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RESEARCH ARTICLE

MAGNETIC AND ELECTRONIC SPECTRAL STUDIES OF FOUR, FIVE AND SIX COORDINATED COMPLEXES OF SUBSTITUTED HYDRAZIDE AND HYDRAZONES WITH DIVALENT NICKEL AND COBALT METAL IONS

Saurabh Bhardwaj¹, Renu Saraswat² and Nupur Chatterji²

1. PGT Chemistry, Meerut Public School, Meerut.
2. Associate Professor, Department of Chemistry, Meerut College, Meerut.

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Abstract

Metal complexes of divalent Nickel and Cobalt metal ions have been synthesized with picolinic acid hydrazide (PH), ortho-hydroxy acetophenone picolinoyl hydrazone (APH) and ortho-hydroxy acetophenone iso-nicotinoyl hydrazone (AIH) ligands and were isolated at both high pH and low pH. These complexes were characterized by elemental analyses and also by electronic spectral studies and magnetic measurements. Ligands PH and AIH act as tridentate, while APH is tetradentate. All form two types of complexes, depending upon pH of the reaction mixture. At high pH complexes formed are monomeric while at low pH complexes were found to be dimeric. Dimerisation is initiated by enolic oxygen which acts like a bridging ligand between two metal ions.

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Introduction:-

Metal-ligand interactions involving a large pH range and non-aqueous solvents present many interesting points requiring further elucidation. In the former case, it has been claimed that the reaction product undergoes dimerisation depending upon the pH of the medium. Attempts have been made in the present paper to investigate this aspect on the basis of magnetic and spectral data. Researchers have paid attention to hydrazones and their complexes with metal ions because they act as very important stereochemical models in the field of coordination chemistry on account of ease of their preparation and versatility in structure. It has been established that the carbonyl linkage i.e. C=O in hydrazides is accountable for the biological activities such as anti bacterial, antifungal, antitumor and herbicidal (1,2). More recently development of new drug metal complexes have gained attention and special interest in the area of coordination chemistry (3,4). Complexes of transition metals of substituted hydrazones play remarkable role in a number of catalytic reaction like polymerisation, asymmetric cyclopropanation and oxidation (5-7). Structural characterisation of some of the complexes of hydrazides have revealed some interesting information about them like their efficacy and tendency to serve as planar pentadentate ligands in its complexes (8-11) along with its tridentate character (12). These ligands not only show keto-enol tautomerism but also can coordinate in monoanionic (13), dianionic (14), neutral (14) or tetraanionic (15) forms with the metal ions having either the coordination number six or seven (14) producing mononuclear as well as binuclear species. However it is also an established fact that it all is dependent on the reaction conditions like metal ion, its concentration, nature of hydrazide and pH of the medium (16). Coordination chemistry of some substituted aroyl hydrazones has revealed combining of donor positions like as protonated amide or deprotonated amide oxygen, an imine nitrogen

Corresponding Author:- Saurabh Bhardwaj

Address:- PGT Chemistry, Meerut Public School, Meerut.

(> C=N-) of hydrazone ($R_2C=N-NR_2'$) moiety as well as some additional donor positions (generally Nitrogen or Oxygen) presented given by aldehyde or ketone to form the Schiff base (17).

The magnetic measurements are of immense importance in determining the nature of bond and stereochemistry of the complexes. The interpretations revealed by the studies of the electronic spectra and magnetic properties of many complexes formed by the metal ions of 3-d transition series and the consequential implementation of ligand-field theory were a major element in the renaissance of transition metal chemistry in the 1960s (18).

The complexes of divalent nickel and cobalt are most extensively studied, because their structures exemplify some important fundamental orbital and electronic principles relevant to the critical study of coordination compounds. The most interesting feature of these metal ions is the exhibition of varied stereochemistries, viz., square planar (19), tetrahedral(20), square pyramidal (21), tetragonal (22) or pentagonal bipyramidal (23).

The pyridine based acid hydrazides and their corresponding hydrazones with o-hydroxyacetophenone, provide suitable coordination sites in the form of phenolic and ketonic oxygen. These compounds may act differently depending upon pH of the reaction mixture. Thus, the ligands chosen for the present studies exhibit keto \rightleftharpoons enolic tautomeric forms. These compounds, therefore, are best suited for carrying out basic studies on bridged complexes.

The present studies have, therefore, been initiated in the direction of evaluating the bonding, structure, geometry and other characteristics of metal chelates. The present ligands have potential donor sites, viz., pyridine nitrogen, ketonic or enolic amide oxygen, hydrazinic or phenolic oxygen and azomethine nitrogen, which are suitably placed for coordination. The interesting feature is the presence of two oxygen atoms and either of them may act as a bridging atom in between the two atoms of metal.

Physical Measurements

Magnetic Measurements

The measurements of magnetic susceptibility of powdered complexes, at room temperature were carried out by Guoy's balance. Mercury(II) tetrathiocyanatocobaltate(II) $[HgCo(CNS)_4]$ ($\chi_g=16.442 \times 10^{-6}$ CGS units at 293°A) was used as a calibrant. Tube constant was calculated from time to time to check the satisfactory working of the apparatus.

Electronic Spectral Measurements

The electronic spectra of the complexes at room temperature were recorded in ethanol, dimethylformamide or nujol mull on a Cary-14 automatic recording spectrophotometer. These measurements were carried out at Indian Institute of Technology, Kanpur.

(iii) pH Measurements

The pH of the solutions was measured at room temperature by Elico (LI-10) pH meter, using combined electrodes.

(iv) Molecular Weight Measurements

measurement of molecular weight was made by Beckmann's cryoscopic method

(v) Chemical Analyses

The metal contents in all the complexes were estimated as under:

A known quantity of the complex was heated with a very small amount of concentrated sulphuric acid and then repeatedly with concentrated nitric acid until all the organic matter was decomposed. The residue was then dissolved in doubly distilled water or sometimes dilute hydrochloric acid was added to it and made upto a known volume, from which the metals were estimated by standard literature methods (24).

The microanalyses of carbon(C), hydrogen (H) and nitrogen (N) for all the compounds were carried out by the Microanalytical Division, CDRI, Lucknow.

