



## RESEARCH ARTICLE

## SYNTHESIS AND CHARACTERIZATION OF SOME METAL COMPLEXES WITH IBA AS LIGAND DERIVED FROM 2-BENZOYLINDANE-1,3-DIONE

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## ABSTRACT

The present investigation are based on the synthesis and characterization of metal complexes with Schiff's bases  $\alpha$ - (1, 3- dioxo- indan- 2-yl) - benzylidene- aniline (IBA) derived from 2-Benzoylindane-1,3-Dione by condensing it with primary aryl amine (aniline) in absolute alcohol. 2-Benzoylindane-1,3-Dione was prepared by claisen-condensation. The Co (II), Ni(II), Cu (II), Zn (II), Cd (II), Fe (III), V (III) and Cr (III) complexes of the Schiff's bases have been prepared in the reactions and investigated their structures by physicochemical methods. The formulation and structure of the ligands have been screened by their chemical analysis, IR, PMR and mass-spectral studies. The PMR spectrum of the metal complexes in quite similar to the PMR spectrum of the IBA with slight change in the position of PMR signals. The metal complexes are thermally stable at higher temperature. Results show that the complexes exhibit partial ionic character, though the complexes are covalent. The mass-spectra of this IETS showed the molecular ion peak as a base peak at  $m/z$  261. The enolic formulation for the IBA got an additional support by a positive ferric chloride test. The structure of ligand has been confirmed by their mass-spectral studies.

**Key words:** Metal Complexes, Schiff's bases, 2-Benzoylindane-1,3-Dione

## INTRODUCTION:

Schiff's bases or anills have been found to be immense importance and versatile complexing agents. large number of transition metal complexes have been synthesized and charatarised with schiff's bases which have been proved of wide utility, semicarbazone and thiosemicarbazone have joined special attention due to their activity against protozoa, influenza, small pox, malaria, tuber-culosis<sup>1-2</sup>, and antitumor activity of their meatal complexes.<sup>3-4</sup> Metal complexes of thiosemicarbazone have emerged as new class of chemotherapeutic agent which exhibit inhibitory activity against most cancers through inhibition of a crucial enzyme, obligatory for DNA biosynthesis and cell division. Due to wide range of medicinal use of metal complexes of semicarbazone/ thiosemicarbazone. Co(II), Ni(II), Cu(II) etc. metal complexes with these ligands have been prepared and reported.<sup>5-8</sup>

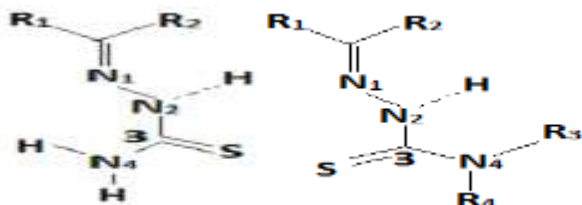
Because of their versatile biological activity and prospective use as drugs.<sup>9</sup> Owing to the interest they generate through a variety of biological prosperties ranging from anticancer,<sup>10</sup> antitumor,<sup>11</sup> antifungal,<sup>12</sup> antibacterial<sup>13</sup> antimalarial,<sup>14</sup> antitilarial,<sup>15</sup> antiviral,<sup>16</sup> anti

- HIV,<sup>17</sup> activities, thiosemicabazones and their metal complexes have been extensively studied.

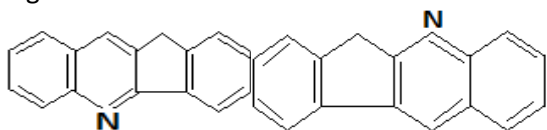
The ability of thiosemicarbazone molecule to chelate with traces of metals in the biological system is believed to be a reason for their activity. The lipophilicity of thio semi carbazone controls the rate of entry of trace metals into the cell. This modified by cordination and some side effects may be decreased<sup>87-88</sup>. It has been proved that thiosemcarbazone block DNA synthesis in mammalian cells big by inhibiting the enzymes, ribonucleosidedi-phosphate reductase, presumably either via chelation with an iron ion required by the enzymes or because a performed metal chellate of the inhibitor interacts with the target enzyme<sup>18</sup>. The reports also point out the capacity of thiosemicarbazone to saver the DNA stands<sup>19</sup>. The antitumor activities of Mn (II), Ni (II), and Cu (II) chelates of anthracene -9 - carboxyldehyde thiosemi-carbazone (7)<sup>20</sup> and the cytotoxic activity of phenylglyoxal bis (thiosemicarbazone) against Ehrlichascitess carcinoma cells have been reported. Platinum complexes of 2-acetylpyriden thiosemicarbazone have been synthesized in which intermolecular hydrogen bonds,  $\pi$ - $\pi$  and weak pt-pt and pt- $\pi$  contacts lead to aggregation and to a two- dimensional supra molecular assembly. The

complexes were found to have a completely lethal effect on Gram +ve bacteria.

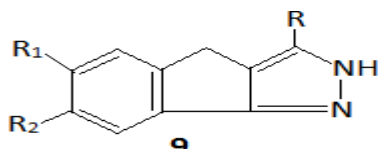
Thiosemicarbazones are thio urea derivatives obtained by condensation of thiosemicarbazide or N(4)-substituted thiosemicarbazide with a suitable aldehyde or ketone. The thiosemi- carbazones are represented by the general formula and when N(4) is substituted they can be represented by the general formula.



11H-indeno[1,2-b] quinoline and 6H-indeno[2,1-b] quinoline have been synthesized and screened for their carcinogenic and antitumor activities.<sup>21, 22</sup>



Houliham and his coworkers<sup>23</sup> synthesizes 3-substituted-2,4-dihydroindeno(1,2-C)pyrazoles and screened them for their antihypertensive, contraceptive and abortifacient activity. At a level of 1-100mg/day, pyrazoles<sup>24</sup> act as antifertility agent in rats and 2-200 mg/ Kg behaved as antihypertensive agents.



R<sub>1</sub> = H, Cl, CH<sub>3</sub> and OCH<sub>3</sub>

R<sub>2</sub> = H and OCH<sub>3</sub>

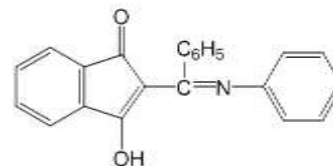
R = 2-, 3-, 4- pyridyl, 2- furyl, 2- thienyl, Phenyl and substituted phenyl.

