

**SYNTHESIS, ELEMENTAL ANALYSIS, IR, <sup>1</sup>H NMR, UV-VISIBLE, ESR, TGA, POWDER XRD CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF CO(II), CU(II), ZN(II) AND CD(II) COMPLEXES DERIVED FROM SCHIFF'S BASE DCPAHNMA**

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### ABSTRACT

The condensation reaction between 2-(2-(2,6-dichlorophenylamino)phenylacetohydrazide with 2-hydroxy-1-naphthaldehyde results in the formation of complexes of the type  $ML^2$  and  $ML^1$  [where  $M=Co(II)$ ,  $Cu(II)$  and  $M^1=Zn(II)$ ,  $Cd(II)$ ]. The Schiff's base of hydrazone behaves as monobasic tridentate ligand containing ONO coordinating sites with the metal ions to yield mononuclear complexes. The Schiff's base were characterized by IR and <sup>1</sup>H NMR and the nature of bonding and stereochemistry of the metal complexes have been deduced from elemental analysis, conductance measurements, magnetic susceptibility, Uv-Visible, IR, <sup>1</sup>H NMR, ESR, TGA and powder X-ray diffraction data. The synthesized Schiff's base DCPAHNMA and its metal complexes were tested for their antimicrobial activity against Gram positive and Gram negative bacterium as well as against fungi in order to check the biological potency.

**KEYWORDS:** Schiff's base, Naphthaldehyde, XRD, TGA and antimicrobial activity.

### INTRODUCTION

Interest in the study of Schiff's base hydrazones has been growing because of their antimicrobial, anti-tuberculosis and anti-tumor activity.<sup>[1]</sup> Schiff's bases play an important

role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff's base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species.<sup>[2]</sup> Coordination compounds derived from aryl hydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications.<sup>[3]</sup> Schiff's bases are organic compounds possessing the azomethine functional group. The hydrazones belong to this huge class of azomethines, characterized by the grouping  $>C=N-N<$ , they are distinguished from the other members of this class *viz.* imines, oximes etc., by the presence of inter linked nitrogen atoms. Hydrazones are usually obtained by condensing hydrazides with aldehydes or ketones.<sup>[4]</sup> In view of the importance of such hydrazones, the present study is concerned with the synthesis and characterization of hydrazone ligand and their Co(II), Cu(II), Zn(II) and Cd(II) metal complexes derived from condensation of 2-(2-(2,6-dichlorophenylamino) phenylacetohydrazide with 2-hydroxy-1-naphthaldehyde. The synthesized compounds were screened for their antimicrobial activity.

## EXPERIMENTAL

**Physical measurements:** The used chemicals are analytical grade reagents and no need of further purification. The elemental analyses (CHN) were obtained from Thermo finnigam Italy, FLASH EA 1112 series. Magnetic susceptibilities were measured on a Guoy balance at room temperature using  $Hg[Co(SCN)_4]$  as calibrant. The molar conductance of the complexes was measured on ELICO CM-82 Conductivity Bridge in DMF solution at a concentration of  $10^{-3}M$ . Infrared spectra of the ligand and its metal(II) complexes in KBr pellets were recorded in the spectral range  $4000-350\text{ cm}^{-1}$  with Perkin Elmer Spectrum one FT-IR spectrometer.  $^1H$  NMR spectra were recorded on AMX-400 NMR spectrometer, using TMS as internal standard and DMSO as a solvent. Electronic spectra were recorded on an Elico SL-164 DOUBLE BEAM UV-Vis Spectrophotometer in the range of 200-1200 nm. ESR measurements were carried on a BRUKER Biospin GmbH spectrometer, working at a microwave frequency of 9.10 GHz. The thermal degradation study of complexes has been carried out on Universal Perkin Elmer Thermal Analyzer. The powder-XRD spectra were recorded on Phillips PW 3710 diffractometer attached to a digitized computer along with graphical assembly using  $CuK\alpha$  radiation source.

