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 $MX_2 \cdot n(\text{INH-DCB})$ [$M = \text{Co(II)}$ or Ni(II) , $X = \text{Cl}^-$, Br^- , NO_3^- , NCS^- , or CH_3COO^- , $n = 2$; $X = \text{ClO}_4^-$, $n = 3$] 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 $R-\text{CO}-\text{NH}-\text{NH}_2$, their corresponding aroylhydrazones $R-\text{CO}-\text{NH}-\text{N}=\text{CH}-R'$, 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

$MX_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Co}^{2+}$ or Ni^{2+} ; $X = \text{Cl}^-$, Br^- , NO_3^- or CH_3COO^-) were obtained from SD Fine Chemicals Ltd (Mumbai, India) and were used as such: $M(\text{NCS})_2$ ($M = \text{Co}^{2+}$ or Ni^{2+}). 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]. $M(\text{ClO}_4)_2$ ($M = \text{Co}^{2+}$ or Ni^{2+}) 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 $M(\text{ClO}_4)_2$ 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.

FIGURE 1: N-isonicotinamido-2',4'-dichlorobenzaladimine (INH-DCB).

On cooling at room temperature, the coloured complexes precipitated out in each case. They were filtered, washed with ethanol and recrystallized, and dried over P_2O_5 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 concentrate H_2SO_4 and H_2O_2 [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 $\pm 0.01^\circ C$ 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 CsI in the range of $200\text{--}4000\text{ cm}^{-1}$. Diffused reflectance spectra of the solid compounds were recorded on a Beckmann DK-2A spectrophotometer at CDRI, Lucknow, India. Thermogravimetric studies of the complexes were carried out in static air with open sample holder and a small boat, the heating rate was $6^\circ C/\text{min}$.

Antibacterial activity was done by the paper-disc plate method. The nutrient agar medium (peptone, beef extract, NaCl, and agar-agar) and 5 mm diameter paper discs (Whatman number 1) were used. The compounds were dissolved in DMSO in 500 and 1000 ppm concentrations. The filter paper discs were soaked in different solutions of the compounds, dried, and then placed in the petri dishes previously seeded with the test organisms (*Escherichia coli* and *Klebsiella aerogenes*). The plates were incubated for 24–30 hours at $28 \pm 2^\circ C$ and the inhibition zone around each disc was measured. The antifungal activity was evaluated against *Fusarium oxysporum* and *Macrophomina phaseolina* using standard food poisoning technique and a procedure recommended for

testing new chemicals [18]. The linear growth of the fungus was recorded by measuring the diameter of the fungus colony after 96 hours and the percentage inhibition was calculated as $100(C-T)/C$, where C and T are the diameters of the fungus colony in the control and test plates, respectively.

Results and discussion

The reaction of cobalt(II) and nickel(II) salts with INH-DCB results in the formation of $MX_2 \cdot (INH-DCB)_n$ [$M = Co(II)$ or $Ni(II)$; $X = Cl^-$, Br^- , NO_3^- , NCS^- , or CH_3COO^- , $n = 2$; $X = ClO_4^-$, $n = 3$] (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 $250^\circ C$. These complexes are generally soluble in common organic solvents. The conductance measurement indicates that the chloro, bromo, nitrato, thiocyanato, and acetato complexes of cobalt(II) and nickel(II) are essentially nonelectrolytes in nitrobenzene, while the perchlorato 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 μ_{eff} from the spin-only value. The magnetic moment of tetrahedral cobalt(II) complexes with an orbitally non-generate 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 4T_g ground term and exhibit μ_{eff} 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 $3d^8$ 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

