates that no work has been reported on the synthesis and characterization of cobalt(II) and nickel(II) complexes of Quinolino[3,2-b][1,5]benzodiazepine (QBD),

Methylquinolino[3,2-b][1,5]benzodiazepine (MQBD),
Quinolino[3,2-b][1,5]benzooxazepine (QBO),
Methylquinolino[3,2-b][1,5]benzooxazepine (MQBO),
2-(2-napthylthio)-quinoline-3-carbaldehyde (NQTC) and
6-methyl-2-(2-napthylthio)-quinoline-3-carbaldehyde (MNQTC).

In this chapter, author reports the isolation of solid complexes of cobalt(II) and nickel(II) with QBD, MQBD, QBO, MQBO, NQTC and MNQTC ligands. These new cobalt(II) and nickel(II) complexes were characterized by elemental analysis, IR, UV-Visible, $^1$H NMR spectral data, magnetic and molar conductance measurements.

2.3 Materials and methods

2.31 Materials

All the chemicals used in the present study are of AR grade. Where analytical grade chemicals were not available, laboratory grade chemicals were purified and employed. Among the solvents employed, dimethyl formamide and dimethyl sulphoxide were of spectroscopic grade and the remaining were of AR grade.

2.32 Methods

Melting points of ligands and complexes were determined on Tosniwal hot stage melting point apparatus and are uncorrected.

a. Estimation of cobalt

The cobalt content in the complex was determined volumetrically by EDTA method. A known weight of the complex was decomposed with concentrated nitric acid and evaporated almost to dryness. The residue was then dissolved in water and the cobalt content was determined using xylenol orange indicator.
b. Estimation of nickel

The nickel content in the complexes was brought into solution by decomposing the complex by repeated evaporation with concentrated nitric acid and estimated gravimetrically by dimethylglyoxime method. A few drops of concentrated hydrochloric acid was added to the nickel solution of the decomposed complex and heated to 70–80 °C. The nickel(II) was precipitated as nickel (II) dimethylglyoximate by addition of slight excess of 1% ethanolic solution of dimethylglyoxime, followed by immediate addition of dilute ammonia solution (1:4) drop wise with constant stirring until the precipitation started and then in slight excess. The resulting complex precipitated was allowed to stand on water bath for 20-40 min and the supernatant solution was tested for completion of precipitation. The solution was cooled to a room temperature and filtered through previously weighed sintered glass crucible. The precipitate was washed with distilled water until free from chloride. It was dried at 110–120 °C for about one hour and weighed as [Ni(C4H7O2N2)2].

c. Estimation of chloride

The chloride content was estimated gravimetrically as AgCl. Accurately weighed sample (0.2 g) was evaporated repeatedly with aqueous ammonia to affect hydrolysis and finally boiled with aqueous ammonia. The precipitate was coagulated with about 5 g of ammonium nitrate and then filtered. The precipitate was washed thoroughly with water and washings were collected in the same beaker. The total bulk of solution was acidified with concentrated nitric acid and heated to boiling. The solution was treated with 0.1N AgNO3. The precipitate of silver chloride was boiled for a while and allowed to settle. The precipitate was filtered through a previously
weighed sintered glass crucible, and washed several times with water followed by alcohol. The precipitate was dried at 120°C, weighed as AgCl.

d. **Estimation of perchlorate**

The perchlorate content in the complexes was estimated by fusion with sodium nitrate and the reduced chloride content was determined as AgCl gravimetrically.

e. **Estimation of nitrogen**

The nitrogen content in the complexes was estimated by Duma’s method and Kjeldhal’s method.

### 2.33 Microelemental analysis

Quantitative microanalysis for elements carbon and hydrogen of the complexes provide useful data in determining the molecular formulae of the complexes under analyses. The carbon and hydrogen microanalysis were done at Department of Chemistry, University of Mysore, Mysore.

### 2.34 Molecular weight determination

**Rast’s method**

The molecular weight of the complexes was determined by Rast’s method using biphenyl. A known weight of the biphenyl (~0.25 g) was mixed with known weight of the complex (~0.25 g) and the mixture was melted to form homogeneous mixture and allowed to solidify on cooling. Using a sensitive thermometer, the melting point of mixture and biphenyl were determined. The depression in freezing point, \( \Delta T_f \) was obtained by the difference between the two melting points and the molecular weight was calculated by using the relation

\[
M = \frac{(1000 \times K_f \times w)}{(W \times \Delta T_f)}
\]
Where $K_f$ is the molal depression constant of biphenyl, which had been determined by the method using naphthalene (known molecular weight) as the solute instead of the complex, $w$ and $W$ are the weight of the complex and biphenyl (in g), respectively.

2.35 Physical techniques used for the characterization of complexes

a. Electrical conductance measurements

The electrical conductance measurements were done to see whether the anions of the metal salts remain inside or outside the coordination sphere of the central metal atom. The conductance data were obtained in freshly prepared $10^{-3}$ M DMF solution employing EQUIPTRONICS digital conductivity meter model EQ-DCM-P.

b. Magnetic susceptibility measurements

The magnetic susceptibility measurements of the complexes were done in order to find out the effective magnetic moment per each metal atom in the complexes. The number of unpaired electrons `$n$' possessed by the metal ion can be determined from the effective magnetic moment of the metal ion. From knowledge of the number of unpaired electrons, it is possible to infer the valence state of the metal ion in a complex.

Magnetic susceptibilities of the solid complexes were measured employing Gouy balance at room temperature ($28\pm2^\circ$C) using $\text{Hg}[\text{Co(CNS)}_4]$ i.e. mercury(II) tetrathiocyanato cobaltate(II), as a calibrant for standardizing the Gouy tube. The previously weighed and calibrated Gouy tube was uniformly filled with finely powdered complexes up to the mark and recording the weights with and without magnetic field. The process of recording repeated thrice and the mean of the three observations were taken as apparent change in weight. The effective magnetic
moments per metal atom were calculated from the corrected magnetic susceptibilities using the relation

$$\mu_{\text{eff}} = 2.84(\chi_M T)^{1/2} \text{ BM}$$

Where $\chi_M$ is the corrected magnetic susceptibility and $T$ is the temperature in kelvin at which measurements were made for diamagnetism of other atoms and groups in the complexes using Pascal’s constants.

c. UV-Visible spectra

The UV-Visible spectral measurements were used for assigning the stereochemistries of metal ions in the complexes based on the positions and number of d-d transition peaks. The electronic spectra of the coloured complexes in the UV-Visible region were measured using SHIMADZU double beam spectrophotometer. The working range of the spectrophotometer was 800-200 nm. The spectra of the complexes were recorded using N,N’-dimethylformamide as a solvent at $10^{-3}$ M concentration.

In some cases the electronic spectra of the complexes in solution may not reflect the true stereochemistries of the complexes, in such cases the diffuse reflectance spectra is useful to predict the geometry of the complexes in the solid state. The diffuse reflectance spectral measurements were made on a Pye Unicam SP8-100 UV/Vis spectrometer with MgO as reflectance standard.

d. Infrared spectra

Generally, a comparison of the infrared spectrum of the ligand and that of its complex is useful to find out the atom or atoms through which the ligand is coordinated to the metal atom.

Complete analysis of the spectra has not been attempted. However, attention has been focused on a limited number of bands, which provide considerable structural
information in order to suggest the most probable manner of coordination of the ligands with the metal ions. When the anions are polyatomic (nitrate, sulphate, perchlorate) the infrared spectral measurements are helpful in determining whether the anionic groups are coordinated or not, and if coordinated, to determine the particular atoms involved in coordination.