### Synthesis of compounds

#### *Preparation of ethyl-2-(2-(2, 6-dichlorophenylamino)phenyl)acetate*

The drug Sodium 2-(2-(2,6-dichlorophenylamino)phenyl)acetate on acid hydrolysis gives 2-(2-(2,6-dichlorophenylamino)phenyl)acetic acid which further upon esterification gives ethyl 2-(2-(2,6-dichlorophenylamino)phenyl)acetate.

#### *Preparation of 2-(2-(2, 6-dichlorophenylamino)phenyl)acetohydrazide*

Equimolar mixture of ester (0.01 M) and hydrazine hydrate (0.01 M) in 30 ml ethanol was taken in a round bottom flask. The reaction mixture was refluxed for 6-7 hrs, solvent was evaporated on water bath and solid separated was collected, the product was washed with absolute alcohol and recrystallized from alcohol.

#### *Preparation of Schiff's base DCPAHNMA*

The Schiff's base were prepared by condensation of 2-(2-(2,6-dichlorophenylamino)phenyl)acetohydrazide with 2-hydroxy-1-naphthaldehyde (0.01 mol) in an alcoholic medium was refluxed on a water bath for 4-5 hrs in presence of few drops of hydrochloric acid. The reaction mixture was cooled to room temperature, the separated Schiff's base 2-(2-(2,6-dichlorophenyl amino) -N'- (1-hydroxynaphthlen-2-yl) methylene) acetohydrazide [DCPAHNMA] were filtered, washed with alcohol. The purity of the Schiff's base DCPAHNMA was checked by TLC.

#### *Preparation of complexes*

To the hot solution of the Schiff's base DCPAHNMA (0.001 mol) in ethanol (50 ml), a hot ethanolic solution of respective metal chlorides (0.001 mol) in ethanol (20 ml) was added, refluxed on water bath 4-5hrs. The reaction mixture was then treated with sodium acetate (0.5 g) and the refluxing was continued further for 2 hrs. The resulting reaction mixture was then decomposed by pouring into distilled water (80-100 ml), the colored complex separated out was collected by filtration, washed with distilled water, then with hot ethanol and dried in vacuum over anhydrous calcium chloride. The complexes were analyzed for their metal and chloride contents by standard methods.<sup>[5]</sup>

## RESULTS AND DISCUSSION

Table 1. Analytical, magnetic susceptibility and molar conductance data of the Schiff's base DCPAHNMA and its complexes

Ligand / Complex Empirical formula	Mol. wt.	M. P. (°C)	Yield (%)	Elemental analysis (%): Found (Calc.)					$\mu_{\text{ef}}$ B.M	$\lambda_{\text{M}}$ Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
				M	C	H	N	Cl		
[DCPAHNMA] C <sub>25</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	463	230	80	--	64.66 (64.61)	4.12 (4.04)	9.05 (9.09)	15.27 (15.22)	–	–
[Co(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	985.6	>300	65	5.98 (5.93)	60.93 (60.95)	3.68 (3.64)	8.53 (8.49)	14.39 (14.38)	4.89	20.04
[Cu(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	990.2	275	70	6.42 (6.38)	60.65 (60.66)	3.66 (3.68)	8.49 (8.51)	14.32 (14.31)	1.93	22.23
[Zn(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl]	564.2	298	72	11.59 (11.60)	53.22 (53.18)	3.22 (3.24)	7.45 (7.44)	18.85 (18.86)	Dia	21.22
[Cd(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl]	611.2	265	68	18.39 (18.31)	49.13 (49.11)	2.97 (2.91)	6.88 (6.81)	17.40 (18.37)	Dia	24.32

Table 2. Characteristic IR frequencies of the ligand DCPAHNMA and its complexes (cm<sup>-1</sup>)