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 $\text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (BM)
		Metal	C	H	N	Anion			
$\text{CoCl}_2 \cdot 2(\text{INH-DCB})$	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
$\text{CoBr}_2 \cdot 2(\text{INH-DCB})$	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
$\text{Co}(\text{NO}_3)_2 \cdot 2(\text{INH-DCB})$	75	7.60 (7.65)	40.68 (40.96)	2.28 (2.33)	14.40 (14.52)	—	765 (771)	1.8	4.7
$\text{Co}(\text{NCS})_2 \cdot 2(\text{INH-DCB})$	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
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2(\text{INH-DCB})$	70	7.65 (7.71)	46.77 (47.05)	3.09 (3.13)	10.87 (10.98)	—	760 (765)	1.9	4.8
$\text{Co}(\text{ClO}_4)_2 \cdot 3(\text{INH-DCB})$	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
$\text{NiCl}_2 \cdot 2(\text{INH-DCB})$	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
$\text{NiBr}_2 \cdot 2(\text{INH-DCB})$	68	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
$\text{Ni}(\text{NO}_3)_2 \cdot 2(\text{INH-DCB})$	72	7.61 (7.65)	40.78 (40.96)	2.29 (2.33)	14.13 (14.52)	—	765 (771)	1.8	3.2
$\text{Ni}(\text{NCS})_2 \cdot 2(\text{INH-DCB})$	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
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2(\text{INH-DCB})$	75	7.66 (7.71)	46.81 (47.05)	3.10 (3.13)	10.79 (10.98)	—	760 (765)	1.9	2.8
$\text{Ni}(\text{ClO}_4)_2 \cdot 3(\text{INH-DCB})$	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

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} known as amide-I band and (ii) strong band in the $1500\text{--}1600 \text{ cm}^{-1}$ region, known as amide-II band. The origin of these bands in hydrazones, that is, the carbonyl absorption responsible for the amide-I band, is likely to be lowered [25] infrequently by the NH group as in normal amides. The amide-I band in INH-derivative, however, appears at 1700 and 1655 cm^{-1} [26, 27]. In the IR spectra of the complexes a considerable negative shift in $\nu(\text{C}=\text{O})$ is observed indicating a decrease in the stretching force constant of $\text{C}=\text{O}$ as a consequence of coordination through the carbonyl-oxygen atom of the free base. The amide-II band appears at the normal position in the NH-deformation rather than the C–N link. In all the hydrazones, the absorptions such as $1540, 1520 \text{ cm}^{-1}$ have been assigned to amide-II absorption. The NH stretching absorption in free ligand occurs at ~ 3300 and 3220 cm^{-1} [28] which remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom.

Another important band occurs at $\sim 1585 \text{ cm}^{-1}$ attributed to $\nu(\text{C}=\text{N})$ (azomethine) mode [29–31]. In spectra

of all the complexes this band is shifted to lower wave number and appears in $1525\text{--}1555 \text{ cm}^{-1}$ region, respectively, indicating the involvement of N-atom of the azomethine group in coordination [32–34].

The strong bands observed at $1520\text{--}1575 \text{ cm}^{-1}$ and $1000\text{--}1080 \text{ cm}^{-1}$ are tentatively assigned [29, 30, 35] to asymmetric and symmetric $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ 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 $395\text{--}505 \text{ cm}^{-1}$ in the complexes under study, which are tentatively assigned to $\nu(\text{M}-\text{O})/\nu(\text{M}-\text{N})$ modes [25].

Anions

In both perchlorato complexes, the presence of the ν_3 at $\sim 1100 \text{ cm}^{-1}$ and ν_4 at $\sim 625 \text{ cm}^{-1}$ bands indicates that the T_d 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: $780\text{--}860 \text{ cm}^{-1}$ for M-SCN and $690\text{--}720 \text{ cm}^{-1}$ for M-SCN group [40]. The NCS frequency (ν_3) is also different for the two isomers $450\text{--}490 \text{ cm}^{-1}$ for the M-SCN and $400\text{--}440 \text{ cm}^{-1}$ for M-SCN

TABLE 2: Infrared absorption frequencies (cm^{-1}) of Co^{2+} and Ni^{2+} complexes INH-DCB.