Infrared spectra of free ligands and their metal complexes were recorded using SHIMADZU FTIR-8400S spectrophotometer with KBr pellets in the region 4000-250 cm\(^{-1}\).

e. Proton magnetic resonance studies

The \(^1\)H NMR study is of help in locating precisely the donor site or sites of a ligand, usually \(^1\)H NMR spectral studies on ligands and their metal complexes are performed to confirm the mode of coordination predicted from the IR data. On complexation, generally a deshielding effect on the heteroatom proton resonance will be observed. The chemical shift towards lower fields is ascribed to the electron withdrawal by a metal from the donor atom and the noticeable deshielding effect supports its coordination.

JEOL 60 MHz spectrometer was used for recording the proton NMR spectra employing TMS as internal reference and DMSO-\(d_6\) as solvent at ambient temperature.

f. X-ray diffraction studies

X-ray diffraction study is useful for the investigation of crystal structure of metal complexes. Generally, the crystal structure of a substance determines the diffraction pattern of that substance or more specifically, the shape and size of the unit cell determines the angular positions of the diffraction lines and the arrangement of the atoms within the unit cell determines the relative intensities of the lines. Since the
structure determines the diffraction pattern, it should be possible to go in the reverse i.e. from the pattern one can arrive at the structure.

The X-ray diffraction patterns of the complex in powder form was recorded on a DE-CER P 12 X-ray machine with a diffractogram, using Cu-Kα radiation filtered by a nickel foil over a range of diffraction angle, 2θ = 3-80°, where θ is the Bragg’s angle and the wavelength of the radiation was 1.5418 Å.

2.4 Experimental

2.41 General procedure for the synthesis of ligands

a. Synthesis of Quinolino[3,2-b][1,5]benzodiazepine (QBD)

2-Chloro-3-quinolinecarbaldehyde (0.958 g, 5 mmol) dissolved in small amount of acetic acid was taken in a 100 ml borosil beaker. o-Phenylenediammine (0.541 g, 5 mmol) and a pinch of potassium iodide were then added. The whole mixture was made into slurry and was irradiated by placing the beaker in a microwave oven for about 10 minutes. The completion of the reaction was monitored by TLC. The product obtained was poured into ice-cold water, the solid separated was filtered, dried, recrystallized and its physical constants were determined.

![Quinolino[3,2-b][1,5]benzodiazepine (QBD)](image)

**Analysis:** Calc. for C_{16}H_{11}N_{3}; C, 78.35; H, 4.52; N, 17.13%; Found: C, 78.52; H, 4.76; N, 17.35 %; IR (KBr, cm⁻¹): 3330 (N-H); 1576 (C=C); 1658 (C=N); 2924 (C-H, aromatic); \(^1\)H NMR (DMSO-d6): δ 10.65 (s, 1H, NH); 8.4 (s, 1H, H-C=N); 7.2-7.8 (m, 9H, Ar-H)
b. Synthesis of Methylquinolino[3,2-b][1,5]benzodiazepine (MQBD)

Mixture of 2-Chloro-6-methylquinoline-3-carbaldehyde (1.569 g, 5 mmol) dissolved in small amount of acetic acid and o-Phenylenediammine (0.541 g, 5 mmol) was taken in a 100 ml borosil beaker and a pinch of potassium iodide was then added. The whole mixture was made into slurry and was irradiated by placing the beaker in a microwave oven for about 10 minutes. The completion of the reaction was monitored by using TLC. The product obtained was poured into ice-cold water, the solid separated was filtered, dried, recrystallized and its physical constants were determined.

Methylquinolino[3,2-b][1,5]benzodiazepine (MQBD)

Analysis: Calc. for C_{17}H_{13}N_{3}; C, 78.74; H, 5.05; N, 16.20 %; Found: C, 78.89; H, 5.25; N, 16.35 %; IR (KBr, cm\(^{-1}\)): 3332 (N-H); 1578 (C=C); 1662 (C=N); 2928 (C-H, aromatic); \(^1\)H NMR (DMSO-d\(_6\)): \(\delta\) 10.80 (s, 1H, NH); 8.6 (s, 1H, H-C=N); 7.1-8.2 (m, 11H, Ar-H); 2.7 (s, 3H, CH\(_3\));

c. Synthesis of Quinolino[3,2-b][1,5]benzoxazepine (QBO)

Mixture of 2-aminophenol (0.11 g, 1 mmol), KOH (0.057 g, 1 mmol) and 2 ml of DMSO were taken in a 100 ml borosil beaker. 2-Chloroquinoline-3-carbaldehyde (1 mmol, 0.192 g) and a pinch of KI were then added. The mixture was irradiated for about two minutes in a microwave oven. The reaction was monitored by means of TLC. The product obtained was then hydrolyzed by pouring into ice-cold water. The final product separated as a solid on acidification with dilute HCl was then filtered, dried, purified and physical constants were determined.
Quinolino[3,2-b][1,5]benzoxazepine (QBO)

**Analysis:** Calc. for C_{16}H_{10}N_{2}O; C, 78.03; H, 4.09; N, 11.38 %; Found: C, 78.21; H, 4.23; N, 11.52 %; IR (KBr, cm^{-1}): 1022 (C-O-C); 1566 (C=C); 1651 (C=N); 2924 (C-H, aromatic); {^1}H NMR (DMSO-d_{6}); δ 8.3 (s, 1H, H-C=N); 7.1-8.0 (m, 9H, Ar-H);

d. Synthesis of Methylquinolino[3,2-b][1,5]benzoxazepine (MQBO)

Mixture of 2-aminophenol (0.11 g, 1 mmol), KOH (0.057 g, 1 mmol) and 2 ml of DMSO were taken in a 100 ml borosil beaker. 2-Chloro-6-methylquinoline-3-carbaldehyde (1 mmol, 0.314 g) and a pinch of KI were then added. The mixture was irradiated for about two minutes in a microwave oven. The reaction was monitored by means of TLC. Obtained product was then hydrolyzed by pouring into ice-cold water. The final product separated as a solid on acidification with dilute HCl was then filtered, dried, purified and physical constants were determined.

Methylquinolino[3,2-b][1,5]benzoxazepine (MQBO)

**Analysis:** Calc. for C_{16}H_{12}N_{2}O; C, 78.44; H, 4.65; N, 10.76 %; Found: C, 78.65; H, 4.83; N, 11.01 %; IR (KBr, cm^{-1}): 1025 (C-O-C); 1569 (C=C); 1653 (C=N); 3053 (C-H, aromatic); {^1}H NMR (DMSO-d_{6}); δ 8.4 (s, 1H, H-C=N); 7.3-8.0 (m, 11H, Ar-H); 2.6 (s, 3H, CH_{3});
e. Synthesis of 2-(2-naphthylthio)-quinoline-3-carbaldehyde (NQTC)

Into a mixture of 2-Chloroquinoline-3-carbaldehyde (0.958 g, 5 mmol), 2-naphthalenethiol (0.8 g, 5 mmol) and potassium carbonate (1.38 g, 10 mmol), anhydrous dimethylformamide (50 ml) was added. The mixture was heated at 80-90 °C for 2 h with constant stirring and was then cooled to room temperature. The product was separated on an alumina (neutral) column using methylene chloride as eluant.

\[
\text{2-(2-naphthylthio)-quinoline-3-carbaldehyde (NQTC)}
\]

