



## DIVALENT NICKEL AND COPPER COMPLEXES WITH LIGANDS DERIVED FROM ACID HYDRAZIDES AND DIACETYL

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### ABSTRACT

Picolinic acid hydrazide (PH) and isonicotinic acid hydrazide (INH) react with diacetyl to form complexes containing open chain tetradentate ligands, through an *in situ* process in presence of nickel and copper salts. The complexes were isolated and characterized as five coordinate with the aid of elemental analyses, magnetic, electronic and infrared spectral studies. Attempts to obtain the free ligands were unsuccessful but its solid complexes can be isolated. Diacetyl-bis-picolylhydrazide  $\text{DA(PH)}_2$  coordinates through azomethine and pyridine nitrogen atoms while diacetyl-bis-isonicotinoylhydrazide  $\text{DA(INH)}_2$  does so through azomethine nitrogen and amido oxygen atoms giving rise to the complexes of the  $[\text{MDA(PH)}_2\text{X}_2]$  or  $[\text{MDA(INH)}_2\text{X}_2]$  type where  $\text{X} = \text{Cl, Br, NO}_3$  or  $\text{NCS}$  and  $\text{M} = \text{nickel (II) and copper (II)}$ . Magnetic and electronic spectra are consistent with five coordinate geometries. The metal–ligand vibrations in the far infrared spectra are discussed.

**Key words :** Nickel, Copper, Acid hydrazide, Diacetyl.

### INTRODUCTION

Pyridine based metal complexes have been found to be versatile chelating agents and recently their complexes with various metal ions have extensively been studied<sup>1–3</sup>. No attempts appear to have been made to condense pyridine based acid hydrazides with  $\alpha$ -diketones. However, few reports are available on the reactions of acid hydrazides with  $\beta$ -diketones to yield acid hydrazones<sup>3–5</sup>. The present paper deals with the synthesis and characterisation of five-coordinated complexes of nickel and copper formed during the reaction of acid hydrazide and diacetyl.

### EXPERIMENTAL

Ethyl-2-picolinate and isonicotinic acid hydrazide were obtained from Koch–Light and diacetyl from BDH, (England), respectively. All other chemicals used were of reagent grade.

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### Synthesis of ligands and complexes

The picolinic acid hydrazide (PH) was synthesized by heating a mixture of ethyl-2-picolinate (0.01 mole) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (0.01 mole) at a reflux temperature on a water bath for four hours. The acid hydrazide so obtained was recrystallised from ethanol, m.p.  $\sim 99.5^\circ$ .

### DA(PH)<sub>2</sub> complexes

Methanolic solutions ( $50\text{ cm}^3$ ) of PH (1.0 mole) and diacetyl (0.5 mole) were added to a solution of copper salts (0.5 mole) in methanol and the mixture was boiled under reflux for three hours. The resulting bright green crystalline precipitate was filtered off, washed with ethanol, methanol, acetone, ether and dried *in vacuo*.

Methanolic solutions of pH (1.0 mole) and diacetyl (0.5 mole) were mixed with methanolic solutions of nickel salts (0.5 mole). The brown mixture was refluxed on a water bath for ten hours and then concentrated to half its volume and kept overnight. The reddish brown crystals were filtered off, washed with methanol, ether and dried *in vacuo*.

### DA(INH)<sub>2</sub> complexes

A methanolic ( $50\text{ cm}^3$ ) solution of INH (1.0 mole) and diacetyl (0.5 mole) were mixed and copper salts (0.5 mole) solutions in methanol were added. On boiling under reflux for four hours, the brown solution became yellowish green; heating was continued for further six hours. The crystals were filtered, washed with methanol, acetone, ether and dried *in vacuo*.

A deep brown colour developed, when methanolic solutions of INH (1.0 mole) and diacetyl (0.5 mole) were mixed with a methanolic solution of nickel salts (0.5 mole) and the solution was boiled under reflux for eight hours and then concentrated and kept overnight in a refrigerator. The brown crystals separated were filtered off, washed with methanol, ether and dried *in vacuo*. All the complexes are stable upto  $300^\circ$  and are soluble in DMF but insoluble in other common organic solvents.

Metal bromide and thiocyanates were synthesised by adding KBr or  $\text{NH}_4\text{NCS}$  to an ethanolic solution of metal chlorides, stirring mechanically for four hours and filtering off the precipitate of KCl or  $\text{NH}_4\text{Cl}$ .

