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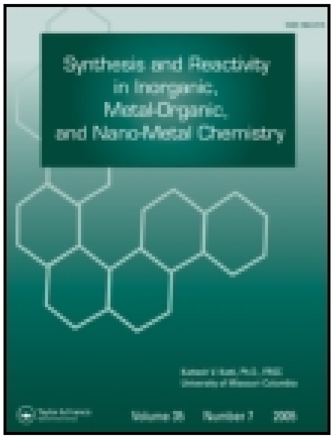

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STUDIES ON COMPLEXES OF COBALT(II), NICKEL(II), COPPER(II), AND CADMIUM(II) WITH ACETOPHENONE AND 4-HYDROXYACETOPHENONE SALICYLOYL AND ISONICOTINOYLHYDRAZONES

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STUDIES ON COMPLEXES OF COBALT(II), NICKEL(II), COPPER(II), AND CADMIUM(II) WITH ACETOPHENONE AND 4-HYDROXYACETOPHENONE SALICYLOYL AND ISONICOTINOYLHYDRAZONES

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ABSTRACT

Metal(II) complexes of the types $[M(L)_mCl_2(H_2O)_n]$ and $[Cu(L')SO_4(H_2O)_2]$ [M=Co(II), Ni(II), Cu(II) and Cd(II), L=acetophenone salicyloylhydrazone (ASH) OHC_6H_4CO-$NHN{=}C(CH_3)C_6H_5$, $m = 2$, $n = 2$; 4-hydroxyacetophenone salicyloylhydrazone (4-HOASH), $m = 2$, $n = 0$; acetophenone isonicotinoylhydrazone (AINH), $NC_5H_4CONHN{=}C(CH_3)$-C_6H_5, $m = 1$, $n = 2$; 4-hydroxyacetophenone isonicotinoyl-

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hydrazone (4-HOAINH), $NC_5H_4CONHN{=}C(CH_3)$-C_6H_4OH, $m = 1$, $n = 2$, and $L' = $ 4-HOAINH and 4-HOASH] were prepared and characterized by elemental and thermal analyses, molar conductance, magnetic susceptibility, infrared, electronic, NMR, ESR and X-ray powder diffraction studies. Some of the complexes were screened against *E. coli* and *Aspergillus niger* to explore their biological activity.

INTRODUCTION

Salicylic- and isonicotinic acid hydrazides and their hydrazones form a variety of complexes with metal ions.[1–3] INH is used as isoniazid for treatment of tuberculosis and its activity is enhanced on chelation with copper(II).[4] The salicylhydrazine is reported to have biological activity. Acetophenone salicyloylhydrazone (ASH), 4-hydroxyacetophenone salicyloylhydrazone (4-HOASH), acetophenone isonicotinoylhydrazone (AINH) and 4-hydroxy acetophenone isonicotinoylhydrazone (4-HOAINH) (Fig. 1) possess a number of potential bonding sites which may form complexes with interesting structural and biological properties. In this paper we report the synthesis, characterization and biological activity of hitherto uninvestigated 3d- bivalent metal complexes of the title hydrazones.

EXPERIMENTAL

Materials and Methods

The chemicals used were of analytical, reagent or equivalent grade. Acetophenone and 4-hydroxyacetophenone were obtained from Central

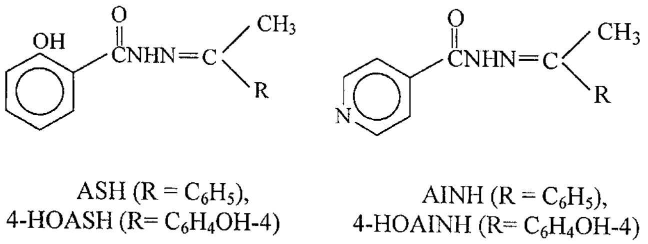
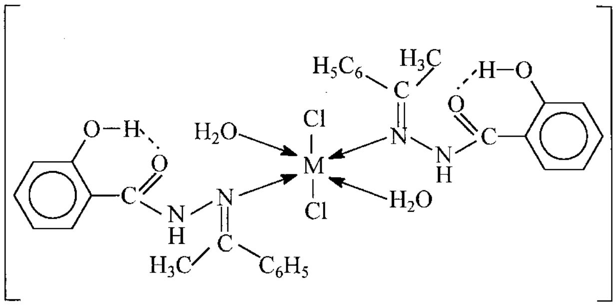
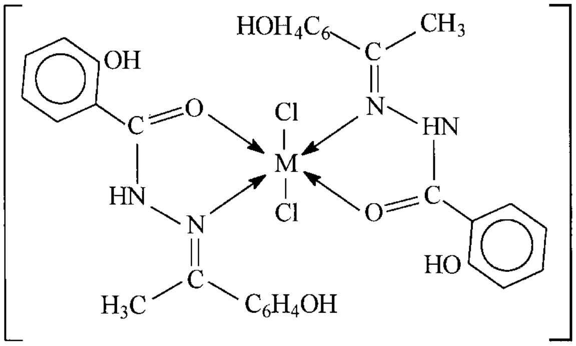


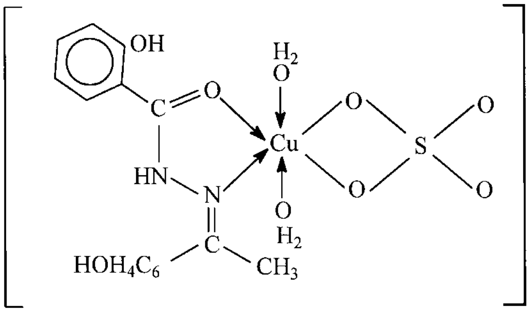
Figure 1. Structures of the ligands.