Analysis: Calc. for C\textsubscript{20}H\textsubscript{13}NOS; C, 76.16; H, 4.15; N, 4.44%; Found: C, 76.35, H; 4.32; N, 4.63%; IR (KBr, cm\textsuperscript{-1}): 760 (-CSC-); 1710 (aldehyde CHO); 1570 (C=C); 1650 (C=N); 2950 (C-H, aromatic); \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}): \delta 9.6 (s, 1H, -CHO); 7.4-8.6 (m, 11H, Ar-H)

f. Synthesis of 6-methyl-2-(2-naphthylthio)-quinoline-3-carbaldehyde (MNQTC)

Into a mixture of 2-Chloro-6-methylquinoline-3-carbaldehyde (1.57 g, 5 mmol), 2-naphthalenethiol (0.8 g, 5 mmol) and potassium carbonate (1.38 g, 10 mmol), anhydrous dimethylformamide (50 ml) was added. The mixture was heated at 80-90 °C for 2 h and was then cooled to room temperature. The product was separated on an alumina (neutral) column using methylene chloride as eluant.

\[
\text{6-methyl-2-(2-naphthylthio)-quinoline-3-carbaldehyde (MNQTC)}
\]
Analysis: Calc. for C_{21}H_{13}NOS; C, 76.57; H, 4.59; N, 4.25%; Found: C, 76.73, H; 4.32; N, 4.68%; IR (KBr, cm\(^{-1}\)): 762 (-CSC-); 1713 (aldehyde CHO); 1652 (C=\(\equiv\)N); 2925 (C-H, aromatic); \(^1\)H NMR (DMSO-\(d_6\)): \(\delta\) 2.9 (s, 3H, CH\(_3\)); 9.7 (s, 1H, -CHO); 7.5-8.6 (m, 10H, Ar-H).

2.42 General procedure for the preparation of complexes

a. Cobalt(II) complexes of QBD and MQBD

\(\text{CoX}_2.6\text{H}_2\text{O} (5 \text{ mmol, where } X=\text{Cl}, \text{NO}_3^-, \text{ClO}_4^-)\), 1g of lithium chloride and 10 mmol of QBD/MQBD were successively dissolved in 50 ml of dry methanol under nitrogen, gaseous chloride was then introduced into this solution under cooling for 15 minutes. The resulting crystals were filtered off and washed with methanol. They were redissolved in ethanol on a water bath and the ethanol was slowly evaporated on the boiling water bath. Further, slow evaporation of the solution at room temperature resulted in the formation of violet crystalline compounds.

b. Cobalt(II) complexes of QBO and MQBO

To a solution of \(\text{CoX}_2.6\text{H}_2\text{O} (1 \text{ mmol, where } X=\text{Cl}, \text{NO}_3^-, \text{ClO}_4^-)\), in dry benzene, (25 cm\(^3\)) the ligand QBO/MQBO (2 mmol) was added and the mixture was stirred for 5 hour at room temperature. The resulting solution was concentrated to about 3 cm\(^3\) and cooled. A small quantity of petroleum ether was added to the concentrated solution and the precipitated complex was filtered, washed with petroleum ether and recrystallized by using CHCl\(_3\)/petroleum ether mixture and then dried under vaccum.

c. Cobalt(II) complexes of NQTC and MNQTC

An alcoholic solution of the ligand NQTC/MNQTC (2 mmol, 50 ml) and \(\text{CoX}_2.6\text{H}_2\text{O} (1 \text{ mmol, where } X=\text{Cl}, \text{NO}_3^- \text{ or ClO}_4^-)\) was refluxed for 8 hours and its volume was reduced in a rotary evaporator until a light blue precipitate appeared.
After cooling, the solid was filtered off, washed with water, methanol and ether, and then dried under reduced pressure at room temperature.

d. Nickel(II) complexes of QBD and MQBD

The hot solution (0.5 mmol, 50 ml) of appropriate nickel(II) salt (NiX₂ where X=Cl⁻, NO₃⁻ or ClO₄⁻ in ethanol) was slowly added to 50 ml of (1.0 mmol) hot ethanolic solution of the ligand with continuous stirring. The reaction mixture was warmed on a water bath at 60-70 °C for about 2 hours. The coloured precipitates obtained in each case after cooling to room temperature were filtered, washed several times with absolute alcohol, finally with ether and dried in an evacuated desiccator over anhydrous silica gel.

e. Nickel(II) complexes of QBO and MQBO

To a 25 cm³ (5 mmol) solution of NiX₂.nH₂O (X= Cl⁻, NO₃⁻ or ClO₄⁻) in dry benzene, the ligand QBO/MQBO (10 mmol) was added and the mixture was stirred for 5 hours at room temperature. The resulting solution was concentrated to about 3 cm³ and cooled. A small quantity of petroleum ether was added to the concentrated solution and the precipitated complex was filtered, washed with petroleum ether and recrystallized by using chloroform/petroleum ether mixture and then dried under vacuum.

f. Nickel(II) complexes of NQTC and MNQTC

A solution of NQTC/MNQTC (2 mmol) in 25 cm³ methanol was added dropwise, with stirring, to a solution of NiX₂.nH₂O (1 mmol, where X=Cl⁻, NO₃⁻ or ClO₄⁻) in methanol (25 cm³). The mixture was refluxed for 6 hours and its volume was reduced until a light yellow precipitate appeared. After cooling, the solid was filtered off, washed with water, methanol and ether, and dried under reduced pressure at room temperature.
2.5 Results and discussion

The analytical data and physical properties of the ligands and their complexes are given in Table 2.1-2.7. The elemental analyses indicates that the stoichiometry of metal: ligand was 1:2 for cobalt(II) and nickel(II) complexes with (QBD), (QBO), (NQTC), (MQBD), (MQBO) and (MNQTC) correspond to the general molecular formula $[ML_2X_2]$ where $M=$Co(II) or Ni(II); $L=$QBD, QBO, NQTC, MQBD, MQBO or MNQTC; $X=$Cl, NO$_3^-$ or ClO$_4^-$. These quantitative analysis data are in good agreement with the chemical formulae of the synthesized cobalt(II) and nickel(II) complexes.

The newly synthesized cobalt(II) and nickel(II) complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC are crystalline in nature. All complexes are quite stable at room temperature except the nitrate containing complexes, which are hygroscopic in nature. The cobalt(II) complexes are blue in colour excluding cobalt(II) perchlorate complex, which is slightly yellowish in colour, whereas the nickel(II) complexes are green in colour. All the complexes are insoluble in water and also in common organic solvents, but all complexes are freely soluble in coordinating solvents like DMF and DMSO.

2.5.1 Molar conductance

a. Cobalt(II) complexes

The molar conductance values of the Co(II) complexes are presented in Table 2.2(a). The molar conductance values measured in DMF at $10^{-3}$ M for the new complexes lie in the range 14.8 to 30.82 mho cm$^2$ mol$^{-1}$ indicating the non-electrolytic nature of the complexes due to charge neutralization of metal ion with an anionic ligand. This indicates that the anions are coordinated to the central metal ion and
this is consistent with the stoichiometry assumed for the complexes on the basis of analytical data.

b. Nickel(II) complexes

The molar conductance values of the Ni(II) complexes are presented in Table 2.2(b). The molar conductance values measured in DMF at $10^{-3}$ M for these new complexes lie in the range 18.9 to 42.1 mho cm$^2$ mol$^{-1}$ which are slightly higher than the values expected for non-electrolytes. This indicates that the anions are coordinated to the central metal ion. The slightly higher values than those expected for non-electrolytes in the cases are due to partial replacement of the anion by the strong donor solvent molecule and the two species may exist in equilibrium. Further, dissociation of coordinated halides in DMF leading to substantially high conductance has been reported in literature also$^{183}$. Therefore, the complexes may perhaps be considered as non-electrolytes.

