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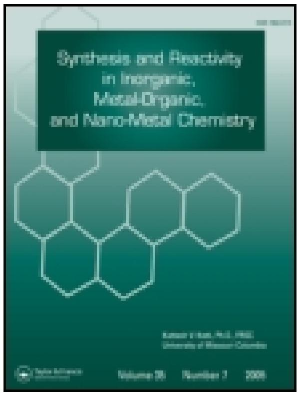

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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, AND BIOLOGICAL ACTIVITY OF N-ISONICOTINOYL- N′-THIOBENZOYLHYDRAZINE COMPLEXES OF Co(II), Ni(II), Cu(II), AND Zn(II)

Nand K. Singh [a] & Dileep K. Singh [a]
[a] Department of Chemistry, Banaras Hindu University, 221 005, India

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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, AND BIOLOGICAL ACTIVITY OF N-ISONICOTINOYL-N′-THIOBENZOYLHYDRAZINE COMPLEXES OF Co(II), Ni(II), Cu(II), AND Zn(II)

Nand K. Singh* and Dileep K. Singh

Department of Chemistry, Banaras Hindu University,
221 005 India

ABSTRACT

A new ligand, N-isonicotinoyl-N′-thiobenzoylhydrazine (HINTB), has been prepared by the reaction of isonicotinic acid hydrazide and carboxymethyl dithiobenzoate. The addition complexes $[M(HINTB)_2Cl_2]$ $[M = Co(II), Ni(II), Zn(II)]$, $[Cu(HINTB)Cl_2]$, $M(HINTB)_2(CH_3COO)_2$ $[M = Co(II), Ni(II)]$ and deprotonated complexes $[Cu(INTB)(CH_3COO)]$ and $[Zn(INTB)_2]$ have been prepared and characterized by elemental analyses, magnetic susceptibility, electronic, NMR and IR spectral data. The room temperature ESR spectra of $[Cu(HINTB)Cl_2]$ and

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*Corresponding author. E-mail: nksingh@banaras.ernet.in

[Cu(INTB)(CH_3COO)] are characteristic of monomeric and dimeric species, respectively. The ligand and the complexes have been screened for activity against a number of fungi and bacteria.

INTRODUCTION

The literature shows that some work has been done on the transition metal complexes of pyridine carboxylic acid hydrazides and their hydrazones[1–11]. The transition metal complexes of a few thiohydrazides and their N-substituted derivatives have also been reported[12–17]. Pyridine carboxylic acid hydrazides, particularly isonicotinic acid hydrazide, show biological activity. Similarly, thiohydrazides which are structurally similar to thiosemicarbazides also exhibit a wide variety of biological activities viz., antifungal, antibacterial and antitumor. In view of this, a new ligand, N-isonicotinoyl-N′-thiobenzoylhydrazine (HINTB), containing the pyridine carboxylic acid and thiohydrazide moities has been synthesized (Fig. 1) and representative 3D metal complexes have been prepared, characterized by various physicochemical techniques and their biological activity against several fungi and bacteria tested.

EXPERIMENTAL

Starting Materials

All chemicals used were of analytical reagent or equivalent grade. Isonicotinic acid hydrazide (INH) was purchased from Sigma Chemical Co.,

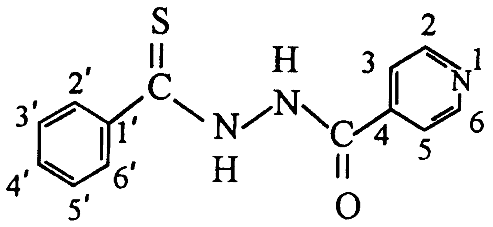


Figure 1. Structure of the ligand (HINTB).

U.S.A. Ammonium polysulfide[18] and carboxymethyl dithiobenzoate[19] were prepared by literature methods.

