Synthesis, Biological, Spectral, and Thermal Investigations of Cobalt(II) and Nickel(II) Complexes of N-Isonicotinamido-2',4'-Dichlorobenzalaldimine

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A new series of 12 complexes of cobalt(II) and nickel(II) with N-isonicotinamido-2',4'-dichlorobenzalaldimine (INH-DCB) with the general composition MX 2 · n(INH-DCB) [M = Co(II) or Ni(II), X = Cl − , Br − , NO3 − , NCS − , or CH3COO − , n = 2; X = ClO4 − , n = 3] have been synthesized. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, infrared, electronic spectra, magnetic susceptibility, and conductivity measurements. An octahedral geometry has been suggested for all the complexes. The metal complexes were screened for their antifungal and antibacterial activities on different species of pathogenic fungi and bacteria and their biopotency has been discussed.

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INTRODUCTION

Interest in the study of hydrazones has been growing because of their antimicrobial, antituberculosis, and antitumour activity [1–8]. Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH [9]. The remarkable biological activity of acid hydrazides R−CO−NH−NH2, their corresponding aroylhydrazones R−CO−NH−N=CH−R′, and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant importance in the past [10–13]. In view of the versatile importance of hydrazones, we herein describe the synthesis and identification of the Co(II) and Ni(II) complexes of N-isonicotinamido-2',4'-dichlorobenzalaldimine (INH-DCB) (Figure 1).

EXPERIMENTAL

MX 2 · nH2O (M = Co2+ or Ni2+; X = Cl − , Br − , NO3 − or CH3COO − ) were obtained from SD Fine Chemicals Ltd (Mumbai, India) and were used as such: M(NCS) 2 (M = Co2+ or Ni2+). They were prepared by mixing metal chloride (in ethanol) and ethanolic solution of potassium thiocyanate in 1 : 2 molar ratio. Precipitated KCl was filtered off and the filtrate having respective metal thiocyanate was used immediately for complex formation [14]. M(ClO4) 2 (M = Co2+ or Ni2+) were prepared by the addition of an ethanolic solution of sodium perchlorate to respective metal chloride solution. White precipitate of NaCl was filtered off and the filtrate containing M(ClO4) 2 was used as such for complex formation. The ligand INH-DCB was synthesized in the laboratory by the following method. Isonicotinic acid hydrazide (INH) (0.01 mol) was dissolved in 10 mL of 95% ethanol. To this solution, 2,4-dichlorobenzaldehyde (0.01 mol) was added in 95% ethanol (10 mL). The mixture was refluxed on a water bath for 1-2 hours. The partial removal of solvent on a water bath followed by cooling produced crystalline product, which was collected by filtration, washed with cold ethanol, and dried under vacuum (yield 80%). The purity of the ligand was checked by TLC, IR spectra, and melting point.

Synthesis of the complexes

A general method has been used for the preparation of all the complexes. A hot ethanolic solution of the corresponding cobalt(II) or nickel(II) salt was mixed with a hot ethanolic solution of the ligand (in 1 : 2 or 1 : 3 molar ratio). The reaction mixture was refluxed on water bath for about 2-3 hours.
On cooling at room temperature, the coloured complexes precipitated out in each case. They were filtered, washed with ethanol and recrystallized, and dried over P2O5 under vacuum.

**Physical measurements and analytical estimations**

The cobalt(II) and nickel(II) ions in their metal complexes were estimated complexometrically with EDTA using murexide and erichrome black-T as an indicator after decomposing the complexes with concentrated H2SO4 and H2O2 [15]. The halogens and thiocyanate were estimated by Volhard’s method [16]. The perchlorate was estimated by the method suggested by Kurz et al [17]. The nitrogen content was determined by Kjeldahl method. The molecular weight of the complexes was determined in laboratory cryoscopically in freezing nitrobenzene using a Beckmann thermometer of ±0.01°C accuracy. The conductivity measurements were carried out, at room temperature in nitrobenzene, using a conductivity bridge and dip-type cell operated at 220 volts AC mains. The magnetic measurements on powder form of the complexes were carried out at room temperature on Evans’s balance using anhydrous copper(II) sulfate as calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer infrared spectrophotometer model Spectrum 1000 in infrared spectra of the complexes were recorded on a Perkin-Elmer infrared spectrophotometer model Spectrum 1000 in the range of 200–4000 cm−1.