[M(ASH)$_2$Cl$_2$(H$_2$O)$_2$] [M(II) = Co, Ni, Cu, and Cd]



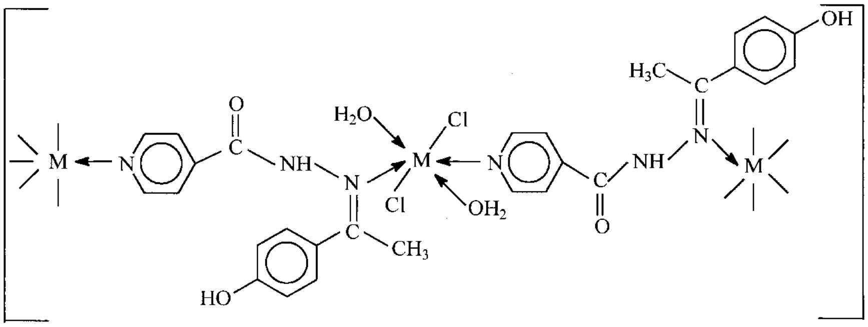
[M(4-HOASH)$_2$Cl$_2$]
[M(II) = Co, Ni, Cu, and Cd]



[Cu(4-HOASH)SO$_4$(H$_2$O)$_2$]

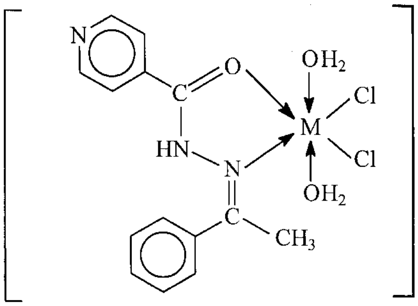
Figure 2. Representative structures of the complexes.

(continued)



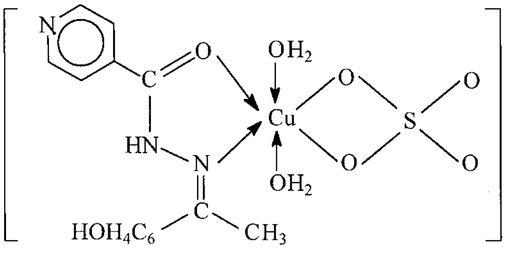
$[\mathrm{M(4\text{-}HOAINH)Cl_2(H_2O)_2}]$

$[\mathrm{M(II)} = \mathrm{Co, Ni, Cu\ and\ Cd}]$



$[\mathrm{M(AINH)Cl_2(H_2O)_2}]$

$[\mathrm{M(II)} = \mathrm{Co, Ni, Cu\ and\ Cd}]$



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

Figure 2. Continued.

Drug House, New Delhi, and were used without further purification. Acetophenone and 4-hydroxyacetophenone salicyloylhydrazones were prepared by refluxing salicyloylhydrazine (10 mmol, 1.52 g) in ethanol (30 mL) with acetophenone (10 mmol, 1.20 mL) or 4-hydroxyacetophenone (10 mmol, 1.36 g, 20 mL) in ethanol (50 mL) for 7 h, respectively. Acetophenone and 4-hydroxyacetophenone isonicotinoylhydrazones were prepared by refluxing isonicotinoylhydrazine (10 mmol, 1.36 g) and acetophenone (10 mmol, 1.20 g, 20 mL) in ethanol (30 mL) or 4-hydroxyacetophenone (10 mmol, 1.36 g, 20 mL) in ethanol (50 mL) for 7–8 h, respectively. The compounds which precipitated during the reaction were filtered and washed with ethanol. They were recrystallized from hot ethanol. The hydrazones were characterized by elemental analyses, hydrazine determination, infrared and NMR spectra.

Synthesis of Complexes

The AINH and ASH complexes were synthesized by adding an aqueous ethanol (50:50, v/v) solution (25 mL) of the metal chloride (5 mmol) to a hot ethanol (50 mL) solution of AINH (10 mmol, 2.39 g) or ASH (10 mmol, 2.54 g), respectively. The reaction solution was heated on a water bath for ~1 h. The compounds which precipitated during heating were filtered and washed several times with distilled water, ethanol and finally with ether before drying over anhydrous calcium chloride in a desiccator.

The complexes of 4-HOASH and 4-HOAINH were prepared by mixing an aqueous ethanol (50:50, v/v) solution (25 mL) of the metal chloride/sulfate (10 mmol) and 4-HOASH (10 mmol, 2.70 g) or 4-HOAINH (10 mmol, 2.56 g) in the same solvent (25 mL). The reaction solution was refluxed for ~8 h with shaking at regular intervals. The compounds which precipitated during heating were filtered and washed several times with distilled water to remove the unreacted metal salts, if any, then with ethanol and finally with ether before drying over anhydrous calcium chloride in a desiccator.

Analyses and Physical Measurements

The complexes were analysed for metal content using literature procedures[5] after decomposing them with aqua regia followed by sulfuric acid. Sulfate and chloride were determined gravimetrically as $BaSO_4$ or AgCl, respectively. Hydrazine was determined volumetrically by titrating with $KBrO_3$ after hydrolysing the complexes in ~6N HCl using methyl orange as an indicator.[6] Carbon, hydrogen and nitrogen were determined microanalytically on a Perkin Elmer 240 DC elemental analyser. The water content in the complexes was determined by heating a known amount of sample to a constant weight at 100, 130, 150 and 180 °C.

Molar conductances in DMSO solution (10^{-3} M) were measured at room temperature on a Systronics 304 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] Electronic spectra of the ligands and complexes were recorded on a Cary 2390 spectrophotometer in Nujol mulls. IR spectra were recorded on a JASCO 5300 spectrophotometer KBr or Nujol mulls. ESR spectra of the complexes were recorded on a Varian X band E4 spectrometer. NMR spectra were recorded on a JEOL FX 90Q spectrometer in DMSO-d_6 using TMS as an internal reference. XRD data were collected on a Seifert ID-300 diffractometer using CuK^{α} radiation.