N-Isonicotinoyl-N′-thiobenzoylhydrazine (HINTB)

N-Isonicotinoyl-N′-thiobenzoylhydrazine (HINTB) was prepared by reacting solutions of isonicotinic acid hydrazide (3.5 g, 25 mmol) and carboxymethyl dithiobenzoate (5.3 g, 25 mmol) each dissolved separately in 50 mL of 0.5 N NaOH, and allowing the mixture to stand at room temperature for 2 h. The product precipitated by adding dropwise dilute acetic acid to this reaction mixture. It was filtered, washed with water, dried and recrystallized from hot ethanol, m.p. 186 °C. Yield, 4.5 g (70%).

Preparation of the Complexes

$[M(HINTB)_2Cl_2]$ and $[Cu(HINTB)Cl_2]$

$[M(HINTB)_2Cl_2]$ ($M = Co(II)$, Ni(II) and Zn(II)) and $[Cu(HINTB)Cl_2]$ were prepared by refluxing 20 mL of methanolic solutions each of the respective metal(II) chlorides (1 mmol) and HINTB (0.514 g, 2 mmol) in the presence of HCl (5–6 drops) for 15 minutes on a water bath. The precipitated complexes were filtered, washed with methanol and dried in vacuo.

$M(HINTB)_2(CH_3COO)_2$, $[Cu(INTB)(CH_3COO)]$, and $[Zn(INTB)_2]$

$M(HINTB)_2(CH_3COO)_2$ ($M = Co(II)$ and Ni(II)), $[Cu(INTB)(CH_3COO)]$ and $[Zn(INTB)_2]$ were prepared by adding 20 mL of a methanolic solution of HINTB (0.257 g, 1 mmol) to an aqueous-methanolic (50% v/v) solution of the respective metal(II) acetate (0.5 mmol) in the presence of sodium acetate (0.5 g) and digesting the reaction mixture for about 30 minutes in a boiling water bath. The precipitated complexes were filtered, washed with methanol-water mixture (50 v/v), water and finally with ethanol and dried in vacuo.

Analyses and Physical Measurements

The complexes were analysed for their metal content following standard procedures[20] after decomposition with aqua regia followed by H_2SO_4. Chloride and sulfur were determined as silver chloride and barium sulphate, respectively. Carbon, hydrogen and nitrogen were determined on a Carlo Erba microanalyzer. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday balance using [$Co(NCS)_4Hg$] as calibrant. Electronic spectra were recorded on a Cary 2390 UV-Vis spectrophotometer as Nujol mulls[21]. IR spectra were recorded in the region 4000–400 cm^{-1} as a KBr discs on a Jasco FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were obtained in DMSO-d_6 on a Jeol FX-90Q spectrometer using TMS as internal reference. ESR spectra of the complexes were recorded on an X-band model EPR-112 spectrometer using DPPH ($g = 2.0036$) as a $\langle g \rangle$ marker.

Fungicidal Screening

The antifungal activity was evaluated by the spore germination technique[22]. A stock solution prepared by dissolving 2 mg/mL of each compound in DMSO was serially diluted with sterilized distilled water up to four dilutions, giving concentrations of 1000, 750, 500 and 250 μg/mL. Spores of the test fungi *Stemphylium* sp., *Fusarium udum*, *Alternaria tennuissima* and *Helminthosporium rostratum* grown on potato dextrose agar medium were incorporated into culture tubes containing the various concentrations of the compounds separately and thoroughly agitated in order to break up the spore clumps. A drop of the suspensions was transferred on clear slides which were then kept in Petri dishes containing moist cotton. A parallel set of control samples was also maintained without the compound using water and a solvent-water (50% v/v) mixture. The Petri dishes were incubated at $25 \pm 1\,^{\circ}C$ for 24 h. The counts of germinated spores were made from three random microscopic fields of each slide in order to calculate the inhibition percentage using the following formula:

$$\text{Inhibition percentage} = 1 - \frac{\text{Germination in treatment}}{\text{Germination in control}} \times 100.$$

Bactericidal Screening

The antibacterial activity of the ligand and its complexes was evaluated by the Agar plate diffusion technique[23]. A stock solution of 1000 μg/mL was made by dissolving 1 mg of each compound in 1 mL DMSO. Filter paper (Whatmann no. 4) discs (6 mm diameter) were soaked in solutions of the test compounds and placed, after drying off the solvent, on Muller Hinton agar plates containing lawn cultures of different bacteria.

