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Research Article

SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE METAL COMPLEXES DERIVED FROM 3, 5-DICHLOROSALICYLALDEHYDE AND 2-AMINO-4-CHLOROBENZOIC ACID

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ABSTRACT

The synthesis and spectroscopic studies of some metal complexes with bidenate schiff bases are reported here. These schiff base were derived by condensing aldehyde like 3,5-dichlorosalicylaldehyde with amino compound like 2-amino-4-chlorobenzoic acid. The complexes were characterized on the basis of elemental analysis, molar conductivity, spectral (^{1}H, IR,Esr and electronic) as well as thermal analysis. All the complexes exhibit octahedral geometry with 1:2 (metal : ligand) stiochiometry.

Keywords: Schiff base, 3,5-dichlorosalicylaldehyde, 2-amino-4-chlorobenzoic acid, Metal complexes.

INTRODUCTION

The co-ordination chemistry of schiff bases as mutidenate ligands gained much importance for more than two decades because of their uses as models in biological systems[1-4]. There is continuing interest in transition metal complexes of schiff bases because of the presence of both nitrogen and oxygen donor atoms in the backbone of these ligands, some of these complexes have been exhibit interesting physical and chemical activities. Schiff base have also been used for analytical purposes in the determination of metal ions and some schiff base derivatives [5-6]. Investigation on the complexing ability of metal with model ligands assit in the understanding of the function of the physiological systems. Among the complexing ligands, schiff bases have special interest due to their industrial and biological applications[7-11]. A large number of schiff bases and their metal complexes have been found to posses important biological and catalytic activity[12-13], Due to their great flexibility and diverse structural aspects, wide ranges of schiff base have been synthesized and their complexation behavior studied[14].

These results motivated us to prepare the complexes and characterize then making the present paper that deals the preparation of Schiff base ligand and its metal complexes characterize by the elemental analysis, magnetic susceptibility, molar conductivity measurements, electronic spectra, infrared, ^{1}H NMR spectrum to determine the mode of co-ordination and geometry.

MATERIAL AND METHODS

Chemicals

All chemicals like 3,5-dichlorosalicylaldehyde, 2-amino-4-methyl phenol, metal chloride salts and solvents used were reagent grade (Alfa aesar/Avra/spectrum) products and were used as such without further purifications.

Synthesis of Schiff base (DABC)

The Schiff base was prepared by condensation of 3,5-dichlorosalicylaldehyde (0.01 mol) with 2-amino-4-chlorobenzoic acid (0.01 mol) and the mixture was refluxed for 2-3hrs. The resulting solution was kept under 0 ºC. The product was obtained and collected by filtration washed several times with ethanol and recrystallized from hot ethanol and dried in a vacuum desiccator. The melting point of the ligand was found to be 150 ºC. The color is red.

Preparation of the complexes

The complexes of Co(II), Ni(II), Cu(II), Zn(II) were prepared by refluxing respective metal chloride in ethanolic solution of ligand (1:1). The resulting mixture was refluxed for 2-4 hrs at 70-80 ºC. On cooling colored solid product was collected by filtration and then washed several times with diethyl ether until the washing become colorless. The product was dried in air and stored in desiccators over anhydrous $CaCl_2$ under vacuum.

Experimental analysis

Elemental analysis **(**C, H and N) was carried out on elemental analyzer Flash EA 112 series. Electronic spectra of the metal complexes in DMSO were recorded on a Perkin Elmer Lambda 35 spectrophotometer. Infrared spectra (4000 – 400 cm^{-1}) of the ligands and metal complexes were obtained using KBr discs, on perkin elmer RX1. Magnetic susceptibility measurements of the complexes were carried out by Gouy balance using $Hg[Co(CNS)_4$ as calibarant. The molar conductance measurements were carried out in DMSO (10^{-3} M) using Digisun Electronic digital conductivity meter DI-909 Having dip-type cell calibrated with KCl . The ^{1}H NMR spectra were recorded on Mercury Plus 300 MHz NMR spectrometer by employing TMS on internal standard.

