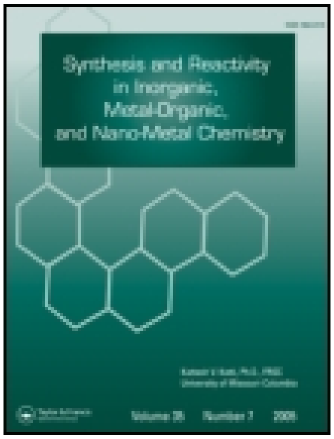
This article was downloaded by: [University of Waikato]
On: 15 July 2014, At: 09:38
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

STUDIES ON COMPLEXES OF Co(II), Ni(II), Cu(Il), AND Cd(II) WITH ACETOPHENONE AND 4-HYDROXYACETOPHENONE BENZOYLHYDRAZONES

B. Singh [a] , K. K. Narang [b] & Rachana Srivastava [a]
[a] Department of Chemistry , Banaras Hindu University , Varanasi, 221 005, India
[b] Department of Applied Chemistry , Institute of Technology, Banaras Hindu University , Varanasi, 221 005, India
Published online: 09 Dec 2011.

To cite this article: B. Singh , K. K. Narang & Rachana Srivastava (2001) STUDIES ON COMPLEXES OF Co(II), Ni(II), Cu(Il), AND Cd(II) WITH ACETOPHENONE AND 4-HYDROXYACETOPHENONE BENZOYLHYDRAZONES, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 31:8, 1375-1386, DOI: 10.1081/SIM-100107204

To link to this article: http://dx.doi.org/10.1081/SIM-100107204

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

SYNTH. REACT. INORG. MET.-ORG. CHEM., 31(8), 1375–1386 (2001)

STUDIES ON COMPLEXES OF Co(II), Ni(II), Cu(II), AND Cd(II) WITH ACETOPHENONE AND 4-HYDROXYACETOPHENONE BENZOYLHYDRAZONES

B. Singh,*[1] K. K. Narang,[2] and Rachana Srivastava[1]

[1]Department of Chemistry, Banaras Hindu University,
Varanasi-221 005, India
[2]Department of Applied Chemistry, Institute of
Technology, Banaras Hindu University,
Varanasi-221 005, India

ABSTRACT

Metal(II) complexes of the types $[M(L)_2Cl_2] \cdot H_2O$ and $[Cu(4\text{-}HOABH)SO_4(H_2O)_2]$ [M = Co(II), Ni(II), Cu(II) and Cd(II), L = acetophenone benzoylhydrazone (ABH), $C_6H_5CONH\text{-}N{=}C(CH_3)C_6H_5$ and 4-hydroxyacetophenone benzoylhydrazone (4-HOABH), $C_6H_5CONHN{=}C(CH_3)C_6H_4OH$], were prepared and characterized by elemental and thermal analyses, molar conductance, infrared, ESR and electronic spectral studies. Some of the complexes were screened against *E. coli* and *Aspergillus niger* for biological activity.

---

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

INTRODUCTION

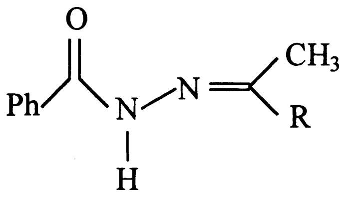
The copper(II) complexes of 2-pyridinecarboxaldehyde 2-pyridylhydrazone[1] and salcylaldehyde benzoylhydrazone[2] show antitumor activity. The transition metal complexes of isonicotinoylhydrazine have been found to be useful in polymer coating inks and pigments[3]. Monoacyl hydrazones and acyl dihydrazones have been found to be flexidentate ligands and form complexes of structural and biochemical interest[4].