Table 2.1: Analytical and physical properties of ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield %</th>
<th>Melting Point (°C)</th>
<th>Colour</th>
<th>Found (Calculated) %</th>
<th>Mol.wt Found (calcd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>C$<em>{16}$H$</em>{11}$N$_{3}$ QBD</td>
<td>78</td>
<td>125</td>
<td>Yellow</td>
<td>78.52 (78.35)</td>
<td>4.76 (4.52)</td>
</tr>
<tr>
<td>C$<em>{17}$H$</em>{12}$N$_{3}$ MQBD</td>
<td>74</td>
<td>129</td>
<td>yellow</td>
<td>78.89 (78.74)</td>
<td>5.25 (5.05)</td>
</tr>
<tr>
<td>C$<em>{16}$H$</em>{12}$N$_{2}$O QBO</td>
<td>81</td>
<td>135</td>
<td>Yellow</td>
<td>78.21 (78.03)</td>
<td>4.23 (4.09)</td>
</tr>
<tr>
<td>C$<em>{17}$H$</em>{12}$N$_{2}$O MQBO</td>
<td>76</td>
<td>138</td>
<td>yellow</td>
<td>78.65 (78.44)</td>
<td>4.83 (4.65)</td>
</tr>
<tr>
<td>C$<em>{20}$H$</em>{13}$NOS NQTC</td>
<td>85</td>
<td>158</td>
<td>Yellow</td>
<td>76.35 (76.16)</td>
<td>4.32 (4.15)</td>
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<tr>
<td>C$<em>{21}$H$</em>{15}$NOS MNQTC</td>
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<td>165</td>
<td>yellow</td>
<td>76.73 (76.57)</td>
<td>4.68 (4.59)</td>
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Table 2.2(a): Analytical and physical properties of Co(II) complexes

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<tr>
<th>Complex</th>
<th>Yield %</th>
<th>Found (Calculated) %</th>
<th>ΩM mhos cm² mol⁻¹</th>
<th>Mol. wt Found (calcd.)</th>
</tr>
</thead>
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<tr>
<td>[Co(QBD)₂Cl₂]</td>
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<td>C: 61.95 (57.35)</td>
<td>12.88 (13.55)</td>
<td>14.8</td>
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<tr>
<td>[Co(MQBD)₂Cl₂]</td>
<td>82</td>
<td>H: 3.58 (3.57)</td>
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<tr>
<td>[Co(QBO)₂Cl₂]</td>
<td>85</td>
<td>N: 12.88 (13.55)</td>
<td>12.88 (13.55)</td>
<td>14.8</td>
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<tr>
<td>[Co(MQBO)₂Cl₂]</td>
<td>82</td>
<td>M: 9.35 (9.5)</td>
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<td></td>
</tr>
<tr>
<td>[Co(NQTC)₂Cl₂]</td>
<td>79</td>
<td>Cl: 11.56 (11.43)</td>
<td>11.56 (11.43)</td>
<td>14.8</td>
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<tr>
<td>[Co(MNQTC)₂Cl₂]</td>
<td>79</td>
<td>C: 61.95 (57.35)</td>
<td>12.88 (13.55)</td>
<td>14.8</td>
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<tr>
<td>[Co(QBD)₂(NO₃)₂]</td>
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<td>[Co(MQBD)₂(NO₃)₂]</td>
<td>78</td>
<td>N: 12.88 (13.55)</td>
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<tr>
<td>[Co(QBO)₂(NO₃)₂]</td>
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<td>M: 9.35 (9.5)</td>
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<td>[Co(MQBO)₂(NO₃)₂]</td>
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<td>11.56 (11.43)</td>
<td>14.8</td>
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<tr>
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<tr>
<td>[Co(MNQTC)₂(NO₃)₂]</td>
<td>79</td>
<td>H: 3.58 (3.57)</td>
<td>9.35 (9.5)</td>
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<tr>
<td>[Co(QBD)₂(ClO₄)₂]</td>
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<td>12.88 (13.55)</td>
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<td>[Co(MQBD)₂(ClO₄)₂]</td>
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<td>[Co(QBO)₂(ClO₄)₂]</td>
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<td>14.8</td>
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<td>[Co(MQBO)₂(ClO₄)₂]</td>
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<td>C: 61.95 (57.35)</td>
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<tr>
<td>[Co(NQTC)₂(ClO₄)₂]</td>
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<tr>
<td>[Co(MNQTC)₂(ClO₄)₂]</td>
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<td>N: 12.88 (13.55)</td>
<td>12.88 (13.55)</td>
<td>14.8</td>
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Table 2.2(b): Analytical and physical properties of Ni(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield %</th>
<th>Found (Calculated) %</th>
<th>Ω_M mhos cm² mol⁻¹</th>
<th>Mol. wt Found (calcd.)</th>
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</thead>
<tbody>
<tr>
<td>[Ni(QBD)₂Cl₂]</td>
<td>85</td>
<td>60.3 (61.9)</td>
<td>3.7 (3.5)</td>
<td>11.5 (11.4)</td>
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<tr>
<td>[Ni((MQBD)₂Cl₂]</td>
<td>75</td>
<td>64.4 (63.0)</td>
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<td>13.0 (12.9)</td>
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<tr>
<td>[Ni(QBO)₂Cl₂]</td>
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<td>60.9 (61.7)</td>
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<td>9.1 (9.0)</td>
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<td>3.5 (3.7)</td>
<td>8.8 (8.6)</td>
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<td>3.3 (3.4)</td>
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2.52 Magnetic behaviour

a. Cobalt(II) complexes

The symmetry properties, the electronic and oxidation state of the central metal ion in the complexes are more often discussed in terms of magnetic data than on the basis of isomerism. The nature of the ground state for tetrahedral cobalt(II) ion...
suggest that the orbital contribution to the magnetic moment is quite small. The spin-only moment \( [4s(s+1)^{1/2}] \) should be 3.9 BM, while the maximum magnetic moment expected for a \( d^7 \) ion with orbital contribution is 5.2 BM \( [4s(s+1) + L (L+1)] \) \( (L=3; s=3/2) \). The tetrahedral complexes of Co(II) are expected to have magnetic moments given by

\[
\mu_{\text{eff}} = \mu_{\text{spin-only}}(1-4\lambda / 10 Dq)
\]

Where \( \lambda = -170 \text{ cm}^{-1} \) and \( \mu_{\text{spin-only}} = 3.991 \text{ BM} \). \( \mu_{\text{eff}} \) = corrected for temperature independent paramagnetism. Thus, the magnetic moments of tetrahedral complexes lie in the range 4.3-4.8 BM\(^{184}\), which is confirmed by \( \text{Hg(Co(NCS)_{4})} \) complex that has a magnetic value of 4.33 BM.

The octahedral cobalt(II) complexes can exist in two possible states which are high spin complexes with a magnetic moment of 4.3-5.2 BM and low spin complexes with a magnetic moment 1.70-1.85 BM\(^{185}\). The magnetic properties of high spin octahedral cobalt(II) complexes are governed by the orbitally degenerate ground term \( ^4T_{1g} \) which is arising from the \( t_{2g}^5 e_g^2 \) electronic configuration, this provides an orbital contribution to the magnetic moment. At room temperature, magnetic moments of these complexes are experimentally found to be in the range 4.7-5.2 BM. Figgis and Nyholm\(^{188}\) presented the view that these high spin complexes vary considerably with temperature. Low spin (spin pair) octahedral Co(II) complexes have the \( ^2E_g \) ground term arising from the \( t_{2g}^6 e_g^1 \) electronic configuration and the magnetic moment of these complexes is expected to be invariant with temperature and found to be in the range 1.70-1.85 BM.