RESULTS AND DISCUSSION

All the metal complexes are colored, solid, stable at room temperature and non – hygroscopic in nature. The analytical ans physical data of ligand and their metal complexes are recorded in table 1. The metal complexes exhibit 1:2 stoichiometry.

Infrared spectra of the Schiff base and its complexes

The infrared frequencies of the schiff base ligand and its complexes are given in figure 1. The Infra-red spectrum of ligand presents a broad peak at 3062cm^{-1} is corresponding to the OH group and shifted to the lower frequencies in the complexes which shows the co-ordination – OH group to the metal ion shown in table 2. The γCH=N frequency in the ligand at 1612cm^{-1} is also shifted to lower frequency shows that the co-ordination to the metal ion. A band at 1665cm^{-1} is assigned to γC=O stretching frequency in the spectrum of free schiff base which is also shifted to lower frequency ranging from 1662-1610cm^{-1} in all the metal complexes. This indicates the involvement of oxygen atom of carbonyl group in the metal ions. In the low frequency region, bands at 600 - 800cm^{-1} range are assigned to M – N and bands at 400 – 500cm^{-1} range are assigned to M – O.

Table 1: Analytical data and physical data of the ligand and its complexes

Compound	Molecular formula	Mol. Weight	Color	Melting point	Elemental analysis Calculated/(Observed)			Ω cm^{-1}
					C	H	N	
Ligand	$C_{14}H_8Cl_3NO_3$	344	Red	150	49.02 (48.80)	2.45 (2.34)	4.20 (4.06)	-
DABC.Co	$[Co(C_{14}H_6Cl_3NO)_2]Cl_2$	818.99	Light pink	>300	41.06 (42.00)	1.97 (2.05)	3.42 (3.72)	142
DABC.Ni	$[Ni(C_{14}H_6Cl_3NO)_2]Cl_2$	818.75	Light green	>300	41.07 (42.06)	1.97 (2.10)	3.42 (3.67)	102
DABC.Cu	$[Cu(C_{14}H_6Cl_3NO)_2]Cl_2$	823.61	Olive green	298	40.83 (41.02)	1.96 (2.02)	3.40 (3.48)	117
DABC.Zn	$Zn[(C_{14}H_6Cl_3NO)_2]Cl_2$	825.45	Light yellow	290	40.74 (41.23)	1.95 (2.11)	3.39 (3.95)	122