From the detailed survey of the literature on condensed heterocyclic ring systems, it is evident that indenoquinolines and indenopyrazoles show various pharmacological and biological properties. Some 10-substituted indenoquinolines are potent analgesics and anti-inflammatory agents. Among pyrazoles fused to carbocyclic and heterocyclic ring systems, indenopyrazoles occur at a unique position because of their wide spectrum of physiological properties. With this fact a series of substituted indenopyrazoles has been reported.

Indenoquinolines and indenopyrazoles consist of indane-1, 3-dione moiety which may be responsible for their biological activity. This suggests that indanedione

derivatives may possibly exhibit this property also. The Schiff's bases have been reported to be good complexing agents.

The present investigation aims at evolving  $\alpha$ - (1, 3-dioxo- indan- 2-yl) - benzylidene- aniline (IBA) as ligands by utilizing 2-benzoylindane-1,3-dione and aniline etc. as starting materials, and formation of their metal derivatives.



$\alpha$ - (1, 3- dioxo- indan- 2-yl) - benzylidene- aniline (IBA), (L<sub>3</sub>H) (C<sub>22</sub>H<sub>15</sub>O<sub>2</sub>N)

In the present work, the reactions of following metal derivatives of the IBA ligand have been isolated and characterized. i.e. Cobalt (II) chloride, Nickel (II) chloride, Copper (II) chloride, Zinc (II) chloride, Cadmium (II) chloride, Iron (III) chloride, Vanadium (III) chloride, Chromium (III) chloride

#### MATERIAL AND METHODS:

##### Material:

All the chemicals used in this investigation were of good quality and analytical grade and were purchased from standard chemical agencies. Methanol and ethanol were first dried by refluxing over quicklime for four to six hours and then distilled over sodium wire.<sup>25,26</sup> Acetaldehyde, Benzaldehyde and Acetone were dried over aluminium isopropoxide and then distilled fractionally before use.<sup>27</sup> Benzene and Aniline were purified and dried before use. Anhydrous metal salts (mostly chlorides) of Co(II), Ni(II), Cu(II) Zn(II), V(III), Cr(III) and Fe(III)(all Fluka, A.G. and B.D.H.) were used as such after confirming their purity by chemical analysis.

##### Analytical methods:

The composition of ligands and their metal derivatives was determined by elemental analysis such as quantitative analysis of carbon, hydrogen, nitrogen, halogen and metal ions by known standard methods. These studies were carried out in case of few selected ligands and their metal derivatives<sup>28</sup>.

Metal ions were estimated by known standard methods. The complexes were dissolved by decomposing first with concentrated nitric acid and then in hydrochloric acid. The solution was then heated to dryness or neutralized by suitable ways depending upon the method of analysis Iron<sup>29</sup>, Cobalt<sup>30</sup>, Nickel<sup>31</sup>, Copper<sup>32</sup>, Zinc etc. were estimated by known standard methods.

**Physical Measurements:****1. Molar Conductance:**

The variation in molar conductance of the metal complexes could be confirmed by molar conductance measurements of the complexes.

The reciprocal of the resistance is termed the conductance measured is reciprocal ohms or  $\Omega^{-1}$ . The resistance of a sample of homogeneous solution, length (l), and cross section area (a), is given by:-

$$R = \rho \cdot l/a \dots\dots\dots (1)$$

$$\rho = \frac{R \cdot a}{l} \dots\dots\dots (2)$$

$\rho$  is a characteristic property of the material termed the resistivity. It is given by

When "l" and "a" are measured in meters and square meter than " $\rho$ " is measured in  $\Omega$  meters. The reciprocal of resistivity is the conductivity (K). The conductivity of 1 mole of the material is called molar conductance. a/l is characteristic of conductivity cell, called cell constant.

The molar conductance of some selected metal derivatives has been determined by using sensitive conductivity bridge. First, the cell constant is determined. The cell ( $\kappa = a/l$ ) must be evaluated by calibration with a solution of accurately known conductivity e.g. a standard Potassium chloride solution.

**2. Magnetic susceptibility measurements.**

The magnetic susceptibility of the synthesized metal complexes was determined by using "Gouy's" balance. The weights were measured by means of electrical balance. By changing the magnetic field change in weight of the compounds were recorded to determine their magnetic susceptibility values. The formula used is given as formula:-

$$\chi_m = \frac{2mgL}{m^2H^2} \text{ C.G.S. Units} \dots\dots\dots (1)$$

Where:-

m = Change in mass of sample in magnetic field(H),

g = acceleration due to gravity at that place.

L = Length of compound in the tube.

$m^2$  = mass of compound field in the tube.

The molecule susceptibility is given by equation:

$\chi_M = \chi_m \times \text{molecular weight of the compound}$

or  $\chi_M = \chi_m \times M \dots\dots\dots (2)$

The magnetic susceptibility after diamagnetic correction is given by relation

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M T} \text{ B.M.} \dots\dots\dots (4)$$

Where, T is absolute temperature copper sulphate was used as calibrant in all these determinations.

**3. Infra-Red measurement:**

Infra-red spectra of the ligands and their metal derivatives were recorded on Perkin - Elemer, 842-infrared spectrometer using KBr Pallets in the region of 400 - 4000  $\text{cm}^{-1}$ .

**4. N.M.R. Studies:**

The PMR spectra of ligands and their metal complexes have been recorded by sending samples to research laboratory at K.U Kurushetra(Haryana) and CDRI lucknow. The NMR- studies helped in determining the structure and stereochemistry of the ligands and their metal derivatives.

**5. Mass - Spectral studies:**

The mass- spectrum of ligand and some metal derivatives were recorded on MS- 12, mass- spectrometer operating at 70ev. The data given in parentheses represent relative intensities of peaks corresponding to the base peak taken as 100.

**Synthesis of ligands:**

In present investigation  $\alpha$ - (1, 3- dioxo- indan - 2-yl) benzylidene aniline (IBA) ligand has been used to form its metal derivatives.