RESULTS AND DISCUSSION

Reactions of AINH and 4-HOAINH with metal(II) salts yielded complexes possessing a 1:1 metal-ligand ratio. ASH and 4-HOASH reacted with metal(II) chloride and formed the complexes having only a 1:2 metal-ligand stoichiometry. The complexes are insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they are slightly to fairly soluble in DMF and DMSO.

$$MCl_2 \cdot nH_2O + 2AINH \xrightarrow[\text{heat}]{H_2O\text{-}EtOH} [M(AINH)Cl_2(H_2O)_2] + AINH + (n-2)H_2O$$

$$MCl_2 \cdot nH_2O + 4\text{-}HOAINH \xrightarrow[\text{heat}]{H_2O\text{-}EtOH} [M(4\text{-}HOAINH)Cl_2(H_2O)_2] + (n-2)H_2O$$

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

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

			Found (Calcd.) %									
Complexes	Colour (Formula wt.)	Melting point/dec. pt. (°C)	Metal	Anion Cl^-/SO_4^{2-}	C	H	N	Hydrazine	Molar Conductance ($\Omega_M^{-1}mol^{-1}cm^2$)	μ_{eff} (B.M.)	Yield %	H_2O
AINH	White	162–63	–	–	70.43	5.41	17.50	13.2	–	–	65	–
$C_{14}H_{13}N_3O$	(239.00)				(70.29)	(5.44)	(17.57)	(13.2)				
$[Co(AINH)Cl_2(H_2O)_2]$	Violet	219–20	14.3	17.4	41.38	4.18	10.11	8.1	9.9	4.81	60	8.6
$C_{14}H_{17}Cl_2CoN_3O_3$	(404.9)		(14.5)	(17.5)	(41.48)	(4.19)	(10.30)	(7.9)				(8.9)
$[Ni(AINH)Cl_2(H_2O)_2]$	Green	200–01	14.0	17.4	41.38	4.21	10.06	8.0	21.2	3.10	59	8.5
$C_{14}H_{17}Cl_2N_3NiO_3$	(404.7)		(14.5)	(17.5)	(41.51)	(4.20)	(10.37)	(7.9)				(8.9)
$[Cu(AINH)Cl_2(H_2O)_2]$	Green	195–97	15.5	17.1	41.11	4.00	10.11	7.7	11.1	2.01	62	8.4
$C_{14}H_{17}Cl_2CuN_3O_3$	(409.5)		(15.4)	(17.3)	(41.02)	(4.15)	(10.25)	(7.8)				(8.8)
$[Cd(AINH)Cl_2(H_2O)_2]$	White	201–02	24.3	15.2	36.66	3.65	9.40	7.3	–	–	68	8.1
$C_{14}H_{17}CdCl_2N_3O_3$	(438.4)		(24.5)	(15.5)	(36.64)	(3.70)	(9.16)	(7.0)				(8.2)
4-HOAINH	Yellow	280–82	–	–	66.40	5.55	15.48	11.5	–	–	72	–
$C_{14}H_{13}N_3O_2$	(255)				(66.60)	(5.57)	(15.60)	(11.8)				
$[Co(4\text{-}HOAINH)Cl_2(H_2O)_2]$	Brown	225–26^d	13.8	16.5	39.66	4.00	10.00	7.1	10.1	5.10	61	8.5
$C_{14}H_{17}Cl_2CoN_3O_4$	(420.9)		(14.0)	(16.8)	(39.91)	(4.03)	(9.97)	(7.6)				(8.5)
$[Ni(4\text{-}HOAINH)Cl_2(H_2O)_2]$	Light green	220–22^d	13.6	16.6	39.64	4.00	9.80	7.1	–	2.96	58	8.1
$C_{14}H_{17}Cl_2N_3NiO_4$	(420.7)		(13.9)	(16.8)	(39.93)	(4.04)	(9.98)	(7.6)				(8.5)
$[Cu(4\text{-}HOAINH)Cl_2(H_2O)_2]$	Green	212–14^d	15.1	16.5	39.06	3.87	9.66	7.1	–	1.86	69	8.0
$C_{14}H_{17}N_3Cl_2CuO_4$	(425.5)		(14.9)	(16.7)	(39.48)	(3.99)	(9.87)	(7.5)				(8.5)
$[Cu(4\text{-}HOAINH)SO_4(H_2O)_2]$	Dark green	250–51^d	14.0	21.0	37.00	3.61	9.00	7.0	4.9	1.96	65	7.6
$C_{14}H_{17}CuN_3O_8S$	(450.5)		(14.1)	(21.3)	(37.30)	(3.77)	(9.32)	(7.1)				(8.0)

(continued)