### Magnetic and spectral measurements

Magnetic susceptibilities were measured by the Gouy's method using  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  as calibrant. IR spectra in KBr pellets were recorded on a Perkin-Elmer 337 ( $4000\text{--}250\text{ cm}^{-1}$ ) instrument and far IR ( $650\text{--}200\text{ cm}^{-1}$ ) in nujol mull on a Beckmann I.R. 12 spectrophotometer. The electronic spectra of the complexes in DMF were recorded on a Carl Zeiss Specor UV-vis-spectrophotometer.

Nickel was estimated by EDTA titrations using Eriochrome Black-T as indicator. The copper content was determined iodometrically. Microanalysis (C, H and N) were performed at



Microanalytical Division, C.D.R.I., Lucknow. The poor solubility of the complexes in common organic solvents and water precluded determination of either conductance or molecular weight.

## RESULTS AND DISCUSSION

The elemental analyses indicate the general formula of the complexes to be  $MLX_2$  where  $M = Cu(II)$  or  $Ni(II)$ ;  $L = DA(PH)_2$  or  $DA(INH)_2$  and  $X = Cl, Br, NO_3$  or  $NCS$ . Tests for anions are consistent with their presence inside the coordination sphere.

### Infrared spectra

A comparison of the spectra of free ligands with those of  $DA(PH)_2$  complexes reveal changes in pyridine ring vibrations. The band I of these vibrations shows an upward shift of  $15\text{ cm}^{-1}$  while band II and III show a downward shift of  $5\text{ cm}^{-1}$ . The ring breathing mode at  $\sim 990\text{ cm}^{-1}$  increases in frequency and appears at  $\sim 1005\text{ cm}^{-1}$ . These changes suggest that pyridine–nitrogen coordinates to the metal atom in  $DA(PH)_2$  complexes. In the spectra of complexes of  $DA(INH)_2$ , such changes are not observed in the pyridine ring vibrations; thus ruling out the possibility of pyridine–nitrogen coordination<sup>6–8</sup>.

In the spectra of  $DA(INH)_2$  complexes, amide I band [ $\nu(C=O)$ ] appear at  $1640\text{ cm}^{-1}$  showing a downward shift and amide II band [ $\nu(CN)$ ] at  $1540\text{ cm}^{-1}$  showing an upward shift, while amide III band [ $\delta(NH)$ ] splits into two bands appearing at  $1220$  and  $1380\text{ cm}^{-1}$ , respectively. The amide IV band ( $C=O$  in plane deformation mode) shows an upward shift and appears at  $\sim 500\text{ cm}^{-1}$ . All these changes are consistent with amide oxygen coordination to the metal atom<sup>9</sup>.

The band  $\sim 1635$  and  $845\text{ cm}^{-1}$  may be assigned to  $NH$  deformation coupled with  $OCN$  antisymmetric vibrations and  $NH$  out-of-plane bending modes, respectively. These bands disappear from the spectra of complexes and new bands appear at  $\sim 1330$  and  $1280\text{ cm}^{-1}$ , respectively. The bands at  $\sim 1620$ – $1610\text{ cm}^{-1}$  and  $\sim 1590\text{ cm}^{-1}$  in the free ligands assignable to  $\nu(CN)$  vibrations, show a downward shift of  $10$ – $20\text{ cm}^{-1}$  indicating that azomethine nitrogen takes part in coordination<sup>10,11</sup>. Thus, it appears that diacetyl has reacted with each amino group of both the hydrazide molecules. Such types of metal template synthesis have been reported earlier wherein one acetylacetone or even one acetone molecule reacts with the two available amino groups leading to ring closure and hence to give macrocyclic molecule<sup>12</sup>. This contention finds support in the presence of new bands in the spectra of the complexes  $\sim 2925$ ,  $1355$ ,  $1270$  and  $680\text{ cm}^{-1}$  characteristic of the diacetyl moiety and may be assigned to  $\nu(CH_3)$ ,  $\nu(C-CH_3)$ ,  $\delta_{sym}(CH_3)$  and ring deformation modes<sup>13</sup>, respectively. The absence of strong bands at  $\sim 1530\text{ cm}^{-1}$  characteristic of bonded carbonyl, shows that both the oxygen atoms of diacetyl have reacted with two molecules of  $PH$  or  $INH$  forming  $DA(PH)_2$  or  $DA(INH)_2$  species as metal chelates.