Acetophenone benzoylhydrazone (ABH) and 4-hydroxyacetophenone benzoylhydrazone (4-HOABH) (Fig. 1) have a number of potential bonding sites such as the carbonyl oxygen, phenolic oxygen, the azomethine and imine nitrogens. Further, ABH differs from 4-HOABH in having a C_6H_5 moiety in place of C_6H_4OH. We have, therefore, synthesized Co(II), Ni(II), Cu(II) and Cd(II) complexes of ABH and 4-HOABH to study the effect of this moiety on the composition, general properties, bonding and stereochemistry of the complexes. The structures of the complexes have been investigated by using infrared, electronic, magnetic susceptibility and ESR spectral studies. Antifungal and antibacterial activities of some of the complexes have also been studied. The results are described in the present paper.

EXPERIMENTAL

Materials and Methods

The chemicals used in the present investigations were of analytical reagent grade. Acetophenone, 4-hydroxyacetophenone (Central Drug House, New Delhi) and metal salts (British Drug House, Bombay) were used as obtained.



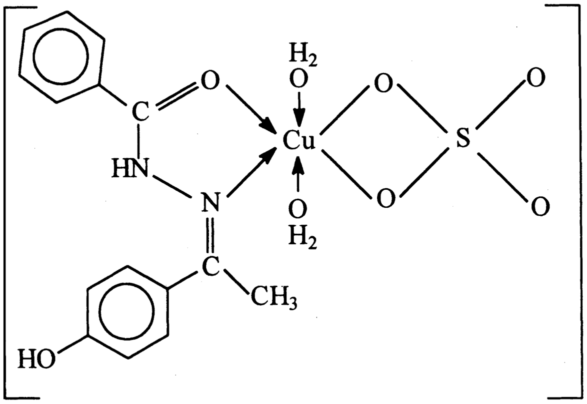
[R = C_6H_5 for ABH and 4-HOC_6H_4 for 4-HOABH]

Figure 1. Structures of the ligands.

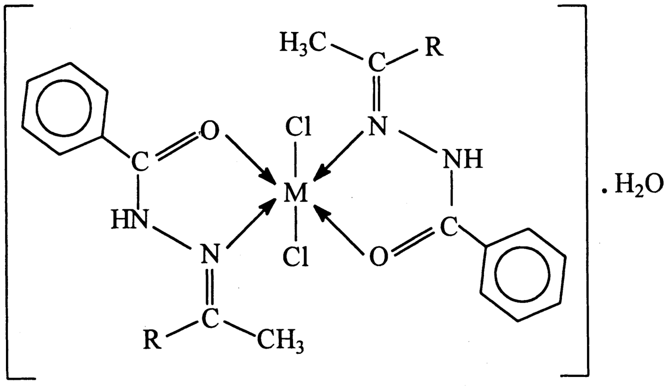
Table I. Analytical and Physico-chemical Data of the Metal Complexes

