



## Synthesis and characterization of transition metal complexes with benzimidazolyl-2-hydrazones of salicylidene acetone and salicylidene acetophenone

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### ABSTRACT

A series of complexes of the type  $[M_2L_2Cl_2]$ , where  $L = 2$ -(salicylidene acetone- 2'-imino) amino benzoimidazole (HSAIAB) and 2-(salicylidene acetophenone- 2'- imino) amino benzimidazole (HSAPIAB),  $M = Cu(II)$ ,  $Co(II)$ ,  $Ni(II)$  and  $Zn(II)$ , have been synthesized and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared spectral studies. The results are in consistent with tridentate chelation of ligand with azomethine nitrogen, ring nitrogen and oxygen atom. The fungi toxicity of the ligands & their complexes against some fungal pathogen has been studied.

**Keywords:** Benzimidazolyl-2-hydrazones, salicylidene acetone, salicylidene acetophenone and Transition metal complexes.

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### INTRODUCTION

Schiff base complexes have undergone a phenomenal growth during the recent years because of the versatility offered by these complexes in the field of industries[1,2], catalysis[3] and in biological system[4,5] etc. In this way, the synthesis, structural investigation and reaction of transition metal Schiff bases have received a special attention, because of their biological activities as antitumoral, antifungal and antiviral activities[6]. Thus, Schiff base hydrazones are also interesting from the point of view of pharmacology. Hydrazone derivatives are found to possess antimicrobial[7], antitubercular[8], anticonvulsant[9] and anti-inflammatory[10] activities. Particularly, the antibacterial and antifungal properties of hydrazones and their complexes with some transition metal ions was studied and reported by Carcelli et al.[11]. In addition, complexes of salicylaldehyde benzoylhydrazone were shown to be a potent inhibitor of DNA synthesis and cell growth[12]. This hydrazone also has mild bacteriostatic activity and a range of analogues has been investigated as potential oral ion chelating drugs for genetic disorders such as thalasemia[13, 14].

Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands[15-19], we report here the synthesis and structural studies on the complexes of  $Cu(II)$ ,  $Co(II)$ ,  $Ni(II)$  and  $Zn(II)$  with some hydrazone derivatives containing benzimidazole moiety such as 2-(salicylidene acetone- 2'-imino) amino benzoimidazole (HSAIAB) and 2-(salicylidene acetophenone- 2'-imino) amino benzimidazole (HSAPIAB).

## EXPERIMENTAL SECTION

**Material and Method**

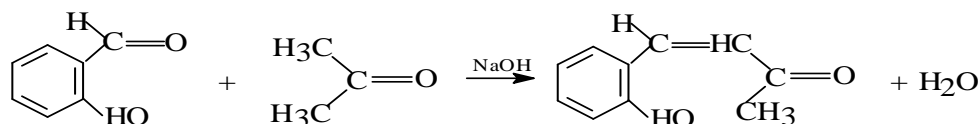
Reagent grade chemicals were used in the present study. The solvents were purified before use by standard process. The starting material such as 2-hydrazinobenzimidazole was synthesized according to literature method[20].

**Preparation of Ligands**

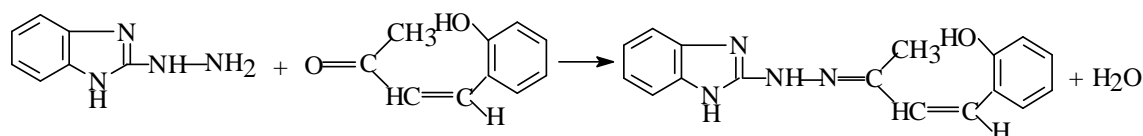
The ligands used in the present investigation were benzimidazolyl-2-hydrazone of aldehydes and ketones such as Salicylidene acetone and salicylidene acetophenone have been synthesized by condensing 2-hydrazinobenzimidazole with respective aldehydes and ketone in the following manner.