The square planar stereochemistry is rare for cobalt(II) complexes. These are invariably low-spin types with room temperature magnetic moments lies in the range 2.1-2.9 BM, indicating one unpaired electron.
In the present study, the effective magnetic moments value for cobalt(II) complexes of QBD, MQBD, QBO, MQBO, NQTC and MNQTC calculated from corrected magnetic susceptibility were found to be in the range 4.41-5.18 BM and are presented in Table 2.3. The room temperature magnetic moments value support the high spin nature of octahedral geometry for the above mentioned Co(II) complexes.\textsuperscript{49,61,72,89,182,186}

b. Nickel(II) complexes

Nickel(II) a d\textsuperscript{8} ion, having two unpaired electrons can form paramagnetic complexes having either four coordinated tetrahedral or six coordinated octahedral geometry. The magnetic susceptibility, which decides a particular geometry, is controlled by many factors like strength of the ligand field and degree of spin orbit coupling. Nickel(II) complexes show magnetic moments in the range 2.9-3.3 BM and 3.6-4.1 BM, respectively for octahedral and tetrahedral geometry.\textsuperscript{187}

In this study, the nickel(II) complexes of QBD, MQBD, QBO, MQBO, NQTC and MNQTC were found to have magnetic moment values in the range 2.94-3.45 BM (Table 2.3). Hence, octahedral geometry may be proposed for the complexes.

2.53 Electronic spectra

a. Cobalt (II) complexes

The chemistry of Co(II) is associated mostly with three distinct stereochemical configurations and sometimes a fourth one. They are tetrahedral, octahedral, square planar and trigonal bipyramidal. Because stereochemical diversity of cobalt(II) ion its spectra have been widely studied.

The regular tetrahedron splits the d-orbital into a doublet and triplet. In tetrahedral structure the d\textsuperscript{7} cobalt(II) ion is symmetrical, involving a filled lower doublet and a half-filled triplet. In this case, the pairing of electrons cannot be true
that the favoring the pairing of electrons often produce other structures such as square planar or octahedral. Due to the presence of center of symmetry the octahedral Co(II) complexes have less intense spectrum than that of tetrahedral Co(II) complexes, therefore tetrahedral Co(II) complexes show more intense colour and characterized by a strongly structured peak in visible region\textsuperscript{185,188}.

For d\textsuperscript{7} ions of Co(II) in tetrahedral crystal field, show three quartet transitions but the splitting of the free ion, ground term F is the reverse of that in octahedral field. These transitions can be assigned as \(^{4}A_{2}(F) \rightarrow ^{4}T_{2}(F)\), \(^{4}A_{2}(F) \rightarrow ^{4}T_{1}(F)\) and \(^{4}A_{2}(F) \rightarrow ^{4}T_{1}(P)\), respectively. The transition \(^{4}A_{2}(F) \rightarrow ^{4}T_{2}(F)\), is observed in the near IR region\textsuperscript{185}.

The Co\textsuperscript{2+} ion has the d\textsuperscript{7} electronic configuration, which in octahedral fields may give rise to either high spin \(t_{2g}^{5}e_{g}^{2}\) or low spin \(t_{2g}^{6}e_{g}^{1}\) complexes. The ground term \(^{4}T_{1g}\) is arising from the high spin octahedral complexes having \(t_{2g}^{5}e_{g}^{2}\) configuration. In general, the solution of cobalt(II) complexes having high spin octahedral geometry exhibit three d-d transition at ca. 13000 cm\(^{-1}\), which may be assigned to the lowest energy transition \(^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F) (v_{1})\), and other intense band in the visible region ca. 16000 cm\(^{-1}\), often with a shoulder on the low energy side. Since the transition \(^{5}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)\) is essentially a two electron transition form \(t_{2g}^{5}e_{g}^{4}\) to \(t_{2g}^{3}e_{g}^{4}\), it is expected to be weak, and the usual assignment is

\[^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F) (v_{2})\]
\[^{4}T_{1p}(F) \rightarrow ^{4}T_{1g}(P) (v_{3})\]

In some cases it is probable that the transitions \(^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F) (v_{2})\) is not observed at all, but that the fine structure arises from term splitting due to spin-orbit coupling or to distortions from regular octahedron symmetry\textsuperscript{185,189}.
The electronic spectra of present complexes exhibit three bands in the visible region. The spectral data are given in Table 2.3 and spectra are presented in Figures 2.1-2.3. These new cobalt(II) complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC show the lowest energy bands in the visible region 13310-14402 cm\(^{-1}\) pertaining to \(\text{^4}T_{1g}(F) \rightarrow \text{^4}T_{2g}(F)\) \((\nu_1)\) transitions. The other two absorption bands observed at 14766-15090 cm\(^{-1}\) and 15906-16490 cm\(^{-1}\) region which are characteristic to \(\text{^4}T_{1g}(F) \rightarrow \text{^4}A_{2g}(F)\) \((\nu_2)\) and \(\text{^4}T_{1g}(F) \rightarrow \text{^4}T_{1g}(P)\) \((\nu_3)\) transitions, respectively in an octahedral environment\(^{185,189}\). The more intense band observed in new complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC beyond 36818 cm\(^{-1}\) are charge transfer bands. These electronic spectral data were consistent with the high spin octahedral configuration around the cobalt(II) ion\(^{61,72,89}\).

![Figure 2.1: Electronic spectra of [Co(QBD)\(_2\)Cl\(_2\)].](image-url)
Synthesis and Structural elucidation of Co(II) and Ni(II) complexes.

Figure 2.2: Electronic spectra of [Co(QBO)₂Cl₂].

Figure 2.3: Electronic spectra of [Co(NQTC)₂Cl₂].
b. Nickel(II) complexes

The nickel(II) ion has $d^8$ outer electronic configuration which gives rise to the triplet and singlet terms in the increasing order of energy $^3F$, $^1D$, $^3P$, $^1G$, $^1S$. It forms a large number of complexes, the main structural type being octahedral, tetrahedral or square planar.

Six coordinate nickel(II) complexes are almost always high spin complexes having either regular or distorted octahedral stereochemistries. The $^3F$ ground terms is split in an octahedral field giving rise to the triplet terms ($^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$). Thus three spin allowed transitions are expected.

$$
^3A_{2g} \rightarrow ^3T_{2g}, (v_1), \; ^3A_{2g} \rightarrow ^3T_{1g} (F), (v_2), \; ^3A_{2g} \rightarrow ^3T_{1g} (P), (v_3),
$$

These three transitions are observed in the regions 7000-13000, 11000-20000 and 20000-28000 cm$^{-1}$. Transitions to spin singlet levels are sometimes observable, the $^3A_{2g} \rightarrow ^1E_g$ band being in the region 11000-15000 cm$^{-1}$ and the $^3A_{2g} \rightarrow ^1T_{1g}$ band in the 17000-15000 cm$^{-1}$. While $v_1$ and $v_3$ bands are normally symmetrical, the $v_2$ band often shows a shoulder or appear as a doublet.