The reaction of cobalt(II) and nickel(II) salts with INH-DCB results in the formation of MX2 · (INH-DCB)2 [M = Co(II) or Ni(II); X = Cl−, Br−, NO3−, NCS−, or CH3COO−, n = 2; X = ClO4−, n = 3] (Table 1). All the complexes are quite stable and could be stored for months without any appreciable change. The complexes do not have sharp melting points but decompose above 250°C. These complexes are generally soluble in common organic solvents. The conductance measurement indicates that the chloro, bromo, nitrito, thiocyanato, and acetato complexes of cobalt(II) and nickel(II) are essentially nonelectrolytes in nitrobenzene, while the perchlorate complexes dissociate in nitrobenzene and behave as 1 : 2 electrolytes [19]. The molecular weights determined cryoscopically are in broad agreement with the conductance data (Table 1).

**Magnetic susceptibility**

The observed magnetic moments of cobalt(II) complexes of INH-DCB are given in Table 1. The theory of magnetic susceptibility of cobalt(II) ion was given originally by Schlapp and Penney [20] and the best summary of results on the magnetic behaviour of cobalt compound is that of Figgis and Nyholm [21]. The observed values of magnetic moment for cobalt(II) complexes are generally diagnostic of the coordination geometry about the metal ion. The low-spin square-planar cobalt(II) complexes may be 2.9 BM, arising from one unpaired electron plus an apparently large orbital contribution [21]. Both tetrahedral and high-spin octahedral cobalt(II) complexes possess three unpaired electrons but may be distinguished by the magnitude of the deviation of μeff from the spin-only value. The magnetic moment of tetrahedral cobalt(II) complexes with an orbitally nongenerate ground term is increased above the spin-only value via contribution from higher orbitally degenerate terms and occurs in the range 4.2–4.7 BM [22]. Octahedral cobalt(II) complexes however maintain a large contribution due to 3T2g ground term and exhibit μeff in the range 4.8–5.6 BM [23]. The magnetic measurements on the complexes reported herein 4.7–5.1 BM show that all are paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration.

Magnetic behavior of octahedral nickel(II) complexes is relatively simple. Nickel(II) has the electronic configuration 3d8 and should exhibit a magnetic moment higher than expected for two unpaired electrons in octahedral (2.8–3.2 BM) and tetrahedral (3.4–4.2 BM) complexes whereas its square-planar complexes would be diamagnetic. This increase in the magnetic moment value from that of the spin-only value has been discussed by Nyholm [24] who considered it to be due to

![Figure 1: N-isonicotinamido-2',4'-dichlorobenzaladimine (INH-DCB).](image-url)
to some “mixing in” of upper state via spin-orbit coupling. The paramagnetism observed for the present series of complexes ranges from 2.6–3.2 BM (Table 1) which is consistent with the octahedral stereochemistry of the complexes.

**Infrared spectra**

INH-DCB is expected to act as tridentate one, the possible coordination sites being pyridinic-nitrogen, azomethine-nitrogen, and amide group. A study and comparison of the IR spectra of INH-DCB and its cobalt(II) and nickel(II) complexes imply that the ligand INH-DCB is bidentate in nature with carbonyl-oxygen and azomethine-nitrogen as two coordination sites. The IR-data are presented in Table 2.