Ligand/ complexes	$\nu_{\text{OH}}$	$\nu_{\text{NH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
DCPAHNMA	3412	3112	1668	1600	1289	-	-	-
[Co(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	-	3114	1638	1582	1336	523	432	-
[Cu(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	-	3110	1642	1583	1308	525	434	-
[Zn(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl]	-	3113	1645	1578	1319	529	424	357
[Cd(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl]	-	3116	1637	1569	1315	530	425	352

Table 3. Electronic spectral data and ligand field parameters of Co(II) and Cu(II) complexes of Schiff's base DCPAHNMA (cm<sup>-1</sup>)

Complexes	Transition in cm <sup>-1</sup>			Dq (cm <sup>-1</sup> )	B <sup>1</sup> (cm <sup>-1</sup> )	$\beta$	$\beta\%$	$\nu_2/\nu_1$	$\nu_3/\nu_1$	LFSE (Kcalmol <sup>-1</sup> )
	$\nu_1$	$\nu_2$	$\nu_3$							
[Co(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	9650	16530	19100	880	831	0.855	14.41	1.71	1.97	15.09
[Cu(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	16225 - 12765			1449	-	-	-	-	-	24.84

Table 4. ESR data of the Cu(II) complex of the ligand DCPAHNMA

Complex	$g_{\parallel}$	$g_{\perp}$	$g_{av}$	$g_{iso}$	G
[Cu(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	2.210	2.048	2.103	2.157	4.54

Table 5. Thermal decomposition of Zn(II) complex of the ligand DCPAHNMA

Complex	Stage	Peak temp. TG (°C)	Loss of mass (%)		Probable Assignments
			Practical	Theoretical	
Zn(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl	–	–	–	–	Zn(C <sub>25</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> Cl <sub>2</sub> )Cl
	I	245.00	6.32	6.38	↓ -Cl <sub>2</sub> Zn(C <sub>25</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> Cl)
	II	445.00	47.61	47.70	↓ -C <sub>13</sub> H <sub>10</sub> NCl Zn(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> )
	III	600.00	78.40	78.69	↓ -C <sub>11</sub> H <sub>6</sub> O Zn(CH <sub>2</sub> N <sub>2</sub> O) ↓ ZnO

Table 6. X-Ray diffraction data of Zn(II) complex of the ligand DCPAHNMA

Peak No.	2θ	θ	Sinθ	Sin <sup>2</sup> θ	h <sup>2</sup> +k <sup>2</sup> +l <sup>2</sup>	h k l	a in Å	Relative Intensity (%)	d-spacing in Å <sup>0</sup>	
									Obs.	Calcd.
1	5.722	2.861	0.049	0.002	1	1 0 0	15.430	100.00	15.429	15.429
2	11.691	5.845	0.101	0.010	4	2 0 0	15.431	29.65	7.562	7.556
3	17.901	8.950	0.155	0.024	10	3 1 0	15.430	23.00	4.950	4.950
4	18.871	9.435	0.163	0.026	11	3 1 1	15.431	14.99	4.698	4.698
5	21.226	10.613	0.184	0.033	14	3 2 1	15.430	34.96	4.182	4.182
6	23.833	11.916	0.206	0.042	17	4 1 0	15.430	38.08	3.730	3.730
7	26.072	13.036	0.225	0.050	20	4 2 0	15.431	25.61	3.185	3.185
8	27.987	13.993	0.241	0.058	23	– – –	15.431	12.05	2.725	2.725
9	32.827	16.413	0.282	0.079	32	4 4 0	15.431	4.40	2.545	2.545
10	35.224	17.613	0.302	0.091	37	6 1 0	15.430	7.47	2.442	2.442
11	36.767	18.383	0.315	0.099	40	6 2 0	15.430	3.75	1.574	1.574
12	58.561	29.280	0.489	0.239	96	8 4 4	15.430	3.02	1.488	1.488
13	62.313	31.157	0.517	0.267	107	9 5 1	15.430	6.83	1.224	1.223
14	77.946	38.973	0.628	0.395	159	– – –	15.430	8.97	1.023	1.022

Table 7. Antimicrobial activity data of the ligand DCPAHNMA and its metal complexes