Methods Of Calculations

Magnetic Susceptibility

Magnetic susceptibility (χ_g) of complexes has been calculated from the formula,

$$\chi_g = \frac{1}{W} (\alpha v + \beta f)$$

where ,

| | | |
|----------|---|---|
| W | = | Weight of the substance in grams, |
| α | = | volume susceptibility of air (-0.029×10^{-6} CGS units at 293°A) |
| β | = | tube constant |
| f | = | pull on the substance (including the pull on empty tube) |

For applying the diamagnetic corrections, using Pascal's constants(25), it is convenient to deal with in terms of susceptibility per mole (χ_m) of the compound, using the formula,

$$\chi_m = \chi_g \times \text{molecular weight}$$

The effective magnetic moment is then calculated with the help of the following formula.

$$\mu_{\text{eff.}} = 2.839 \sqrt{\chi_m \times T}$$

Where T = temperature in absolute units.

Ligand field Parameters

The calculation of various ligand field parameters viz., Ds, Dt, Dq^{xy}, Dq^z and parameters of Normalised Spherical Harmonic (NSH) Hamiltonian Theory (26) , viz., DS, DT, DQ, DQ^L and DQ^Z have been made .

Experimental

SYNTHESIS OF PICOLINIC ACID HYDRAZIDE (PH)

It was synthesised by refluxing ethyl-2-picolinate and hydrazine hydrate (99%) in 1:1 molar ratio on a water bath for five hours. On cooling, white crystalline product was obtained. It was filtered and recrystallised from ethanol when colourless needle shaped crystals (m.pt. 101°) were obtained. Yield ~ 85%. Calcd. for C₆H₇N₃O: C(52.55); H(5.11); N(30.65) percent. Found : C(52.42); H(5.09); N(30.77) percent.

SYNTHESIS OF ORTHO-HYDROXYACETOPHENONE PICOLINOYL HYDRAZONE (APH)

It was prepared by refluxing ethanolic solutions of picolinic acid hydrazide (0.1M) and o-hydroxyacetophenone (0.1M) for about three hours. On cooling, white product was obtained, which was filtered. It was recrystallised from ethanol, when shining colourless crystals (m.pt., 214°) were obtained. Yield ~ 75%. Calculated. for C₁₄H₁₃N₃O₂ : C(65.88); H(5.09); N(16.47) percent: Found : C(65.99); H(5.23); N(16.63) percent.

SYNTHESIS OF ORTHO-HYDROXYACETOPHENONE ISO-NICOTINOYL HYDRAZONE (AIH)

It was synthesised by mixing ethanolic solutions of iso-nicotinic acid hydrazide (0.1M) and o-hydroxyacetophenone (0.1M). The solution was refluxed on a water bath for four hours and cooled. A white product separated out. It was filtered and recrystallised from ethanol and needle shaped crystals (m.pt., 200°) were obtained. Yield ~ 80%. Calculated. for C₆H₇N₃O : C(52.52); H(5.11); N(30.65) percent: Found : C(52.42); H(5.09); N(30.77) percent. The ligands were also subjected to TLC to check their purity.

Methods of preparation and isolation of complexes

Two types of nickel (II) and cobalt (II) complexes with PH , APH and AIH were synthesised at low and high pH as follows:

NICKEL (II) COMPLEXES

Low pH complexes

Ethanolic solutions of PH (100 ml; 0.01 mole) and nickel (II) chloride (100 ml; 0.005 mole) were mixed with continuous stirring . Then the mixture (pH~2.3) was refluxed for about 4 hours. This solution was then concentrated on a sand bath to half its volume and kept overnight. The light blue crystals thus obtained were filtered and recrystallised from ethanol and dried under vacuum. Yield ~ 50%. Nickel hydrazones were obtained by first refluxing ethanolic solutions of PH or INH (100 ml; 0.01 mole) and o-hydroxyacetophenone (25 ml; 0.011 mole) followed by adding an ethanolic solution of nickel (II) chloride (50 ml; 0.005 mole) dropwise with constant shaking. The reaction mixture (pH ~ 2.2.-2.7) was refluxed for about 3 hrs., concentrated and kept overnight. Light bluish or greenish crystals were obtained. These crystals after filtration were washed with acetone, recrystallised from ethanol and dried under vacuum. Yield ~ 50-55%.

The analytical data of the complexes reveal their formulae to be $\text{Ni}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2\text{Cl}_2$, $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)\text{Cl}$ and $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)_2$, respectively and their results are given in Table (A).

The complexes do not undergo decomposition on keeping in air and are stable upto 275° . They are soluble in water, ethanol and dimethylformamide.

High pH Complexes

To a warm ethanolic solution of nickel (II) chloride (50 ml; 0.01 mole) and PH (50 ml; 0.02 mole), an ethanolic solution of potassium hydroxide was added dropwise with constant stirring, till pH became ~ 4.9 . Then the refluxing of the reaction mixture was done for 1 hr, when a green precipitate was obtained. It was cooled, filtered, washed with ethanol and ether and finally dried under vacuum. Yield $\sim 70\%$.

The ethanolic solution of PH (50 ml; 0.02 mole) was refluxed with o-hydroxyacetophenone (25 ml; 0.021 mole) for 1 hr. To the hot solution, warm ethanolic solution of nickel (II) chloride (100 ml; 0.01 mole) was added gradually. The pH was then raised to ~ 5.0 by dropwise addition of ethanolic solution of potassium hydroxide, when the blue solution changed to olive green. On refluxing it for 1 hr., a precipitate was obtained. It was then filtered then washed with ethanol and ether and finally dried under vacuum. Yield $\sim 50\%$.

Ethanolic mixture of INH (150 ml; 0.04 mole) and o-hydroxyacetophenone (25 ml; 0.042 mole) was refluxed for 1 hr. To this, was added a hot ethanolic solution of nickel (II) chloride (100 ml; 0.02 mole). The resulting brown solution did not show any perceptible precipitation even after raising the pH to 5.2. The solution was then kept in a refrigerator for 48 hrs, whereby orange-red crystals got separated from the oily liquid, which were separated by filtration, washed with ethanol, ether and dried in an oven at 110° . Yield $\sim 35\%$.