Complex	$\nu(\text{NH})$	Amide-I	$\nu(\text{C}=\text{N})$ azomethinic	$\nu(\text{M}-\text{N})/\nu(\text{M}-\text{O})$
INH-DCB	3300 m	1700 vs	1585 s	—
	3220 w	1655 vs		
$\text{CoCl}_2 \cdot 2(\text{INH-DCB})$	3305 m	1670 vs	1525 m	490 m, 398 w
	3220 w	1605 vs		
$\text{CoBr}_2 \cdot 2(\text{INH-DCB})$	3302 m	1670 s	1530 vs	492 m, 402 w
	3220 w	1610 vs, 1580 m		
$\text{Co}(\text{NO}_3)_2 \cdot 2(\text{INH-DCB})$	3300 m	1680 s	1555 s	502 m, 398 w
	3220 w	1620 s		
$\text{Co}(\text{NCS})_2 \cdot 2(\text{INH-DCB})$	3302 m	1670 vs	1525 m	505 m, 400 w
	3220 w	1620 vs, br		
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2(\text{INH-DCB})$	3300 m	1670 vs	1530 s	499 m, 402 w
	3220 w	1600 vs, br		
$\text{Co}(\text{ClO}_4)_2 \cdot 3(\text{INH-DCB})$	3300 m	1660 s	1532 s	498 m, 398 w
	3225 w	1605 s		
$\text{NiCl}_2 \cdot 2(\text{INH-DCB})$	3305 m	1660 vs	1530 s	490 m, 398 w
	3220 w	1605 vs		
$\text{NiBr}_2 \cdot 2(\text{INH-DCB})$	3302 m	1670 s	1555 m	495 m, 395 w
	3220 w	1600 vs, br		
$\text{Ni}(\text{NO}_3)_2 \cdot 2(\text{INH-DCB})$	3300 m	1680 s	1525 m	502 m, 398 w
	3222 w	1620 s		
$\text{Ni}(\text{NCS})_2 \cdot 2(\text{INH-DCB})$	3300 m	1670 s	1530 sh	505 m, 400 w
	3222 w	1605 vs		
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2(\text{INH-DCB})$	3305 m	1660 s	1525 m	500 m, 402 w
	3220 w	1605 s		
$\text{Ni}(\text{ClO}_4)_2 \cdot 3(\text{INH-DCB})$	3300 m	1662 s	1530 m	505 m, 410 w
	3220 w	1660 vs		

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 (ν_1), C–S stretch (ν_3), and N–C–S bending (ν_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 nitrate complexes at ~ 1500 and 1300 cm^{-1} are attributed to ν_4 and ν_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 $\sim 200 \text{ cm}^{-1}$ 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 nitrate 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 $\nu_{\text{asym}}(\text{COO}^-)$ of free acetate ions are at $\sim 1560 \text{ cm}^{-1}$ and 1416 cm^{-1} , respectively. In the unidentate complex (structure a) $\nu(\text{C}=\text{O})$ is higher than $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu(\text{C}-\text{O})$ is lower than $\nu_{\text{asym}}(\text{COO}^-)$. As a result, the separation between the two $\nu(\text{CO})$ is much larger in unidentate complexes than that of free ion. The opposite trend is observed in the bidentate complex, the separation between the $\nu(\text{CO})$ 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	ν_2 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$	ν_3 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	Dq (cm^{-1})	B (cm^{-1})	β	Dq/B	ν_1 (cm^{-1})
$\text{CoCl}_2 \cdot 2(\text{INH-DCB})$	15500	20830	861	956	0.853	0.90	7955
$\text{CoBr}_2 \cdot 2(\text{INH-DCB})$	15450	20670	858	953	0.850	0.90	7806
$\text{Co}(\text{NCS})_2 \cdot 2(\text{INH-DCB})$	15400	20500	855	950	0.848	0.90	7836
$\text{Co}(\text{NO}_3)_2 \cdot 2(\text{INH-DCB})$	15500	20830	861	956	0.853	0.90	7955
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2(\text{INH-DCB})$	15400	20500	855	950	0.848	0.90	7830
$\text{Co}(\text{ClO}_4)_2 \cdot 3(\text{INH-DCB})$	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	ν_1	ν_2	ν_3	Dq (cm^{-1})	B (cm^{-1})	β
$\text{NiCl}_2 \cdot 2(\text{INH-DCB})$	9090	15150	25000	909	988	0.91
$\text{NiBr}_2 \cdot 2(\text{INH-DCB})$	9600	16200	24400	960	1043	0.96
$\text{Ni}(\text{NO}_3)_2 \cdot 2(\text{INH-DCB})$	9900	16660	24390	990	1076	0.99
$\text{Ni}(\text{NCS})_2 \cdot 2(\text{INH-DCB})$	9800	16700	24500	980	1065	0.98
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2(\text{INH-DCB})$	9600	15385	25640	960	1043	0.96
$\text{Ni}(\text{ClO}_4)_2 \cdot 3(\text{INH-DCB})$	9900	16660	24390	990	1076	0.99

the bridging complexes (structure c), however, two $\nu(\text{CO})$ are close to the free ion values. The present complexes show infrared absorption frequency bands corresponding to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ at ~ 1610 and 1370 cm^{-1} , respectively. These observations indicate that both the acetate groups in present complexes are unidentate [50, 51].