The spectra of nitrate complexes show various bands at  $\sim 1260$ ,  $1050$  and  $830\text{ cm}^{-1}$  consistent with monodentate nature of nitrate group. The spectra of thiocyanato complexes show new bands at  $\sim 2130\text{ v(CN)}$ ,  $825\text{ v(CS)}$  and also  $480\text{ cm}^{-1}$  (NCS bending), respectively which are characteristic of the N-bonded monodentate thiocyanate group.

### Magnetic and electronic spectral studies

The magnetic moments of copper and nickel complexes lie in the range  $1.74\text{--}1.82\text{ }\mu_{\text{B}}$  and  $2.68\text{--}2.88\text{ }\mu_{\text{B}}$  range at room temperature, respectively. The magnetic moments for copper complexes are well within the range reported for these having an orbitally degenerate ground state<sup>14</sup>. The magnetic moments of nickel complexes are however, low, but values as low as  $2.50\text{ }\mu_{\text{B}}$  have also been reported<sup>15,16</sup>. The values are well within the range reported for five-coordinate complexes. The slight lowering may be attributed to distortion of the molecule from idealised symmetry, however, the values indicate that metal-metal interactions are absent<sup>16</sup>.

The solution spectra of copper complexes show an intense band at  $\sim 14750\text{--}15300\text{ cm}^{-1}$  and broad bands at  $\sim 16800\text{--}17650$  and  $22000\text{--}23000\text{ cm}^{-1}$ . The spectra are comparable to those of five-coordinated square pyramidal complexes of copper (II) whose structures have been established by X-ray measurements<sup>17-18</sup>. The various bands, therefore, can be assigned to;  ${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$  [ $10300\text{--}10800\text{ cm}^{-1}$ ],  ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$  [ $14750\text{--}15300\text{ cm}^{-1}$ ] and  ${}^2\text{B}_1 \rightarrow {}^2\text{E}$  ( $16800\text{--}17650\text{ cm}^{-1}$ ) assuming energy level sequence  ${}^2\text{E} > {}^2\text{B}_1 > {}^2\text{A}_1 > {}^2\text{B}_2$  of  $\text{C}_{4v}$  symmetry<sup>19</sup>.

The solution spectra of nickel complexes show spectral bands discernable in the  $8000\text{--}8500$ ,  $10250\text{--}10750$ ,  $14500\text{--}15500$ ,  $22250\text{--}23250$  and  $26600\text{--}27200\text{ cm}^{-1}$  regions. These spectral bands are consistent with those predicted for five-coordinated nickel complexes whose structures have been established by X-ray crystallographic measurements<sup>20</sup>. It is interesting, however, that for a similar set of donor atoms in a regular trigonal bipyramid, only one band is expected in the near i.r. region at  $\sim 7000\text{ cm}^{-1}$ , while two bands are expected for regular square-pyramidal structure, one at  $\sim 7500$  and other at  $\sim 10800\text{ cm}^{-1}$ <sup>18</sup>. The spectra are consistent with those reported for five-coordinate square-pyramidal<sup>21</sup>. However, to consider the structure to be distorted square-pyramidal is quite reasonable. The various bands can be assigned to  ${}^3\text{B}_1 \rightarrow {}^3\text{B}_2$  ( $8000\text{--}8500\text{ cm}^{-1}$ ),  ${}^3\text{B}_1 \rightarrow {}^3\text{E}^{\text{a}}$  ( $\sim 10000\text{ cm}^{-1}$ ),  ${}^2\text{B}_1 \rightarrow {}^3\text{A}_2$  ( $\sim 14000\text{ cm}^{-1}$ ) and  ${}^3\text{B}_1 \rightarrow {}^3\text{E}^{\text{b}}$  ( $\sim 22500\text{ cm}^{-1}$ ), respectively, assuming the effective symmetry to be  $\text{C}_{4v}$ . Considering that description for  $\text{D}_{4h}$  complexes applies equally well to square pyramidal  $\text{C}_{4v}$  complexes utilizing various energy transitions, the values of ligand field parameters,  $\text{D}_{\text{qxy}}$  and  $\text{D}_{\text{qz}}$  have been calculated<sup>22</sup>. The value indicate that the equatorial ligand field is much stronger than the axial field produced by anions.