**1. Synthesis of 2 - Benzoylindan - 1,3 dione<sup>33,34</sup>:**

A mixture of redistilled diethylphalate (58.5g, 0.25mol), acetophenone (32.5g, 0.25ml) and freshly prepared sodium methoxide(14.5g, 0.25mol) was in dry benzene in a two necked flask with a mercury sealed stirrer and a condenser on a water bath for 4 hour. Benzene was distilled off and the unreacted diethylphalate and acetophenone were removed by steam distillation. The non- volatile residue was diluted with water and filtered. The unreacted diethylphalate and acetophenone were extracted from the filtrate by shaking it with ether and separated. The aqueous layer was acidified with hydrochloric acid(pH 3). It gave light yellow solid, which on crystallization from ethanol solution gave light yellow needles, m.p. 112<sup>o</sup>, (Lit<sup>1</sup>, m.p. 110-120<sup>o</sup>). The yield was 3.5g. The product was characterized by IR and PMR studies.

**2. Synthesis of  $\alpha$ - (1,3- dioxo-indane- 2-yl) Benzylidene aniline(IBA):<sup>34</sup>**

A mixture of 2-benzoylindane-1,3-dione(3.0g, 0.01mol) and freshly distilled aniline (1.25g, 0.014mol) was heated under reflux in presence of a few drops of glacial acetic acid and solvent dry benzene (30ml) for four hours. After reflux the reaction mixture was cooled in ice water. The solvent was distilled off. The residue after cooling deposited as dark green solid. This was dissolved in absolute ethanol and re-crystallized from ethanol solution as dark green needles, m.p. 132<sup>o</sup>, the yield

obtained was found to be 2.85g (80% base on 2-substituted benzoyl indane – 1,3-dione). The product was characterized by IR and PMR studies.

#### Preparation of metal derivatives:

The present investigation is based upon the reactions between metal ions and ligand. The metal complexes of metal ions Co(II), Ni(II), Cu(II), Zn(II), Cd(II), V(II), Cr(II), and Fe(III) with ligand, IBA has been prepared in different molar ratios of metal to ligand. The general reactions may be represented as follows:

#### 1. Reactions of ligands with bivalent metal ions; M(II) in MeOH solvent: –

(i) 1:1 molar ratio Reactions: –



(ii) 1:2 molar ratio Reactions:–



[x= Cl, M= Co(II), Ni(II), Cu(II), Zn(II), Cd(II)],  
[x= 3, and y= 2, for Co(II), Ni(II) complexes].

#### 2. Reactions of ligands with trivalent metal ions in MeOH solvent: –

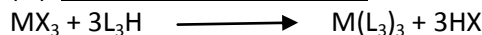
(i) 1:1 molar ratio reactions: –



(ii) 1:2 molar ratio reactions: –



(iii) 1:3 molar ratio Reactions: –



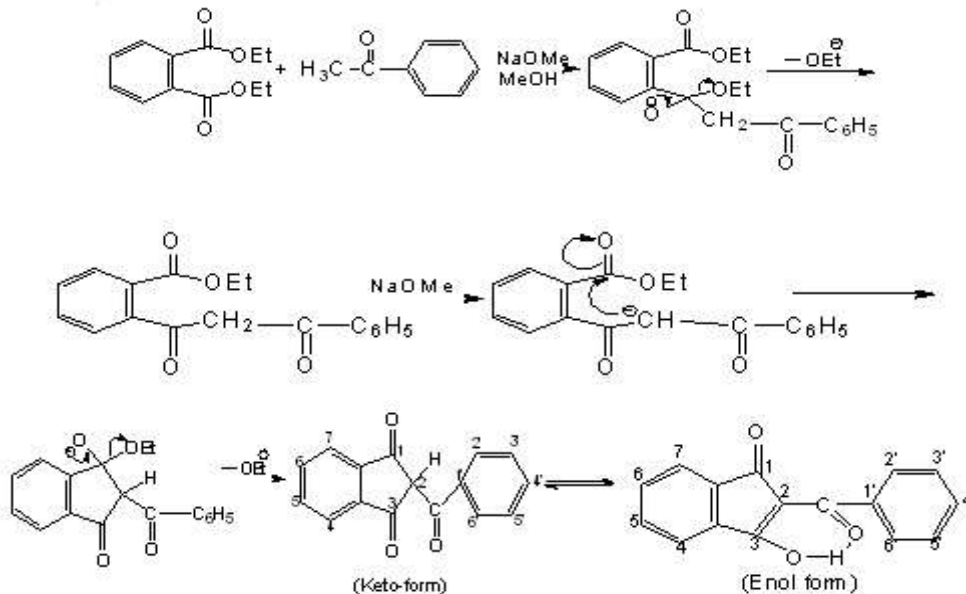
[x= Cl, M= V(III), Cr(III) and Fe(III)], [x= 2, and y= 1].

#### RESULTS AND DISCUSSIONS

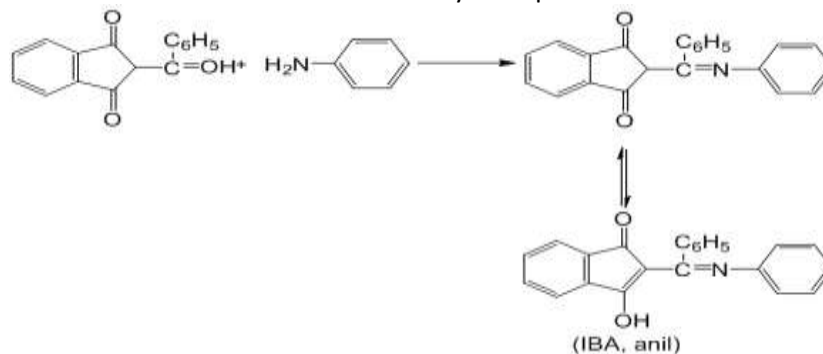
This work includes the synthesis of IBA as ligand and their metal derivatives and their characterization by spectral studies and elemental analysis. In the present work, the reactions of following anhydrous metal chlorides and the IBA ligands have been studied; the metal derivatives of the ligands have been isolated and characterized. i.e. Cobalt (II) chloride, Nickel (II) chloride, Copper (II) chloride, Zinc (II) chloride, Cadmium (II) chloride, Iron (III) chloride, Vanadium (III) chloride, Chromium (III) chloride