Test compound	Antibacterial activity of zone of inhibition (in mm) (conc. in µg mL <sup>-1</sup> )		Antifungal activity of zone of inhibition (in mm) (conc. in µg mL <sup>-1</sup> )	
	<i>E. coli</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>A. flavous</i>
DCPAHNMA	10	10	09	10
[Co(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	19	18	18	17
[Cu(C <sub>25</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]	12	11	16	17
[Zn(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl]	18	18	17	18

[Cd(C <sub>25</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )Cl]	13	13	12	13
Streptomycin	24	25	--	--
Clotrimazole	--	--	25	24

FIGURE-1

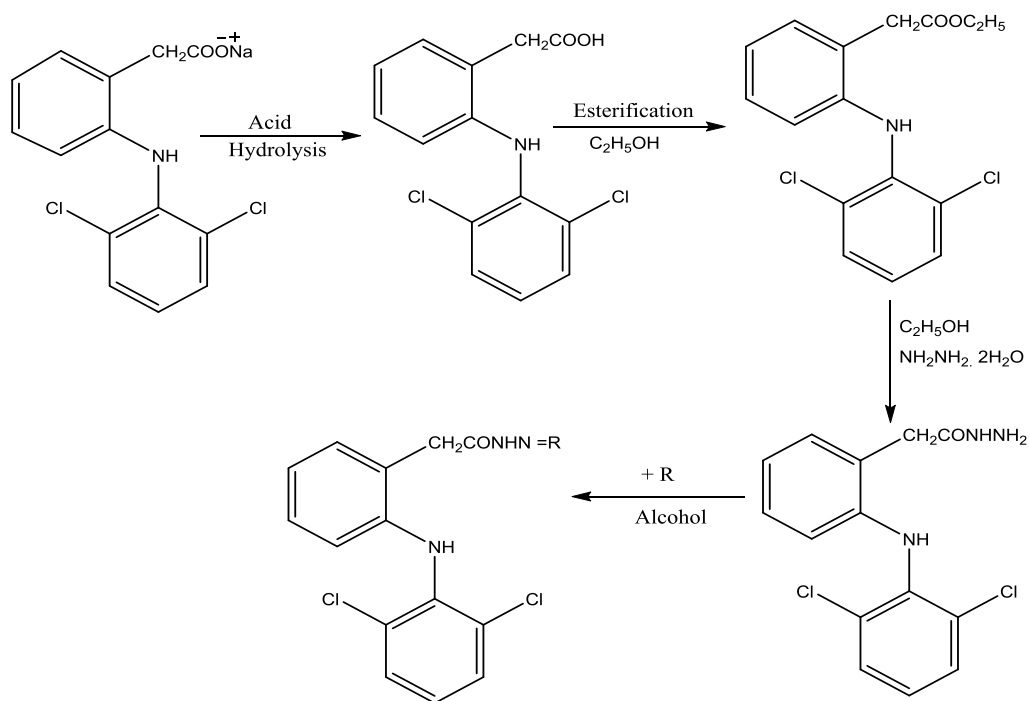
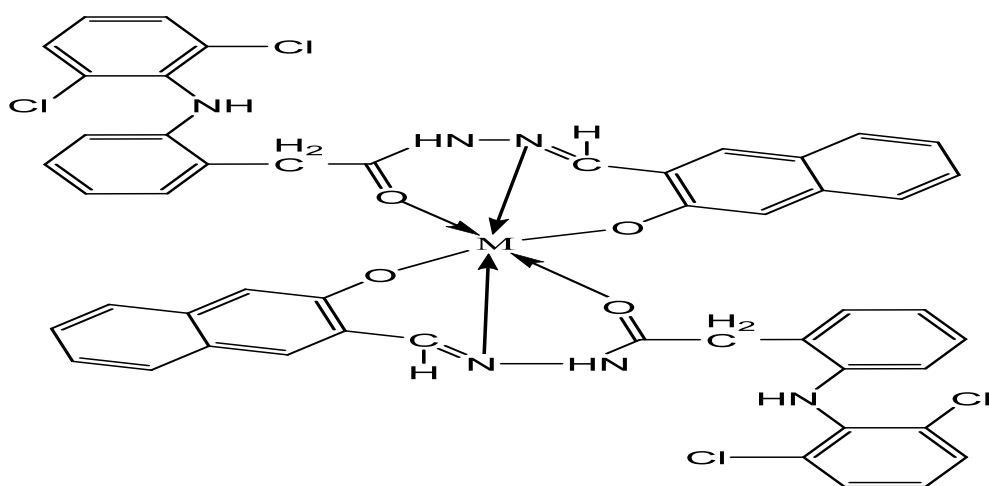
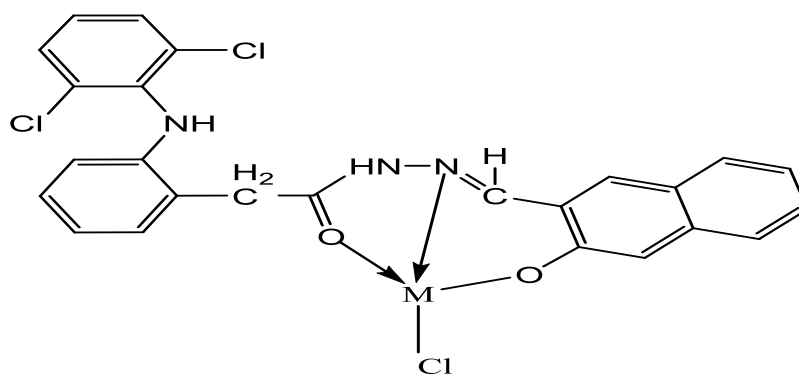