Table I. Continued

Complexes	Colour (Formula wt.)	Melting point/dec. pt. (°C)	Found (Calcd.) %						Molar Conductance ($\Omega_M{}^{-1}$mol^{-1}cm^2)	μ_{eff} (B.M.)	Yield %	H_2O
			Metal	Anion $Cl^-/SO_4{}^{2-}$	C	H	N	Hydrazine				
[Cd(4-HOAINH)$Cl_2(H_2O)_2$]	Yellow	235–37^d	23.6	14.6	35.30	3.63	8.76	6.4	–	–	70	7.1
$C_{14}H_{17}CdCl_2N_3O_4$	(474.4)		(23.7)	(14.9)	(35.40)	(3.58)	(8.85)	(6.7)				(7.6)
ASH	White	205–7	–	–	70.35	5.31	11.18	12.5	–	–	70	–
$C_{15}H_{14}N_2O_2$	(254)				(70.86)	(5.51)	(11.02)	(12.6)				
[Co(ASH)$_2Cl_2(H_2O)_2$]	Purple	220–22	8.5	10.6	53.32	4.81	8.15	9.3	10.1	4.86	65	5.0
$C_{30}H_{32}Cl_2CoN_4O_6$	(673.9)		(8.7)	(10.5)	(53.42)	(4.74)	(8.31)	(9.5)				(5.3)
[Ni(ASH)$_2Cl_2(H_2O)_2$]	Green	180–82	8.6	10.4	53.35	4.68	8.25	9.3	9.6	3.30	60	5.1
$C_{30}H_{32}Cl_2N_4NiO_6$	(673.7)		(8.7)	(10.5)	(53.43)	(4.74)	(8.31)	(9.5)				(5.3)
[Cu(ASH)$_2Cl_2(H_2O)_2$]	Blue	195–96	9.5	10.4	53.20	4.65	8.14	9.3	22.7	2.01	58	5.2
$C_{30}H_{32}Cl_2CuN_4O_6$	(678.5)		(9.3)	(10.5)	(53.05)	(4.71)	(8.25)	(9.4)				(5.3)
[Cd(ASH)$_2Cl_2(H_2O)_2$]	White	250–52	15.2	9.7	49.37	4.30	7.82	8.6	10.7	–	66	6.4
$C_{30}H_{32}CdCl_2N_4O_6$	(727.4)		(15.4)	(9.8)	(49.49)	(4.39)	(7.70)	(8.8)				(6.9)
4-HOASH	Yellow	242–44	–	–	66.8	5.20	10.80	11.6	–	–	70	–
$C_{15}H_{14}N_2O_3$	(270)				(66.66)	(5.18)	(10.37)	(11.8)				
[Co(4-HOASH)$_2Cl_2$]	Violet	240–42^d	8.6	10.3	53.56	4.10	8.45	9.2	–	4.88	60	–
$C_{30}H_{28}Cl_2CoN_4O_6$	(669.9)		(8.8)	(10.6)	(53.74)	(4.17)	(8.36)	(9.5)				
[Ni(4-HOASH)$_2Cl_2$]	Green	190–92^d	8.7	10.7	53.70	4.22	8.25	9.4	8.9	3.21	65	–
$C_{30}H_{28}Cl_2N_4NiO_6$	(669.7)		(8.8)	(10.6)	(53.75)	(4.18)	(8.36)	(9.5)				
[Cu(4-HOASH)$_2Cl_2$]	Dark green	200–02^d	9.3	10.6	53.26	4.20	8.10	9.6	11.1	1.89	60	–
$C_{30}H_{28}Cl_2CuN_4O_6$	(674.5)		(9.4)	(10.5)	(53.37)	(4.15)	(8.30)	(9.5)				
[Cu(4-HOASH)$SO_4(H_2O)_2$]	Green	220–22^d	13.5	20.4	38.70	3.80	6.00	6.8	8.9	1.96	65	7.5
$C_{15}H_{18}CuN_2O_9S$	(465.5)		(13.6)	(20.6)	(38.66)	(3.86)	(6.01)	(6.9)				(7.7)
[Cd(4-HOASH)$_2Cl_2$]	White	244–45^d	15.3	9.9	49.71	3.80	7.53	8.7	–	–	58	–
$C_{30}H_{28}CdCl_2N_4O_6$	(723.4)		(15.5)	(9.8)	(49.76)	(3.87)	(7.74)	(8.8)				

d = decomposition temperature.

$$MCl_2 \cdot nH_2O + 2ASH \xrightarrow[\text{heat}]{H_2O\text{-}EtOH} [M(ASH)_2Cl_2(H_2O)_2] + (n-2)H_2O$$

$$MCl_2 \cdot nH_2O + 4\text{-}HOASH \xrightarrow[\text{heat}]{H_2O\text{-}EtOH} [M(4\text{-}HOASH)_2Cl_2] + nH_2O$$

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

$$[M(II) = Co, Ni, Cu \text{ and } Cd; n = 0, 2, 6]$$

The complexes $[M(ASH)_2Cl_2(H_2O)_2]$ and $[M(AINH)Cl_2(H_2O)_2]$ melt in the 180–252 °C temperature range while $[M(4\text{-}HOASH)_2Cl_2]$ and $[M(4\text{-}HOAINH)Cl_2(H_2O)_2]$ decompose in the 190–251 °C temperature range.

The molar conductances (4.9–28.7 Ω_M^{-1} cm^2 mol^{-1}) in DMSO of the complexes suggest non-electrolytic behaviour. The slightly higher values of $[Ni(AINH)Cl_2(H_2O)_2]$ and $[Cu(ASH)_2Cl_2(H_2O)_2]$ complexes are due to partial dissociation of the anion by DMSO.[8] Dehydration studies of the hydrated complexes in the 100–180 °C temperature range showed the presence of coordinated water in the complexes.

Magnetic Measurements

The magnetic moment values of the cobalt(II) and nickel(II) complexes are indicative of an octahedral geometry.[9] The μ_{eff} values of the copper(II) complexes correspond to one unpaired electron and give no definite information regarding the coordination geometry around the metal ion.

Electronic Spectra

In the spectra of ASH absorption bands (Table II) are observed at 31,250, 41,322 and 45,870 cm^{-1} while the spectrum of AINH shows bands at 34,246, 40,322 and 48,076 cm^{-1}, respectively. The bands are observed at 29,410, 40,650 and 46,290 cm^{-1} in the spectrum of 4-HOASH and at 33,333, 42,016 and 47,169 cm^{-1} in that of 4-HOAINH. The first two bands may be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of >C=O and >C=N moieties and the third absorption band may be due to the $\pi \rightarrow \pi^*$ transition of the benzene moiety. These bands were observed at lower energies in the spectra of the complexes indicating involvement of the carbonyl oxygen and/or azomethine nitrogen in bonding.