The plates were incubated at an optimum growth temperature of 37 °C. The zones of inhibition around the discs were measured after 24 h. The test bacteria included (a) *Staphylococcus aureus*, (b) *Staphylococcus epidermidis*, (c) *Enterococcus faecalis*, (d) *Escherichia coli*, (e) *Pseudomonas aeruginosa*, (f) *Proteus vulgaris*, (g) *Shigella flexneri*, (h) *Vibrio cholerae* and (i) *Staphylococcus aureus* (ATCC 25923). All experiments were performed in duplicate and gentamicin was used as a standard drug.

RESULTS AND DISCUSSION

All of the complexes are insoluble in water, ethanol and methanol but are soluble in polar organic solvents such as DMF and DMSO. Zn(II) and Cu(II) give deprotonated ligand complexes, [Zn(INTB)$_2$] and Cu(INTB)(CH$_3$COO)], respectively, formed by loss of one proton from each ligand, other metal salts yield non-deprotonated complexes (Table I). The complexes formed by Co(II), Ni(II) and Cu(II) acetates melt in the temperature range 190–260 °C but [Zn(INTB)$_2$] and the metal(II) chloride complexes do not melt up to 300 °C. The formation of the ligand and the complexes may be represented by the following equations:

$$\begin{aligned}&C_6H_5CSSCH_2COOH + (C_5H_4N)CONHNH_2 \underset{AcOH}{\overset{NaOH}{\longrightarrow}}\\&\qquad C_6H_5CSNHNHCO(C_5H_4N)(HINTB) + HSCH_2COOH \qquad (1)\end{aligned}$$

$$[M(H_2O)_6]Cl_2 + 2HINTB \overset{MeOH}{\longrightarrow} [M(HINTB)_2Cl_2] + 6H_2O \qquad (2)$$

$$M = Co(II), Ni(II)$$

$$CuCl_2{\cdot}2H_2O + HINTB \overset{MeOH}{\longrightarrow} [Cu(HINTB)Cl_2] + 2H_2O \qquad (3)$$

$$ZnCl_2 + 2HINTB \overset{MeOH}{\longrightarrow} [Zn(HINTB)_2Cl_2] \qquad (4)$$

$$\begin{aligned}&M(CH_3COO)_2{\cdot}4H_2O + 2HINTB \underset{AcONa}{\overset{MeOH}{\longrightarrow}}\\&\qquad M(HINTB)_2(CH_3COO)_2 + 4H_2O \qquad (5)\end{aligned}$$