			Found (Calcd.)%								
Complexes	Colour (Formula Wt.)	Dec. p./Mp.	Metal	Anion (Cl^-/SO_4^{2-})	C	H	N	Hydrazine	Molar Conductance (Ω^{-1} mol^{-1}cm^2)	μ_{eff} (B.M.)	Yield (%)
$[Co(ABH)_2Cl_2]\cdot H_2O$	Violet	220–22	9.33	11.00	57.68	4.68	8.87	10.11	10.67	4.89	60
$C_{30}H_{30}N_2O_3Cl_2Co$	(624.0)		(9.45)	(11.37)	(57.69)	(4.48)	(8.97)	(10.25)			
$[Co(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	Light blue	210–11^d	9.20	10.51	57.88	4.68	6.86	10.66	–	4.99	62
$C_{30}H_{32}N_2O_3Cl_2Co$	(640.0)		(9.36)	(10.46)	(57.77)	(4.48)	(6.86)	(10.26)			
$[Ni(ABH)_2Cl_2]\cdot H_2O$	Green	180–82	9.11	11.22	57.55	4.33	3.88	10.11	22.6	2.83	71
$C_{30}H_{30}N_2O_3Cl_2$	(627.7)		(9.41)	(11.39)	(57.44)	(4.22)	(3.66)	(10.26)			
$[Ni(4\text{-}HOABH)Cl_2]\cdot H_2O$	Green	190–92^d	9.33	11.51	57.66	4.46	6.77	10.66	–	3.22	66
$C_{30}H_{32}N_2O_7Cl_2Ni$	(643.7)		(9.51)	(11.29)	(57.36)	(4.66)	(6.86)	(10.26)			
$[Cu(4\text{-}HOABH)SO_4(H_2O)_2]$	Green	160–62^d	13.36	13.71	58.48	4.56	7.33	8.50	7.95	2.09	72
$C_{30}H_{32}N_2O_7SCu$	(467.5)		(13.58)	(13.98)	(58.68)	(4.86)	(7.57)	(8.65)			
$[Cu(ABH)_2Cl_2]\cdot H_2O$	Blue	185–86	10.00	11.11	57.00	4.02	8.05	10.01	19.60	1.96	61
$C_{30}H_{30}N_2O_3Cl_2Cu$	(628.5)		(10.10)	(11.29)	(57.29)	(4.33)	(8.66)	(10.18)			
$[Cu(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	Blue	190–92^d	15.22	17.44	44.11	3.11	6.33	7.66	16.01	1.95	70
$C_{30}H_{32}N_2O_3Cl_2Cu$	(629.5)		(15.62)	(17.47)	(44.20)	(3.00)	(6.44)	(7.87)			
$[Cd(ABH)_2Cl_2]\cdot H_2O$	White	249–50	16.50	10.55	27.11	3.00	3.99	10.88	22.70	–	66
$C_{30}H_{32}N_2O_3Cl_2Cd$	(677.4)		(16.90)	(10.46)	(27.29)	(3.03)	(4.24)	(11.33)			
$[Cd(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	White	235–37^d	16.60	10.20	27.00	3.02	6.88	9.90	–	–	70
$C_{30}H_{32}N_2O_3Cl_2Cd$	(693.4)		(16.66)	(10.99)	(27.02)	(3.00)	(6.91)	(9.60)			

d = decomposition temperature.



$[Cu(4\text{-}HOABH)SO_4(H_2O)_2]$



$[M(L)_2Cl_2].H_2O$

$[M(II) = Co, Ni, Cu$ and $Cd]$, $[R = C_6H_5, C_6H_4OH\text{-}4]$

Figure 2. Representative structures of the complexes.

Benzoylhydrazine was prepared by refluxing methyl benzoate (10 mmol, 13.6 mL) with hydrazine hydrate (10 mmol, 5.0 mL) in ethanol (30 mL) for ~7 h. A white compound separated on standing over night. This was filtered and washed with distilled water. The pure hydrazide was obtained by recrystallization from hot benzene.

Acetophenone benzoylhydrazone and 4-hydroxyacetophenone benzoylhydrazone were prepared by refluxing the benzoylhydrazine (10 mmol, 1.36 g) with acetophenone (10 mmol, 1.20 mL) or 4-hydroxyacetophenone (10 mmol, 1.36 g) in ethanol (50 mL) for ~8 h. The hydrazones precipitated during the reaction and were filtered and recrystallized from hot ethanol.

The hydrazones were characterized by elemental analyses, hydrazine determination and infrared spectra.

Synthesis of Complexes

The ABH complexes were synthesized by adding an aqueous ethanol (50:50, v/v) solution (25 mL) of the metal chloride or sulfate (5 mmol) to a hot ethanol solution (50 mL) of ABH (10 mmol, 4.76 g). The reaction solutions were heated on a water bath for ~1 h. The compounds which precipitated during the reaction were filtered and washed with distilled water and ethanol to remove unreacted metal salts and ligand, if any. They were finally washed with diethyl ether and dried over anhydrous calcium chloride in a desiccator under reduced pressure.

The complexes of 4-HOABH were prepared by heating a suspension of the finely powdered ligand (5 mmol, 2.54 g) in an aqueous ethanol (50:50, v/v) solution (50 mL) of the metal chloride/sulfate (10 mmol). During the reaction of the ligand dissolved and the colour of the solution changed indicating reaction between the metal salt and the hydrazone. The solution was poured in a beaker and the complexes precipitated during evaporation of the solvent. The compounds were filtered and washed several times with hot distilled water to remove unreacted metal salts followed by ethanol and finally with diethyl ether. They were dried in a desiccator at room temperature under reduced pressure.