The analytical data of the complexes reveal their formulae to be $\text{Ni}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{Cl}$, $\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2)$ and $\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2)_2$, respectively and the results are given in Table (A).

The complexes formed with PH and APH ligands are insoluble in water, ethanol, partially soluble in methanol and soluble in dimethylformamide, whilst the AIH complex is soluble in dimethylformamide only.

COBALT (II) COMPLEXES

Low pH Complexes

Cobalt (II) chloride (0.01 mole) and PH (0.02 mole) were first dissolved in ethanol (100 ml.) and mixed with constant stirring. The reaction mixture (pH ~ 2.5) was refluxed for about 5 hours and kept overnight. Brown crystals separated out, which were filtered, washed with ethanol, ether and dried under vacuum. Yield $\sim 55\%$.

Ethanolic solutions of PH or INH (100 ml; 0.02 mole) and o-hydroxyacetophenone (25 ml; 0.021 mole) were mixed and refluxed for 1 hour. A hot solution of cobalt (II) chloride in ethanol (75 ml; 0.01 mole) was dropwise added to it. The reaction mixture (pH $\sim 2.1-2.5$) was refluxed for another 4 hours and kept overnight. Bright crystals (ranging from light to dark brown), separated were then filtered and washed with ethanol, acetone and dried under vacuum. Yield $\sim 55-60\%$.

The analyses of the complexes conform to the formulae $\text{Co}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2\text{Cl}_2$, $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)\text{Cl}$ and $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)_2$, respectively and the data are given in Table (B). The complexes are stable upto 300° . They are soluble in water and ethanol, but are insoluble in other organic solvents.

High pH complexes

To a solution of cobalt (II) chloride (100ml; 0.01 mole) and PH(100ml; 0.033 mole) in ethanol, an ethanolic solution of potassium hydroxide was added dropwise till its pH become ~ 4.5 . The reaction mixture was refluxed for an hour. The precipitate so obtained was filtered after cooling, washed with ethanol, ether and dried under vacuum. Yield $\sim 60\%$.

100 ml. ethanolic solution of PH (0.025 mole) and o-hydroxyacetophenone (0.028 mole) was refluxed for one hour. A hot ethanolic solution of cobalt (II) chloride (100 ml; 0.01 mole) was gradually added to it and pH raised to ~ 5.0 , as in preceding para. Refluxing of the reaction mixture was done for two hours. The red precipitate obtained was filtered, washed with ethanol, ether and dried in an oven at 110° . Yield $\sim 50\%$.

INH (0.025 mole) and o-hydroxyacetophenone (0.028 mole) were mixed in 100 ml. ethanol and refluxed for an hour. A brown solution was obtained on adding a warm solution of cobalt (II) chloride in ethanol (100 ml; 0.02 mole). On adding ethanolic potassium hydroxide solution, the solution developed a dark blue colour at pH~5.1. It was concentrated and kept overnight. Fine bluish red crystals were obtained. These crystals were then filtered and washed successively with ethanol, ether and dried under vacuum. Yield ~ 45%.

The analyses of the complexes conform to the formulae $\text{Co}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{Cl}$ and $\text{Co}(\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2)$ respectively and the results are given in Table (B).

The complexes are stable upto 290°. They are insoluble in water and ethanol, but soluble in dimethylformamide.

The bromo complexes of nickel (II) and cobalt (II) with PH and APH (at low pH) were prepared by the method of Denk and Madan (27). Their corresponding nitrate complexes were synthesised by taking the nitrate salts of the metals. Preparation of thiocyanato complexes were made by adding potassium thiocyanate to the metal chloride solution. The preparations of bromo, nitrate and thiocyanato complexes were also attempted for all the three ligands, but with APH (at high pH) and AIH (at low as well as high pH) similar products were obtained (as confirmed by analytical and i.r. spectral measurements).

Results And Discussion:-

(i) Analytical studies

Tables (A) and (B) list the complexes investigated together with their analytical data and colours. The results indicate that PH and AIH complexes synthesised at low pH have 1:2 metal to ligand stoichiometry, whereas the corresponding ratio is 1:1 in all the remaining complexes.

However, the molar ratio of M:L was varied between 1:1 and 1:3 in different synthetic procedures and the same product was obtained in all reactions. The complexes formed at low pH can be represented by the general formulae : $\text{M}(\text{PH})_2\text{X}_2$, $\text{M}(\text{APH})\text{X}$ and $\text{M}(\text{AIH})_2$, and those at high pH by : $\text{M}(\text{PH})\text{X}$, $\text{M}(\text{APH})$ and $\text{M}(\text{AIH})$; where $\text{M}=\text{Ni}(\text{II})$ or $\text{Co}(\text{II})$ and $\text{X}=\text{Cl}$, Br , NO_3 or NCS . The molecular weights of $\text{M}(\text{AIH})_2$ and $\text{M}(\text{APH})\text{X}$ determined cryoscopically and consistent with their formulae. However, the ratio of observed and calculated molecular weights for $\text{M}(\text{PH})\text{X}$, $\text{M}(\text{APH})$ and $\text{M}(\text{AIH})$ ranges between 1.92-2.02, which can be taken as an indication of their dimeric nature. The tests for anions are show in $\text{M}(\text{PH})_2\text{X}_2$, but in $\text{M}(\text{PH})\text{X}$ and $\text{M}(\text{APH})\text{X}$, these are given only after decomposing the complexes, showing thereby that X is in the coordination sphere. The formation of complexes of two sort , viz., monomeric and dimeric, indicate that the ligands exists in two forms i.e at low pH in keto form and at high pH in the enol form , as shown below :



MAGNETIC AND ELECTRONIC SPECTRAL STUDIES

NICKEL (II) COMPLEXES

The magnetic data for nickel (II) complexes at room temperature are reported in Table (C) and (D). The low pH complexes of PH, APH and AIH show magnetic moments in the range 2.78-3.06 B.M. These values are comparatively lower than expected for six- (2.80-3.20 B.M.) or five-coordinate (3.20-3.40 B.M.) nickel (II) complexes and may be probably related to the presence of low symmetry components in these complexes. The magnetic moments of nickel (II) complexes of PH and APH synthesised at high pH are much lower than the corresponding compounds at low pH. It appears that the substandard magnetic moments (2.40-2.60 B.M.) for these compounds may be due to metal-metal exchange coupling through enolic oxygen bridging (vide i.r.).