Table I. Analytical Data and Physical Properties of HINTB and Its Complexes

Compound Empirical Formula	F. wt.	Colour/ Yield (%)	Analyses Found (Calc.) % M	 C	 H	 N	 S	 Cl	M.p. (°C)	μ_{eff} (B.M.)
HINTB		Yellow	–	60.97	4.09	15.90	11.98	–	186	–
$C_{13}H_{11}N_3SO$	257.31	(70)		(60.68)	(4.30)	(16.33)	(12.46)			
$[Co(HINTB)_2Cl_2]$		Greenish	9.06	49.06	2.95	13.82	9.47	10.80	> 300	5.20
$C_{26}H_{22}N_6S_2O_2Cl_2Co$	644.46	yellow (45)	(9.14)	(48.46)	(3.44)	(13.04)	(9.95)	(11.00)		
$[Ni(HINTB)_2Cl_2]$		Light brown	9.40	48.35	3.10	13.08	10.20	10.53	> 300	3.20
$C_{26}H_{22}N_6S_2O_2Cl_2Ni$	644.22	(55)	(9.11)	(48.48)	(3.44)	(13.05)	(9.95)	(11.01)		
$[Cu(HINTB)Cl_2]$		Black	15.85	40.03	2.80	11.26	8.68	18.58	260	2.03
$C_{13}H_{11}N_3SOCl_2Cu$	391.76	(40)	(16.22)	(39.86)	(2.83)	(10.73)	(8.18)	(18.10)		
$[Zn(HINTB)_2Cl_2]$		Yellow	10.70	47.86	3.16	12.69	10.33	10.67	> 300	–
$C_{26}H_{22}N_6S_2O_2Cl_2Zn$	650.91	(45)	(10.04)	(48.00)	(3.41)	(12.91)	(9.85)	(10.89)		
$[Co(HINTB)_2](CH_3COO)_2$		Dirty green	8.12	51.74	3.61	12.70	9.84	–	190	4.75
$C_{30}H_{28}N_6S_2O_6Co$	691.64	(50)	(8.52)	(52.09)	(4.08)	(12.15)	(9.27)			
$[Ni(HINTB)_2(CH_3COO)_2]$		Brick red	9.10	51.50	3.50	12.40	9.76	–	260	2.98
$C_{30}H_{28}N_6S_2O_6Ni$	691.40	(60)	(8.49)	(52.12)	(4.08)	(12.16)	(9.28)			
$[Cu(INTB)(CH_3COO)]$		Green	16.25	48.10	3.20	11.29	8.21	–	230	1.43
$C_{15}H_{13}N_3SO_3Cu$	378.90	(45)	(16.77)	(47.55)	(3.46)	(11.09)	(8.46)			
$[Zn(INTB)_2]$		Light yellow	10.92	54.18	3.40	14.93	11.09	–	> 300	–
$C_{26}H_{20}N_6S_2O_2Zn$	578.00	(35)	(11.31)	(54.03)	(3.49)	(14.54)	(11.09)			

$$M = Co(II), Ni(II)$$

$$Cu(CH_3COO)_2 \cdot H_2O + HINTB \xrightarrow[AcONa]{MeOH} [Cu(INTB)(CH_3COOH)] + CH_3COOH + H_2O \quad (6)$$

$$Zn(CH_3COO)_2 \cdot 4H_2O + 2HINTB \xrightarrow[AcONa]{MeOH} [Zn(INTB)_2] + 2CH_3COOH + 4H_2O \quad (7)$$

Magnetic Moments and Electronic Spectra

The magnetic moment and electronic spectral data of the complexes are given in Tables I and II, respectively. The magnetic moment of 4.75 B.M. for $[Co(HINTB)_2](CH_3COO)_2$ lies in the range reported for tetrahedral cobalt(II) complexes. It shows two bands at 15,820 and 16,780 cm^{-1} which may be assigned to the split components of the $^4A_2 \rightarrow {}^4T_1(P)$ transition, usually observed for tetrahedral cobalt(II) complexes. $[Co(HINTB)_2Cl_2]$ shows a magnetic moment of 5.2 B.M. and exhibits two bands at 16,890 and 19,085 cm^{-1} which may be assigned to the $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g}(P)$ transitions, respectively, in an octahedral geometry of cobalt(II). The magnetic moments of $[Ni(HINTB)_2X_2]$ suggest their octahedral structure

Table II. Electronic Spectral Data for the Complexes and Their Assignments

Compound	Band Maxima (cm^{-1})	Assignments
HINTB	26455	L
$[Co(HINTB)_2](CH_3COO)_2$	15820, 16780, 25775, 33115	$^4A_2 \rightarrow {}^4T_1(P)$, C.T., L
$[Co(HINTB)_2Cl_2]$	16890, 19085, 33555	$^4T_{1g} \rightarrow {}^4A_{2g}, {}^4T_{1g}(P)$, L
$[Ni(HINTB)_2(CH_3COO)_2]$	14285, 24040, 33335	$^3A_{2g} \rightarrow {}^3T_{1g}(F), {}^3T_{1g}(P)$, L
$[Ni(HINTB)_2Cl_2]$	14045, 23925, 33110	$^3A_{2g} \rightarrow {}^3T_{1g}(F), {}^3T_{1g}(P)$, L
$[Cu(INTB)(CH_3COO)]$	15770, 20575, 35210	Envelope of $^2B_{1g} \rightarrow {}^2A_{1g}, {}^2B_{2g}, {}^2E_g$C.T., L
$[Cu(HINTB)Cl_2]$	16890, 28410, 34245	Envelope of $^2B_{1g} \rightarrow {}^2A_{1g}, {}^2B_{2g}, {}^2E_g$C.T., L
$[Zn(INTB)_2]$	32680	C.T.
$[Zn(HINTB)_2Cl_2]$	28410	C.T.