Analyses and Instrumentation

The complexes were analysed for their metal content using literature procedures[5] after decomposition with aqua regia followed by sulfuric acid, sulfate and chloride were determined gravimetrically as $BaSO_4$ and AgCl, respectively. Hydrazine was determined volumetrically by titrating with

$KBrO_3$[6] after hydrolysing the complexes in 6N HCl for ~4 h. Carbon, hydrogen and nitrogen were determined microanalytically on a Perkin Elmer 240 DC elemental analyser.

Molar conductances in DMSO solution (10^{-3} M) were measured at room temperature on a Systronics conductivity meter. Room temperature magnetic susceptibilities were determined on a Cahn Faraday balance using $[CoHg(SCN)_4]$ as standard and were corrected for diamagnetism[7]. The electronic spectra of the ligands and complexes were recorded on a Cary 2390 spectrophotometer in Nujol. IR spectra were recorded in Nujol mulls on a JASCO FT-IR 5300 spectrophotometer.

RESULTS AND DISCUSSION

Reaction of ABH and 4-HOABH with metal(II) salts yielded complexes having 1:1 and 1:2 metal-ligand stoichiometries. Formation of the complexes may be shown below.

$$MCl_2 \cdot nH_2O + 2L \xrightarrow[\text{heat}]{H_2O\text{-}EtOH} [M(L)_2Cl_2] \cdot H_2O + (n-1)H_2O$$

$$CuSO_4 \cdot 5H_2O + 4\text{-HOABH} \xrightarrow[\text{heat}]{H_2O\text{-}EtOH} [Cu(4\text{-HOABH})SO_4(H_2O)_2] + 3H_2O$$

$$[M(II) = \text{Co, Ni, Cu and Cd},\ L = \text{ABH or 4-HOABH}]$$

The complexes are insoluble in water and common organic solvents such as ethanol, methanol, benzene, chloroform but are slightly soluble in DMF and DMSO. They melt with decomposition in the 180–250 °C temperature range. The $[M(4\text{-HOABH})_2Cl_2]\cdot H_2O$ complexes decompose in the 180–237 °C temperature range. The hydrated complexes lose water molecules at 110–180 °C. The low molar conductances (16.6–27.5 Ω_M^{-1} cm^2 mol^{-1}) of the complexes suggest that they are non-electrolytes[8] in solution.

Magnetic Measurements

The magnetic moment of the cobalt(II) and nickel(II) complexes lie in the range reported for octahedral geometry[9]. The μ_{eff} values of the copper(II) complexes indicate the presence of one unpaired electron and give no definite information about the geometry.

Electronic Spectra

In the spectrum of ABH absorption bands are observed at 35,714, 43,859 and 47,619 cm^{-1} while in that of 4-HOABH they were observed at 35,971, 45,454 and 48,544 cm^{-1} which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of $>C{=}O$ and $>C{=}N$ groups, respectively. The corresponding bands of the metal complexes are observed at lower energies at 32,258–35,714, 40,985–45,045 and 45,454–47,719 cm^{-1}, respectively, indicating bonding of $>C{=}O$ and $>C{=}N$ groups to the metal ions.

The spectrum of $[Co(ABH)_2Cl_2] \cdot H_2O$ shows two absorption bands at 15,060 (ν_2) and 19,607 (ν_3) cm^{-1} while that of $[Co(4\text{-}HOABH)_2Cl_2] \cdot H_2O$ exhibits two bands at 14,471 (ν_2) and 18,050 (ν_3) cm^{-1}. They are assigned to the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(P)$ (ν_3) transitions, respectively. These features are characteristic of octahedral geometry of the complexes as indicated by the magnetic susceptibility measurement.

The absorption bands at 12,820 (ν_2) and 22,935 (ν_3) cm^{-1} in the spectrum of $[Ni(ABH)Cl_2] \cdot H_2O$ and at 14,637 (ν_2) and 24,154 (ν_3) cm^{-1} in that of $[Ni(4\text{-}HOABH)_2Cl_2] \cdot H_2O$ are attributed to the ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3T_{1g}(P)$ (ν_3) transitions[10], respectively, and show an octahedral geometry for the complexes[11].