Generally, all amides show two absorption bands, (i) the carbonyl absorption band near 1640 cm\(^{-1}\) and (ii) strong band in the 1500–1600 cm\(^{-1}\) region, which are tentatively assigned [29, 30, 35] to asymmetric and symmetric ν(C=O) + ν(C=N) of pyridine ring and pyridine ring breathings and deformations remain practically unchanged in frequency and band intensities revealing noninvolvement of pyridinic-nitrogen and metal bond. The overall IR spectral evidence suggests that the INH-DCB acts as bidentate ligand and coordinate through amide-oxygen and azomethine-nitrogen atoms forming a five-membered chelate ring. In the far IR spectral region, the bands in the ligand are practically unchanged in these complexes. However, some new bands with medium to weak intensities appear in the regions 395–505 cm\(^{-1}\) in the complexes under study, which are tentatively assigned to ν(M-O)/ν(M-N) modes [25].

**Anions**

In both perchlorato complexes, the presence of the ν\(_{1}\) at ~ 1100 cm\(^{-1}\) and ν\(_{4}\) at ~ 625 cm\(^{-1}\) bands indicates that the T\(_{4}\) symmetry of ClO\(_{4}\)\(^{-}\) is maintained in all the complexes. This, therefore, suggests the presence of ClO\(_{4}\)\(^{-}\) outside the coordination sphere in the complexes [31, 36, 37]. The CN stretching frequency (ν\(_{1}\)) is generally lower for M-SCN complexes than for M-SCN complexes [38]. Bailey et al [39] suggested the region near or above 2100 cm\(^{-1}\) for S-bonding, below this for N-bonding. The CS stretching frequency (ν\(_{2}\)) was assigned in the following regions: 780–860 cm\(^{-1}\) for M-SCN and 690–720 cm\(^{-1}\) for M-SCN group [40]. The NCS frequency (ν\(_{3}\)) is also different for the two isomers 450–490 cm\(^{-1}\) for the M-SCN and 400–440 cm\(^{-1}\) for M-SCN.

### Table 1: Analytical conductivity, molecular weight, and magnetic data of Co\(^{2+}\) and Ni\(^{2+}\) complexes of INH-DCB.

| Complex          | Yield (%) | Analysis: found (calcd) (%) | Mol wt found (calcd) | Ω\(_{M}\) (Ohm cm\(^{2}\) mol\(^{-1}\)) | \(\mu_{eff}\) (BM) |
|------------------|-----------|-----------------------------|----------------------|---------------------------------------|-------------------|
| **Metal**        | **C**     | **H**                      | **N**                | **Anion**                             |                   |
| CoCl\(_{2}\) -2(INH-DCB) | 72        | 8.16 (8.21)                | 43.23 (43.45)       | 2.46 (2.50)                          | 11.58 (11.69)     | 9.79 (9.88)      | 714 (718) | 1.9 | 5.1 |
| CoBr\(_{2}\) -2(INH-DCB) | 68        | 7.27 (7.31)                | 38.49 (38.66)       | 2.19 (2.23)                          | 10.30 (10.40)     | 19.65 (19.82)   | 804 (807) | 2.4 | 4.9 |
| Co(NO\(_{3}\))\(_{2}\) -2(INH-DCB) | 75        | 7.60 (7.65)                | 40.68 (40.96)       | 2.28 (2.33)                          | 14.40 (14.52)     | —                | 765 (771) | 1.8 | 4.7 |
| Co(NCS)\(_{2}\) -2(INH-DCB) | 70        | 7.68 (7.73)                | 43.79 (44.03)       | 2.30 (2.35)                          | 14.55 (14.67)     | 15.08 (15.20)   | 758 (763) | 2.3 | 5.0 |
| Co(CH\(_{2}COO\))\(_{2}\) -2(INH-DCB) | 70        | 7.65 (7.71)                | 46.77 (47.05)       | 3.09 (3.13)                          | 10.87 (10.98)     | —                | 760 (765) | 1.9 | 4.8 |
| Co(CIO\(_{4}\))\(_{2}\) -3(INH-DCB) | 65        | 5.09 (5.17)                | 40.79 (41.05)       | 2.32 (2.36)                          | 10.95 (11.05)     | 17.34 (17.45)   | 380 (1140) | 51.9 | 4.9 |
| NiCl\(_{2}\) -2(INH-DCB) | 70        | 8.17 (8.21)                | 43.20 (43.45)       | 2.46 (2.50)                          | 11.09 (11.69)     | 9.78 (9.88)      | 713 (718) | 2.1 | 3.1 |
| NiBr\(_{2}\) -2(INH-DCB) | 70        | 7.28 (7.31)                | 38.49 (38.66)       | 2.19 (2.23)                          | 10.00 (10.40)     | 19.63 (19.82)   | 800 (807) | 2.2 | 2.9 |
| Ni(NO\(_{3}\))\(_{2}\) -2(INH-DCB) | 72        | 7.61 (7.65)                | 40.78 (40.96)       | 2.29 (2.33)                          | 14.13 (14.52)     | —                | 765 (771) | 1.8 | 3.2 |
| Ni(NCS)\(_{2}\) -2(INH-DCB) | 70        | 7.68 (7.73)                | 43.79 (44.03)       | 2.30 (2.35)                          | 14.16 (14.67)     | 14.98 (15.20)   | 758 (763) | 2.3 | 2.6 |
| Ni(CH\(_{2}COO\))\(_{2}\) -2(INH-DCB) | 75        | 7.66 (7.71)                | 46.81 (47.05)       | 3.10 (3.13)                          | 10.79 (10.98)     | —                | 760 (765) | 1.9 | 2.8 |
| Ni(CIO\(_{4}\))\(_{2}\) -3(INH-DCB) | 68        | 5.09 (5.17)                | 40.89 (41.05)       | 2.32 (2.36)                          | 10.92 (11.05)     | 17.38 (17.45)   | 381 (1140) | 50.9 | 3.2 |
Table 2: Infrared absorption frequencies (cm$^{-1}$) of Co$^{2+}$ and Ni$^{2+}$ complexes INH-DCB.