#### Synthesis of Ligand IBA

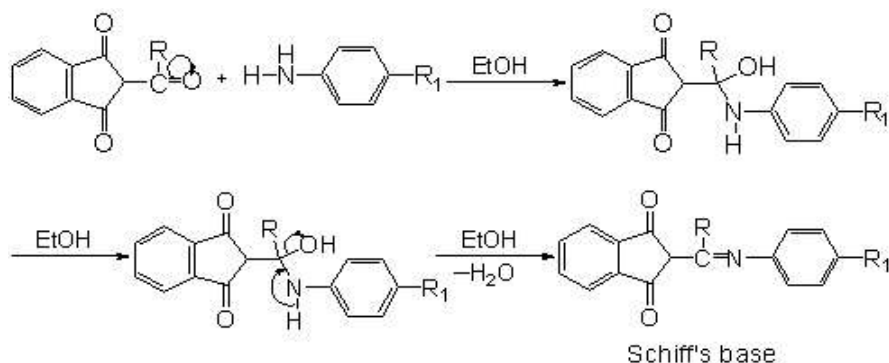
The starting material 2-Benzylidene-1, 3-dione was prepared by the claisen condensation and diethylphalate under the influence of sodium methoxide. The reaction proceeded through the following steps:



In the next step the IBA was prepared by refluxing 2-benzoyl indan-1,3-dione and aniline in absolute ethanol. Dark green needles were obtained as a solid Schiff's base. The reaction may be represented as follows:



Mechanism of synthesis of IBA:



Where  $R = C_6H_5$ ,  $R_1 = H$

### Indeno-Benzylidene-aniline (IBA):

#### Structure of the ANIL (IBA):

The structure of the IBA has been elucidated by elemental analysis, IR, PMR and mass-spectral studies. The IR and PMR data have been presented in the table 1. IR-spectra of the IBA showed strong absorption bands at 1715, 1640, 1570 and  $1500\text{ cm}^{-1}$  along with other bands. These absorptions may be assigned to non-bonded  $\alpha,\beta$ -unsaturated  $>C=O$  group in a five membered ring Ketone, chelated carbonyl group,  $>C=O-H-O$  and enolic double bond respectively. The absorption at  $3630\text{ (s)}\text{ cm}^{-1}$  may be due to  $\nu$ -OH (phenolic) and band at  $3040\text{ cm}^{-1}$  may be due to  $\nu$ -C-H, stretch (Aryl). The absorption bands in region

$1380\text{-}1340\text{ cm}^{-1}$  may be assigned to  $\nu$ -C-H stretching frequency in aniline and bands in the region  $850\text{-}730\text{ cm}^{-1}$  may be assigned to  $\nu$ -C-H in benzene ring. The strong absorption at  $1040\text{-}940\text{ cm}^{-1}$  may be attributed to  $\nu$ -C-O frequency in five membered ring.

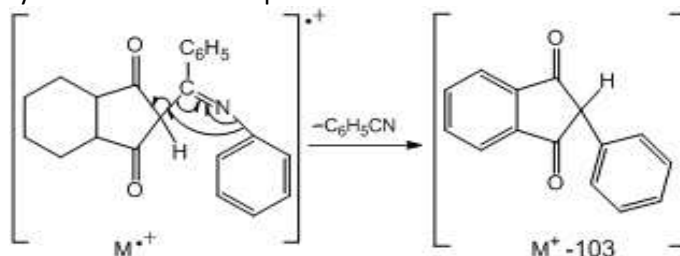
The structure of IBA further supported by its 90 MHz PMR spectrum which displayed a complex, multiplets in the region 7.50-7.80 $\delta$  which may be assigned to seven protons of the IBA ( $C_3\text{-H}$ ,  $C_4\text{-H}$ ,  $C_5\text{-H}$ ,  $C_6\text{-H}$  and  $C_7\text{-H}$ ) The  $C_3\text{-OH}$  (enolic) signal appeared as a broad signal at  $\delta$  14.30-14.40 The enolic formulation for the anil (IBA) got an additional support by a positive ferric chloride test.

Table 1: The principle IR and PMR spectral data of IBA

Sr. No.	Spectral data	Assignments
	(A) IR (Nujol) $\text{cm}^{-1}$	
1	3630 (s)	$\nu$ (O-H), stretch, (phenolic)
2	3040 (s)	$\nu$ (C-H), str. (Aryl)
3	1715 (s)	$\nu$ (C=O), str. (In five membered ring)
4	1640 (s)	Chelated $\nu$ C=O, str.
5	1610, 1450 (s)	$\nu$ C=N, str.
6	1570 (s), 1500 (w)	$\nu$ C=C, str. (Benzene ring)
7	1380 (m), 1340 (m)	$\nu$ C-N, str. (Aniline)
8	1040 (s), 940 (s)	$\nu$ C-O, str. (five membered ring)
9	850 (m), 760 (m) and 730 (m)	$\nu$ (C-H), str. (Benzene ring)
	(B) PMR ( $\text{CDCl}_3$ ) $\delta$	
1	7.50 – 7.80 (m)	7H; $C_3\text{-H}$ , $C_4\text{-H}$ , $C_5\text{-H}$ , $C_6\text{-H}$ and $C_7\text{-H}$
2	14.30 (br)	5H, (Aniline ring, $C_2\text{-H}$ to $C_6\text{-H}$ )

Abbreviations: str = stretch, s = sharp, w = weak, m = medium, br = broad.

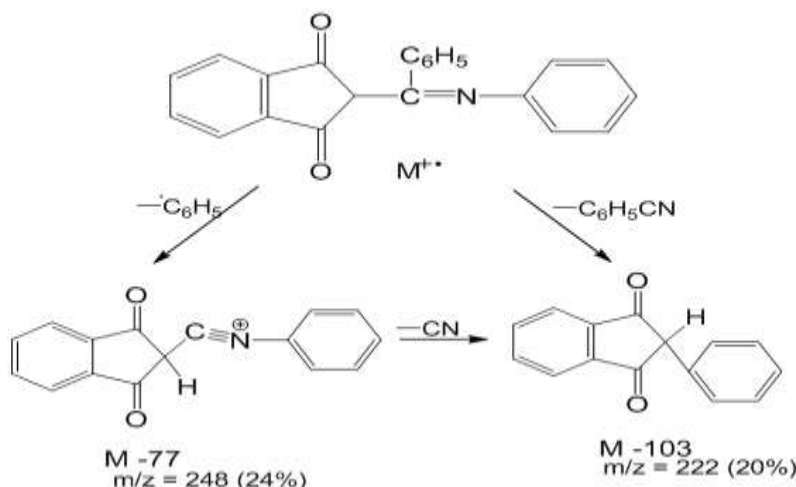
Finally, the structure of the IBA has been confirmed by its mass spectrum which showed the molecular ion peak at  $m/z$  325 (94% intensity). The base peak of the spectrum was, however located at  $m/z$  77 ( $-C_6H_5$ ). The mass spectra showed  $M+1$  ion peaks. The most probable structure for the  $M+1$  ion peak seems to be the one derived through the loss of the most acidic hydrogen located at C2 of the indan-dione moiety. The  $M+1$  ion peak



The mass spectra showed prominent peaks corresponding to loss of  $C_6H_5$   $m/z$  248(24%) and  $M+103$  ion peak due to loss of  $C_6H_5CN$  at  $m/z$  222(20%). The  $M+1$

appeared at  $m/z$  324(44). The fragmentation process commences with the elision of a  $C_6H_5$  radical from the molecular ion with a base peak at  $m/z$  77. The resultant  $M+103$  ions subsequently lose a  $CN$  ( $m/z$  26) radical to afford ions corresponding to  $M+103$ . These ions could also arise partially through the direct loss of phenyl cyanide from the molecular ion as shown below.