The ligand field parameters, such as crystal field splitting energy ($10\,D_q$), interelectronic repulsion parameter (B'), nephalauxetic ratio (β), percentage covalency (β^0) and ligand field stabilization energy (LFSE) have been evaluated for cobalt(II) and nickel(II) complexes[12]. The values of these parameters in Table II are indicative of considerable metal-ligand orbital overlap.

The copper(II) complexes of ABH and 4-HOABH shows only one absorption band at 12,670 and 14,865 cm^{-1}, respectively, which is assigned to the ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition on the basis of a distorted octahedral geometry[13].

ESR Spectra

The ESR spectrum of $[Cu(4\text{-}HOABH)SO_4(H_2O)_2]$ shows a broad signal yielding a g-value of 2.005. This may be due to dipolar exchange and unresolved hyperfine interactions[14]. The spectrum also supports the octahedral structure of the copper(II) complex.

Table II. Electronic Spectral Data of Complexes

	Band maxima			Ligand field parameters				
Complexes	ν_1	ν_2	ν_3	$10D_q$ (cm^{-1})	B′ (cm^{-1})	β	β^0 (%)	LFSE $kJ \cdot mol^{-1}$
$[Co(ABH)_2Cl_2] \cdot H_2O$	–	15,060	19,607	8,015	916	0.94	5.6	76.2
$[Ni(ABH)_2Cl_2] \cdot H_2O$	–	12,820	22,935	7,645	849	0.82	23.0	110.7
$[Cu(ABH)_2Cl_2] \cdot H_2O$	14,815	–	–	14,815	–	–	–	106.1
$[Co(4\text{-}HOABH)_2Cl_2] \cdot H_2O$	–	14,471	18,050	7,794	820	0.84	15.5	74.6
$[Ni(4\text{-}HOABH)_2Cl_2] \cdot H_2O$	–	14,367	24,154	8,822	803	0.76	24.1	125.9
$[Cu(4\text{-}HOABH)_2 SO_4(H_2O)_2]$	14,044	–	–	14,044	–	–	–	90.4
$[Cu(4\text{-}HOABH)_2Cl_2] \cdot H_2O$	14,760	–	–	14,760	–	–	–	105.3

Infrared Spectra

The spectrum of ABH exhibits bands at 3270, 1640, 1624 and 996 cm^{-1} while that of 4-HOABH at 3265, 1660, 1625 and 998 cm^{-1} which are attributed to ν(NH), ν(C=O), ν(C=N) and ν(N–N), respectively. A band at 3320 cm^{-1} is assigned to ν(OH) in the spectrum of 4-HOABH.

In the metal complexes, ν(C=O) shifted to lower frequency by 5–15 cm^{-1} and suggests bonding through the carbonyl oxygen[15].

The ν(C=N) band is observed in the 1605–1620 cm^{-1} region in the spectra of ABH and 4-HOABH complexes indicating that the azomethine nitrogen is involved in bonding[16]. The ν(N–N) band shifted from 996–998 cm^{-1} in the ligand to higher frequency (1000–1010 cm^{-1}) in the complexes which further supports bonding through the azomethine nitrogen[17]. The band due to ν(OH) remains unaltered compared to the ligand indicating non-involvement of the phenolic oxygen in bonding. Thus, both hydrazones behave as bidentate ligands bonding through the carbonyl oxygen and azomethine nitrogen. All complexes show a broad band in the 3400–3600 cm^{-1} region indicating the presence of water molecules. [Cu(4-HOABH)$SO_4(H_2O)_2$] shows bands in the 950–900, 760–750 and 660–650 cm^{-1} region due to wagging, twisting and rocking modes characteristic of coordinated water. In [Cu(4-HOABH)$SO_4(H_2O)_2$] three new bands appeared at 950, 1050 and 1220 cm^{-1} which suggest the presence of the chelating sulfate group[18].