| Complex                  | $\nu$(NH)  | Amide-I  | $\nu$(C=N) azomethinic | $\nu$(M–N)/$\nu$(M–O) |
|--------------------------|-----------|----------|-------------------------|------------------------|
| INH-DCB                  | 3300 m    | 1700 vs  | 1585 s                  | —                      |
| CoCl$_2$·2(INH-DCB)      | 3305 m    | 1670 vs  | 1525 m                  | 490 m, 398 w           |
| CoBr$_2$·2(INH-DCB)      | 3302 m    | 1670 s   | 1530 vs                 | 492 m, 402 w           |
| Co(NO$_3$)$_2$·2(INH-DCB)| 3300 m    | 1680 s   | 1555 s                  | 502 m, 398 w           |
| Co(NCS)$_2$·2(INH-DCB)   | 3302 m    | 1670 s   | 1525 m                  | 505 m, 400 w           |
| Co(CH$_3$COO)$_2$·2(INH-DCB)| 3300 m | 1670 vs | 1530 s                 | 499 m, 402 w           |
| Co(ClO$_4$)$_2$·3(INH-DCB)| 3300 m  | 1660 s   | 1532 s                  | 498 m, 398 w           |
| NiCl$_2$·2(INH-DCB)      | 3305 m    | 1660 s   | 1530 s                  | 490 m, 398 w           |
| NiBr$_2$·2(INH-DCB)      | 3302 m    | 1670 s   | 1555 s                  | 495 m, 395 w           |
| Ni(NO$_3$)$_2$·2(INH-DCB) | 3300 m    | 1680 s   | 1525 m                  | 502 m, 398 w           |
| Ni(NCS)$_2$·2(INH-DCB)   | 3300 m    | 1670 s   | 1530 s sh               | 505 m, 400 w           |
| Ni(CH$_3$COO)$_2$·2(INH-DCB)| 3305 m | 1660 s   | 1525 m                  | 500 m, 402 w           |
| Ni(ClO$_4$)$_2$·3(INH-DCB)| 3300 m    | 1662 s   | 1530 m                  | 505 m, 410 w           |