77 ions could also lose a molecule of  $CO$  to afford ions at  $M+105$  (12%). The fragmentation pattern of the anil may be presented as follows:



### Synthesis of Metal derivatives:

The metal derivatives of the ligand were prepared by refluxing the reaction mixture of the metal salt and the ligand in methanol for 1-3 hours on water bath. The colored solid products were obtained which were insoluble in water, ether and alcohols. The products were thermally stable at high temperature ( $> 300^\circ C$ ). These properties suggest the polymeric nature of the complexes.

The metal complexes have been prepared in different molar ratios in the reactions as follow:

(i) Reaction with bivalent metal ions:

(1) 1:1 molar ratio reactions:



[M= Co (II) and Ni (II), X= Cl]

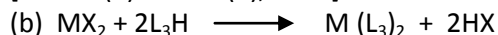


[M= Cu (II) and Zn (II) and Cd (II), X= Cl]

(2) 1:2 - molar ratio reactions:



[M= Co (II) and Ni (II), X= Cl]



[M= Cu (II) and Zn (II) and Cd (II), X= Cl]

(ii) Reaction with trivalent metal ions:

(1) 1:1 molar ratio reactions:



(2) 1:2 - molar ratio reactions:



(3) 1:3 - molar ratio reactions:



[M= Fe (III), V (III) and Cr (III), X= Cl,  $L_3H$ = IBA ligand]

### Structure of metal derivatives:

The structures of the isolated metal derivatives have been determined by spectral studies, magnetic moment values and molar conductivity measurements. The color, physical state and measured magnetic moment data of the metal derivatives of the IBA have been given in the table 2

Table 2: The physical state, colour and magnetic moment data of the metal complexes of the ligand, IBA

S. No.	Complex	Colour and Physical state	Magnetic moment $\mu_{\text{eff}}$ . R.M.
1.	Co L <sub>3</sub> .Cl. 3CH <sub>3</sub> OH	Dirty green, solid	4.80
2.	Co (L <sub>3</sub> ) <sub>2</sub> . 2CH <sub>3</sub> OH	Green, solid	.....
3.	Ni L <sub>3</sub> Cl. 3CH <sub>3</sub> OH	Yellowish-green, solid	3.20
4.	Ni(L <sub>3</sub> ) <sub>2</sub> . 2CH <sub>3</sub> OH	Yellowish-green, solid	.....
5.	Cu L <sub>3</sub> Cl	Yellowish-green, solid	1.73
6.	Cu(L <sub>3</sub> ) <sub>2</sub>	Yellowish-green, solid	.....
7.	Zn L <sub>3</sub> Cl	Green, solid	.....
8.	Zn (L <sub>3</sub> ) <sub>2</sub>	Green, solid	.....
9.	Cd L <sub>3</sub> Cl	Yellow brown, solid	.....
10.	Cd (L <sub>3</sub> ) <sub>2</sub>	Yellow brown, solid	.....
11.	Fe L <sub>3</sub> Cl <sub>2</sub> .2CH <sub>3</sub> OH	Yellowish-green, solid	5.70
12.	Fe (L <sub>3</sub> ) <sub>2</sub> Cl .CH <sub>3</sub> OH	Yellowish-green, solid	.....
13.	Fe (L <sub>3</sub> ) <sub>3</sub>	Yellowish-green, solid	.....
14.	V L <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH	Yellowish-green, solid	3.75
15.	V (L <sub>3</sub> ) <sub>2</sub> Cl. CH <sub>3</sub> OH	Yellowish-green, solid	.....
16.	V (L <sub>3</sub> ) <sub>2</sub>	Yellowish-green, solid	.....
17.	Cr (L <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH	Yellow brown, solid	3.72
18.	Cr (L <sub>3</sub> ) <sub>2</sub> Cl.CH <sub>3</sub> OH	Yellow brown, solid	.....
19.	Cr (L <sub>3</sub> ) <sub>3</sub>	Yellow brown, solid	.....

Where, L<sub>3</sub>H = Ligand anion (C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>N)<sup>-</sup>

#### IR and PMR spectral studies:

The observed principal IR spectral data of the metal derivatives of the IBA has been given in the table 3.

The IR-spectra of the complexes does not show absorption band in the region 3650-3600cm<sup>-1</sup> for  $\nu$ O-H (Phenolic). The absence of  $\nu$ O-H (phenol) suggests its bonding with metal ion through oxygen atom of (O-H) group. The sharp bands in the region 3060-3020cm<sup>-1</sup> and 2960-2920cm<sup>-1</sup> may be attributed to stretching vibrations of (C-H) bond in aromatic ring. Sharp bands in the region 1700-1695cm<sup>-1</sup> could be assigned to  $\nu$ C=O vibrations in five membered ring the lowering in  $\nu$ C=O frequency relative to ligand may be due to its bonding with the metal ion. The band in the region 1640-1440cm<sup>-1</sup> may be assigned to  $\nu$ C=N frequency and IR band at 1320-120cm<sup>-1</sup> is due to stretching frequency of (C-N) bond. The absorption bands in the region 1060-950cm<sup>-1</sup> may be attributed to  $\nu$ C-O stretching frequency. The band at 850-

820cm<sup>-1</sup> and 350-340-cm<sup>-1</sup> may be due to  $\nu$ M-O vibrations The IR band in the region 275-250cm<sup>-1</sup> may be assigned to  $\nu$ M-Cl Vibrations. The sharp band in the region 4.4-410cm<sup>-1</sup> may be attributed to stretching frequency of (M-N) bands.