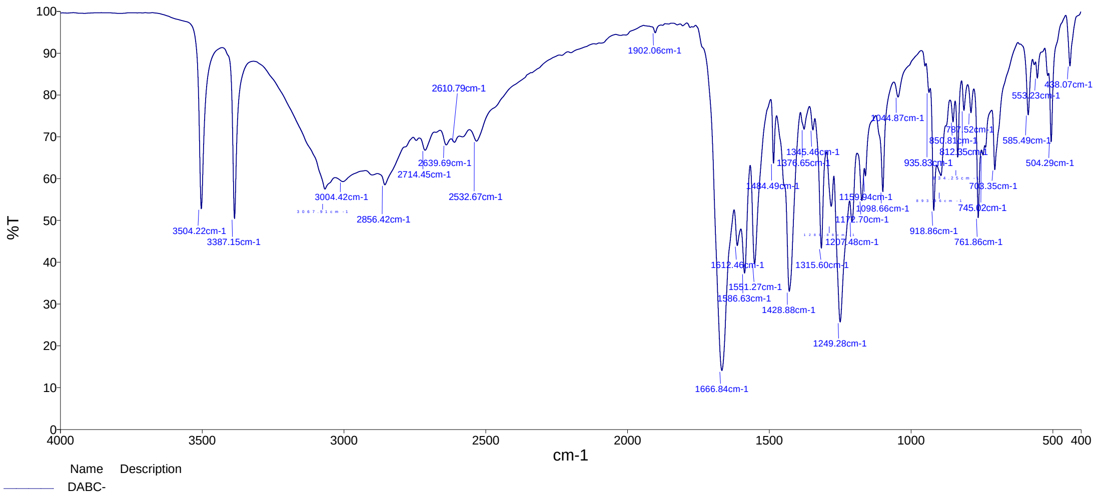

Fig. 1: IR spectrum of ligand - DABC

Table 2: Infrared spectra of the Schiff base and its complexes

Compound	γ_{OH}	$\gamma_{C=N}$	$\gamma_{C=O}$	$\gamma_{C\text{-}O}$	$\gamma_{M\text{-}N}$	$\gamma_{M\text{-}O}$
Ligand (DABC)	3387	1612	1666	1376	-	-
DABC.CoCl$_2$	3306	1585	1613	1302	609	467
DABC.NiCl$_2$	3302	1587	1612	1301	611	474
DABC.CuCl$_2$	3136	1595	1639	1335	671	519
DABC.ZnCl$_2$	3298	1586	1614	1301	663	468

Electronic spectra

- The spectrum of Co(II) complex showed absorptions 19,230 cm^{-1} assigned to and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transitions. The cobalt(II) complex shows a magnetic moment of 4.88BM at room temperature. This high value suggests that the magnetic moment and co-ordination number six for the central cobalt(II) ion and octahedral geometry[15].
- The electronic spectra of the Nickel(II) complex exhibit absorption bands at 18,348 cm^{-1} and 25,000 assigned to $^3A_{2g} \longrightarrow {}^4T_{1g}(P)$, $^3A_{2g} \longrightarrow {}^4T_{1g}(F)$ transitions respectively in an octahedral geometry[16]. The value of magnetic moment 3.12BM may be taken as additional evidence for its octahedral structure.
- The electronic spectra of Copper(II) complex exhibit absorption band at 17,921cm^{-1} mainly due to$^2E_g \longrightarrow {}^2T_{2g}$ transition suggesting octahedral geometry 1.72BM suggestive octahedral nature of the complex[17].

^{1}HNMR and Zn-NMR

The ^{1}HNMR spectrum of the ligand and Zn complex in DMSO shows the following signals given in Table 4. The proton NMR spectrum of the ligand is shown in figure. The signal due to azomethine proton appeared as singlet at 7.68ppm. Another singlet corresponding to one proton is observed in the range 14.0-15.98ppm, due to phenolic –OH group is downfield in the Zn complex. The phenyl multiplet is seen at 6.6-7.0ppm are seen downfield in complex, whereas the acidic –OH is seen at 9.2ppm is also downfield in Zn complex.

ESR spectra of Cu(II) complexes

ESR spectral studies of Cu(II) complex provide information of the metal ion environment is shown in figure 2. The ESR spectra of Cu(II) complex shows intense band with average g = 2.1550 at room temperature. The values of average g value and shape of ESR signals suggests distorted octahedral co-ordination around Cu(II) ions.

Table 3: Electronic data of Schiff base and its complexes

Compound	UV-Visible bands (cm^{-1})	μ eff (BM)
Ligand (EAB)	-	-
Co(II) complex	19,230	4.88
Ni(II) complex	18,348;25,000	3.12
Cu(II) complex	17,921	1.78
Zn(II) complex	-	-

Table 4: ^{1}HNMR of the Schiff base and its Zn(II) complexes

Compound	-CH=N (δppm)	Aromatic protons (δppm)	-OH	-COOH
Ligand	7.68	6.6-7	14.3	9.2
Zn-complex	8.08	6.8-7.4	14.8	10.2

