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Research Article

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Synthetic, spectral, magnetic and antibacterial studies of schiff base transition metal complexes of bis-[(1-(5-chloro-2-hydroxyphenyl) ethanone)-diaminopropane]

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ABSTRACT

A Schiff base bis-[(1-(5-chloro-2-hydroxyphenyl) ethanone)-diaminopropane] was synthesized via the reaction of 1-(5-chloro-2-hydroxyphenyl) ethanone) with 1, 3 diaminopropane and investigated by CHN elemental analyses, IR spectra, ^{1}H NMR. The infrared spectral data exhibited the main positions of functional groups present in the Schiff base. ^{1}H NMR data reveals that all signals belonging to the main functional groups in the Schiff base. The Schiff base complexes have been synthesized from CHPEDAP with Mn(II), Co(II), Cr(III), Ni(II), Cu(II), Zn(II) and Cd(II) ions and characterized by elemental analyses, spectral (^{1}H NMR, FT-IR and electronic spectra), magnetic susceptibility measurements. The Schiff base and the complexes have been screened for antibacterial activity against E. coli, S. typhy, S. aureus, P. aeruginosa and K. pneumonie bacterial species using Agar well diffusion method. The study shows that the Schiff base complexes show more antibacterial activity compared to ligand.

Key words: Schiff base, 1-(5-chloro-2-hydroxyphenyl) ethanone, diffuse reflectance, magnetic and antibacterial.

INTRODUCTION

Metal complexes of Schiff base have played a central role in the development of coordination chemistry [1]. Various Schiff base complexes have been widely studied because they have antimicrobial, anticancer, analgesic, anti-inflammatory, anti-fertility and herbicidal applications [2-3]. Chelating ligands containing N, S and O donor atom show broad biological activity and are of special interest because of the ways in which they are bonded to the metal ions [4]. It is known that existence of metal ions bonded to biologically active compounds may enhance their activities [5-8].

A novel Schiff base ligand derived from 1-(5-chloro-2-hydroxyphenyl)ethanone and 1, 3diaminopropane and its transition metal complexes with different metal acetates were prepared and their spectral properties were investigated [9]. Hence it was thought of interesting to study the reactions of this Schiff base [CHPEDAP] and its metal complexes with Mn(II), Co(II), Cr(III), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions. In this communication we report, the synthesis and characterization of new transition metal complexes that have been obtained. Antimicrobial activity of ligand and its complexes has also been reported.

EXPERIMENTAL SECTION

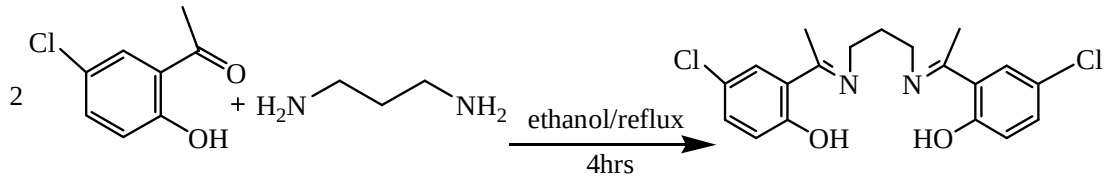
All the chemicals were of A.R. grade and used as received. 1-(5-chloro-2-hydroxyphenyl) ethanone was prepared by known methods [10-13]. The solvents were purified by standard methods [14].

The ^{1}H NMR spectra of ligand and elemental analysis were obtained from micro analytical unit. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}. The diffuse reflectance spectra of the complexes were recorded on Varian Cary-5E UV-visible spectrophotometer. The magnetic

moment measurement were made on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. The ligand and the metal complexes have been screened for antibacterial activity against *E. coli, S. typhy, S. aureus, P aeruginosa* and *K. pneumonie* bacterial species using cup plate agar diffusion method.

Synthesis of Schiff base ligand[CHPEDAP]

To the solution of 1-(5-chloro-2-hydroxyphenyl) ethanone (25ml, 0.02M) in ethanol, 1, 3 diaminopropane was added (2:1) drop wise and the reaction mixture was refluxed on a water bath for 4 hours. After cooling a pale yellow colored crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and m.p. It was also characterized by IR and ^{1}H NMR spectral studies. Yield of CHPEDAP: 61%.



1-(5-Chloro-2-hydroxy-phenyl)-ethanone

bis[1-(5-Chloro-2-hydroxy-phenyl)-ethanone -diaminopropane]

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm)

The ^{1}H NMR spectra of ligand were recorded in $CDCl_3$ at 300 MHz on a Bruker DRX-300 NMR spectrometer with TMS as an internal reference.

δ 6.75-7.04 (6H, m, Ar-H), 1.65 (2H, s(b) -OH), 2.34 (6H, s, $-CH_3$), 3.65-3.76 (4H, t, $-CH_2$).

Synthesis of metal complexes

All the metal complexes were prepared in a similar way by following method.