The PMR Spectrum of the metal complexes shows resemblance with the PMR spectra of the ligand with minor difference in the position of PMR signals. This may be due to environmental effect on the protons. The most of the PMR signals in the spectra of complexes were observed at the expected values as observed in PMR spectra of the ligand. The PMR signal due to (O-H) phenolic observed in ligand spectra at 14.30 (broad) was absent in the PMR spectra of the complexes. This indicates its participation in metal-ligand bonding. This observation supports the formation of metal complexes with the ligand.

Table 3: The principle IR – spectral data of 1:1 molar ratio complexes of the ligand, IBA

Sr. No.	CoL <sub>3</sub> Cl. 3CH <sub>3</sub> OH cm <sup>-1</sup>	NiL <sub>3</sub> Cl. 3CH <sub>3</sub> OH cm <sup>-1</sup>	CuL <sub>3</sub> Cl cm <sup>-1</sup>	ZnL <sub>3</sub> Cl cm <sup>-1</sup>	Cd <sub>3</sub> Cl cm <sup>-1</sup>	Fe L <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH cm <sup>-1</sup>	V L <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH cm <sup>-1</sup>	Cr L <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH cm <sup>-1</sup>	Assignments
1	.....	.....	.....	.....	.....	.....	.....	.....	u(O-H) (Phenolic)
2	3050 (s)	3040 (s)	3060 (s)	3030 (s)	3045 (s)	3060 (s)	3020 (s)	3040 (s)	u(C-H) (Aryl)
3	2960 (m)	2940 (m)	2940 (s)	2950 (s)	2930 (s)	2950 (s)	2920 (s)	2940 (m)	u(C-H) str
4	1690 (s)	1700 (s)	1680 (s)	1695 (s)	1705 (s)	1685 (s)	1690 (s)	1705 (s)	u (C=O), str (five membered ring)
5	1600, 1430 (s)	1610, 1440 (s)	1630, 1430 (s)	1640, 1410 (s)	1630, 1420 (s)	1640, 1420 (s)	1610, 1420 (s)	1630, 1420 (s)	u (C=N), str
6	1550 (s)	1570 (s)	1540 (s)	1560 (s)	1540 (s)	1550 (s)	1545 (m)	1530 (m)	u (C=C) (benzene)
7	1330 (m)	1310 (s)	1290 (s)	1300 (s)	1320 (s)	1290 (s)	1280 (s)	1320 (s)	u (C-N), str
8	1060-930 (s)	1050-940 (s)	1040-920 (s)	1070-950 (s)	1060-920 (s)	1030-940 (s)	1050-930 (s)	1020-940 (s)	u(C-O), str
9	860-730 (s)	850-720 (s)	840-720 (s)	860-720 (s)	870-730 (s)	840-720 (s)	850-730 (s)	840-710 (s)	u (C-H) (benzene)
10	800 (s), 350 (s)	820, 340 (s)	830, 350 (s)	820, 340 (s)	820, 350 (s)	850, 320 (s)	850, 350 (s)	820, 340(s)	u (M-O) stretch
11	260 (s)	240 (s)	275 (s)	280 (s)	260 (s)	270 (s)	260 (s)	250 (s)	u (M-Cl) stretch
12	420 (s)	410 (s)	420 (s)	430 (s)	420 (s)	425 (s)	430 (s)	440 (s)	u (M-N), stretch

Abbreviations: s= sharp, m= median,

str= stretch,

L<sub>3</sub><sup>-</sup> = Ligand anion, (C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>N)<sup>-</sup>



**The Magnetic moment measurements:**

The magnetic behavior of the complexes was studied by measuring their magnetic moments by using Gouy's method. The magnetic moment values of the complexes are given in the table 2

The Cobalt (II) complexes of the ligand (IBA) showed their magnetic moments in the range 4.80-4.90 B.M. Normally the spin-free octahedral Cobalt (II) complexes (d7) show the magnetic moments in the range 4.30-5.20 B.M. These results suggest that Cobalt (II) complexes with this ligand (IBA) are magnetically paramagnetic in nature and high spin complexes.

The observed magnetic moments of Nickel (II) complexes of the ligand lie in the range 3.10-3.20 B.M. At room temperature. The expected magnetic moments of Ni (II) (d8) spin-free complexes lies in the range of 2.90-3.40 B.M. These results suggest that Ni (II)- IBA complexes are paramagnetic and show antiferromagnetism at room temperature.

The measured magnetic moments of Copper (II) complexes of the ligand is found to be 1.73 B.M. This value is in resemblance to the expected magnetic moment values in the range 1.75-1.80 B.M. For spin free Cu (II) (d9) complexes. This suggests that Copper (II) complexes are paramagnetic and bear square planer or distorted

octahedral geometry according to Jahn-Teller distortions. Zinc (II) and Cd (II) complexes have zero magnetic moments. Thus these complexes are diamagnetic in nature with tetrahedral geometry as expected. The Iron (III), Vanadium (III) and Chromium (III) complexes are paramagnetic in nature with their magnetic moments 5.70 B.M., 3.75B.M. And 3.72 B.M. Respectively. The complexes exhibit ferromagnetic behavior in the applied magnetic field. These results suggest spin-free octahedral geometry of the complexes.

**Molar Conductivity Measurements:**

The molar conductivity of few of the complexes in 1:1 molar ratio have been measured in anhydrous DMSO solvent at room temperature, 25°C. The observed molar conductivity values of the complexes are shown in the table 4. The observed conductivity values of the complexes lies in the range -190-250 mhos-cm<sup>2</sup>-mole. These results show that the complexes exhibit partial ionic character, though the complexes are covalent. The complexes are insoluble in common organic solvents. This suggests the polymeric nature of the complexes. But the possibility of their feebly ionic nature cannot be ruled out on the basis of their observed conductivity values. Moreover the complexes are solid of high M.P. (250° and above)