Figure 1. Synthesized structure of the Schiff's base DCPAHNMA



Where M = Co(II), and Cu(II)

Figure 2. Proposed structure of the synthesized Co(II) and Cu(II) complexes



Where  $M = \text{Zn(II)}$  and  $\text{Cd(II)}$

**Figure 3. Proposed structure of the synthesized Zn(II) and Cd(II) complexes**

The elemental analysis data indicates that the stoichiometry of the complexes are 1:2 (metal to ligand ratio) for Co(II) and Cu(II) and 1:1 (metal to ligand ratio) for Zn(II) and Cd(II) complexes. The prepared complexes were sparingly soluble in common organic solvents but soluble in DMF and DMSO. The observed molar conductance values measured in DMF solution fall in the range  $20\text{--}22 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating that the complexes are non-electrolytic in nature.<sup>[6]</sup> The measured magnetic moment values of Co(II) and Cu(II) complexes are 4.89 BM and 1.93 BM., shows the calculated magnetic moment values of Co(II) and Cu(II) complexes in the range of 4.54–4.95 BM and 1.90–2.10 BM respectively and indicates their octahedral geometries.<sup>[7]</sup>

#### *Infrared spectral data of the Schiff's base and its complexes*

The characteristic absorption bands of the free ligand are shifted on complexation and new vibrational bands characteristic of complexation appeared showing that ligand DCPAHNMA behaves as monobasic tridentate manner coordinating through carbonyl oxygen, phenolic oxygen and azomethine nitrogen. The IR Spectra of ligand DCPAHNMA exhibit characteristic absorption at  $3112 \text{ cm}^{-1}$  due to  $\nu_{\text{N-H}}$  vibrations, but in all complexes they show negligible change ( $0\text{--}6 \text{ cm}^{-1}$ ) due to non involvement in the complexation.<sup>[8]</sup> The sharp band appears at  $1668 \text{ cm}^{-1}$  due to the keto  $\nu_{\text{C=O}}$  stretching vibrations in case of Schiff's base but in the spectra of all the complexes observed lower shift ( $23\text{--}32 \text{ cm}^{-1}$ ) and a new band appears in the region  $1645\text{--}1636 \text{ cm}^{-1}$  indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the carbonyl oxygen atom to the metal ion.<sup>[9]</sup> A strong band at  $1600 \text{ cm}^{-1}$  due to  $\nu_{\text{C=N}}$  stretching in case of Schiff's base DCPAHNMA, but in the spectra of all the complexes show the lower shift ( $18\text{--}31 \text{ cm}^{-1}$ ) and a new band appears in the region  $1582\text{--}1569 \text{ cm}^{-1}$  in all the complex confirms the coordination of azomethine