C.T. = Charge transfer; L = Intraligand.

which is supported by the occurrence of two bands in the regions 14,045–14,285 and 23,925–24,040 cm^{-1} for the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3T_{1g}(P)$, respectively. The magnetic moment of [Cu(HINTB)Cl_2] is normal and corresponds to the presence of one unpaired electron. A lower value of the magnetic moment (1.43 B.M.) for [Cu(INTB)(CH_3COO)] suggests antiferromagnetic interaction between two Cu(II). The presence of a broad band at 15,770–16,890 cm^{-1} suggests a square-planar geometry for the copper(II) complexes.

The high-energy band in the ligand at 26,455 cm^{-1} and in the complexes at 28,000–35,000 cm^{-1} may be assigned to intra-ligand or charge-transfer transitions.

NMR Spectra

The ^1H NMR spectrum of HINTB shows a signal at δ 11.8 ppm due to two NH protons which disappears on D_2O exchange. A multiplet is observed between δ 7.87–8.34 ppm due to the benzene ring protons. In addition, two doublets at δ 7.76 and 9.10 ppm are observed for the pyridine ring protons. The assignments for the pyridine ring protons have been made by comparing the ^1H NMR spectrum of HINTB with that of isonicotinic acid hydrazide, INH (Table III). The ^1H NMR spectra of [Zn$(INTB)_2$] and [Zn$(HINTB)_2Cl_2$] show the pyridine ring protons almost at the same positions as those of HINTB, indicating non-involvement of ring nitrogen in bonding. The spectra of [Zn$(INTB)_2$] and [Zn$(HINTB)_2Cl_2$] show a signal at δ 11.85 and 11.79 ppm, respectively, for the NH proton(s).

The ^{13}C NMR spectrum of HINTB (Table IV) shows 11 signals, of which two at δ 197.69 and 160.50 ppm are due to the C=S and C=O carbons, respectively. By comparing the spectra of INH and HINTB, the chemical shifts for the pyridine and benzene ring carbons are: (δ, ppm) C(4), 143.40; C(2), C(6), 150.50; C(3), C(5), 121.47; C′(1), C′(4), 131.87, 131.33; C′(2), C′(6), 127.58, 127.91; C′(3), C′(5), 128.24, 129.65.

The low solubility of [Zn$(INTB)_2$] and [Zn$(HINTB)_2Cl_2$] precluded the recording of their ^{13}C NMR spectra.

ESR Spectra

The solid state ESR spectrum of [Cu(INTB)(CH_3COO)] at room temperature shows a strong absorption at 3275 G ($\Delta Ms = 1$ transition) with a g_{av} value of 2.08 and a weak absorption at 1675 G ($\Delta Ms = 2$ transitions) with $g = 4.06$, indicating the dimeric nature of the complex. The room

Table III. ^{1}H NMR Spectral Data (δ, ppm)

Compound	NH	Phenyl Ring	Pyridine Ring
INH	10.40 (s, 1H)	–	9.00 (d, 2H, J = 6 Hz); 7.90 (d, 2H, J = 6 Hz)
HINTB	11.80 (s, 2H)	7.87–8.34 (m, 5H)	9.10 (d, 2H, J = 6 Hz); 7.76 (d, 2H, J = 6 Hz)
[Zn(INTB)$_2$]	11.85 (s, 1H)	7.90–8.16 (m, 5H)	9.00 (d, 2H, J = 6 Hz); 7.76 (d, 2H, J = 6 Hz)
[Zn(HINTB)$_2$Cl$_2$]	11.79 (s, 2H)	7.93–8.40 (m, 5H)	9.03 (d, 2H, J = 6 Hz); 7.79 (d, 2H, J = 6 Hz)

Table IV. ^{13}C NMR Spectral Data (δ, ppm)

Compound	>C=O	>C=S	C_4	$C_{3,5}$	$C_{2,6}$	C'_1, C'_4	C'_2, C'_6	C'_3, C'_5
INH	163.99	–	140.26	121.03	150.18	–	–	–
HINTB	160.50	197.69	143.40	121.47	150.50	131.87 131.33	127.58 127.91	128.24 129.65

temperature spectrum of [Cu(HINTB)Cl$_2$] shows only a strong absorption at 3225 G ($g_{av} = 2.115$).