**Table 4: Molar conductivity data of 1:1 molar ratio complexes of the ligand IBA measured at room temp, 25°C.**

Sr. No.	Complex	Conc. of solution in DMSO	Observed conductance micro mhos	Cell constant	Specific conductance mictomhos	Molar conductance cm <sup>2</sup> /g. mol
1.	Co L <sub>3</sub> Cl. 3CH <sub>3</sub> OH	1x10 <sup>-3</sup> M	1900	0.1	190.0	190.0
2.	Ni L <sub>3</sub> Cl. 3CH <sub>3</sub> OH	1x10 <sup>-3</sup> M	1950	0.1	195.0	195.0
3.	Cu L <sub>3</sub> Cl	1x10 <sup>-3</sup> M	1970	0.1	197.0	197.0
4.	Zn L <sub>3</sub> Cl	1x10 <sup>-3</sup> M	1960	0.1	196.0	196.0
5.	Cd L <sub>3</sub> Cl	1x10 <sup>-3</sup> M	1990	0.1	199.0	199.0
6.	FeL <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH	1x10 <sup>-3</sup> M	2500	0.1	250.0	250.0
7.	V L <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH	1x10 <sup>-3</sup> M	2450	0.1	245.0	245.0
8.	CrL <sub>3</sub> Cl <sub>2</sub> . 2CH <sub>3</sub> OH	1x10 <sup>-3</sup> M	2470	0.1	247.0	247.0

**Mass- Spectral Studies:**

The structure of the ligand, IBA and few of its complexes has been determined by mass-spectral studies. The mass-spectra of these compounds displayed the presence of molecular ion peaks (M+), base peaks and M+-1 ion peaks at the expected m/z values and showed also an interesting fragmentation pattern.

The mass-spectra of the ligand and its metal derivatives showed intense molecular ion peaks which also constituted the base peak of each spectrum. All these spectra showed also M+-1 ion peaks of variable intensity. The mass spectra of the ligand (IBA) showed M+ ion peak at m/z, 325 (94%) M+-1 ion peak at m/z 324 (44%). The M+-1 ion peak seems to be derived through the loss of the most acidic hydrogen located at C2 of the indane moiety. The fragmentation process begins with the loss of C6H5 radical, m/z, 77. The resultant M+-C6H5 ions subsequently lose a CN2 (m/z 26) radical to afford M+-C6H5 ions. These ions could also arise partially through the direct loss of phenyl cyanide from the molecular ion (M+) reported earlier<sup>16,17</sup>. Mass-spectra showed prominent peaks due to loss of C6H5 (m/z,77) at m/z 248 and M+-103 ion peak due to loss of C6H5CN (103) at m/z 222 (20%). the M+-77 ions fragment to lose CO to afford ions at M+-105 (12%).

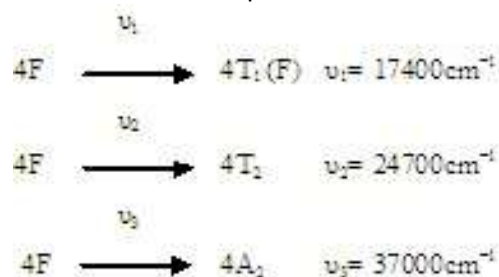
The mass spectra of Co (II), Ni (II) and Cu (II) complexes of the ligand (IBA) displayed fragmentation pattern similar to the ligand. The molecular ion peaks M+, and M+-1 base peaks were observed at expected positions with variable intensities. The mass-spectra of Co (II), Ni (II) and Cu (II) displayed molecular ion peaks, (M+) at m/z 418, m/z 514 and m/z 423 respectively and M+-1 ion peaks were observed at m/z 417 m/z 513 and m/z 422 in mass-spectra of these complexes respectively. In the mass spectra of these complexes prominent peaks due to loss of C6H5 radical (m/z 77), CN radical (m/z 26), C6H5CN (m/z 105), CO (m/z 28) were observed similar as in the mass spectra of the ligand (IBA). These observations support the complex formation and their structure.

**Electronic Spectral Studies:**

The electronic spectral studies of Iron (III), Chromium (III) and Ni (II) complexes have been carried out. Iron (III) is isoelectronic with manganese (II) thus energy level diagrams of Fe(III) and Mn (II) thus energy level diagrams of Fe (III) and Mn (II) are identical and give identical electronic spectra. Iron (III) complexes show charge transfer bands in the near 4v region and very weak spin-forbidden d-d bands. Such bands are reported in octahedral surrounding of Fe (III) ions. The electronic spectra of Fe (III) complex with the ligand (IBA) in 1:1

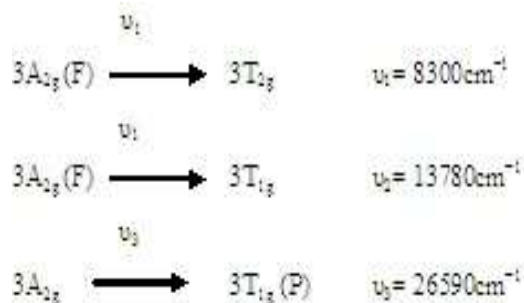
molar ratio displays three absorption bands at 31780 cm<sup>-1</sup>, 17690cm<sup>-1</sup> and 8379cm<sup>-1</sup>

Chromium (III) ion (d<sup>3</sup>) show the magnetic moments as spin-only values in Cr (III) octahedral complexes which is observed in Cr (III)- IBA complexes. The ground state term for a Cr (III) (d<sup>3</sup>) ion is 4F. the electronic spectra of Cr (III) complexes indicate three spin-allowed.



Such absorption bands have been observed in considerable number of Cr (III) octahedral complexes.

The nickel (II) complexes with the ligand (IBA) are characterized by following transitions

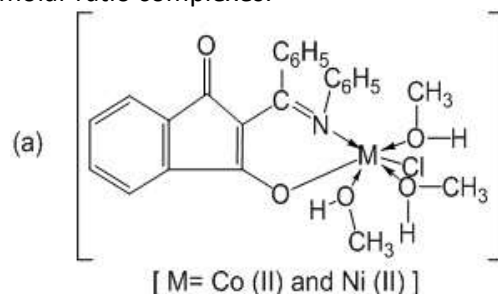


The  $\nu_1$  absorption band splits in the components with maxima at 7060cm<sup>-1</sup> and 8280cm<sup>-1</sup>. This split is assigned to lowering in symmetry from regular octahedral geometry of the six coordinated Ni (II) complexes.