**Synthesis of Salicylidene acetone**

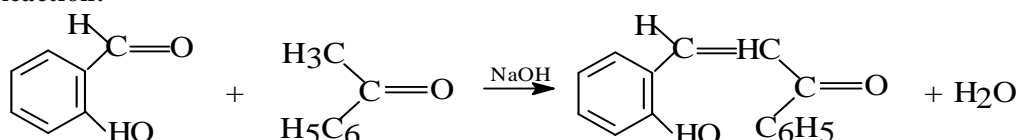
This compound was synthesised as per the following manner. A mixture of salicylaldehyde and acetone in 1:1 molar ratio was prepared. It was added to a solution of NaOH (10 gm in 100 ml water and 80 ml ethanol) with a constant stirring, during which a red coloured precipitate was formed. The precipitate was filtered and washed with cold water to eliminate unreacted NaOH and was dried at room temperature upon filter paper. It was recrystallised from hot rectified spirit. The sample was dried in vacuo over fused calcium chloride and then analysed.

**Reaction:****Synthesis of 2-(salicylidene acetone- 2'- imino) amino benzoimidazole (HSAIAB)**

To a warm ethanolic solution of 2-hydrazinobenzimidazole (0.01 mol in 20ml) ethanolic solution of salicylidene acetone (0.01 mole in 20 ml) was added and the above mixture was refluxed on a water bath for 4 hours. It was concentrated and allowed to stand overnight when dark yellow coloured precipitate was separated out. It was filtered washed and recrystallised from ethanol. The sample was dried in vacuo over fused calcium chloride and then analysed.

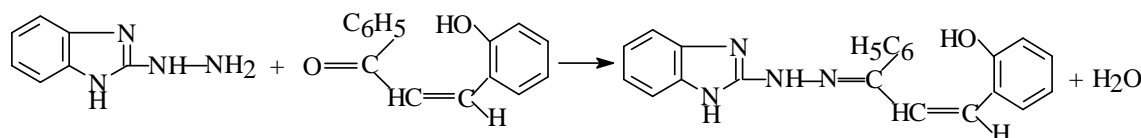
**Reaction:****Synthesis of salicylidene acetophenone**

Salicylidene acetophenone was synthesised by adopting an identical procedure as in case of synthesized of salicylidene acetone by the reaction of salicylaldehyde with acetophenone in presence NaOH (10 gm in 100 ml water and 80 ml ethanol), a deep brown coloured precipitate was formed. The precipitate was filtered at pump and washed with cold water to eliminate unreacted NaOH and was dried at room temperature upon filter paper. It was recrystallised from hot rectified spirit. The sample was dried in vacuo over fused calcium chloride and then analysed.

**Reaction:**

**Synthesis of 2-(salicylidene acetophenone- 2'- imino amino) benzimidazole (HSAPIAB)**

To a warm ethanolic solution of 2-hydrazinobenzimidazole (0.01 mol in 20ml) ethanolic solution of salicylidene acetophenone (0.01 mole in 20 ml) the above mixture was refluxed on a water bath for 4 hours. It was concentrated and allowed to stand overnight when dark brown coloured precipitate was separated out. It was filtered washed and recrystallised from ethanol. The sample was dried in vacuo over fused calcium chloride and then analyzed

**Reaction:****Preparation of the complexes**

A hot ethanolic solution of the ligand HSAIAB/ HSAPIAB (0.01 mol in 20 ml) was mixed with an ethanolic solution of respective hydrated metal (II) chloride (0.01 mol in 20 ml) and the mixture was refluxed on a water bath for 3 to 4 hours followed by addition of few drops of conc. NH<sub>3</sub> solution, when coloured precipitates of metal complexes were obtained in each cases. The precipitates were filtered, washed with ethanol followed by ether and finally dried in vacuo over fused CaCl<sub>2</sub>.

**Analysis and Physical measurements:**

The metal contents in the complexes were determined gravimetrically following standard procedure[21]. Sulphur was determined as BaSO<sub>4</sub>. The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (model CL-01-06, cell constant 0.5 cm<sup>-1</sup>) using 1x10<sup>-3</sup>M solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined by using a MLW-CHN micro analyser. FTIR spectra in KBr pellets were recorded on a Varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a Perkin-Elmer spectrophotometer. Thermo gravimetric analysis was done by Netzch-429 thermo analyzer.