The AIH complex synthesised at high pH shows a magnetic moment 0.45 B.M., a value in the range often observed for spin paired ions and suggests square planar environment around the metal atom.

The spectra of the solution of $[\text{Ni}(\text{PH})_2]\text{X}_2$ and $[\text{Ni}(\text{AIH})_2]$ are similar and show two bands that are identically positioned ~ 11350-11800 and 16250-16950 cm^{-1} with a shoulder ~ 9700-10500 cm^{-1} . This presence of the shoulder must have been there due to of the splitting of the first band into two components, which indicates that tetragonal distortion is there in case of such complexes. The band at ~ 28500 cm^{-1} emerges as a broad band. The spectra of these complexes can best be interpreted by assuming the effective symmetry to be D_{4h} . Thus, the various bands can be assigned to: ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$ (F) (9700-10500 cm^{-1}); ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_{2g}$ (F) (11350-11800 cm^{-1}); ${}^3\text{B}_{1g} \rightarrow {}^3\text{A}_{2g}$ (F)

(16250-16950 cm^{-1}) and ${}^3\text{B}_{1g} \rightarrow {}^3\text{A}_{2g}(\text{P})$, ${}^3\text{E}_g$ (28500 cm^{-1}) [13]. It is found that the bands formed in these complexes do not follow any regular pattern, so it may be concluded that they are anion independent.

The solution spectra of $[\text{Ni}(\text{APH})\text{X}]$, $[\text{Ni}(\text{PH})\text{X}]_2$ and $[\text{Ni}(\text{APH})]_2$ are interestingly similar, but are quite different from those of $[\text{Ni}(\text{PH})_2]\text{X}_2$ and $[\text{Ni}(\text{AIH})_2]$ and four bands, viz., 8100-8700 cm^{-1} , 10200-11000 cm^{-1} , 14500-16000 cm^{-1} and 22500-23500 cm^{-1} are discernable. These bands are consistent with those of five coordinate ones, whose structures have been established by X-ray measurements. Thus, assuming the effective symmetry to be C_{4v} , the bands can be assigned to: ${}^3\text{B}_1 \rightarrow {}^3\text{B}_2$ (8100-8700 cm^{-1}); ${}^3\text{B}_1 \rightarrow {}^3\text{E}^a$ (10200-11000 cm^{-1}); ${}^3\text{B}_1 \rightarrow {}^3\text{A}_2$ (14500-16000 cm^{-1}) and ${}^3\text{B}_1 \rightarrow {}^3\text{E}^b$ (22500-23500 cm^{-1}). The symmetry of the complexes is, however, lower than C_{4v} due to the presence of donor atoms of unequal strengths and different sizes. Six coordinate Ni (II) complexes may possess O_h or D_{4h} symmetry. There is no splitting of the ν_1 band, which is generally observed in the D_{4h} symmetry. Thus complexes, under study, possess distorted octahedral geometry.

The complexes $[\text{Ni}(\text{AIH})_2]$, however, appears to be quite distinct from other complexes in being orange-red in colour and diamagnetic in nature. Its solution spectra exhibits two bands ~ 15500 and 19000 cm^{-1} with a weak shoulder at 14200 cm^{-1} . The former band characteristic of square planar geometry, may be assigned to first spin allowed transition, ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$. The bands at 19000 and 14200 cm^{-1} may be due to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ and spin-forbidden ${}^1\text{A}_{1g} \rightarrow {}^3\text{B}_{1g}$ transitions respectively. The energies of these bands are comparable to d-d bands observed for other square planar Schiff's base complexes.

The intense higher energy bands $\sim 34600 \text{ cm}^{-1}$ observed in the spectra of all complexes except those of $[\text{Ni}(\text{PH}_2)]\text{X}_2$ and $[\text{Ni}(\text{PH})\text{X}]_2$ may be due to ligand $\pi-\pi^*$ transition of the phenolic group.

COBALT (II) COMPLEXES

The magnetic moments of $[\text{Co}(\text{PH})_2]\text{X}_2$, $[\text{Co}(\text{APH})\text{X}]$ and $[\text{Co}(\text{AIH})_2]$ at room temperature lie in the range 4.84-5.04 B.M., whereas they are anomalously low (~ 3.90 and 4.20 B.M.) for $[\text{Co}(\text{PH})\text{X}]_2$ and $[\text{Co}(\text{APH})]_2$. The former values are in the range reported for high spin five- or six-coordinate complexes, while the latter values are too low to be predicted for tetrahedral (4.40-4.87 B.M.) or octahedral (4.70-5.20 B.M.) complexes of cobalt (II). It appears that the sub-normal values are due to metal-metal exchange interaction through enolic oxygen bridging. The magnetic moment of $(\text{Co}(\text{AIH})_2)$ is 4.45 B.M. at room temperature. It is, however, not isomorphous with other cobalt compounds.

The solution spectra of $[\text{Co}(\text{PH})_2]\text{X}_2$ and $[\text{Co}(\text{AIH})_2]$ show two bands discernable at ~ 8200 , 8650 cm^{-1} and ~ 15800 , 16200 cm^{-1} , respectively with a broad band envelope $\sim 20000 \text{ cm}^{-1}$ having two bands ~ 18000 and 22000 cm^{-1} . The spectra are consistent with the octahedral environment around the metal atom. However, the chances of an idealised symmetry are remote due to the presence of donor atoms of unequal strength and size. The various bands can be assigned to: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$; ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively in order of increasing energy. Distortion of the molecule gives rise to multiple bands and this is consistent with the lower symmetry elements present in these compounds. The amount of distortion cannot be calculated since the splitting of bands is not observed in the spectra of complexes.