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 $15,400\text{--}15,500 \text{ cm}^{-1}$ and the other in the $20,500\text{--}20,830 \text{ cm}^{-1}$ 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, ν_1 , ν_2 , and ν_3 are observed to be free from shoulders, the ligand field parameters D_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]:

$$\begin{aligned}
 \nu_1 &= 5D_q - 7.58 + \frac{1}{2}(225B^2 + 100D_q^2 + 180D_qB)^{1/2}, \\
 \nu_2 &= 15D_q - 7.58 + \frac{1}{2}(225B^2 + 100D_q^2 + 180D_qB), \\
 \nu_3 &= (225B + 100D_q + 180D_qB)^{1/2}.
 \end{aligned}
 \tag{1}$$

The methods of calculation of ligand field parameters from the ligand field spectra of octahedral $\text{Co}(\text{II})$ complexes have been discussed by Reedijk et al [55]. The energy of ν_1 corresponds to $10D_q$ for weak field and the value of D_q is obtained from it. With these assignments, B and D_q have also been observed (Table 3).

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 ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_1)$, $\sim 16,000 \text{ cm}^{-1}$ due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\nu_2)$, and $\sim 25,000 \text{ cm}^{-1}$ for ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_3)$ 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 $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ 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 nitrate complexes. All the complexes are thermally stable up to 165°C . After that deligation process started and in temperature range $165\text{--}270^\circ\text{C}$, one mol of INH-DCB is lost, which is confirmed by mass loss of $37.20\%\text{--}41.96\%$ at this stage. Another mol of INH-DCB is lost in the $280\text{--}390^\circ\text{C}$ temperature

TABLE 5: Thermoanalytical results obtained for Co²⁺ of INH-DCB.

Complex	Decomp temp (°C)		Decomp product	Weight loss (%)	
	Initial	Final		Theor	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 Ni²⁺ of INH-DCB.

Complex	Decomp temp (°C)		Decomp product	Weight loss (%)	
	Initial	Final		Theor	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)			
	<i>E. coli</i>		<i>K. aerogenus</i>	
	500	1000	500	1000
INH-DCB	6	8	5	8
CoCl ₂ ·2(INH-DCB)	9	11	8	10
CoBr ₂ ·2(INH-DCB)	9	10	8	11
Co(NO ₃) ₂ ·2(INH-DCB)	10	12	9	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	9	11
NiBr ₂ ·2(INH-DCB)	8	10	7	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

range. Finally at ~ 615°C, metal-oxide (Co₃O₄ 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

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)					
	<i>F oxysporum</i>			<i>M phaseolina</i>		
	50	100	200	50	100	200
INH-DCB	41	50	55	40	50	55
CoCl ₂ ·2(INH-DCB)	44	51	57	42	55	59
CoBr ₂ ·2(INH-DCB)	44	50	57	43	54	61
Co(NO ₃) ₂ ·2(INH-DCB)	43	51	56	44	56	62
Co(NCS) ₂ ·2(INH-DCB)	48	56	61	47	56	63
Co(CH ₃ COO) ₂ ·2(INH-DCB)	45	54	60	45	55	60
Co(ClO ₄) ₂ ·3(INH-DCB)	44	50	57	45	56	60
NiCl ₂ ·2(INH-DCB)	43	49	54	43	51	57
NiBr ₂ ·2(INH-DCB)	44	49	54	43	52	57
Ni(NO ₃) ₂ ·2(INH-DCB)	44	49	55	44	53	56
Ni(NCS) ₂ ·2(INH-DCB)	47	56	62	48	58	63
Ni(ClO ₄) ₂ ·3(INH-DCB)	45	54	59	44	53	57
Bavistin	84	100	100	80	99	100

FIGURE 2: (a) Suggested structure of $[M(\text{INH-DCB})_3] (\text{ClO}_4)_2$ ($M = \text{Co}^{2+}$ or Ni^{2+}); (b) suggested structure of $[M(\text{INH-DCB})_2\text{X}_2]$ ($M = \text{Co}^{2+}$ or Ni^{2+} ; $\text{X} = \text{Cl}^-$, Br^- , I^- , NCS^- , or NO_3^-).

by measuring the diameter of colony after 96 hours and the percentage inhibition was calculated as $100 (C-T)/C$, 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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