nitrogen to metal.<sup>[10]</sup> The strong band observed at  $3412\text{ cm}^{-1}$  due to phenolic OH stretching vibrations in Schiff's base, the strong band disappeared in all the complexes indicates the involvement of oxygen in coordination to the metal ion via deprotonation.<sup>[11]</sup> The band appears at  $1289\text{ cm}^{-1}$  due to  $\nu_{\text{C-O}}$  in the Schiff's base, this band shifted to higher frequency in the region  $1308\text{-}1336\text{ cm}^{-1}$  in all the complexes indicates involvement in bonding with complexation.<sup>[12]</sup> The new band appears in region  $523\text{-}530\text{ cm}^{-1}$  due to  $\nu_{\text{M-O}}$  and  $424\text{-}434\text{ cm}^{-1}$  due to  $\nu_{\text{M-N}}$  respectively in all the complexes.<sup>[13,14]</sup> The sharp new band appears at  $357\text{ cm}^{-1}$  and  $352\text{ cm}^{-1}$  due to presence of  $\nu_{\text{M-Cl}}$  bond in the Zn(II) and Cd(II) complexes respectively.<sup>[15]</sup>

### ***<sup>1</sup>H NMR spectral data of the Schiff's base DCPAHNMA and Zn(II) complex***

The fine singlet at  $\delta 12.35$  (s, 1H, CONH) and  $\delta 10.00$  were assigned to protons of the amide -NH and -NH respectively in case of Schiff's base and are unaffected in the complex indicates non-involvement of N of -NH group.<sup>[16]</sup> A signal due to  $\text{CH}_2$  proton appears at  $\delta 2.52$ . The signal due to azomethine proton of ligand shows a downfield shift and appears around  $\delta 9.1$  (s, 1H, HC=N) in the spectra of Zn(II) complex, indicates the coordination of the azomethine group to the metal ion through nitrogen.<sup>[17]</sup> This downfield shift is due to deshielding of the =CH proton. All these observation supported the IR spectral data. The thirteen aromatic protons of the ligand have resonated as multiplet in the region  $\delta 7.00\text{-}7.89$  (m, 13H, Ar-H). A proton due to -OH group at 2-position of naphthaldehyde ring has resonated as a singlet at  $\delta 11.46$  in case of ligand which has also been disappeared in the complex indicating the involvement of phenolic oxygen in the coordination via deprotonation.<sup>[18]</sup>

### ***Electronic spectral analysis data***

The electronic spectral data of Co(II) and Cu(II) complexes of the Schiff's base (DCPAHNMA) were recorded in DMF solution at  $10^{-3}$  M concentration and are given in table 3. They have been studied with a view to obtaining more information on the stereochemistry of the complexes and to procure more support for the conclusion deduced with the help of magnetic data. The electronic spectra of the Co(II) complex gave two absorption bands at  $9650\text{ cm}^{-1}$  and  $19100\text{ cm}^{-1}$ , due to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_1)$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$  transitions.<sup>[19]</sup> The bands due to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$  transitions could not be observed because of its very low intensity. The position of  $\nu_2$  band has been calculated ( $16530\text{ cm}^{-1}$ ) by using the equation  $\nu_2 = \nu_1 + 10Dq$ . These transitions suggest