The absorption maxima of the ligand field bands in the spectra of $[\text{Co}(\text{APH})\text{X}]$, $[\text{Co}(\text{PH})\text{X}]_2$ and $[\text{Co}(\text{APH})]_2$ are nearly identical and show three bands in 9200-10450, 16800-17500, 22200-23250 cm^{-1} regions which resembles the spectra of five-coordinate complexes, structures of which have been authenticated by X-ray measurements. These complexes are isomorphous with the corresponding nickel (II) complexes. This also points towards the pentacoordination around the cobalt ion. The tri- and tetradentate nature of PH and APH, presence of one anion the coordination sphere, dimeric nature of $[\text{Co}(\text{PH})\text{X}]_2$ and $[\text{Co}(\text{APH})]_2$, conclusively point towards their square pyramidal geometry. Thus by assuming that the effective symmetry to be C_{4v} , the various bands may be assigned to: ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{B}_1$ (9200-10650 cm^{-1}); ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{E}$ (16800-17500 cm^{-1}) and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{A}_2(\text{P})$ (22200-23250 cm^{-1}). This symmetry is, however, lower than C_{4v} , since the donor set, e.g. $\text{N}_2\text{O}_2\text{X}$ or N_2O_3 cannot conform to idealised symmetry. Applying the statement that the tensor Hamiltonian for C_{4v} group is identical with that for D_{4h} the description of D_{4h} applies well in the square pyramidal complexes conforming of C_{4v} symmetries. Various parameters used to define the distortion viz., Dt , Dq^{xy} , and Dq^z are calculated and included in Table (E) and (F).

The solution spectra of $[\text{Co}(\text{AIH})_2]$ is quite different from the spectra of other compounds described herein. The broad high intensity bands are observed ~ 5850 and $\sim 15800 \text{ cm}^{-1}$ and are multistructured, perhaps due to the mixing in of metal d-orbitals with ligand functions. The spectral bands are consistent with the tetrahedral environmental around the metal atom and may be assigned to, ${}^4\text{A}_2 \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively.

Table (A):- Analytical Data Of Nickel (Ii) Complexes.

| Complex | Colour | Found (%) | | | | | Calculated (%) | | | | |
|--|---------------|-----------|-------|------|-------|---------|----------------|-------|------|-------|---------|
| | | Ni | C | H | N | Halogen | Ni | C | H | N | Halogen |
| $[\text{Ni}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]\text{Cl}_2$ | Light blue | 14.68 | 35.52 | 3.39 | 20.98 | 17.39 | 14.54 | 35.67 | 3.46 | 20.82 | 17.58 |
| $[\text{Ni}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]\text{Br}_2$ | Greenish blue | 11.72 | 29.43 | 2.72 | 17.21 | 32.68 | 11.91 | 29.22 | 2.84 | 17.05 | 32.47 |
| $[\text{Ni}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2](\text{NO}_3)_2$ | Blue | 12.71 | 31.74 | 3.21 | 24.73 | - | 12.85 | 31.52 | 3.06 | 24.52 | - |
| $[\text{Ni}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2](\text{NCS})_2$ | Light green | 13.31 | 37.16 | 3.02 | 24.71 | - | 13.08 | 37.43 | 3.12 | 24.95 | - |
| $[\text{Ni}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{Cl}]_2$ | Green | 25.31 | 31.41 | 2.72 | 18.35 | 15.20 | 25.51 | 31.29 | 2.60 | 18.25 | 15.43 |
| $[\text{Ni}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{Br}]_2$ | Light green | 21.09 | 26.07 | 2.01 | 15.51 | 29.01 | 21.37 | 26.20 | 2.18 | 15.29 | 29.12 |
| $[\text{Ni}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{NO}_3]_2$ | Light green | 23.01 | 28.31 | 2.25 | 21.65 | - | 22.86 | 28.04 | 2.33 | 21.80 | - |
| $[\text{Ni}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{NCS}]_2$ | Olive green | 23.00 | 33.41 | 2.49 | 22.41 | - | 23.22 | 33.24 | 2.37 | 22.16 | - |
| $[\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)\text{Cl}]$ | Light blue | 16.61 | 48.49 | 3.65 | 12.32 | 10.00 | 16.85 | 48.24 | 3.44 | 12.06 | 10.19 |
| $[\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)\text{Br}]$ | Blue | 14.71 | 43.00 | 3.21 | 10.92 | 20.51 | 14.94 | 42.77 | 3.05 | 10.69 | 20.37 |
| $[\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)\text{NO}_3]$ | Blue | 15.87 | 44.57 | 3.01 | 15.23 | - | 15.66 | 44.83 | 3.20 | 14.94 | - |
| $[\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)\text{NCS}]$ | Blue | 15.52 | 48.81 | 3.42 | 14.87 | - | 15.83 | 48.55 | 3.23 | 15.10 | - |
| $[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2)]_2$ | Olive green | 18.69 | 53.52 | 3.79 | 13.31 | - | 18.83 | 53.89 | 3.52 | 13.47 | - |
| $[\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2)_2]$ | Bluish green | 10.16 | 59.00 | 4.02 | 14.99 | - | 10.35 | 59.28 | 4.23 | 14.82 | - |
| $[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2)]_2$ | Orange red | 18.67 | 54.11 | 3.40 | 13.62 | - | 18.83 | 53.89 | 3.52 | 13.47 | - |

Table (B):- Analytical Data Of Cobalt (Ii) Complexes.

| Complex | Colour | Found (%) | | | | | Calculated (%) | | | | |
|--|-----------------|-----------|-------|------|-------|---------|----------------|-------|------|-------|---------|
| | | Co | C | H | N | Halogen | Co | C | H | N | Halogen |
| $[\text{Co}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]\text{Cl}_2$ | Brown | 14.71 | 35.41 | 3.31 | 20.98 | 17.25 | 14.58 | 35.65 | 3.46 | 20.79 | 17.57 |
| $[\text{Co}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]\text{Br}_2$ | Light brown | 12.11 | 29.42 | 2.71 | 17.23 | 32.21 | 11.94 | 29.21 | 2.84 | 17.04 | 32.46 |
| $[\text{Co}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2](\text{NO}_3)_2$ | Light brown | 12.63 | 31.63 | 3.19 | 24.31 | - | 12.89 | 31.51 | 3.06 | 24.51 | - |
| $[\text{Co}(\text{C}_6\text{H}_7\text{N}_3\text{O})_2](\text{NCS})_2$ | Light brown | 13.29 | 31.41 | 3.31 | 24.76 | - | 13.12 | 37.42 | 3.11 | 24.94 | - |
| $[\text{Co}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{Cl}]_2$ | Chocolate brown | 25.41 | 31.01 | 2.71 | 18.47 | 15.63 | 25.56 | 31.25 | 2.68 | 18.22 | 15.40 |
| $[\text{Co}(\text{C}_6\text{H}_6\text{N}_3\text{O})\text{Br}]_2$ | Reddish | 21.2 | 26.0 | 2.0 | 15.0 | 29.32 | 21.4 | 26.1 | 2.1 | 15.2 | 29.10 |