IR Spectra

The IR spectrum of HINTB in KBr shows two bands at 3240 and 3135 cm^{-1} due to ν(NH). The bands at 1700, 830 and 970 cm^{-1} are assigned to ν(C=O), ν(C=S) and ν(N-N), respectively. The spectra of M(HINTB)$_2$X$_2$ (X = CH$_3$COO and Cl) and [Cu(HINTB)Cl$_2$] show a strong band in the 1610–1676 cm^{-1} region due to ν(C=O). A shift to lower frequency of 24–90 cm^{-1} indicates the involvement of the carbonyl oxygen in bonding. Bonding through the sulfur of C=S is not indicated because ν(C=S) remains practically unchanged in the complexes (Table V). However, the ν(N-N) frequency shows a shift to higher frequency of 20–50 cm^{-1} indicating that one hydrazinic nitrogen is coordinated to the metal ion. The pyridine ring vibrations in all the complexes remain unchanged as compared to the ligand (1000, 635 cm^{-1}) indicating that the ring nitrogen is not involved in bonding. Thus, HINTB behaves as a neutral bidentate ligand in M(HINTB)$_2$X$_2$ and [Cu(HINTB)Cl$_2$], bonding through the carbonyl oxygen and one hydrazinic nitrogen. The spectra of [Cu(INTB)(CH$_3$COO)] and [Zn(INTB)$_2$] show the

Table V. Important IR Spectral Bands (cm^{-1}) and Their Assignments[a]

Compound	ν(N-H)	ν(C=O)/ν(NCO)	ν(N-N)	ν(C=S)	Pyridine Ring	ν_{as}(C-O), ν_S(C-O)
HINTB	3240 s, 3135 m	1700 s	970 m	830 s	1000 m, 635 m	–
[Co(HINTB)$_2$Cl$_2$]	3250 m, 3100 m	1610 s	1020 m	820 s	1000 m, 635 m	–
[Ni(HINTB)$_2$Cl$_2$]	3280 s, 3160 w	1612 s	1028 m	827 s	1001 m, 630 w	–
[Cu(HINTB)Cl$_2$]	3225 w, 3101 w	1615 s	1030 w	830 s	1000 m, 630 m	–
[Zn(HINTB)$_2$Cl$_2$]	3240 w, 3130 w	1616 s	1032 s	835 m	1000 m, 635 w	–
[Co(HINTB)$_2$](CH$_3$COO)$_2$	3200 m, 3110 w	1676 s	990 m	827 s	1000 m, 640 w	1508 s, 1437 m
[Ni(HINTB)$_2$(CH$_3$COO)$_2$]	3240 w, 3115 w	1610 m	1020 m	831 w	1000 m, 625 m	1570 b, 1330 w
[Cu(INTB)(CH$_3$COO)]	– 3100 w	1540 m	1020 m	830 s	1000 m, 625 w	1540 m, 1420 w
[Zn(INTB)$_2$]	– 3100 w	1535 w	1030 m	830 m	1000 m, 640 w	–

[a] b = broad, s = strong, m = medium, w = weak.