octahedral geometry for Co(II) complex. The ligand field parameters such as  $Dq$ ,  $B'$ ,  $\beta$  and  $\beta\%$  have been calculated by using band-fitting equation given by Billing and Underhill.<sup>[20]</sup> The crystal field splitting energy ( $Dq$ ) value of  $880\text{ cm}^{-1}$ , is well within the range reported for most of the octahedral Co(II) complexes.<sup>[21]</sup> The Co(II) complex under present investigation possess Racha parameter  $B'$   $831\text{ cm}^{-1}$ . The Racha parameter  $B'$  is less than free ion value  $971\text{ cm}^{-1}$ , suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio ( $\beta$ ) for the present Co(II) complex is  $0.855\text{ cm}^{-1}$ . This is less than one, suggesting partial covalency in the metal ligand bond. The values  $Dq$ ,  $\beta\%$ , LFSE and  $\nu_2/\nu_1$  suggest the octahedral geometry for Co(II) complex.<sup>[22]</sup> The Cu(II) complex exhibits a broad asymmetric band in the region  $12765\text{-}16225\text{ cm}^{-1}$  with a maxima at  $14480\text{ cm}^{-1}$  in an distorted octahedral geometry.<sup>[23]</sup> The crystal field splitting energy ( $Dq$ ) and LFSE value of Cu(II) complex is obtained as  $1449\text{ cm}^{-1}$  and  $24.84\text{ kcalmol}^{-1}$  respectively.<sup>[24]</sup>

#### ***ESR Spectral data[Cu(C<sub>25</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]***

Electron spin resonance spectra (ESR), a branch of absorption spectroscopy, is the study of interaction between electron magnetic moments arising from systems possessing one or more unpaired electrons and an applied field. The room-temperature ESR spectrum of the [Cu(C<sub>25</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>] complex displayed a poorly resolved broad asymmetric signal with spin Hamiltonian parameters range  $g_{\parallel}=2.210$  and  $g_{\perp}=2.048$ . From the observed value given in table 4, it is clear that  $g_{\parallel} > g_{\perp} > 2.00277$  which suggests that the complex is present in distorted octahedral geometry consistent with the earlier reports.<sup>[25]</sup> The unpaired electron lies predominantly in the  $d_{x^2-y^2}$  orbital and  $g_{\parallel}$  value is below 2.3, hence  $g_{\parallel}=2.210$  indicates the covalent nature of the metal ligand bond.<sup>[26]</sup> For the present Cu(II) complex, the  $G=4.54$  indicates that there is no exchange interaction in the Cu(II) complex.

#### ***Thermal study of Zn( C<sub>25</sub>H<sub>18</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>)Cl complex***

The decomposition study of the [Zn( C<sub>25</sub>H<sub>18</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>)Cl] complex has been carried out. In order to get the additional information about the structure, evidence for the absence/presence of water molecules and the thermal behavior of the complex was studied by the thermogravimetric data.<sup>[27]</sup> The thermal decomposition of Zn(II) complex with probable assignments given in the table 5. In the thermogram of the [Zn( C<sub>25</sub>H<sub>18</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>)Cl], the thermal degradation of the complex starts with the cleavage at  $245.00^{\circ}\text{C}$ . The observed weight loss 6.32% for Cl<sub>2</sub> molecules is in agreement with the theoretical weight loss 6.38%. The second inflection point results in decomposition of the complex around  $445.00^{\circ}\text{C}$ , with

the loss of mass 47.61%. The observed weight loss 47.61% which accounts for the loss of  $[C_{13}H_{10}NCl]$ , is in agreement with the theoretical weight loss of 47.70%. On further heating the thermogram showed a weight loss 78.40% at  $600.00^{\circ}C$  due to loss of  $[C_{11}H_6O]$ . The theoretical weight loss at this temperature 78.69% is well agreement with the observed weight loss. Thereafter, the compound showed a gradual decomposition up to  $1000.00^{\circ}C$  and onwards due to the loss of organic ligand.<sup>[28]</sup> The weight of the residue left corresponds to the formation of zinc oxide. The thermal behavior of the complex is in agreement with the absence of coordinated water molecule.<sup>[29]</sup>