**Table-1: Analytical and physical data of the complexes**

Sl no	Compounds	Colours	$\Lambda_m^a$	Cl Found (Calcd)	C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	M Found (Calcd)
1	HSAIAB	dark yellow	-	-	41.36 (41.39)	0.20 (0.23)	45.42 (45.46)	-
2	HSAPIAB	dark brown	-	-	45.42 (45.45)	0.17 (0.21)	43.36 (43.39)	-
3	[Co(SAIAB) <sub>2</sub> Cl <sub>2</sub> ]	Pink	10.16	9.94 (9.97)	52.90 (52.92)	1.95 (1.97)	14.49 (14.53)	8.25 (8.28)
4	[Ni(SAIAB) <sub>2</sub> Cl <sub>2</sub> ]	Greenish blue	8.28	9.95 (9.98)	52.93 (52.96)	1.94 (1.97)	14.50 (14.54)	8.26 (8.29)
5	[Cu(SAIAB) <sub>2</sub> Cl <sub>2</sub> ]	Light blue	11.25	9.86 (9.90)	52.27 (52.30)	1.91 (1.95)	14.33 (14.36)	8.82 (8.86)
6	[Zn(SAIAB) <sub>2</sub> Cl <sub>2</sub> ]	White	12.85	9.84 (9.88)	52.01 (52.06)	1.92 (1.95)	14.25 (14.29)	9.02 (9.05)
7	[Co(SAPIAB) <sub>2</sub> Cl <sub>2</sub> ]	Violet	14.24	8.45 (8.49)	58.95 (58.99)	1.87 (1.91)	12.48 (12.51)	7.01 (7.05)
8	[Ni(SAPIAB) <sub>2</sub> Cl <sub>2</sub> ]	Dark green	8.67	8.46 (8.50)	59.01 (59.04)	1.88 (1.91)	12.50 (12.52)	6.97 (7.00)
9	[Cu(SAPIAB) <sub>2</sub> Cl <sub>2</sub> ]	Light blue	11.52	8.41 (8.44)	58.35 (58.40)	1.86 (1.90)	12.34 (12.39)	7.52 (7.55)
10	[Zn(SAPIAB) <sub>2</sub> Cl <sub>2</sub> ]	Pale yellow	9.60	8.41 (8.43)	58.14 (58.17)	1.87 (1.90)	12.30 (12.34)	7.66 (7.71)

<sup>a</sup>Ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>

## RESULTS AND DISCUSSION

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (Table-1). The complexes are highly coloured and insoluble in water and common organic solvents but soluble in highly coordinating solvents such as dioxane, DMF and DMSO. They are non hygroscopic, highly stable under normal conditions and all of them decompose above 250<sup>0</sup>C. The molar conductance data values in DMSO for the complexes indicate them to be non-electrolyte in nature.

### IR spectra

The ligands HSAIAB and HSAPIAB are formed by condensation of 2-hydrazinobenzimidazole with a condensation product of salicylaldehyde with acetone / acetophenone in presence of NaOH. Formation of the second precursor is confirmed by its IR spectra. It contains an intense band at ~ 1650 cm<sup>-1</sup> which may be due to  $\nu_{C=O}$  carbonyls. Another broadband around ~ 3300 cm<sup>-1</sup> is attributed to phonetic -OH and a band seen around ~1675 cm<sup>-1</sup> may be due to  $\nu_{C=C}$  formed by the condensation of salicylaldehyde with the ketones.

Formation of ligands HSAIAB and HSAPIAB by the condensation of above precursors with 2-hydrazinobenzimidazole is proved by change in the IR spectra of the starting materials. The most notable change in the IR spectra is the disappearance of the -NH<sub>2</sub> stretching vibration and appearance of an intense band at ~ 1565 cm<sup>-1</sup> due to  $\nu_{C=N}$  (azomethine). The spectra also contain a multiple band system at ~ 1520, ~ 1300 and attributed to  $\nu_{C=N}$  (cyclic) and  $\nu_{C-N}$  (cyclic) of benzimidazole group respectively.

In the IR spectra of all the metal complexes, the position of bands due to  $\nu_{C=N}$  (cyclic) and  $\nu_{C-N}$  (cyclic) remain unchanged there by indicating non-participation of the ring nitrogen atom in coordination. However,  $\nu_{NH}$  band of benzimidazole ring (-N-H) group was found invariably shifted 20-10 cm<sup>-1</sup> towards negative side indicating the coordination of benzimidazole ring NH group to the metal ions. Where as band occurring at ~3100 cm<sup>-1</sup> due to  $\nu_{N-H}$  exocyclic remains practically unaltered indicating its non involvement either in coordination or enolisation. The band at ~3300cm<sup>-1</sup> due to phenolic -OH stretching vibration disappears in IR spectra of metal complexes formed by above ligands and clearly demonstrate the deprotonation of phenolic (OH) group and co-ordination to the metal ion through oxygen atom[22]. This is further substantiated by hypsochromic shift of phenolic  $\nu_{C-O}$  mode around ~1280cm<sup>-1</sup> of the free ligand to ~1500cm<sup>-1</sup> in the spectra of these complexes[23]. This is because C-O assumes a partial double bond character on co-ordination to the metal ion due to drainage of  $\pi$  electron of benzene ring through resonance[24].