The electronic ground state of a planar complex may either be $e^4_b$, $a^2_{1g}$, $b^2_{2g}$, i.e., a spin singlet $^1A_{1g}$ or $e^4_b$, $a^2_{1g}$, $b_{2g}$, $b_{1g}$, i.e., a spin triplet state $^3A_{2g}$ and an excited state $^1A_{2g}$. The low spin state is favoured, if the separation between the $dx^2-r^2$ and $dxy$ orbitals is more than 10000 cm$^{-1}$.

Square planar nickel(II) complexes are commonly orange or red but a few have purple or green colors. Their spectra frequently consist of a strong band around 15000-23000 cm$^{-1}$, with a second band in the range 23000-27000 cm$^{-1}$. These bands are commonly assigned to the transitions $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow ^1B_{1g}$. A further weaker band is sometimes observed in the 11000-15000 cm$^{-1}$ region and this is probably a spin forbidden band. The major difference between the spectra of square
planar complexes and those of octahedral complexes or tetrahedral is the absence of any bands below 10000 cm\(^{-1}\). The absence of such bands confirms that the \(d_{x^2-y^2}, d_{xy}\) separation is invariably greater than this value and accordingly these planar complexes are all diamagnetic\(^{192}\).

The electronic spectral data of Ni(II) complexes are given in Table 2.3 and spectra are presented in Figures 2.4-2.6. The electronic spectra of the present Ni(II) complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC show two bands in the region 12610-16260 cm\(^{-1}\) and 20408-28570 cm\(^{-1}\) due to \(3A_{2g(F)} \rightarrow 3T_{1g(F)}\) (\(\nu_2\)) and \(3A_{2g(F)} \rightarrow 3T_{1g(F)}\) (\(\nu_3\)) transitions, respectively commensurate with octahedral stereochemistry\(^{193-195}\). The spectra of the complexes do not indicate the lowest energy \(3A_{2g} \rightarrow 3T_{2g}\) transition.

![Figure 2.4: Electronic spectra of [Ni(QBD)\(_2\)Cl\(_2\)].](image-url)
Figure 2.5: Electronic spectra of [Ni(QBO)$_2$Cl$_2$].

Figure 2.6: Electronic spectra of [Ni(NQTC)$_2$Cl$_2$].
Table 2.3: Electronic spectra and Magnetic susceptibility measurement data of Co(II) and Ni(II) complexes

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2.54 Infrared spectra of cobalt(II) and nickel(II) complexes

The important IR spectral assignments of the Co(II) and Ni(II) complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC are summarized in Table 2.4 and the representative spectra are presented in Figures 2.7-2.11. The assignments of IR bands were arrived at after a careful comparison of the spectrum of each complex with that of corresponding ligand.

In the IR spectra of the ligand QBD, a strong band at around 1658 cm\(^{-1}\) can be attributed to the \(v(C=N)\). The peaks occurring at 1576 and 3330 cm\(^{-1}\), respectively in the ligand QBD are due to \(v(C=C)\) and \(v(NH)\). In the IR spectra of the complexes the band at 1658 cm\(^{-1}\) shifted to the lower frequency at around 1620 cm\(^{-1}\) suggesting the coordination through the quinoline nitrogen. And also, the band due to \(v(NH)\) suffers a negative shift by 10-25 cm\(^{-1}\) indicating the involvement of azepine nitrogen in the coordination.

The IR spectra of the ligand MQBD shows a strong band at around 1662 cm\(^{-1}\) which is assigned to \(v(C=N)\) vibrations. The peaks occurring at 1578 and 3332 cm\(^{-1}\), respectively are due to \(v(C=C)\) and \(v(NH)\). The shifting of the band at 1662 cm\(^{-1}\) in the IR spectra of the complexes indicates the coordination through the quinoline nitrogen. The band due to \(v(NH)\) suffers a negative shift by 20-25 cm\(^{-1}\) indicates the involvement of azepine nitrogen in the coordination. On the basis of the above interpretation, it is concluded that the MQBD behaves as a bidentate ligand.

The IR spectra of the ligand QBO shows the band at 1651 cm\(^{-1}\) due to the \(v(C=N)\). The bands occurring at 1566 and 2924 cm\(^{-1}\), respectively in the ligand QBO are assigned to \(v(C=C)\), \(v(C-H)\) of the heterocyclic ring. The \(v(COC)\) of the oxazepine moiety is observed at 1022 cm\(^{-1}\). The shift of the bands by 20-35 cm\(^{-1}\) corresponding to 1651 and 1022 cm\(^{-1}\) in the spectra of the complexes indicates that the
coordination is through the nitrogen and oxygen atoms of ligand. With reference to the above observations, it is concluded that the QBO behaves as a bidentate ligand.

In the IR spectra of the ligand MQBO, the \( \nu(C=O) \) of the oxazepine moiety is observed at 1025 cm\(^{-1} \). The bands occurring at 1569 and 3053 cm\(^{-1} \), respectively in the ligand MQBO are assigned to \( \nu(C=\equiv) \), \( \nu(C-H) \) of the heterocyclic ring. It also shows the band around 1653 cm\(^{-1} \) due to \( \nu(C=N) \) vibrations. In the IR spectra of the complexes, the band at 1653 cm\(^{-1} \) suffers a negative shift by 20-40 cm\(^{-1} \) indicating the coordination through the quinoline nitrogen. Also, the band at 1025 cm\(^{-1} \) is shifted to a lower frequency by 25-40 cm\(^{-1} \) indicating the oxygen atom of oxazepine ring is the site of coordination. With reference to the above observations, it is concluded that the MQBO behaves as a bidentate ligand.

In the IR spectra of the ligand NQTC, \( \nu(C=S) \) and \( \nu(CHO) \) are located at around 760 and 1710 cm\(^{-1} \) respectively. The band in the region 1650 cm\(^{-1} \) is assigned to \( \nu(C=N) \). In the IR spectra of the complexes, the band due to \( \nu(C=S) \) shifted to a lower frequency to the extent of 25-35 cm\(^{-1} \) indicating the involvement of sulphur atom of the ligand in bonding with metal ion. The band due to \( \nu(C=N) \) also suffers a negative shift by 25-30 cm\(^{-1} \) indicating the involvement of quinoline nitrogen in the coordination. On the basis of the above interpretation, it is concluded that the NQTC behaves as a bidentate ligand.

In the IR spectra of the ligand MNQTC, \( \nu(C=S) \) and \( \nu(CHO) \) are located at 762 and 1713 cm\(^{-1} \), respectively. The band in the region 1652 cm\(^{-1} \) is assigned to \( \nu(C=N) \). In the IR spectra of the complexes, the negative shift of the band due to \( \nu(C=S) \) to the extent of 20-35 cm\(^{-1} \) indicates the involvement of sulphur atom of the ligand in bonding with metal ion. Also, the band due to \( \nu(C=N) \) suffers a negative shift by 30-35 cm\(^{-1} \) suggesting the involvement of quinoline nitrogen in the coordination.
coordination. On the basis of the above interpretation, it is concluded that the MNQTC behaves as a bidentate ligand.

Further, in the spectra of the complexes a broad band around 3450-3480 cm\(^{-1}\) assignable to \(v(O-H)\) was absent indicating the absence of coordinated water. The absence of coordinated water was also confirmed from the TG studies.

The ligands and their complexes spectra show several common bands, which do not undergo any appreciable shifts. Important of these bands include the band in the 2950-3050 cm\(^{-1}\) regions, which are assigned to C-H stretching of the aromatic ring system. In addition to the appearance of new bands in the 440-475, 510-525 and 350-395 cm\(^{-1}\) range attributed to M-N, M-O and M-S vibrations, respectively seen in the spectra of the metal complexes suggest that the metal ion form bonds with N, O and S atoms of the ligands.