Table VI. Inhibition of Spore Germination by HINTB and Its Complexes

		Percentage inhibition of spore germination in different fungi			
Compound	Conc. (ppm)	*Stermphylium* sp.	*Fusarium udum*	*Alternaria tenuissima*	*H. rostratum*
HINTB	250	16.73	11.25	11.67	14.50
	500	23.11	18.75	14.58	17.71
	750	27.33	34.67	32.67	3.80
	1000	35.55	38.85	47.68	45.61
[Co(HINTB)$_2$Cl$_2$]	250	15.31	19.81	14.06	13.24
	500	31.21	30.35	49.65	52.92
	750	55.85	53.33	51.25	60.26
	1000	71.68	72.81	74.96	68.80
[Ni(HINTB)$_2$Cl$_2$]	250	15.30	13.88	14.20	25.49
	500	20.75	21.78	23.48	26.20
	750	42.00	29.71	29.66	46.34
	1000	44.09	51.55	40.13	54.17
[Cu(HINTB)Cl$_2$]	250	25.65	26.75	34.52	29.04
	500	62.73	59.76	60.05	67.95
	750	80.16	76.61	74.63	78.49
	1000	88.23	85.27	84.16	89.90
[Zn(HINTB)$_2$Cl$_2$]	250	68.15	76.68	73.93	66.90
	500	88.44	81.59	84.85	84.26
	750	89.85	86.14	84.96	89.04
	1000	98.24	96.59	89.53	96.40
[Cu(INTB)(CH$_3$COO)]	250	20.25	21.20	27.04	22.84
	500	56.56	52.75	53.80	58.50
	750	74.20	72.58	70.60	73.28
	1000	79.50	76.54	75.45	79.90
[Zn(INTB)$_2$]	250	58.15	66.68	64.04	56.90
	500	78.44	71.40	74.85	74.50
	750	79.80	75.50	75.04	79.04
	1000	88.24	86.54	79.53	86.40
Control (water)	–	1.02	2.29	0.80	2.11
Control (solvent + water)	–	2.59	3.66	3.50	4.83

absence of one ν(NH) and ν(C=O) and the presence of a new band due to ν(NCO), indicating enolisation of the C=O group and its subsequent deprotonation during complex formation.

$[Ni(HINTB)_2(CH_3COO)_2]$ shows bands at 1570 and 1330 cm^{-1} ($\Delta\nu = 240$ cm^{-1}) due to ν_{as}(C-O) and ν_s(C-O), respectively, indicating the presence of a monodentate acetato group. These bands are observed at 1508 and 1437 cm^{-1} ($\Delta\nu = 71$ cm^{-1}) in $[Co(HINTB)_2](CH_3COO)_2$, suggesting the ionic nature of the acetato group[24]. The corresponding bands in $[Cu(INTB)(CH_3COO)]$ are observed at 1540 and 1420 cm^{-1} ($\Delta\nu =$ 120 cm^{-1}) and indicate the bridging bidentate behaviour of the acetato group and thus explains the dimeric nature of the complex as indicated by the ESR spectrum.

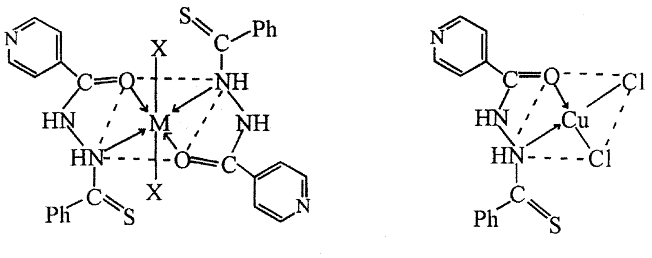
Fungicidal Screening

The results of antifungal activity given in Table VI show that the complexes are fungitoxic against the fungi, *Stemphylium* sp., *Fusarium udum*, *Alternaria tenuissima* and *Helminthosporium rostratum*. The antifungal activity increases with increasing the concentration of the compound and is believed to be due to the presence of the toxophoric groups thiocarbonyl and hydrazine. The ligand HINTB shows fungitoxic activity of 27–48%, whereas, its metal complexes show 30–98% fungitoxicity at the concentrations of 750 and 1000 ppm. $[Zn(HINTB)_2Cl_2]$ and $[Zn(INTB)_2]$