To a hot solution of ligand [CHPEDAP] (0.02M) in 25ml of ethanol a suspension of respective metal salts [acetates of with Mn(II), Co(II), Ni(II), Cr(III),Cu(II), Zn(II) and Cd(II)] was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-11 hours. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield: 45-50%.

Antimicrobial Activity testing

To access the antimicrobial activity of obtained compound Agar well diffusion method[15] was used. The antimicrobial activity was determined by using Mullar Hinton Agar[16]. A loop full culture of each test organism were inoculated in sterilized Nutrient agar and incubated overnight to obtain the broth culture. All the culture were inoculated on Mullar Hinton agar plate by using sterile cotton swab after swabbing well was punched on media and the different dilutions of the compounds were added in to the well with the help of dropper. After addition of sample the plate were incubated at 37^{o}C for 24 hours. After incubation period plates were examined and zone of inhibition were measured

RESULTS AND DISCUSSION

All the complexes are colored solids, air stable and insoluble in water and common organic solvents but found soluble in DMF and DMSO. The analytical data indicate 1:1 metal to ligand stoichiometry for all the complexes (Table 1).

Infrared Spectra (KBr, ν in cm^{-1}):

IR spectra of ligand and metal complexes shows *ν*(C=N) peaks at 1612 cm^{-1} and absence of C=O peak at around 1700-1800 cm^{-1} indicate Schiff base formation. The structurally important vibration bands of the free ligands and their metal complexes which are useful for determining the mode of coordination of the ligand are given in Table 2. The HCADP exhibits a medium intense band at 2922-2925 cm^{-1} due to the intramolecular hydrogen bonded (O-H) [17]. The absence of this band in the spectra of complexes indicates deprotonation of the phenolic group and coordination of the oxygen atom to the metal ion. The strong band in the region 1612–1651 cm^{-1} region may be assigned to the (C=N) (azomethine). In this region, the C=N band may not be pure and it may be associated with the aromatic (C=C) stretching band. Shifting of this band to a lower wave number by 20–40 cm^{-1} in the metal complexes in comparison to the free ligands indicates the coordination of azomethine nitrogen to the metal [18]. The

presence of new bands in the spectra of complexes in the range 515–679 cm^{-1} is attributed to M–N and M–O modes respectively [19].

Table 1: Analytical data of CHPEDAP and its Complexes

S.N.	Compound	Color	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)			
				M	C	H	N
1.	CHPEDAP	Pale Yellow	4	--	66.93 (66.99)	6.35 (6.48)	12.01 (12.11)
2.	[Mn(CHPEDAP)2H_2O]	Cairo Bazaar	9	10.98 (11.00)	52.72 (52.90)	4.00 (4.04)	5.52 (5.61)
3.	[Co(CHPEDAP)2H_2O]	Grayish Brown	4	11.59 (11.70)	52.46 (52.48)	3.95 (4.00)	5.41 (5.56)
4.	[Ni(CHPEDAP)2H_2O]	Sapphire Ice	4	11.50 (11.66)	52.48 (52.51)	4.00 (4.01)	5.45 (5.57)
5.	[Cr(CHPEDAP)2H_2O]	Graish Green	8	11.50 (11.66)	44.88 (45.44)	4.56 (4.62)	5.20 (5.33)
6.	[Cu(CHPEDAP)2H_2O]	Raven Song	11	12.48 (12.49)	52.00 (52.01)	3.86 (3.97)	5.42 (5.51)
7.	[Zn(CHPEDAP) 2H_2O]	Lemon Pie	10	12.70 (12.82)	51.72 (51.82)	3.80 (3.95)	5.38 (5.49)
8.	[Cd(CHPEDAP)2H_2O]	Day Break	9	20.13 (20.18)	47.28 (47.44)	3.56 (3.62)	5.00 (5.03)

Magnetic and Electronic study

The room temperature magnetic moment of Mn(II) complex is 5.98 B.M. suggesting octahedral geometry to the complex [20-22]. The Mn(II) complex shows three bands at 17301, 22988 and 25974 cm^{-1} . These spectral bands are assigned as to the $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G), $^6A_1 \rightarrow {}^4T_{1g}$ (^4G) and $^6A_1 \rightarrow {}^4T_{1g}$ (^4Eg) transitions, respectively towards octahedral structure around Mn(II) ion. The Co(II) complex shows magnetic moment 4.75 B.M. suggest high spin octahedral geometry for Co(II) complex . The electronic spectrum Co(II) complex shows three bands in the regions 7812, 10050 and 16722 cm-1 assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively in an octahedral environment around the cobalt ion. The magnetic moment of Ni(II) complex is 2.86 B.M. which lies in the normal range of octahedral Ni(II) complexes. The electronic spectrum of Ni(II) complex exhibits three bands at 10559 , 17543 and 25188 cm^{-1}. These bands may be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively in octahedral configuration [23-24]. The Cr(III)complex has magnetic moment value 3.79 B.M. which is in good agreement reported for octahedral Cr(III) complexes. The electronic spectrum of this complex exhibits three bands at 14947, 20000 and 31840cm^{-1} which indicates $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ transitions respectively. The observed magnetic moment of Cu (II) complex is found to be 1.89 B.M. suggesting distorted octahedral geometry. The Cu (II) complex shows bands at 17301, 19455 and 20920 cm-1 due to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively towards pseudo octahedral structure around Cu(II) ion [25]. The Zn(II) and Cd(II) complexes are found diamagnetic as expected from their electronic configurations and may have tetrahedral geometry [26].