| | | | | | | | | | | | |
|--|------------------|-----------|-----------|----------|-----------|-------|-----------|-----------|----------|-----------|-------|
| | brown | 0 | 0 | 3 | 0 | | 2 | 9 | 8 | 7 | |
| [Co(C ₆ H ₆ N ₃ O)NO ₃] ₂ | Light brown | 23.1 2 | 28.2 5 | 2.3 0 | 21.9 6 | - | 22.9 2 | 28.0 2 | 2.3 3 | 21.7 9 | - |
| [Co(C ₆ H ₆ N ₃ O)NCS] ₂ | Light brown | 23.4 5 | 33.4 2 | 2.5 3 | 22.2 9 | - | 23.2 8 | 33.2 1 | 2.3 7 | 22.1 4 | - |
| [Co(C ₁₄ H ₁₂ N ₃ O ₂)Cl] | Light brown | 17.0 2 | 48.4 1 | 3.5 3 | 11.9 1 | 10.01 | 16.9 0 | 48.2 2 | 3.4 4 | 12.0 5 | 10.18 |
| [Co(C ₁₄ H ₁₂ N ₃ O ₂)Br] | Brownis h red | 14.8 9 | 42.5 6 | 2.9 1 | 10.5 0 | 20.56 | 14.9 9 | 42.7 5 | 3.0 5 | 10.6 8 | 20.36 |
| [Co(C ₁₄ H ₁₂ N ₃ O ₂)NO ₃] | Brownis h red | 15.5 7 | 44.6 3 | 3.0 9 | 14.7 6 | - | 15.7 1 | 44.8 1 | 3.2 0 | 14.9 3 | - |
| [Co(C ₁₄ H ₁₂ N ₃ O ₂)NCS] | Light brown | 15.9 9 | 48.3 1 | 3.0 2 | 15.3 7 | - | 15.8 8 | 48.5 3 | 3.2 3 | 15.0 9 | - |
| [Co(C ₁₄ H ₁₁ N ₃ O ₂)] ₂ | Red | 18.9 8 | 54.0 4 | 3.4 2 | 13.6 9 | - | 18.8 8 | 53.8 6 | 3.5 2 | 13.4 6 | - |
| [Co(C ₁₄ H ₁₂ N ₃ O ₂)] ₂ | Brown | 10.6 7 | 59.5 1 | 4.0 7 | 15.0 0 | - | 10.3 8 | 59.2 6 | 4.2 3 | 14.8 1 | - |
| [Co(C ₁₄ H ₁₁ N ₃ O ₂)] ₂ | Bluish red | 18.6 1 | 53.9 9 | 3.3 8 | 13.2 2 | - | 18.8 8 | 53.8 6 | 3.5 2 | 13.4 6 | - |

Table (C):- Electronic Spectral And Magnetic Moment Data Of Five-Coordinate Nickel (Ii) Complexes.

| Complex | μ_{eff} (B.M.) , 303K | Spectral bands (cm ⁻¹) | Dt | Ds | Dq ^{xy} | Dq _z | DS | DT | DQ | DQ ^L | DQ ^Z | DT/D Q |
|---------------------------------------|--|--|---------|--------------|------------------|-----------------|----------|----------|-----------|-----------------|-----------------|-----------|
| [Ni(PH)Cl] ₂ | 2.42 | 8300,10350 15000,2320 0 | 23 4 | - 72 6 | 103 5 | 62 5 | 508 2 | 317 2 | 2470 5 | 2845 9 | 1719 7 | 0.128 |
| [Ni(PH)Br] ₂ | 2.50 | 8600,10900, 15450,2350 0 | 26 3 | - 70 4 | 109 0 | 63 0 | 492 8 | 357 9 | 2575 2 | 2998 8 | 1728 1 | 0.139 |
| [Ni(PH)NO ₃] ₂ | 2.44 | 8350,10750, 14400,2320 0 | 27 4 | - 55 1 | 107 5 | 59 6 | 385 7 | 371 4 | 2516 3 | 2955 8 | 1637 2 | 0.148 |
| [Ni(PH)NCS] ₂ | 2.40 | 8250,10800, 14700,2280 0 | 29 1 | - 58 9 | 108 0 | 57 1 | 412 3 | 394 5 | 2502 8 | 2969 7 | 1569 1 | 0.158 |
| [Ni(APH)Cl] | 2.90 | 8650,10750, 15650,2290 0, 34620 | 24 0 | - 76 6 | 107 5 | 65 5 | 536 2 | 325 3 | 2570 8 | 2955 8 | 1800 9 | 0.127 |
| [Ni(APH)Br] | 2.82 | 8550,10750, 15150,2335 0, 34600 | 25 1 | - 68 1 | 107 5 | 63 6 | 476 7 | 340 2 | 2553 2 | 2955 8 | 1748 0 | 0.133 |
| [Ni(APH)NO ₃] | 2.96 | 8700,10950, 14950,2345 0, 34600 | 25 7 | - 61 3 | 109 5 | 64 5 | 429 1 | 348 4 | 2598 6 | 3010 9 | 1774 0 | 0.134 |
| [Ni(APH)NC S] | 2.87 | 8650,11000, 16000,2250 0, 34620 | 26 9 | - 77 7 | 110 0 | 62 9 | 543 9 | 364 6 | 2593 1 | 3024 6 | 1730 1 | 0.140 |
| [Ni(APH)] ₂ | 2.58 | 8550,10950, 15050,2315 0, 34580 | 27 4 | - 62 6 | 109 5 | 61 6 | 438 2 | 371 4 | 2571 3 | 3010 8 | 1692 2 | 0.144 |