Table II. Electronic Spectral Bands of the Metal Complexes and Ligand Field Parameters

Complexes	ν_1	ν_2	ν_3	10Dq (cm^{-1})	B′ (cm^{-1})	β	β^0 (%)	LFSE (kJ mol^{-1})
[Co(AINH)$Cl_2(H_2O)_2$]	–	14,492	18,518	7,704	856	0.88	11.8	73.4
[Ni(AINH)$Cl_2(H_2O)_2$]	9,589	15,529	26,178	9,589	862	0.83	16.5	136.9
[Cu(AINH)$Cl_2(H_2O)_2$]	12,903	–	–	12,903	–	–	–	92.1
[Co(4-HOAINH)$Cl_2(H_2O)_2$]	–	14,502	18,990	7,606	895	0.92	7.8	72.4
[Ni(4-HOAINH)$Cl_2(H_2O)_2$]	9,765	15,432	25,000	9,765	742	0.72	28.0	139.4
[Cu(4-HOAINH)$Cl_2(H_2O)_2$]	13,513	–	–	13,513	–	–	–	96.5
[Cu(4-HOAINH)$SO_4(H_2O)_2$]	15,698	–	–	15,698	–	–	–	112.1
[Co(ASH)$_2Cl_2(H_2O)_2$]	–	15,375	19,230	8,281	871	0.90	10.0	78.8
[Ni(ASH)$_2Cl_2(H_2O)_2$]	–	16,500	24,150	10,907	574	0.56	44.3	155.8
[Cu(ASH)$_2Cl_2(H_2O)_2$]	14,760	–	–	14,760	–	–	–	105.4
[Co(4-HOASH)$_2Cl_2$]	–	14,450	19,607	7,854	924	0.95	4.84	74.8
[Ni(4-HOASH)$_2Cl_2$]	–	14,367	24,140	8,827	803	0.78	22.0	126.1
[Cu(4-HOASH)$_2Cl_2$]	14,110	–	–	14,110	–	–	–	100.7
[Cu(4-HOASH)$SO_4(H_2O)_2$]	15,190	–	–	15,190	–	–	–	108.5

The spectra (Table II) of the cobalt(II) complexes show two absorption bands. They are assigned to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(P)$ (ν_3) transitions, respectively, assuming an octahedral stereochemistry for the complexes.[10]

The $[Ni(ASH)_2Cl_2(H_2O)_2]$ and $[Ni(4\text{-}HOASH)_2Cl_2]$ complexes show two absorption bands which are attributed to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3T_{1g}(P)$ (ν_3) transitions, respectively, while $[Ni(AINH)Cl_2(H_2O)_2]$ and $[Ni(4\text{-}HOAINH)Cl_2(H_2O)_2]$ exhibit three absorption bands which are assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3T_{1g}(F)$ (ν_2) and $^3T_{1g}(P)$ (ν_3), transitions, respectively, on the basis of an octahedral geometry. The octahedral coordination around nickel(II) is further supported by the ν_2/ν_1 ratio for AINH (1.58) and 4-HOAINH (1.61) complexes which lies in the range reported for the nickel (II) complexes with an octahedral geometry.[11]

The ligand field parameters such as crystal field splitting energy (10Dq), inter-electronic repulsion parameters (B'), nephelauxetic ratio (β), percentage covalency (β^0) and ligand field stablization energy (LFSE) have been evaluated for the cobalt(II) and nickel(II) complexes.[12] The values of B' and β are indicative of the reduction in inter-electronic repulsion which is resulting due to the metal-ligand orbital overlap.

Only one broad band is observed in the spectra of the copper(II) complexes at 10,810–15,190 cm^{-1} which may be assigned to the $^2E_g \rightarrow {}^2T_{2g}$ (D) transition on the basis of an octahedral geometry.[13]

ESR Spectra

The spectra of $[Cu(4\text{-}HOASH)SO_4(H_2O)_2]$ and $[Cu(4\text{-}HOAINH)SO_4(H_2O)_2]$ are not resolved. They show peaks (Table III) which are used to evaluate the g values. These are characteristic of interaction between copper ions in the powder complex.

^{1}H NMR Spectra

The spectrum of ASH shows peaks (Table IV) at δ 2.52 (s), 11.36 (s) and 7.40–8.80 (m). AINH exhibits signals at δ 2.52 (s), 10.06 (s) and 7.40–8.43 (m). These peaks are attributed to $-C\underline{H}_3$, $N\underline{H}$ and aromatic protons, respectively. In the spectrum of $[Cd(ASH)_2Cl_2(H_2O)_2]$, the $-N\underline{H}$ peak is observed at the same position and shows non-involvement of the carbonyl oxygen in bonding. The spectrum of $[Cd(AINH)Cl_2(H_2O)_2]$ shows signals at δ 2.52 ($C\underline{H}_3$), 10.55 ($-N\underline{H}$) and 7.40–8.03 (aromatic protons).

Table III. ESR Spectral Data of Complexes

Complexes	Peak Position (G)	g Values
[Cu(4-HOAINH)$SO_4(H_2O)_2$]	3400, 3485, 3560	2.13, 2.07, 2.03
[Cu(4-HOASH)$SO_4(H_2O)_2$]	3040, 3200, 3480	2.38, 2.26, 2.08

A downfield shift in the $-N\underline{H}$ proton suggests bonding of the carbonyl oxygen with the metal ions in these complexes.

^{13}C NMR Spectra

The 22.49 MHz proton decoupled ^{13}C NMR spectrum of ASH exhibits signals (Table IV) at 13.92, 152.45 and 162.20 ppm and that of AINH shows signals at 13.02, 150.03 and 152.25 ppm due to $-\underline{C}H_3$, $>\underline{C}=N$ and $>\underline{C}=O$ carbons, respectively.

The spectra of [Cd(ASH)$_2Cl_2(H_2O)_2$] show deshielding of the azomethine carbon indicating bonding through the azomethine nitrogen, while that of [Cd(AINH)$Cl_2(H_2O)_2$] exhibits signals at 13.28 ($-\underline{C}H_3$), 152.55 ($>\underline{C}=N$) and 152.88 ($>\underline{C}=O$) ppm. The downfield shifts in the carbonyl and azomethine carbons, suggest participation of $>C=O$ and $>C=N$ moieties in bonding.[15,16]

Infrared Spectra

The bands (Table V) appearing at 3300–3148, 1690–1640, 1620–1610 and 990–960 cm^{-1} in the spectra of the hydrazones are attributed to ν(NH),