Antibacterial Studies

All the compounds have been screen for antibacterial activity using cup plate agar diffusion method [27-29]. By measuring the inhibition zone in mm, the compounds were taken at a concentration of 1mg/mL using dimethyl sulphoxide (DMSO) as solvent. Amikacin (100µg/mL) was used as standard for antibacterial activity. The Schiff base and the complexes have been screened for antibacterial activity against *E. coli, S. typhi, S.aureus, P. aeruginosa* and *K. pneumonie* bacterial species**.** The complexes were found to be active against *E.coli, S. typhi* and *K. pneumonie* but showed comparatively moderate activity against *S.aureus* and *P. aeruginosa.*

Table 4: Antimicrobial activity ligand CHPEDAP and its complexes (mm)

S.N.	Compound	*E.coli*	*S.typhi*	*S.aureus*	*P.auruginosa*	*K.pneumonie*
1.	CHPEDAP	08	08	08	09	18
2.	Mn- CHPEDAP	10	15	11	13	08
3.	Co- CHPEDAP	-	10	12	15	20
4.	Ni- CHPEDAP	-	-	-	08	09
5.	Cr- CHPEDAP	12	08	-	08	18
6.	Cu- CHPEDAP	12	10	08	12	08
7.	Zn- CHPEDAP	-	15	15	08	20
8.	Cd- CHPEDAP	-	18	15	20	19
9.	Amikacin	28	28	23	25	22

Including the well diameter of 6 mm. Zone of inhibition in mm (15 or less) resistant, (16-20 mm) moderate and (more than 20 mm) sensitive.

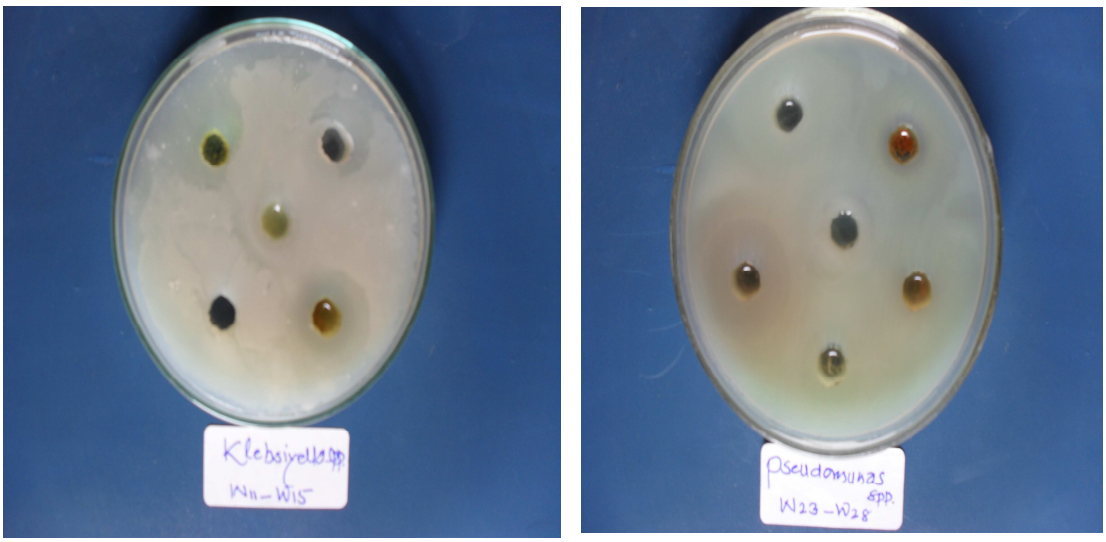


FIG: Photographs Showing the Antibacterial Activity Against *K. Pneumonia* And *P. Auruginosa*

CONCLUSION

From the observed IR spectra the ligand [CHPEDAP] coordinate in a tetradentate manner involving NNOO. The newly synthesized complexes namely [Mn(CHPEDAP)2H_2O], [Co(CHPEDAP)2H_2O], [Ni(CHPEDAP)2H_2O], [Cr(CHPEDAP)2H_2O] possess octahedral geometry, [Cu(CHPEDAP)2H_2O] shows distorted octahedral geometry while [Zn(CHPEDAP)2H_2O] and [Cd(CHPEDAP)2H_2O] possess tetrahedral geometry. All the Schiff base complexes show much more activity towards *K. pneumonie* and *P. auruginosa* and moderate to low activity towards other organisms. It was observed that the structural changes have marked effect on the sensitivity and sensitivity varies with organisms.

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