![Figure 2.7: IR spectra of QBD.](image-url)
Synthesis and Structural elucidation of Co(II) and Ni(II) complexes.

Figure 2.8: IR spectra of QBO.

Figure 2.9: IR spectra of NQTC.
Synthesis and Structural elucidation of Co(II) and Ni(II) complexes.

Figure 2.10: IR spectra of [Co(QBD)$_2$Cl$_2$].

Figure 2.11: IR spectra of [Ni(QBD)$_2$Cl$_2$].
Table 2.4: Some important IR stretching frequencies (cm\(^{-1}\)) of Co(II) and Ni(II) complexes

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<tr>
<th>Complex</th>
<th>ν(C=N)</th>
<th>ν(NH)</th>
<th>ν(COC)</th>
<th>ν(CSC)</th>
<th>ν M-N</th>
<th>ν M-O</th>
<th>ν M-S</th>
<th>ν M-X</th>
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<tr>
<td>[Co(QBD)_2Cl_2]</td>
<td>1615</td>
<td>3320</td>
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<td>--</td>
<td>440</td>
<td>--</td>
<td>350</td>
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<tr>
<td>[Co(QBO)_2Cl_2]</td>
<td>1615</td>
<td>--</td>
<td>995</td>
<td>--</td>
<td>458</td>
<td>510</td>
<td>--</td>
<td>368</td>
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<tr>
<td>[Co(NQTC)_2Cl_2]</td>
<td>1626</td>
<td>--</td>
<td>--</td>
<td>725</td>
<td>469</td>
<td>--</td>
<td>350</td>
<td>364</td>
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<td>998</td>
<td>--</td>
<td>464</td>
<td>518</td>
<td>--</td>
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<tr>
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2.55 Modes of coordination of anions

a. Chloride ion\(^{211-214,86,182,184}\)

The Far-IR spectra of the complexes, shows a sharp band in the region 350-368 and 250-285 cm\(^{-1}\) which are assignable to ν(Co-Cl) and ν(Ni-Cl) vibrations, respectively.

b. Nitrate ion\(^{215-217,70,86,206,212,182}\)

The free nitrate ion has relatively high symmetry and belongs to the point group D\(_{3h}\). This effective D\(_{3h}\) symmetry of free ion is lowered to C\(_{2v}\) after coordination to a metal ion; it can be confirmed by using IR spectral studies.

In general, the free nitrate exhibits three bands at 1380 (\(v_3\)), 830 (\(v_2\)), and 720 (\(v_4\)) cm\(^{-1}\). Upon coordination, this \(v_3\) band (1380 cm\(^{-1}\)) splits into two bands, which occurs around 1500 cm\(^{-1}\)(\(v_4\)) and 1320 cm\(^{-1}\) (\(v_1\)) in the complexes and for unidentate
nitrate ion the magnitude of splitting($\Delta \nu$) between $\nu_4$ and $\nu_1$ is in the 110-150 cm$^{-1}$ range.

The present nitrate complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC showed three IR bands. These three bands are appear at ca. 1480, 1350 and 1020 cm$^{-1}$ which are assigned to $\nu_4$, $\nu_1$ and $\nu_2$ band of coordinated nitrate ions, respectively and the magnitude splitting between $\nu_4$ and $\nu_1$ bands is ~120 cm$^{-1}$ which suggest that the nitrate ions are bonded unidentately to cobalt(II) and nickel(II) ion.

c. Perchlorate ion

The free perchlorate ion exhibits the band at 1100 cm$^{-1}$. Upon coordination, this band splits into a doublet at 1100 cm$^{-1}$ and ~1090 cm$^{-1}$ and a sharp peak at ca. 630 cm$^{-1}$. In the IR spectra of perchlorate complexes of QBD, QBO, NQTC, MQBD, MQBO and MNQTC exhibits the bands at 1120 cm$^{-1}$ and 1070 cm$^{-1}$ and a sharp one at 610 cm$^{-1}$. Thus these absorption bands support monodentate coordination of perchlorate group to the cobalt(II) and nickel(II) ion.

2.56 Proton nuclear magnetic resonance spectra

The $^1$H NMR spectra of the ligands and their complexes have been recorded in DMSO-d$_6$ using TMS as an internal reference. The chemical shift values of the ligands and their corresponding complexes are presented in Table 2.5 and the representative spectra are presented in Figures 2.12-2.15.

The $^1$H NMR spectra of the ligand QBD exhibits the signal at $\delta$ 10.65 ppm is due to N-H proton. The H-C=N proton of QBD appear at $\delta$ 8.4 ppm as a sharp peak. A multiplet appearing in the region $\delta$ 7.2-7.8 ppm is assignable to aromatic protons. In the spectra of cobalt(II) and nickel(II) complexes, all these resonance signals are retained but a sharp signal at $\delta$ 10.65 ppm has completely disappeared indicating that azepine nitrogen atom is the site of coordination.
The $^1\text{H}$ NMR spectra of the ligand MQBD exhibit the signal at $\delta$ 10.80 ppm due to N-H proton. The H-C=N proton of MQBD appear at $\delta$ 8.6 ppm as a sharp peak. A multiplet appearing in the region $\delta$ 7.1-8.2 ppm is assignable to aromatic protons. In the spectra of cobalt(II) and nickel(II) complexes, all these resonance signals are retained but a sharp signal at $\delta$ 10.80 ppm has completely disappeared indicating that azepine nitrogen atom is the site of coordination.

A $^1\text{H}$ NMR spectrum of the ligand QBO exhibit a multiplet in the range $\delta$ 7.1-8.0 is attributed to aromatic protons. The singlet at $\delta$ 8.3 is assigned to H-C=N proton. In the spectrum of the complexes, all the NMR signals of the ligand have appeared in their appropriate places.

A $^1\text{H}$ NMR spectrum of the ligand MQBO exhibit a multiplet in the range $\delta$ 7.3-8.0 is attributed to aromatic protons. The singlet at $\delta$ 8.4 is assigned to H-C=N proton. In the spectrum of the complexes, all the NMR signals of the ligand have appeared in their appropriate places as in the free ligand.

$^1\text{H}$ NMR spectra of the ligand NQTC showed singlet at $\delta$ 9.6 ppm and a multiplet in the range $\delta$ 7.4-8.6 ppm due to -CHO and aromatic protons respectively. $^1\text{H}$ NMR spectra of nickel(II) and cobalt(II) complexes exhibit signals remaining in the same position as in the free ligand.

$^1\text{H}$ NMR spectra of the ligand MNQTC showed singlet at $\delta$ 9.7 ppm and a multiplet in the range $\delta$ 7.5-8.6 ppm due to -CHO and aromatic protons, respectively. $^1\text{H}$ NMR spectra of nickel(II) and cobalt(II) complexes exhibit signals remaining in the same position as in the free ligand.

Thus, $^1\text{H}$ NMR support the conclusion drawn on the basis of IR data regarding the coordination mode of the ligands QBD, QBO, NQTC, MQBD, MQBO and MNQTC with cobalt(II) and nickel(II) ions.
Figure 2.12: $^1$H NMR spectra of ligand QBD.

Figure 2.13: $^1$H NMR spectra of ligand QBO.
Figure 2.14: $^1$H NMR spectra of ligand NQTC.