Table IV. NMR Spectral Data of Ligands and Their Metal Complexes

	^{1}H NMR			^{13}C NMR		
Complexes	$-N\underline{H}$	$-C\underline{H}_3$	Aromatic Protons	$>\underline{C}=O$	$>\underline{C}=N$	$-\underline{C}H_3$
AINH	10.06	2.52	7.40–8.43	152.25	150.03	13.02
[Cd(AINH)$Cl_2(H_2O)_2$]	10.55	2.52	7.40–8.03	152.88	152.55	13.28
ASH	11.36	2.52	7.40–8.80	162.20	152.45	13.92
[Cd(ASH)$_2Cl_2(H_2O)_2$]	11.36	2.52	7.00–8.61	162.36	156.67	13.98

Table V. Important IR Spectral Bands (cm^{-1}) of Ligands and Metal Complexes

Complexes	$\nu(OH)_{H_2O}$	ν(NH)	Amide I/ν(C=O)	ν(C=N)	ν(N–N)	Pyridine Ring Vibrations
AINH	–	3190 s	1690 s	1620 s	990 m	685 s, 415 w
[Co(AINH)$Cl_2(H_2O)_2$]	3408 w	3210 m	1650 m	1610 w	1010 m	685, 415 w
[Ni(AINH)$Cl_2(H_2O)_2$]	3410 w	3200 m	1655 m	1605 w	1015 m	680 m, 410 w
[Cu(AINH)$Cl_2(H_2O)_2$]	3440 w	3210 m	1650 m	1610 w	1010 m	680 m, 410 w
[Cd(AINH)$Cl_2(H_2O)_2$]	3555 w	3200 m	1662 m	1610 m	1015 m	685 m, 415 w
4-HOAINH	–	3280 w	1655 s	1610 s	980 m	680 m, 415 w
[Co(4-HOAINH)$Cl_2(H_2O)_2$]	3440 w	3280 w	1680 s	1604 w	1005 m	690 m, 425 w
[Ni(4-HOAINH)$Cl_2(H_2O)_2$]	3445 w	3275 w	1660 s	1604 w	1010 m	695 m, 435 w
[Cu(4-HOAINH)$Cl_2(H_2O)_2$]	3455 w	3280 w	1665 s	1605 w	1015 m	700 m, 420 w
[Cu(4-HOAINH)$SO_4(H_2O)_2$]	3440 w	3275 w	1650 w	1605 w	1005 w	680 m, 415 w
[Cd(4-HOAINH)$Cl_2(H_2O)_2$]	3446 w	3080 w	1685 w	1605 w	1010 m	695 m, 430 w
ASH	–	3148 m	1640 s	1610 m	972 m	
[Co(ASH)$_2Cl_2(H_2O)_2$]	3420 m	3166 b	1640 s	1600 m	982 m	
[Ni(ASH)$_2Cl_2(H_2O)_2$]	3410 m	3150 b	1642	1604 m	985 w	
[Cu(ASH)$_2Cl_2(H_2O)_2$]	3425 m	3165 b	1640 s	1605 m	1000 w	
[Cd(ASH)$_2Cl_2(H_2O)_2$]	3450 m	3160 b	1640 s	1605 m	980 w	
4-HOASH	–	3300 m	1650 s	1610	960 m	
[Co(4-HOASH)$_2Cl_2$]	–	3300 b	1645 m	1604 m	998 m	
[Ni(4-HOASH)$_2Cl_2$]	–	3310 b	1645 m	1606 m	990 m	
[Cu(4-HOASH)$_2Cl_2$]	–	3305 m	1645 m	1605 m	996 m	
[Cu(4-HOASH)$SO_4(H_2O)_2$]	3435 m	3300 m	1635 m	1605 m	1006 m	
[Cd(4-HOASH)$_2Cl_2$]	–	3305 b	1638 m	1605 m	1006 m	

Table VI. X-Ray Powder Diffraction Data of [Cu(4-HOAINH)$SO_4(H_2O)_2$]

D	$I_{rel.}$	$1/d^2$ $Q_{obs.}$	$1/d^2$ $Q_{cal.}$	h	k	l
8.4892	1000	0.01388	0.01355	1	0	1
7.2613	302	0.01897	0.01896	0	0	2
6.8038	287	0.02160	0.02165	2	0	−2
6.1453	190	0.02480	0.02727	−2	2	1
5.5141	55	0.03289	0.03295	2	−1	1
5.1920	106	0.03710	0.03721	2	0	−3
4.8700	178	0.04216	0.04196	3	−1	0
4.6283	203	0.04668	0.04717	1	−2	2
4.2975	169	0.05415	0.05419	2	0	2
4.1114	56	0.05916	0.05890	3	−1	1
4.0113	62	0.06215	0.06226	2	0	−4
3.8742	379	0.06662	0.06672	−4	2	2
3.6274	116	0.07600	0.07630	4	1	−1
3.4697	515	0.08306	0.08299	−2	4	2
3.3298	70	0.09019	0.08944	3	2	1
3.2115	99	0.09696	0.09685	4	0	1
2.9414	58	0.11558	0.11553	2	−4	2
2.8962	93	0.11922	0.11933	2	−5	0
2.8166	49	0.12605	0.12649	−3	3	5
2.6977	62	0.13741	0.13746	0	2	5
2.5746	54	0.15086	0.15081	−6	3	2
2.3545	45	0.18039	0.18066	3	−6	0
2.3096	62	0.18747	0.18717	1	5	3
2.2612	55	0.19558	0.19569	−4	4	6
2.0176	58	0.24566	0.24567	−2	6	5
1.9510	66	0.26272	0.26266	−1	6	5
1.8981	59	0.27756	0.27742	2	5	−6
1.8794	52	0.28311	0.28129	7	1	1
1.7899	56	0.31214	0.31238	5	−7	1
1.7340	66	0.33258	0.33265	−8	6	4
1.6577	42	0.36391	0.36420	2	8	1
1.6484	49	0.36802	0.36829	−1	6	7
1.6130	53	0.38435	0.38439	−8	2	9
1.5745	47	0.40338	0.40317	5	6	2
1.5646	76	0.50850	0.40852	4	3	6
1.5359	49	0.42391	0.42373	1	4	8
1.5154	33	0.43546	0.43546	1	9	−3
1.5047	45	0.44167	0.44170	8	4	−7
1.4892	37	0.45091	0.45098	−10	6	5
1.4506	45	0.47523	0.47527	6	−5	5
1.3916	77	0.51638	0.51637	−11	3	1
1.3856	55	0.52086	0.52103	4	−8	5
1.3631	67	0.53820	0.52820	8	1	−11
1.3531	59	0.54619	0.54614	−12	1	4