### Far IR spectra

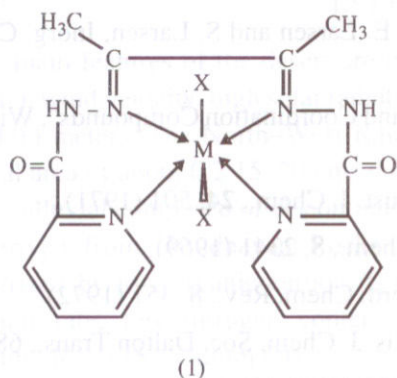
New bands  $\sim 255\text{--}260$  and  $280\text{--}285\text{ cm}^{-1}$  regions may be assigned to  $\text{v(Ni-py)}$  and  $(\text{Cu-py})$  vibrations, respectively in the far IR spectra of the  $\text{DA(PH)}_2$  complexes. These bands



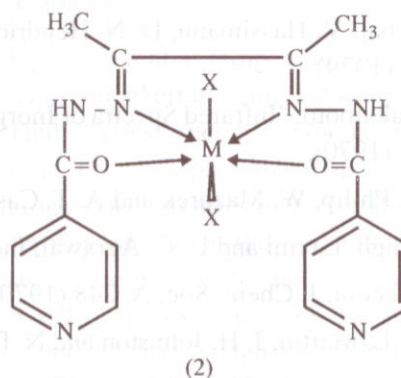
substantiate the coordination of pyridine–nitrogen stretching modes and are well within the range suggested for five–coordinate complexes<sup>23</sup>. However, similar bands are absent in the spectra of DA (INH)<sub>2</sub> complexes. The 16b and 6a vibrations (out–of–plane and in–plane deformations), respectively, of the pyridine ring appear at ~410 and 610 cm<sup>-1</sup> in the spectra DA(PH)<sub>2</sub> ligand. These vibrations show an upward shift of 10–15 and 30–35 cm<sup>-1</sup>, respectively in the DA(PH)<sub>2</sub> complexes, but are unaffected in that of DA(INH)<sub>2</sub>.

These observations substantiate the involvement of pyridine–nitrogen in DA(PH)<sub>2</sub> complexes. The new vibrations appearing in the spectra of DA(INH)<sub>2</sub> complexes at ~300–320 and 440–450 cm<sup>-1</sup> are assigned to  $\nu(\text{Ni–O})$  and  $\nu(\text{Cu–O})$  (amide) respectively. Some new bands appear in the spectra of all the complexes at ~450–490 cm<sup>-1</sup>. The bands at 480–490 cm<sup>-1</sup> in nickel and 460–470 cm<sup>-1</sup> in copper complexes may be assigned to  $\nu(\text{Ni–N})$  and  $\nu(\text{Cu–N})$  (azomethine) vibrations<sup>9</sup>, respectively. The spectra of halocomplexes show various metal–halogen stretching frequencies in the ~280–290 cm<sup>-1</sup> regions  $\nu(\text{Ni–Cl})$ , 225–230 cm<sup>-1</sup>  $\nu(\text{Ni–Br})$ , 270–280 cm<sup>-1</sup>  $\nu(\text{Cu–Cl})$  and 215–220 cm<sup>-1</sup> (Cu–Br), respectively<sup>9</sup>. The nitrate complexes show bands at ~230 and 225 cm<sup>-1</sup> and can be assigned to  $\nu(\text{Ni–ONO}_2)$  and  $\nu(\text{Cu–ONO}_2)$  vibrations, respectively. Thiocyanato complexes show new bands at ~280 and 270 cm<sup>-1</sup> assignable to  $\nu(\text{Ni–NCS})$  and  $\nu(\text{Cu–NCS})$ . All these metal–anion vibrations are consistent with the monodentate nature of nitrate and N–bounded thiocyanate group<sup>9</sup>.

Based on analytical, magnetic, electronic and IR spectral data, structures (1) and (2) may be proposed for these complexes.



M = Cu (II) and Ni (II)  
X = Cl, Br, ONO<sub>2</sub> and NCS



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X = Cl, Br, ONO<sub>2</sub> and NCS

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