Table (D):- Electronic Spectral And Magnetic Moment Data Of Six-Coordinate Nickel (Ii) Complexes.

| Complex | μ_{eff} (B.M.) | Spectral bands | Dt | Ds | Dq ^x | Dq | DS | DT | DQ | DQ ^L | DQ ^Z | DT/D |
|---------|------------------------------|-------------------|----|----|-----------------|----|----|----|----|-----------------|-----------------|------|
|---------|------------------------------|-------------------|----|----|-----------------|----|----|----|----|-----------------|-----------------|------|

| | , 303K | (cm ⁻¹) | | | y | z | | | | | | Q |
|---|--------|---------------------------------------|---------|---------|----------|---------|----------|----------|-----------|-----------|-----------|-------|
| [Ni(PH) ₂]Cl ₂ | 2.96 | 10350,11350, 16500,28520 | 11 4 | - 83 | 113 5 | 93 6 | 584 5 | 154 5 | 2937 9 | 3120 7 | 2572 2 | 0.052 |
| [Ni(PH) ₂]Br ₂ | 2.82 | 9950,11500, 16600,28520 | 17 7 | - 81 | 115 0 | 84 0 | 569 1 | 239 9 | 2878 1 | 3162 0 | 2310 3 | 0.083 |
| [Ni(PH) ₂](NO ₃) ₂ | 3.02 | 9900,11450, 16800,28550 | 17 7 | - 85 | 114 5 | 83 5 | 598 5 | 239 9 | 2864 3 | 3148 2 | 2296 5 | 0.084 |
| [Ni(PH) ₂](NCS) ₂ | 2.86 | 9800,11400, 16250,28500 | 18 3 | - 77 | 114 0 | 82 0 | 539 0 | 248 1 | 2895 3 | 3188 9 | 2308 1 | 0.086 |
| [Ni(AIH) ₂] | 3.05 | 10400,11750, 16950,28500, 34620 | 15 4 | - 83 | 117 5 | 90 6 | 584 5 | 208 8 | 2983 7 | 3230 8 | 2489 5 | 0.070 |

Table (E):- Electronic Spectral Nd Magnetic Moment Data Of Five-Coordinate Cobalt (Ii) Complexes.

| Complex | μ_{eff} (B.M.), , 303K | Spectral bands (cm ⁻¹) | Dt | Ds | Dq ^x _y | Dq ^z | DS | DT | DQ | DQ ^L | DQ ^Z | DT/DQ |
|--|--------------------------------------|------------------------------------|--------------|----------|------------------------------|-----------------|-----------|---------------|-----------|-----------------|-----------------|-------|
| [Co(PH)Cl] ₂ | 3.91 | 9340,16860, 22240 | - 60 6 | 210 3 | 129 0 | 235 1 | 1472 1 | - 821 5 | 4518 9 | 3546 7 | 6463 3 | 0.182 |
| [Co (PH)Br] ₂ | 3.95 | 9250,17100, 22220 | - 61 8 | 205 3 | 129 7 | 237 8 | 1437 1 | - 837 7 | 4557 4 | 3566 0 | 6540 1 | 0.184 |
| [Co (PH)NO ₃] ₂ | 3.90 | 9500,17400, 22550 | - 64 4 | 209 3 | 130 5 | 243 2 | 1465 1 | - 873 0 | 4621 1 | 3588 0 | 6687 4 | 0.189 |
| [Co(PH)NCS] ₂ | 3.98 | 10040,17500, 23240 | - 65 6 | 225 4 | 132 0 | 246 8 | 1577 8 | - 889 2 | 4681 6 | 3629 3 | 6786 2 | 0.190 |
| [Co(APH)Cl] | 4.88 | 10000,17280, 23050 | - 64 8 | 225 3 | 130 5 | 243 9 | 1577 1 | - 878 4 | 4627 5 | 3588 0 | 6706 6 | 0.190 |
| [Co(APH)Br] | 5.02 | 9950,17050, 22840 | - 64 1 | 224 9 | 128 9 | 241 1 | 1574 3 | - 868 9 | 4572 3 | 3544 0 | 6628 9 | 0.190 |
| [Co(APH)NO ₃] | 5.04 | 10040,17360, 22980 | - 66 6 | 223 7 | 129 4 | 246 0 | 1565 9 | - 902 8 | 4626 1 | 3557 7 | 6762 9 | 0.195 |
| [Co(APH)NC S] | 4.82 | 10250,17480, 23150 | - 68 6 | 227 4 | 129 0 | 249 1 | 1591 8 | - 929 9 | 4647 2 | 3546 7 | 6848 1 | 0.200 |
| [Co(APH)] ₂ | 4.20 | 10450,16700, 23180 | - 63 9 | 241 9 | 127 3 | 239 1 | 1693 3 | - 862 2 | 4525 1 | 3500 0 | 6575 3 | 0.191 |

Table (F):- Electronic Spectral And Magnetic Moment Data Of Six-Coordinate Cobalt (Ii) Complexes.

| Complex | μ_{eff} (B.M.), 303K | Spectral bands (cm ⁻¹) | Dq ^{xy} | B |
|---------------------------------------|---------------------------------|------------------------------------|------------------|-----|
| [Co(PH) ₂]Cl ₂ | 5.01 | 8150, 15750, 18000, 22100 | 1019 | 792 |

| | | | | |
|---|------|---------------------------|------|-----|
| $[\text{Co}(\text{PH})_2]\text{Br}_2$ | 5.04 | 8250, 15800, 18050, 22050 | 1031 | 791 |
| $[\text{Co}(\text{PH})_2](\text{NO}_3)_2$ | 4.85 | 8200, 15800, 18100, 22100 | 1025 | 797 |
| $[\text{Co}(\text{PH})_2](\text{NCS})_2$ | 4.92 | 8200, 15850, 18050, 22000 | 1025 | 793 |
| $[\text{Co}(\text{AIH})_2]$ | 4.84 | 8650, 16200, 18100, 21950 | 1081 | 774 |

Conclusion:-

Following conclusions are drawn on the basis of above studies:

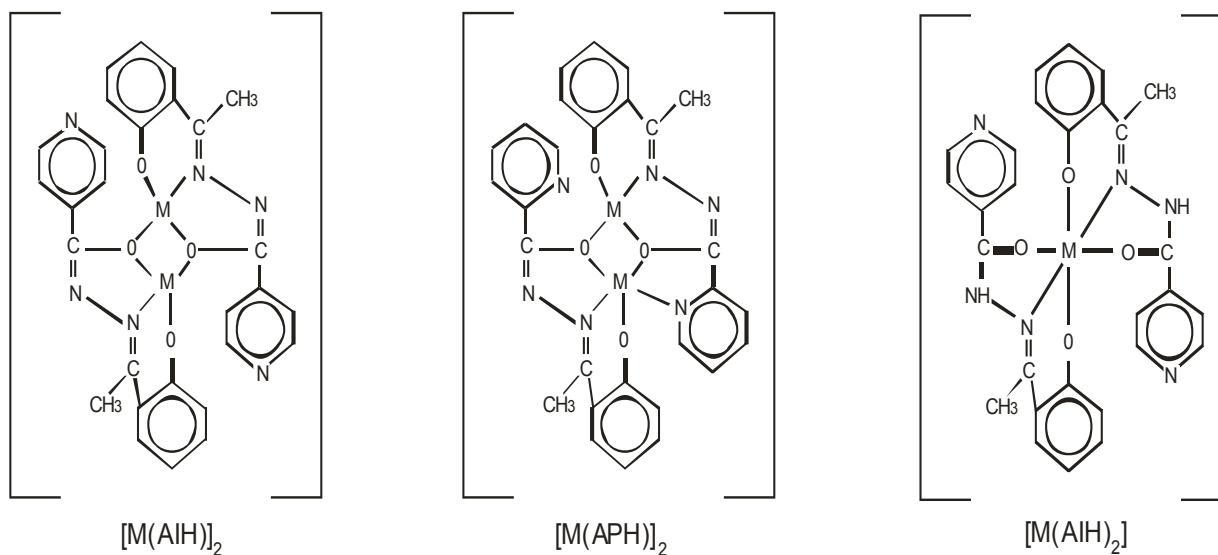
(a) Ligands PH and AIH act as tridentate, while APH is tetradentate. All form two types of complexes, depending upon pH of the reaction mixture.

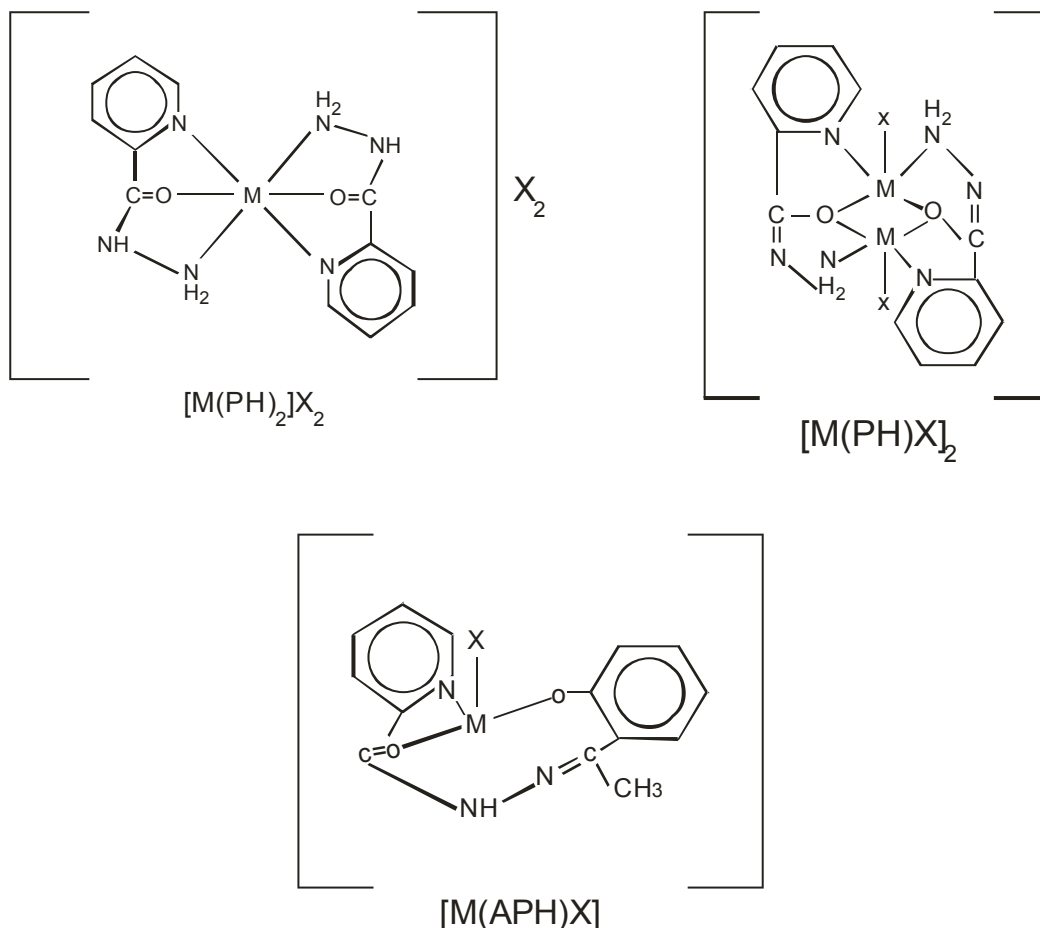
(b) Complexes synthesised at low and high pH are monomeric and dimeric, respectively.

(c) In complexes synthesised at high pH, the dimerisation is initiated by enolic oxygen, which acts as a bridge between the two metal atoms.

(d) In PH and APH complexes, besides phenolic oxygen, ketonic or enolic oxygen and hydrazinic or azomethine nitrogen, pyridine nitrogen also takes part in coordination, while it is not so in AIH complexes.

(e) At low pH, PH and AIH complexes are six coordinate while those of APH are five-coordinate. At high pH, except AIH complexes which are four-coordinate all other complexes are five-coordinate. The following tentative structures can be proposed for the various cobalt and nickel hydrazide and hydrazone complexes





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