Table III. Important IR Spectral Bands (cm^{-1}) and Their Assignments

Complexes	ν(OH)/NH	Amide I ν(C=O)	ν(C=N)	ν(N–N)
ABH	3280 b	1640 s	1614 s	998 w
[Co(ABH)$_2$Cl$_2$]·H_2O	3415 b/3270 m	1635 s	1610 m	1010 w
[Ni(ABH)$_2$Cl$_2$]·H_2O	3410 b/3258 m	1630 s	1610 m	1005 w
[Cu(ABH)$_2$Cl$_2$]·H_2O	3410 b/3260 m	1635 s	1610 m	1010 w
[Cd(ABH)$_2$Cl$_2$]·H_2O	3415 b/3270 w	1635 s	1610 m	995 w
4-HOABH	3320 b/3255 m	1660 s	1625 m	1005 w
[Co(4-HOABH)$_2$Cl$_2$]·H_2O	3311 b/3260 m	1640 s	1608 m	1005 w
[Ni(4-HOABH)$_2$Cl$_2$]·H_2O	3315 m/3265 m	1645 m	1620 m	1010 w
[Cu(4-HOABH)$_2$Cl$_2$]·H_2O	3320 w/3260 m	1635 m	1620 m	1005 w
[Cu(4-HOABH) SO_4]$(H_2O)_2$]	3320 w/3260 m	1650 m	1610 m	1010 w
[Cd(4-HOABH)$_2$Cl$_2$]·H_2O	3320 m/3265 w	1650 w	1605 m	1010 w

Table IV. Antibacterial Activity

Compounds	Zone of Inhibition (cm)		
	500 μg/mL	1000 μg/mL	1500 μg/mL
ABH	0.022	0.024	0.028
$[Cu(ABH)_2Cl_2]\cdot H_2O$	0.866	0.886	0.896
$[Zn(ABH)_2Cl_2]\cdot H_2O$	0.431	0.441	0.466
4-HOABH	0.040	0.048	0.499
$[Cu(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	1.201	1.360	1.440
$[Zn(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	0.781	0.881	0.888

Biological Activity

Acetophenone and 4-hydroxyacetophenone benzoylhydrazones and their Cu(II) and Zn(II) complexes have been screened against *E. coli* (a gram +ve bacteria) and *Aspergllus niger* at three different concentrations, 500, 1000 and 1500 μg/mL. The results are shown in Tables IV and V.

The experimental data show that 4-HOABH has a greater inhibitory effect than ABH which may be due to the presence of the phenolic group in 4-HOABH which is more effective than other groups[19].

The complexes have a greater inhibitory effect than their parent ligands[20]. The region behind the good activity may be the combined effect of metal toxicity and availability of uncoordinated binding sites of ligands which interact with metal trace metals of bacteria and fungi. In the

Table V. Antifungal Activity[a]

Compounds	Percentage of Inhibition		
	500 μg/mL	1000 μg/mL	1500 μg/mL
ABH	++++	+++	++++
$[Cu(ABH)_2Cl_2]\cdot H_2O$	++++	+++	+++
$[Zn(ABH)_2Cl_2]\cdot H_2O$	+++	++	+
4-HOABH	+++	++	+++
$[Cu(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	+++	+	++
$[Zn(4\text{-}HOABH)_2Cl_2]\cdot H_2O$	++	++	++

[a] ++++ = 100% germination, +++ = 75% germination, ++ = 50% germination, + = 25% germination.

4-HOABH metal complexes the phenolic group is uncoordinated so these complexes have greater inhibitory effect that the ABH complexes.

ACKNOWLEDGMENT

The authors thank the Head, Department of Chemistry, Banaras Hindu University, for providing laboratory facilities.