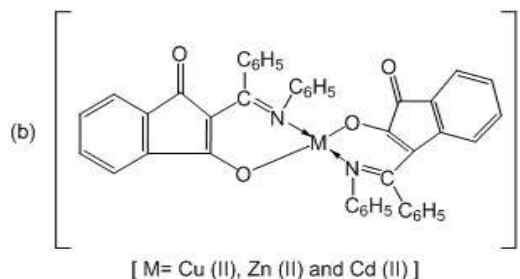
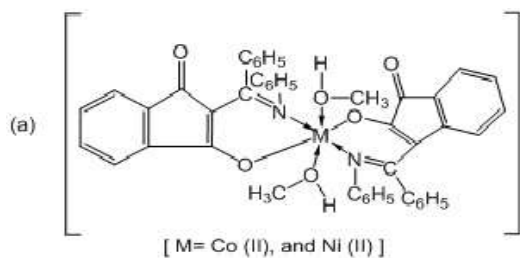
On the basis of the characteristics shown by the metal derivatives of the ligand (IBA) plausible structures of the complexes have been suggested in which the metal ions exhibit tetra and hexa-coordination geometry depending upon the nature of metal ions and ligands. The general structures of the metal complexes may be represented as follow:

1. General structure of bivalent metal complexes:

(i) 1:1- molar ratio complexes:

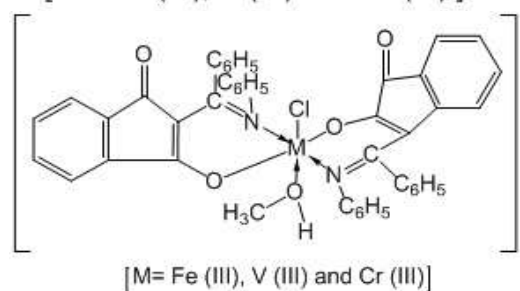
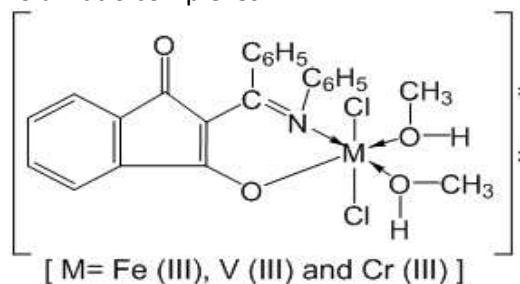


(ii) 1:2 molar ratio complexes:

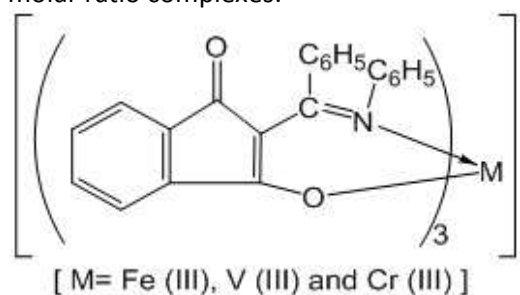


## 2. General structures of trivalent metal complexes:

### (i) 1:1 molar ratio complexes:



### (iii) 1:3 molar ratio complexes:



In 1:1 and 1:2 molar ratio complexes of Co (II), Ni (II), Fe (III), V(III) and Cr (III) ions. The hexa coordination has been achieved by coordination of methanol molecules as donor species similar to coordinated water molecules in aquo complexes of the metal ions.

### SUMMARY:

The coordination chemistry has been recognized as an unique branch of chemistry. Transition metal ions have unique capacity of complex formation with variety of

ligands. This study has originated wide applications in different branches of Science and Engineering. A large number of coordination compounds are of biological importance.

A large number of chemists throughout the world are currently engaged in the synthesis heterocyclic compounds with a view to evaluating their various biological properties. The present investigation aims at supplementing these efforts in the broad area of the synthesis of Schiff's bases (anils) such as IBA and their metal derivatives. The opportunity has also been taken to examine spectral properties of these compounds. The results of the present investigation have been described dealing with the synthesis and spectral studies of heterocyclic ligands with 2-benzoylindane-1,3-dione moiety and their metal derivatives.

From the detailed survey of the literature on condensed heterocyclic ring systems. It is evident that indenoquinolines and indenopyrazoles show various physiological properties such as potent analgesics, antipyretics, anti-inflammatory agents etc.

The general approach towards the synthesis of these Schiff's bases (ligands) consists two step synthesis. In the first step of synthesis the starting materials 2-benzoylindane-1,3-dione. In the next step the IBA was prepared by refluxing 2-benzoyl indan-1,3.dione and aniline in absolute ethanol. Dark green needles were obtained as a solid Schiff's base.

The formulation and structure of the ligands have been screened by their chemical analysis, IR, PMR and mass-spectral studies.

IR-spectra of the IBA showed strong absorption bands at 1715, 1640, 1570 and 1500<sup>cm-1</sup> along with other bands.

The absorption at 3630 (s) <sup>cm-1</sup> may be due too uo-H (phenolic) and band at 3040<sup>cm-1</sup> may be due to uc-H, stretch (Aryl). The absorption bands in region 1380-1340<sup>cm-1</sup> may be assigned to uc-H stretching frequency in aniline and bands in the region 850-730<sup>cm-1</sup> may be assigned to uc-H in benzene ring. The strong absorption at 1040-940<sup>cm-1</sup> may be attributed to uc-o frequency in five membered ring.

The structure of IBA further supported by its 90 MHz PMR spectrum which displayed a complex, multiplets in the region 7.50-7.80δ which may be assigned to seven protons of the IBA (C<sub>3</sub>-H, C<sub>4</sub>-H, C<sub>5</sub>-H, C<sub>6</sub>-H and C<sub>7</sub>-H) The C<sub>3</sub>-OH (enolic) signal appeared as a broad signal at δ 14.30-14.40 The enolic formulation for the anil (IBA) got an additional support by a positive ferric chloride test.

Finally, the structure of the IBA has been confirmed by its mass spectrum which showed the molecular ion peak at

m/z 325 (94% intensity). The base peak of the spectrum was, however located at m/z 77 (-C<sub>6</sub>H<sub>5</sub>).

The PMR Spectrum of the metal complexes shows resemblance with the PMR spectra of the ligand with minor difference in the position of PMR signals. This may be due to environmental effect on the protons. The most of the PMR signals in the spectra of complexes were observed at the expected values as observed in PMR spectra of the ligand.

Results show that the complexes exhibit partial ionic character, though the complexes are covalent. The complexes are insoluble in common organic solvents. This suggests the polymeric nature of the complexes. But the possibility of their feebly ionic nature cannot be ruled out on the basis of their observed conductivity values. Moreover the complexes are solid of high M.P. (250<sup>o</sup> and above). The mass-spectra of these compounds displayed the presence of molecular ion peaks (M<sup>+</sup>), base peaks and M<sup>+</sup>-1 ion peaks at the expected m/z values and showed also an interesting fragmentation pattern.

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