group [40]. Bridging thiocyanate usually gives higher CN stretching frequencies than terminal NCS group [41–43]. In present thiocyanato complexes, three fundamental absorptions C–N stretch ($\nu_1$), C–S stretch ($\nu_3$), and N–C–S bending ($\nu_2$) are identified at ~ 2050, 840, and 475, respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions [41–43]. The occurrence of two strong absorption bands in both the nitrato complexes at ~ 1500 and 1300 cm$^{-1}$ are attributed to $\nu_4$ and $\nu_1$ modes of vibrations of the covalently bonded nitrate groups, respectively. This suggests that nitrate groups are present inside the coordination sphere [44, 45]. If the ($\nu_4 - \nu_1$) difference is taken as an approximate measure of the covalency of nitrate group [46, 47], a value of ~ 200 cm$^{-1}$ for the complexes studied suggests strong covalency for the metal-nitrate bonding. Devi et al [48] have shown that the number and relative energies of nitrate combination frequencies ($\nu_1 + \nu_4$) in the 1700–1800 cm$^{-1}$ region of the infrared spectrum may be used as an aid to distinguish the various coordination modes of the nitrate group. According to Agarwal et al [49], bidentate coordination involves a greater distortion from D$_{3h}$ symmetry than unidentate coordination, therefore, bidentate complexes should show a larger separation of ($\nu_1 + \nu_4$). By an investigation of the spectra of a number of compounds of known crystal structure, Devi et al [48] showed this to be true, the separation of monodentate nitrate groups appeared to be 5–26 cm$^{-1}$ and that for bidentate groups 25–66 cm$^{-1}$. The authors have tried to apply this method to present complexes. In both cases, in all the nitrato complexes, a separation of 15–25 cm$^{-1}$ in the combination bands ($\nu_1 + \nu_4$) in the 1700–1800 cm$^{-1}$ region conclude the monodentate nitrate coordination.

The $\nu_{\text{asym}}$(COO$^-$) of free acetate ions are at ~ 1560 cm$^{-1}$ and 1416 cm$^{-1}$, respectively. In the unidentate complex (structure a) $\nu$(C=O) is higher than $\nu_{\text{asym}}$(COO$^-$) and $\nu$(C–O) is lower than $\nu_{\text{asym}}$(COO$^-$). As a result, the separation between the two $\nu$(CO) is much larger in unidentate complexes than that of free ion. The opposite trend is observed in the bidentate complex, the separation between the $\nu$(CO) is smaller than that of free ion in this case. In
Table 3: Electronic spectral bands (cm\(^{-1}\)) and ligand-field parameters of Co\(^{2+}\) complexes of INH-DCB.

| Complex                | \(\nu_1\) | \(\nu_2\) | \(\nu_3\) | \(\Delta q\) (cm\(^{-1}\)) | \(B\) (cm\(^{-1}\)) | \(\beta\) | \(\Delta q/B\) | \(\nu_1\) (cm\(^{-1}\)) |
|------------------------|-----------|----------|----------|----------------------------|---------------------|---------|-------------|------------------|
| CoCl\(_2\)·2(INH-DCB)  | 15500     | 20830    | 861      | 956                        | 0.853               | 0.90    | 7955        |
| CoBr\(_2\)·2(INH-DCB)  | 15450     | 20670    | 858      | 953                        | 0.850               | 0.90    | 7806        |
| Co(NCS)\(_2\)·2(INH-DCB)| 15400    | 20500    | 855      | 950                        | 0.848               | 0.90    | 7836        |
| Co(NO\(_3\))\(_2\)·2(INH-DCB)| 15500   | 20830    | 861      | 956                        | 0.853               | 0.90    | 7955        |
| Co(CH\(_3\)COO)\(_2\)·2(INH-DCB)| 15400  | 20500    | 855      | 950                        | 0.848               | 0.90    | 7830        |
| Co(ClO\(_4\))\(_2\)·3(INH-DCB) | 15500   | 20830    | 861      | 956                        | 0.853               | 0.90    | 7955        |