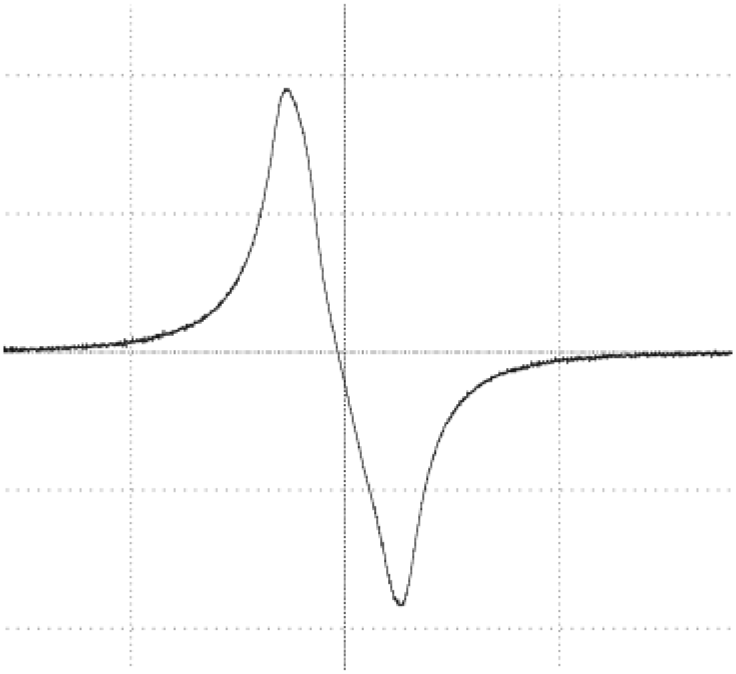

Fig. 2: ESR spectrum of Copper complex

Thermal analysis

In the present investigation heating rates were suitably controlled at 10^0C min^{-1} under nitrogen atmosphere and the weight loss was measured from the ambient temperature up to 800^0C. In the complex of $DABC.CoCl_2$ no weight loss between 60 - 120^0C shows that no water molecule present inside the co-ordination. The maximum and gradual weight loss in the range of 300 - 550^0C is attributable to decomposition of ligand moiety. The residue at above 550^0C indicates non-volatile metal component present in the complex.

Antibacterial studies

The synthesized Schiff base and their corresponding metal complexes were screened against Staphylococcus, Escherischiacolli to assess their potential as antimicrobial agent by diffusion method.

The diffusion method requires filter paper disc, the medium used is muller-hinton agar and diameter of inhibition zone is visually read at 24hour after incubation at 37ºC. The compounds are added on to the filter paper containing this medium. Sterile discs of five millimeter width were impregnated with 10 ml of various compounds of various concentrations of 50 µg/ml, 100 µg/ml and 200µg/ml respectively. Prepared discs were placed onto the top layer of the agar plates and left for 30 minutes at room temperature for compound diffusion. The dishes were incubated for 24 h at 37ºC and the zones of inhibition were recorded in millimeters and the experiment was repeated twice. Chlorophenicol was used as standard. DMF was used as solvent control. The zones of inhibition based upon zone size around the discs were measured. The measured zone of inhibition against the growth of various micro orangism is listed in table 5. It is found that the metal complexes have higher antibacterial activity than the free ligand. Hence on complexation increases the microbial activity. Such increased activity of metal complexes were explained on the basis of complexation.

Table 5: Growth inhibition zone of microbes in mm

Sample	**Organism**	**Zone of inhibition (cm)**		
		A(50 µg/ml)	**B(100 µg/ml)**	**C(200 µg/ml)**
DABC	*E.coli*	0.5	0.6	0.8
DABC	*S.aureus*	0.6	0.7	0.9
Co-DABC	*E.coli*	0.6	0.7	1.0
Co-DABC	*S.aureus*	0.6	0.7	1.0
Cu-DABC	*E.coli*	0.5	0.7	0.8
Cu-DABC	*S.aureus*	0.6	0.7	0.8
Ni-DABC	*E.coli*	0.5	0.6	0.8
Ni-DABC	*S.aureus*	0.7	0.8	1.2
Zn-DABC	*E.coli*	0.5	0.7	0.8
Zn-DABC	*S.aureus*	0.6	0.8	1.0

CONCLUSION

The DABC ligand and its metal complexes of Co(II), Ni(II), Cu(II), Zn(II) were synthesized and characterized. The structural data established on the basis of elemental analysis (C, H, N), infrared, ultra-violet, ^{1}HNMR, magnetic susceptibility of complexes, TGA, ESR were recorded and discussed. Biological studies of these complexes reveal that these complexes show better activity compared to the ligand.

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