Figure 2.15: $^1$H NMR spectra of complex [Co(QBD)$_2$Cl$_2$].
Table 2.5: $^1$H NMR spectral data (δ, ppm) of ligands and their Co(II) and Ni(II) complexes

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<tr>
<th>Ligand/Complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>QBD</td>
<td>10.65 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>MQBD</td>
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</tr>
<tr>
<td>QBO</td>
<td>8.3 (s, 1H, H-C=N), 7.1-8.0 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>MQBO</td>
<td>8.4 (s, 1H, H-C=N), 7.3-8.0 (m, 11H, Ar-H), 2.6 (s, 3H, CH$_3$)</td>
</tr>
<tr>
<td>NQTC</td>
<td>9.6 (s, 1H, -CHO), 7.4-8.6 (m, 11H, Ar-H)</td>
</tr>
<tr>
<td>MNQTC</td>
<td>2.9 (s, 3H, CH$_3$), 9.7 (s, 1H, -CHO), 7.5-8.6 (m, 10H, Ar-H)</td>
</tr>
<tr>
<td>[Co(QBD)$_2$Cl$_2$]</td>
<td>10.95 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-8.8 (m, 9H, Ar-H)</td>
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<tr>
<td>[Co(QBO)$_2$Cl$_2$]</td>
<td>8.3 (s, 1H, H-C=N), 7.5-8.9 (m, 9H, Ar-H)</td>
</tr>
<tr>
<td>[Co(NQTC)$_2$Cl$_2$]</td>
<td>9.6 (s, 1H, -CHO), 7.4-9.0 (m, 11H, Ar-H)</td>
</tr>
<tr>
<td>[Ni(QBD)$_2$Cl$_2$]</td>
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<td>8.3 (s, 1H, H-C=N), 7.5-8.9 (m, 9H, Ar-H)</td>
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<tr>
<td>[Ni(NQTC)$_2$Cl$_2$]</td>
<td>9.6 (s, 1H, -CHO), 7.4-9.0 (m, 11H, Ar-H)</td>
</tr>
</tbody>
</table>

2.57 X-ray diffraction studies$^{231-236}$

a. Cobalt(II) complex

The X-ray powder diffraction data were obtained for [Co(QBO)Cl$_2$] complex. The diffractogram records 19 reflections (Figure 2.16) between 5 and 50° (2θ). The diffraction patterns of this complex have been indexed by standard methods and the unit cell parameters were calculated from the indexed data by trail and error method (Table 2.6). In this study, the unit cell parameters are found to be $a=6.257502$, $b=6.347065$, $c=4.116160$ and the value of $\alpha=85.22^\circ$, $\beta=87.44067$ and $\gamma=67.36$. Within the limits of experimental error, the calculated values of 2θ are in good agreement with the observed 2θ values.
Fig 2.16: X-ray diffraction spectrum of [Co(QBO)\textsubscript{2}Cl\textsubscript{2}] complex.

Table 2.6: X-ray diffraction data of [Co(QBO)\textsubscript{2}Cl\textsubscript{2}] complex

<table>
<thead>
<tr>
<th>Peak</th>
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<th>2θ expt(calc.)</th>
<th>h k l</th>
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b. Nickel(II) complex

The X-ray powder diffraction for [Ni(QBO)Cl₂] complex has been shown in typical X-ray pattern Figure 2.17, it is seen that the complex consists of some reflections between 3-50° (2θ) arising from the diffraction X-rays by planes of metal ions. The interplanar spacing (d) have been calculated (Table 2.7) from the positions of intense peak using Bragg’s relationships i.e., nλ = 2d Sinθ, where λ = wavelength of x-rays used (Cu Kα = 1.5412 Å). In this study, the unit cell parameters are found to be a=11.0748, b=14.0295, c=23.1064 and the value of α=65.60°, β=102.03 and γ=103.39.

Fig 2.17: X-ray diffraction spectrum of [Ni(QBO)₂Cl₂] complex.
Table 2.7: X-ray diffraction data of \([\text{Ni}(\text{QBO})_2\text{Cl}_2]\) complex

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<td>28</td>
<td>2.4113</td>
<td>37.250 (37.248)</td>
<td>1 -1 1</td>
</tr>
<tr>
<td>29</td>
<td>2.2929</td>
<td>39.250 (39.243)</td>
<td>-2 6 4</td>
</tr>
<tr>
<td>30</td>
<td>2.1612</td>
<td>41.750 (41.750)</td>
<td>-2 1 10</td>
</tr>
<tr>
<td>31</td>
<td>2.0338</td>
<td>44.500 (44.500)</td>
<td>3 4 6</td>
</tr>
</tbody>
</table>

In the present case, Co(II) and Ni(II) complexes shown sharp peaks indicating crystalline nature. On the basis of elemental analysis, Infrared, electronic and XRD spectral data, the following octahedral structures for Co(II) and Ni(II) complexes are proposed.
Synthesis and Structural elucidation of Co(II) and Ni(II) complexes.

\[
\text{[M(QBD)\textsubscript{2}X\textsubscript{2}]} \\
\text{M} = \text{Co(II) or Ni(II)}; \\
\text{X} = \text{Cl}^{-}, \text{NO}_3^{-}, \text{ClO}_4^{-}
\]

\[
\text{[M(MQBD)\textsubscript{2}X\textsubscript{2}]} \\
\text{M} = \text{Co(II) or Ni(II)}; \\
\text{X} = \text{Cl}^{-}, \text{NO}_3^{-}, \text{ClO}_4^{-}
\]

\[
\text{[M(QBO)\textsubscript{2}X\textsubscript{2}]} \\
\text{M} = \text{Co(II) or Ni(II)}; \\
\text{X} = \text{Cl}^{-}, \text{NO}_3^{-}, \text{ClO}_4^{-}
\]

\[
\text{[M(MQBO)\textsubscript{2}X\textsubscript{2}]} \\
\text{M} = \text{Co(II) or Ni(II)}; \\
\text{X} = \text{Cl}^{-}, \text{NO}_3^{-}, \text{ClO}_4^{-}
\]

\[
\text{[M(NQTC)\textsubscript{2}X\textsubscript{2}]} \\
\text{M} = \text{Co(II) or Ni(II)}; \\
\text{X} = \text{Cl}^{-}, \text{NO}_3^{-}, \text{ClO}_4^{-}
\]

\[
\text{[M(MNQTC)\textsubscript{2}X\textsubscript{2}]} \\
\text{M} = \text{Co(II) or Ni(II)}; \\
\text{X} = \text{Cl}^{-}, \text{NO}_3^{-}, \text{ClO}_4^{-}
\]
2.6 Conclusion

Co(II) and Ni(II) complexes with different quinoline derivatives such as QBD, MQBD, QBO, MQBO, NQTC, MNQTC have been synthesized and characterized on the basis of elemental analysis, magnetic susceptibility, molar conductance measurements, infrared spectra, proton NMR, X-ray diffraction data. Elemental analysis shows 1:2 metal to ligand stoichiometry for Co(II) and Ni(II) complexes. Infrared spectra reveals that the ligands in Co(II) and Ni(II) complexes behaves as bidentate. These complexes shows coordination number six and octahedral geometry.

On the basis of elemental and spectral data, the following empirical formulae are suggested for the complexes.

\[
[\text{CoL}_2\text{X}_2] \quad \text{and} \quad [\text{NiL}_2\text{X}_3]
\]

where \( L = \) QBD, QBO, NQTC, MQBD, MQBO or MNQTC and \( X = \) Cl\(^{-}\), NO\(_3\)\(^{-}\) or ClO\(_4\)\(^{-}\).
Reference


134. G. Lopez, G. Sauchez, G. Garcia, E. Perez, J. Casabo, E. Molins and