On comparing IR spectra of these ligands with their complexes stretching band corresponding to  $\nu_{C=N}$  (azomethine) group is found to be red shifted by 20-10 cm<sup>-1</sup> indicating the co-ordination of azomethine N atom to the metal ion consequently the new  $\nu_{N-N}$  band showed blue shift by 20-30 cm<sup>-1</sup> there by supporting the coordination of azomethine nitrogen atom to the metal centers.

A pair of sharp bands of moderate intensity are observed in the IR spectra of all the metal complexes, the first band appears at ~520 cm<sup>-1</sup> where as the second one at ~ 450 cm<sup>-1</sup>. These bands are distinctly absent in the spectra of ligands. Considering the sharpness and intensity, former band is attributed to  $\nu_{M-O}$  and later band is attributed to  $\nu_{M-N}$  vibrations.

Although evidence of  $\nu_{M-Cl}$  band could not be brought in the present investigation due to instrumental limitation, the insolubility of the complexes in water and their non-electrolytic nature provide sufficient evidence for the coordination of the counter ions Cl<sup>-</sup> to form neutral complexes.

As evidenced from IR spectral data it is clear that the ligand moiety satisfies 3- coordination number of the metal centre and the fourth coordination number is satisfied by Cl<sup>-</sup>. Absence of any band around ~3500 cm<sup>-1</sup> indicates that neither coordinated nor lattice water is present in the complexes. It is further supported by thermal analysis. The metal centre is unable to coordinate with phenolic oxygen of the ligand coordinating with it through azomethine nitrogen and ring nitrogen, as coordination of phenolic oxygen involves formation of highly stressed 8-membered ring and this indicates involvement of two metal centers as evidenced by elemental analysis.

**Thermal analysis**

Thermal characteristics of the complexes formed by the ligands HSAIAB and HSAPIAB are recorded in Table-2. Thermal behaviour of these complexes is almost the same. The complexes remain stable up to 240°- 340°C indicating the absence of water molecules and then they decompose rapidly. The rapid decomposition denotes loss of ligand moiety. However they do not adhere to constant weight due to decomposition even up to -620°C except [Zn (HSAPIAB) Cl]<sub>2</sub> complex. Thermal stability places the complexes in the following order:

(HSAIAB) complexes: Cu (II) < Ni (II) < Co (II) < Zn (II)

(HSAPIAB) complexes: Co (II) < Ni (II) < Cu (II) < Zn (II)

**Table-2: Important features of thermo gravimetric analysis (TGA)**

Complexes	Total wt. for TG (mg)	Decomposition temperature (°C)	% of residue		Composition of the residue
			Found	Calc.	
3	20.4	280	10.49	10.53	CoO
4	18.6	275	10.42	10.47	NiO
5	22.1	260	11.03	11.09	CuO
6	11.2	290	11.25	11.28	ZnO
7	22.5	250	8.93	8.97	CoO
8	15.2	265	8.88	8.92	NiO
9	16.5	270	9.41	9.46	CuO
10	12.6	280	9.58	9.62	ZnO

**Electronic spectra and magnetic properties**

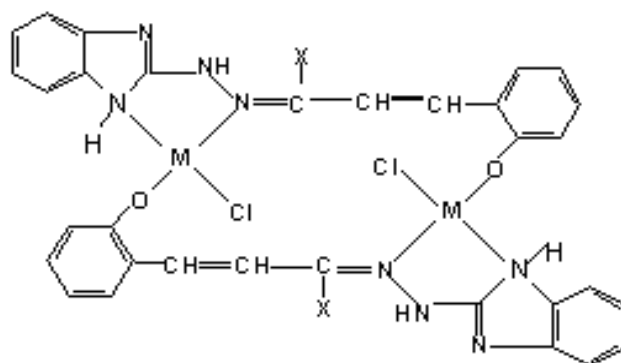
The room temperature magnetic moment value of complexes obtained from ligands HSAIAB and HSAPIAB lie in the normal range for Co (II) complexes. The electronic spectra of these complexes are characterized by two main bands around ~9320-9550 cm<sup>-1</sup> (1072-1047 nm) and ~20,690-21,000 cm<sup>-1</sup> (483-476 nm). These bands are assignable to <sup>4</sup>T<sub>1g</sub>(F)→<sup>4</sup>T<sub>2g</sub>(F) (ν<sub>3</sub>) and <sup>4</sup>T<sub>1g</sub>(F)→<sup>4</sup>T<sub>1g</sub>(P) (ν<sub>3</sub>) transitions respectively.