REFERENCES

1. Sorensen, J.R.J. Copper(II) Complexes in Biochemistry and Pharmacology. Chem. Ber. **1984**, *20* (12), 1110–1113.
2. Pickart, L.; Goodwin, W.H.; Murphy, T.B.; Johnson, D.K. Cytotoxic Chelators and Chelates. Inhibition of DNA Synthesis in Cultured Potent and Human Cells by Aroylhydrazons and by Copper(II) Complex of Salicylaldehyde Benzoylhydrazone. Inorg. Chim. Acta **1982**, *67* (5), 159–165.
3. Cseh, G.; Lienard, P.; Wiedmann, W. Heterocyclic 1:1 Hydrazine-Metal Complex. Pigments for Organic Polymers and Coating Materials. Eur. Pat. Appl. **1990**, 349489: Chem. Abstr. **1990**, *100*, 25554 y.
4. Narang, K.K.; Singh, V.P. Synthesis, Characterization and Biological Activity of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Valeraldehyde Benzoylhydrazones and Valeraldehyde Isonicotinoylhydrazones. Synth. React. Inorg. Met.-Org. Chem. **1993**, *23* (4), 607–627.
5. Vogel, A.I. *A Text Book of Quantitative Inorganic Analysis*; Longmass: London, 1969; 459–587.
6. Narang, K.K.; Lal, R.A. Copper(II), Nickel(II) and Cobalt(II) Complexes of Disalicylaldimine Succinamide and Di(o-hydroxyacetophenoneimine) Succinamide. Transition Met. Chem. **1976**, *1*, 260–263.
7. Earnshaw, A. *Introduction to Magneto-Chemistry*; Academic Press: London, 1968; 35–36.
8. Geary, W.J. The Use of Conductivity Measurements in Organic Solvents for Characterization of Coordination Compounds. Coord. Chem. Rev. **1971**, *7*, 81–122.
9. Dyer, G.; Weak, D.W. Low Spin Co(II) Complexes with Bidentate Ligands. J. Am. Chem. Soc. **1967**, *89* (16), 3983–3987.
10. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968; 299–300.
11. Sacconi, L. Electronic Structure and Stereochemistry of Ni(II). Transition Met. Chem. **1969**, *4*, 199–298.

12. Lever, A.B.P. Electronic Spectra of Some Transition Metal Complexes. Derivation of Dq and B. J. Chem. Educ. **1968**, *45* (11), 711–712.
13. Patel, K.C.; Goldberg, D.E. N-Aroylalkylpolyamine Complexes. Formation Constants of Coordination Compounds N-Benzyl and N′N-Dibenzylethylenediamine with Transition Metal Ions. J. Inorg. Nucl. Chem. **1972**, *34* (11), 3583–3584.
14. Procter, I.M.; Hathaway, B.J.; Nicholls, P. Electronic Properties and Stereochemistry of Cu(II) Ion. Part I. (Ethylenediamine)Cu(II). J. Chem. Soc. A. **1968**, *7*, 1678–1684.
15. Nagano, K.; Kinoshita, H.; Hirakawa, A. Infrared Absorption Spectra of Isonicitinoylhydrazine and Related Compounds. Chem. Pharm. Bull. **1964**, *12* (10), 1198–1206.
16. Narang, K.K.; Singh, V.P. Synthesis, Characterization of Cobalt(II), Nickel(II) and Zinc(II) Complexes with Acetylacetone Bis-Benzoylhydrazine and Acetylacetone Bis-Isonicotinoylhydrazine. Transition Met. Chem. **1993**, *18* (3), 287–290.
17. Braibanti, A.; Dallavale, F.; Pellinghelli, M.A.; Leporati, E. The Nitrogen-Nitrogen Stretching Band in Hydrazine Derivatives and Complexes. Inorg. Chem. **1968**, *7* (7), 1430–1433.
18. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley Interscience: New York, 1986; 284–286.
19. Mishra; L.; Upadhyay, K.K.; Singh, V.K. Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of Some Bis-Heterocyclics as Potential Fungicides. Synth. React. Inorg. Met.-Org. Chem. **1996**, *26* (4), 23–43.
20. Johri, R.B.; Sharma, R.C. Synthesis and Biological Studies of Some Metal Complexes of Benzaldehyde Salicyloylhydrazone. J. Ind. Chem. Soc. **1988**, *LXV* (11), 793–794.

Received February 17, 2000
Accepted June 23, 2001

Referee I: M. T. Caudle
Referee II: I. F. Cheng