Table VII. X-Ray Powder Diffraction Data of [Cd(AINH)Cl$_2$(H$_2$O)$_2$]

D	I$_{rel.}$	1/d^2 Q$_{obs.}$	1/d^2 Q$_{cal.}$	h	k	l
8.3426	681	0.01437	0.01415	1	1	−2
7.8421	214	0.01626	0.01602	2	1	1
7.5165	911	0.01770	0.01752	2	−2	1
6.7880	107	0.02170	0.02177	−3	1	1
6.4861	169	0.02377	0.02370	2	2	−1
6.3277	232	0.02498	0.02488	2	−2	2
5.8325	106	0.02940	0.02954	−1	2	3
5.5268	1000	0.03274	0.03258	−2	3	2
5.3382	153	0.03509	0.03503	3	−2	2
5.2057	152	0.03690	0.03694	2	3	−1
4.8796	201	0.04200	0.04191	4	−2	1
4.6597	166	0.04606	0.04585	−4	2	2
4.6117	166	0.04702	0.04893	1	3	3
4.4782	207	0.04986	0.04978	4	−3	1
4.1804	135	0.05722	0.05721	2	3	3
3.8621	127	0.06704	0.06688	−3	3	4
3.5862	229	0.07776	0.07786	0	3	5
3.4265	97	0.08517	0.08531	3	−2	5
3.3267	343	0.09036	0.09010	6	1	0
3.2012	287	0.09758	0.09757	3	−6	2
2.8555	73	0.12264	0.12261	6	−4	3
2.8113	135	0.12653	0.12651	3	−6	4
2.6379	96	0.14371	0.14374	−1	8	1
2.6082	139	0.14700	0.14701	5	0	6
2.5346	137	0.15566	0.15561	7	3	1
2.4452	188	0.16725	0.16724	−5	5	6
2.3962	140	0.17416	0.17418	−4	6	6
2.3543	139	0.18042	0.18042	−7	1	6
2.2532	157	0.19697	0.19688	4	1	8
2.2097	125	0.20480	0.20478	7	5	1
2.1823	121	0.20998	0.20985	9	1	−3
2.1117	103	0.22425	0.22431	9	2	2
2.0366	132	0.24110	0.24110	−8	8	2
1.9962	136	0.25095	0.25070	10	−3	3
1.9559	147	0.26140	0.26150	6	−10	1
1.9104	99	0.27400	0.27401	7	7	−2
1.8936	133	0.27888	0.27885	8	4	5
1.8717	121	0.28545	0.28547	4	−11	2
1.7200	92	0.33802	0.33795	8	2	−9

(continued)

Table VII. Continued

D	$I_{rel.}$	$1/d^2$ $Q_{obs.}$	$1/d^2$ $Q_{cal.}$	h	k	l
1.6970	133	0.34725	0.34724	−10	9	3
1.6798	107	0.35439	0.35442	4	1	−11
1.6678	123	0.35951	0.35953	0	11	6
1.6467	93	0.36878	0.36889	6	10	1
1.6350	97	0.37408	0.37408	−9	11	1
1.6148	80	0.38350	0.38352	1	9	9
1.5590	160	0.41144	0.41144	−11	10	2
1.5500	173	0.41623	0.41623	13	−5	3
1.5403	245	0.42149	0.42147	1	−8	11
1.5275	189	0.42859	0.42860	−5	2	13
1.5043	236	0.44191	0.44191	9	8	4
1.4870	119	0.45225	0.45230	5	12	2
1.4785	120	0.45746	0.45748	9	9	−3
1.4697	158	0.46296	0.46293	−9	10	8
1.4615	153	0.46817	0.46810	−4	14	4
1.4458	131	0.47839	0.47833	11	−10	5
1.4344	164	0.48603	0.48603	10	−7	9
1.4261	177	0.49170	0.49174	−10	5	11
1.4071	170	0.50507	0.50502	4	11	4
1.3995	161	0.51057	0.51056	3	−7	13
1.3812	107	0.52419	0.52419	7	9	−9
1.3582	97	0.54209	0.54207	12	4	7
1.3478	120	0.55049	0.55038	3	5	14

ν(C=O), ν(C=N) and ν(N–N) modes, respectively. A band at 3260, 3325 and 3320 cm^{-1} is assigned to ν(OH) (phenolic) in the spectra of ASH, 4-HOASH and 4-HOAINH, respectively. The appearance of ν(OH) at lower frequency may be due to inter- and/or intramolecular hydrogen bonding.

In the spectra of $[M(ASH)_2Cl_2(H_2O)_2]$ and $[M(4\text{-HOAINH})Cl_2(H_2O)_2]$, the absorption band due to ν(C=O) is shifted towards higher frequency or remained unaltered indicating non-participation of the carbonyl oxygen in bonding. In the spectra of $[M(4\text{-HOASH})_2Cl_2]$, $[M(AINH)Cl_2(H_2O)_2]$, $[Cu(4\text{-HOASH})SO_4(H_2O)_2]$ and $[Cu(4\text{-HOAINH})SO_4(H_2O)_2]$ complexes, ν(C=O) is observed at lower frequency (1662–1635 cm^{-1}) indicating coordination of the carbonyl oxygen to the metal ion.[17]

In all of the complexes ν(C=N) is observed in the 1615–1595 cm^{-1} region indicating that the azomethine nitrogen is involved in bonding.[18]