Table 4: Electronic spectral bands (cm\(^{-1}\)) and ligand-field parameters of Ni\(^{2+}\) complexes of INH-DCB.

| Complex                | \(\nu_1\) | \(\nu_2\) | \(\nu_3\) | \(\Delta q\) (cm\(^{-1}\)) | \(B\) (cm\(^{-1}\)) | \(\beta\) |
|------------------------|-----------|----------|----------|----------------------------|---------------------|---------|
| NiCl\(_2\)·2(INH-DCB)  | 9090      | 15150    | 25000    | 909                        | 988                 | 0.91    |
| NiBr\(_2\)·2(INH-DCB)  | 9600      | 16200    | 24400    | 960                        | 1043                | 0.96    |
| Ni(NO\(_3\))\(_2\)·2(INH-DCB)| 9900    | 16660    | 24390    | 990                        | 1076                | 0.99    |
| Ni(NCS)\(_2\)·2(INH-DCB)| 9800     | 16700    | 24500    | 980                        | 1065                | 0.98    |
| Ni(CH\(_3\)COO)\(_2\)·2(INH-DCB)| 9600   | 15385    | 25640    | 960                        | 1043                | 0.96    |
| Ni(ClO\(_4\))\(_2\)·3(INH-DCB) | 9900    | 16660    | 24390    | 990                        | 1076                | 0.99    |

The methods of calculation of ligand field parameters from the ligand field spectra of octahedral Co(II) complexes have been discussed by Reedijk et al [55]. The energy of \(\nu_1\) corresponds to \(10\Delta q\) for weak field and the value of \(\Delta q\) is obtained from it. With these assignments, \(B\) and \(\Delta q\) have also been observed (Table 3).

**Electronic spectra**

**Cobalt(II) complexes**

The electronic spectra of all the present cobalt(II) complexes recorded herein are very similar to each other and consist of two bands one in the 15,400–15,500 cm\(^{-1}\) and the other in the 20,500–20,830 cm\(^{-1}\) regions, which clearly indicate the octahedral stereochemistry of the complexes. In Table 3, the band maxima and their assignments and the calculated ligand field parameters are listed. When all the bands, \(\nu_1\), \(\nu_2\), and \(\nu_3\) are observed to be free from shoulders, the ligand field parameters \(\Delta q\) and \(B\) are, in principle, calculated using first-order perturbation theory [52, 53] and the transition energies are given by the following equations [54]:

\[
\nu_1 = 5\Delta q - 7.58 + \frac{1}{2} (225B^2 + 100\Delta q^2 + 180\Delta qB)^{1/2},
\nu_2 = 15\Delta q - 7.58 + \frac{1}{2} (225B^2 + 100\Delta q^2 + 180\Delta qB),
\nu_3 = (225B + 100\Delta q + 180\Delta qB)^{1/2}.
\]

**Nickel(II) complexes**

The electronic spectra of all the complexes recorded herein are very similar to each other and consist of three bands one at \(\sim 10\,000\, \text{cm}^{-1}\) due to \(3A_{2g} \rightarrow 3T_{2g}(\nu_1)\), \(\sim 16\,000\, \text{cm}^{-1}\) due to \(3A_{2g} \rightarrow 3T_{1g}(\nu_2)\), and \(\sim 25\,000\, \text{cm}^{-1}\) for \(3A_{2g} \rightarrow 3T_{2g}(\nu_3)\) which clearly indicate the octahedral stereochemistry of the complexes. In Table 4, the band maxima and their assignments and the calculated ligand field parameters are listed [52–54].

**Thermal studies**

The thermal results of Co(II) and Ni(II) complexes of INH-DCB are briefed in Tables 5 and 6, respectively. Due to the explosive nature of perchlorato complexes, we have investigated only the thermal properties of chloro, bromo, and nitrito complexes. All the complexes are thermally stable up to 165°C. After that deligation process started and in temperature range 165–270°C, one mol of INH-DCB is lost, which is confirmed by mass loss of 37.20–41.96% at this stage. Another mol of INH-DCB is lost in the 280–390°C temperature range.
range. Finally at $\sim 615^\circ C$, metal-oxide (Co$_3$O$_4$ or NiO) formation takes place [49].