Besides the above bands, the spectra possess two shoulders at ~19,580 cm<sup>-1</sup> (510 nm) and ~16,500-17,000 cm<sup>-1</sup> (625-581nm). Here we can obtain values of Dq and B by using energy matrix equation of low <sup>4</sup>T<sub>1g</sub> level. The calculated ν<sub>3</sub> value is ~20,190 cm<sup>-1</sup> which is very close to ν<sub>3</sub>. This is confirmed by the appearance of the shoulder in the region ~19,850 cm<sup>-1</sup>. Thus the shoulder at ~16,500-17000 cm<sup>-1</sup> is assignable to spin forbidden transition <sup>4</sup>T<sub>1g</sub>(F) → <sup>2</sup>T<sub>2g</sub>(G), thus the former shoulder can be assigned to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F) (ν<sub>2</sub>) transition.

The electronic spectral data and μ<sub>eff</sub> value at room temperature for Ni (II) complexes with ligands HSAIAB and HSAPIAB are recorded. The μ<sub>eff</sub> value of these complexes is in fair with the tetragonal six coordinated spin free Ni (II) complexes. These complexes have four bands at ~8,500cm<sup>-1</sup> (1175 nm), ~10,800 cm<sup>-1</sup> (925 nm), ~15,000 cm<sup>-1</sup> (666 nm) and ~25,000 cm<sup>-1</sup> (400 nm) assignable <sup>3</sup>B<sub>1g</sub>→<sup>3</sup>E<sub>g</sub>, <sup>3</sup>B<sub>1g</sub>→<sup>3</sup>B<sub>2g</sub>, <sup>3</sup>A<sub>2g</sub>(F)→<sup>3</sup>T<sub>1g</sub>(F) (ν<sub>1</sub>) and <sup>3</sup>A<sub>2g</sub>(F)→<sup>3</sup>T<sub>1g</sub>(P) (ν<sub>3</sub>) transitions respectively under D<sub>4h</sub> geometry. Various crystal field parameters are found to be in good agreement with proposed geometry.

The electronic spectral data and room temperature μ<sub>eff</sub> values of Cu (II) complexes with ligands HSAIAB and HSAPIAB are recorded. The μ<sub>eff</sub> value in these cases lie in the range 1.71-1.86 B.M. as expected for hexa coordinated spin free Cu (II) complexes either in octahedral or distorted octahedral environment. The electronic spectra of these complexes contain three distinct bands at ~11,000 cm<sup>-1</sup> (909 nm), ~13,400 cm<sup>-1</sup> (784 nm) and ~17,000 cm<sup>-1</sup> (588 nm) assignable to <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>1g</sub> (ν<sub>1</sub>), <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>B<sub>2g</sub> (ν<sub>2</sub>) and <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>E<sub>g</sub> (ν<sub>3</sub>) transitions respectively under D<sub>4h</sub> symmetry.

Based on the foregoing observations the following tentative structures (Fig-1) have been proposed for the present complexes.



(Fig-1)

$M = \text{Co (II)}, \text{Ni (II)}, \text{Cu (II)} \text{ and } \text{Zn (II)}$

$X = -\text{CH}_3 \text{ or } -\text{C}_6\text{H}_5, n = 1 \text{ or } 2.$

### Antifungal activity

The antifungal activity of the complexes has been studied by potato dextrose agar diffusion method in DMSO solvent against *A. niger* and *A. flavus*. The complexes showed good antifungal activity against the species. This may be explained on the basis that their structures mainly possess C=N bonds. Moreover, coordination reduces the polarity [25,26] of the metal ion mainly because of the partial sharing of its positive charge within the chelate ring formed during coordination. This process increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the micro-organism [27-29] thus destroying them more aggressively.

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