Table VIII. X-Ray Powder Diffraction Data of $[Cd(4\text{-}HOAINH)Cl_2(H_2O)_2]$

D	$I_{rel.}$	$1/d^2$ $Q_{obs.}$	$1/d^2$ $Q_{cal.}$	h	k	l
8.1493	863	0.01506	0.01508	2	−1	0
6.1931	1000	0.02607	0.02621	−1	2	1
5.8722	452	0.02900	0.02892	0	2	0
5.5007	446	0.03305	0.03306	2	1	0
5.1271	394	0.03804	0.03789	3	0	0
3.3788	343	0.08759	0.08760	7	0	−2
2.5687	271	0.15156	0.15158	6	0	0
2.4033	308	0.17313	0.17303	6	2	−1
1.8298	401	0.29867	0.29869	2	6	−3
1.6798	327	0.03544	0.35427	0	7	0
1.5986	360	0.39131	0.39133	9	4	1
1.5811	264	0.40002	0.40004	−9	9	6
1.5708	313	0.40528	0.40523	0	0	7
1.5656	305	0.40798	0.40808	7	−7	1
1.5268	467	0.42898	0.42895	2	−1	6
1.4753	424	0.45945	0.45941	9	5	−10

The ν(N—N) band shifted to higher frequency (1015—980 cm^{-1}) in the spectra of the complexes compared to the free hydrazones. This further supports bonding through the azomethine nitrogen.[19] The band due to ν(OH) shifted to higher frequency or remained unaltered indicating non-involvement of the phenolic oxygen in bonding.

The bands observed at 680 cm^{-1} due to in-plane deformation and at 415 cm^{-1} due to out-of-plane deformation modes in the spectrum of 4-HOAINH shifted towards higher frequencies in the spectra of the complexes except in that of $[Cu(4\text{-}HOAINH)SO_4(H_2O)_2]$. This suggests involvement of the pyridine nitrogen in bonding. In the spectrum of AINH these bands are observed at 685 and 415 cm^{-1} which remain unaltered in the spectra of the complexes and suggest non-participation of the pyridine nitrogen in bonding.

In the spectra of $[Cu(4\text{-}HOASH)SO_4(H_2O)_2]$, and $[Cu(4\text{-}HOAINH)\text{-}SO_4(H_2O)_2]$ three new bands appear at 960—985, 1040—1060 and 1210—1250 cm^{-1} and indicate chelate bonding of SO_4^{2-}.

A broad band at 3555—3405 cm^{-1} is assigned to ν(OH) of water in the hydrated complexes. The coordinated nature of water is shown by the presence of bands in the 880—860 and 780—770 cm^{-1} regions due to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively.

X-Ray Powder Diffraction Studies

The X-ray powder diffraction patterns of the complexes [Cd(AINH)$Cl_2(H_2O)_2$], [Cu(4-HOAINH)$SO_4(H_2O)_2$] and [Cd(4-HOAINH) $Cl_2(H_2O)_2$] are indicative of their crystalline nature. The diffraction patterns have been successfully indexed by Ito's method.[21] The shape of the unit lattice and parameters are given in Table IX.

Biological Activity

Acetophenone and 4-hydroxyacetophenone salicyloylhydrazones and their copper(II) and zinc(II) complexes were screened against *E. coli* and *Aspergillus niger* at the three concentrations 500, 1000 and 1500 μg/mL.

Table IX. The Shape of Unit Lattice and Parameters

Complex	Crystal Lattice		V (Å^3)
[Cd(AINH)$Cl_2(H_2O)_2$]	Rhombohedral	a 21.34 Å α 89° b 21.31 Å β 93° c 20.93 Å γ 101°	9318.3970
[Cu(4-HOAINH)$SO_4(H_2O)_2$]	triclinic	a 16.45 Å α 84° b 14.86 Å β 115° c 16.15 Å γ 102°	3471.1381
[Cd(4-HOAINH)$Cl_2(H_2O)_2$]	triclinic	a 53.90 Å α 51° b 16.44 Å β 161° c 35.52 Å γ 133°	7050.7761

Table X. Antifungal Activity of ASH, 4-HOASH, and Their Metal Complexes

	% Germination		
Complexes	500 μg/mL	1000 μg/mL	1500 μg/mL
ASH	+++	++	++
4-HOASH	++	++	++
[Cu$(ASH)_2Cl_2(H_2O)_2$]	++	++	++
[Zn$(ASH)_2Cl_2(H_2O)_2$]·H_2O	+	+	+
[Cu$(4\text{-HOASH})_2Cl_2$]	+++	++	++
[Zn$(4\text{-HOASH})_2Cl_2$]·H_2O	++	++	++

++++ = 100% germination, +++ = 75% germination, ++ = 50% germination, + = 25% germination.

Table XI. Antibacterial Activity of ASH, 4-HOASH, and Their Metal Complexes

	Zone of Inhibition (cm)		
Complexes	500 μg/mL	1000 μg/mL	1500 μg/mL
ASH	0.52	0.58	0.69
4-HOASH	0.66	0.68	0.71
$[Cu(ASH)_2Cl_2(H_2O)_2]$	0.89	0.91	0.98
$[Zn(ASH)_2Cl_2(H_2O)_2]\cdot H_2O$	0.77	0.69	0.70
$[Cu(4\text{-}HOASH)_2Cl_2]$	0.61	0.60	0.79
$[Zn(4\text{-}HOASH)_2Cl_2]\cdot H_2O$	0.69	0.66	0.78

From Tables X and XI it may be inferred that the metal complexes of 4-HOASH and ASH have greater activity than the parent hydrazones which may be due to the chelation effect.[22]

The ligand containing the phenolic moiety is found more effective as compared to other ligands reported earlier.[23] The ligand 4-HOASH containing two phenolic groups shows poor germination and better inhibition against *E. coli* than ASH which is due to the presence of only one phenolic group. The complexes show better inhibitory effect compared to the parent hydrazones. This may be explained as follows. In the complexes the ligands have some uncoordinated donor atoms which enhance the activity of the complexes by bonding with trace element present in biosystem. Thus, the microquanitity of trace elements presents in microorganisms may combine with the uncoordinated site and may inhibit the growth of fungi and bacteria.

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