**Biological properties**

The antimicrobial screening data are presented in Table 7. The table shows that the metal complexes exhibit antimicrobial properties and it is important to note that these complexes exhibit enhanced activity in contrast to the free ligand. The increased lipophilic character of these complexes seems to be responsible for their enhanced potent antibacterial activity. It may be suggested that these complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these microorganisms. It has also been proposed that the ultimate action of the toxicant is the denaturation of one or more proteins of the cell, which as a result, impairs normal cellular processes. The antifungal activity of the cobalt(II) and nickel(II) complexes was evaluated against *F oxysporum* and *M phaseolina* by the agar plate techniques by mixing solutions of the metal complexes in different concentrations in DMF which were then mixed with the medium. The linear growth of the fungus was recorded

| Complex                        | Decomp temp (°C) Initial | Decomp temp (°C) Final | Decomp product | Weight loss (%) Theor | Weight loss (%) Exp |
|-------------------------------|--------------------------|-------------------------|-----------------|-----------------------|---------------------|
| Co(INH-DCB)$_2$·Cl$_2$        | 180                      | 250                     | Co(INH-DCB)Cl$_2$ | 40.94                 | 41.96               |
|                              | 300                      | 360                     | CoCl$_2$        | 81.89                 | 82.91               |
|                              | 500                      | 600                     | Co$_3$O$_4$     | 88.81                 | 89.62               |
| Co(INH-DCB)$_2$·Br$_2$        | 165                      | 235                     | Co(INH-DCB)Br$_2$ | 36.43                 | 37.20               |
|                              | 280                      | 370                     | CoBr$_2$        | 72.86                 | 74.01               |
|                              | 505                      | 610                     | Co$_3$O$_4$     | 90.04                 | 91.26               |
| Co(INH-DCB)$_2$(NO$_3$)$_2$   | 200                      | 260                     | Co(INH-DCB)(NO$_3$)$_2$ | 38.13           | 39.86               |
|                              | 320                      | 390                     | Co(NO$_3$)$_2$  | 76.26                 | 77.36               |
|                              | 500                      | 610                     | Co$_3$O$_4$     | 89.58                 | 90.34               |

**Table 6: Thermoanalytical results obtained for Ni$^{2+}$ of INH-DCB.**

| Complex                        | Decomp temp (°C) Initial | Decomp temp (°C) Final | Decomp product | Weight loss (%) Theor | Weight loss (%) Exp |
|-------------------------------|--------------------------|-------------------------|-----------------|-----------------------|---------------------|
| Ni(INH-DCB)$_2$Cl$_2$          | 190                      | 245                     | Ni(INH-DCB)Cl$_2$ | 40.94                 | 41.62               |
|                              | 290                      | 365                     | NiCl$_2$        | 81.80                 | 82.56               |
|                              | 505                      | 610                     | NiO             | 89.55                 | 90.32               |
| Ni(INH-DCB)$_2$Br$_2$          | 175                      | 235                     | Ni(INH-DCB)Br$_2$ | 36.43                 | 37.38               |
|                              | 285                      | 375                     | NiBr$_2$        | 72.86                 | 73.42               |
|                              | 510                      | 615                     | NiO             | 90.70                 | 91.35               |
| Ni(INH-DCB)$_2$(NO$_3$)$_2$    | 210                      | 270                     | Ni(INH-DCB)(NO$_3$)$_2$ | 38.13           | 39.26               |
|                              | 300                      | 390                     | Ni(NO$_3$)$_2$  | 76.26                 | 77.16               |
|                              | 500                      | 605                     | NiO             | 90.27                 | 91.32               |