Table VII. Antibacterial Activity of HINTB and the Complexes

	Microbial Species								
Compound	a	b	c	d	e	f	g	h	i
HINTB	–	–	–	–	–	–	–	–	–
$[Co(HINTB)_2Cl_2]$	–	–	–	–	+	–	–	–	–
$[Ni(HINTB)_2Cl_2]$	–	–	–	–	+	–	–	–	–
$[Cu(HINTB)Cl_2]$	–	–	–	–	+	–	–	–	–
$[Zn(HINTB)_2Cl_2]$	–	–	–	–	–	–	–	–	–
$[Cu(INTB)(CH_2COO)]$	–	–	–	–	–	–	–	–	–
$[Zn(INTB)_2]$	–	–	–	–	–	–	–	–	–
Gentamicin	–	+	+	–	–	+	+	+	–
Solvent (DMSO)	–	–	–	–	–	–	–	–	–

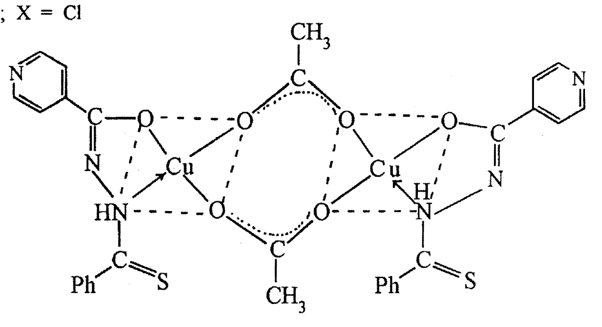
Zone diameter of inhibition >8 mm is taken as sensitive and shown as (+). a, b, c, d etc., denote the bacterial species mentioned in the text.



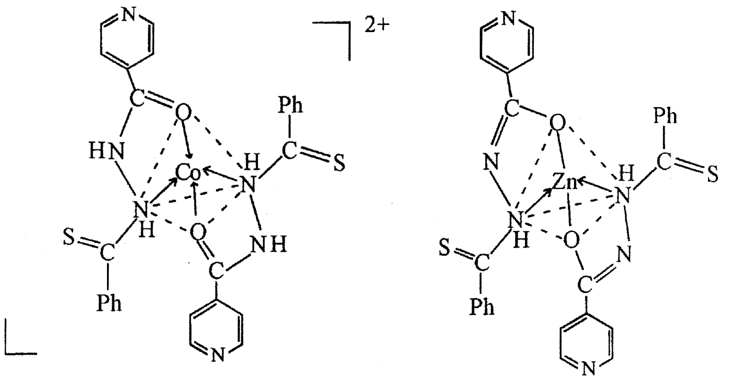
$[M(HINTB)_2X_2]$ $[Cu(HINTB)Cl_2]$

M = Ni; X = CH_3COO, Cl

M = Co, Zn; X = Cl



$[Cu(INTB)(CH_3COO)]$



$[Co(HINTB)_2](CH_3COO)_2$ $[Zn(INTB)_2]$

Figure 2. Proposed structure of the complexes.

show greater fungitoxicity as compared to [Cu(HINTB)Cl_2], [Ni$(HINTB)_2Cl_2$], [Co$(HINTB)_2Cl_2$], [Cu(INTB)(CH_3COO)] and the ligand, as expected due to the greater basic nature of Zn(II) as compared to other metal ions.

Antibacterial Screening

The results of antibacterial screening of HINTB and its complexes against *Staphylococcus aureus* (a), *Staphylococcus epidermidis* (b), *Enterococcus faecalis* (c), *Escherichia coli* (d), *Pseudomonas aeruginosa* (e), *Proteus vulgaris* (f), *Shigella flexneri* (g), *Vibrio cholerae* (h) *and Staphylococcus aureus* (ATCC 25923) (i) are shown in Table VII. It may be observed that [Co$(HINTB)_2Cl_2$], [Ni$(HINTB)_2Cl_2$] and [Cu(HINTB)Cl_2] inhibit the growth of only *Pseudomonas aeruginosa*. [Zn$(HINTB)_2Cl_2$], [Cu(INTB)(CH_3COO)], [Zn$(INTB)_2$] and the ligand are inactive against all of the nine bacteria.

On the basis of the analytical data and physico-chemical studies described above, the proposed structures of the complexes are shown in Fig. 2.

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