#### *X-ray powder diffraction studies of Zn(II) complex*

The X-ray powder diffraction pattern for the Zn(II) complex were show fourteen reflections in the range of  $5.722-77.946$  ( $2\theta$ ) arising from the diffraction of X-ray by planes of complex. The inter planar spacing ( $d$ ) values have been calculated from the position of intense peaks by using Bragg's relation.<sup>[30]</sup> The calculated spacing together with relative intensities with respect to most intense peaks has been recorded in table 6. The  $2\theta$  values with maximum intensity of the peak for the Zn(II) were found to be  $5.72292$  ( $2\theta$ ) which corresponds to  $d=15.430$   $\text{\AA}$ . The experimental values of  $2\theta$  and  $\text{Sin}^2\theta/\text{common factors}$  are recorded for each peak. The experimental  $d$ -spacing values are good agreement with the calculated values. The unit cell calculations have been done for cubic symmetry of the compound. The set of  $h^2+k^2+l^2$  values of the complex were found to be 1, 4, 10, 11, 14, 17, 20, 23, 32, 37, 40, 96, 107 and 159 which corresponds to the planes and the presence of forbidden number 23 and 159 confirms the hexagonal or tetragonal symmetry. From the above results the unit cell constants for hexagonal system were found to be  $a=b=c=15.430$   $\text{\AA}$  for the Zn(II) complex. The Zn(II) complex showed broad peak indicates the amorphous nature.<sup>[31]</sup>

#### *Antimicrobial activity*

The antimicrobial activity of synthesized ligand DCPAHNMA and its Co(II), Cu(II), Zn(II) and Cd(II) complexes were carried out by standard cup-plate method.<sup>[32]</sup> The antimicrobial activity results of the tested compounds are given in the table 7. Antibacterial activity against *E. coli* and *S. aureus* and antifungal activity against *A. niger* and *A. flavous* at  $1000\mu\text{g/ml}$  concentration were carried out.<sup>[33]</sup> The standard drugs *Streptomycin* and *Clotrimazole* were also tested for their antibacterial and antifungal activity at the same concentration under the conditions similar to that of the test compounds. The some factors such as solubility, conductivity, dipole moment, size of metal ions, stability constants of the complexes and their

magnetic moments are also reported to affect the microbial activity of the complexes.<sup>[34]</sup> The enhanced activity of the Schiff's base and its complexes were explained based on chelation theory. On chelation the positive charge of metal is partially shared with the donor atoms present in the ligand, there may be  $\pi$ - electron delocalization over the whole chelating. This increases the lipophilic character of the metal chelate and favors its penetration through the lipid layer of the bacterial membranes. Chelation is not only the criterion for antibacterial activity it is expected to be a function of steric, electronic and pharmacokinetic factors along with mechanistic pathway.<sup>[35]</sup> The obtained results of the synthesized compounds were compared with standard drugs. The Schiff's base DCPAHNMA show very low activity compared to both antibacterial and antifungal activity of standard drugs. For antibacterial activity of Co (II) and Zn (II) obtained good activity compared with ligand. For antifungal activity of Co (II), Cu (II) and Zn (II) obtained good activity compared with ligand.

## CONCLUSION

The elemental analysis, conductivity data, magnetic susceptibility, IR, <sup>1</sup>H NMR spectral observations, electronic spectral data reveals the mononuclear nature of all the synthesized complexes. The non-electrolytic behavior of the complexes confirms the presence of chloride within the coordination sphere. The Co(II) and Cu(II) complexes exhibit octahedral geometry, whereas Zn(II) and Cd(II) complexes exhibit tetrahedral geometry (figure 2 and 3). All the complexes show higher activity than the Schiff's base DCPAHNMA. The complexes of Co(II) and Zn(II) show good antibacterial activity compared with streptomycin standard drug and the complexes of Co(II), Cu(II) and Zn(II) show good antifungal activity compared with clotrimazole standard drug.

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