**Table 7: Antibacterial screening data of INH-DCB and its Co(II) and Ni(II) complexes.**

| Compound                        | Diameter of inhibition zone (mm) (conc in ppm) |
|-------------------------------|-----------------------------------------------|
|                               | *E coli* 500 | 1000 | *K aerogenous* 500 | 1000 |
| INH-DCB                       | 6            | 8    | 5                  | 8    |
| CoCl$_2$·2(INH-DCB)           | 9            | 11   | 10                 | 10   |
| CoBr$_2$·2(INH – DCB)         | 9            | 10   | 8                  | 11   |
| Co(NO$_3$)$_2$·2(INH-DCB)     | 10           | 12   | 10                 | 11   |
| Co(NCS)$_2$·2(INH-DCB)        | 11           | 13   | 10                 | 12   |
| Co(CH$_3$COO)$_2$·2(INH-DCB)  | 10           | 12   | 10                 | 12   |
| Co(ClO$_4$)$_2$·3(INH-DCB)    | 10           | 12   | 9                  | 11   |
| NiCl$_2$·2(INH-DCB)           | 8            | 10   | 10                 | 11   |
| NiBr$_2$·2(INH-DCB)           | 8            | 10   | 10                 | 8    |
| Ni(NO$_3$)$_2$·2(INH-DCB)     | 9            | 11   | 8                  | 10   |
| Ni(NCS)$_2$·2(INH-DCB)        | 10           | 12   | 9                  | 11   |
| Ni(ClO$_4$)$_2$·3(INH-DCB)    | 9            | 11   | 8                  | 10   |
| Streptomycin                  | 16           | 18   | 16                 | 18   |
Table 8: Fungicidal screening data of INH-DCB and its Co(II) and Ni(II) complexes.

| Compound                     | Percentage inhibition after 96 h (conc in ppm) |  |
|------------------------------|-----------------------------------------------|--|
|                              | 50    | 100   | 200   | 50    | 100   | 200   |
| F. oxysporum                 |       |       |       |       |       |       |
| INH-DCB                      | 41    | 50    | 55    | 40    | 50    | 55    |
| CoCl₂·2(INH-DCB)             | 44    | 51    | 57    | 42    | 55    | 59    |
| CoBr₂·2(INH-DCB)             | 44    | 50    | 57    | 43    | 54    | 61    |
| Co(NO₃)₂·2(INH-DCB)          | 43    | 51    | 56    | 44    | 56    | 62    |
| Co(NCS)₂·2(INH-DCB)          | 48    | 56    | 61    | 47    | 56    | 63    |
| Co(CH₃COO)₂·2(INH-DCB)       | 45    | 54    | 60    | 45    | 55    | 60    |
| Co(ClO₄)₂·3(INH-DCB)         | 44    | 50    | 57    | 45    | 56    | 60    |
| NiCl₂·2(INH-DCB)             | 43    | 49    | 54    | 43    | 51    | 57    |
| NiBr₂·2(INH-DCB)             | 44    | 49    | 54    | 43    | 52    | 57    |
| Ni(NO₃)₂·2(INH-DCB)          | 44    | 49    | 55    | 44    | 53    | 56    |
| Ni(NCS)₂·2(INH-DCB)          | 47    | 56    | 62    | 48    | 58    | 63    |
| Ni(ClO₄)₂·3(INH-DCB)         | 45    | 54    | 59    | 44    | 53    | 57    |
| Bavistin                     | 84    | 100   | 100   | 80    | 99    | 100   |

by measuring the diameter of colony after 96 hours and the percentage inhibition was calculated as $100 \times (C-T)/C$, where C and T are the diameters of the fungus colony in the control and test plates, respectively (Table 8).

**CONCLUSION**

The present study revealed octahedral geometry around Co(II) and Ni(II) complexes, in which the ligand INH-DCB acts as a neutral bidentate coordinating through nitrogen and oxygen atoms and thus forming stable five-membered chelates. Tentative structures of the present chelates can be shown in Figures 2(a) and 2(b). The results of antimicrobial activity show that the metal complexes exhibit antimicrobial properties and it is important to note that they show enhanced inhibitory activity compared to the parent ligand. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases.

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