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N, O Donor Schiff Base Polymeric Complexes : Synthesis, Characterization, and Antimicrobial Studies

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ABSTRACT

With a Schiff base ligand created from the condensation of 2,4-dihydroxy acetophenone and p-phenylene diamine, a number of novel polymeric complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) were created. These complexes were then characterised by elemental analysis, IR, and NMR spectrum data. The Schiff base and its polymeric complexes have been investigated for its antibacterial properties.

Keywords : Elemental Analysis, IR, NMR Spectrum Data, Schiff Base, Polymeric Complexes

I. INTRODUCTION

Imines-based compounds have been widely used in chemical synthesis1; several2 of these molecules exhibit considerable biological activity. Schiff base ligands have drawn greater attention in the past ten years, mostly because of their numerous uses in the field of catalysis 3 as well as their antibacterial4 and antifungal5 properties.

Due to their ease in forming stable complexes with the majority of transition metal ions, schiff bases are crucial in inorganic chemistry.6 Since many of these complexes may act as models for biologically significant entities, the area of bioinorganic chemistry has grown and this has boosted interest in Schiff base complexes. For fungicidal, fungistatic, bactericidal, and bacteriostatic activity, Schiff base metal complexes were studied7.

In the present work, the structures of synthesized bis-bidentate ligand and its polymeric metal complexes with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions have been characterized by various physicochemical techniques, namely, elemental analysis and IR and NMR spectral studies, and were also screened for antibacterial activities against some species of pathogenic bacteria.

II. EXPERIMENTAL

Materials and Methodology

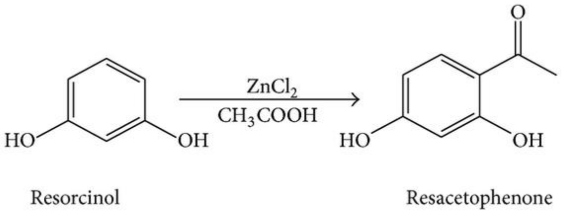
All the chemicals used were of analytical grade. Solvents used were of analytical grade and purified by standard procedures.

Synthesis of Ligand

Synthesis of ligand was carried out in two steps. The first step involved the preparation of 2,4-dihydroxy acetophenone while the second step involved the preparation of ligand.

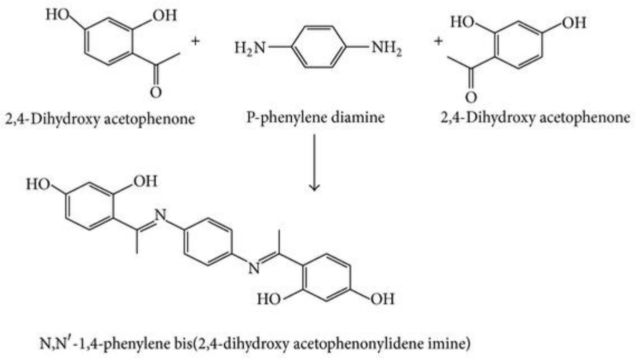
Synthesis of 2,4-Dihydroxy Acetophenone

Anhydrous $ZnCl_2$ (70 g) was dissolved in glacial acetic acid (65 mL) in a 500 mL beaker. The solution was heated on wire gauge up to 140°C, and resorcinol (45 g) was added slowly with constant stirring. The temperature then raised up to 152°C, and the solution began to boil. It was allowed to stand for 30 min and diluted with HCl (50%). The resulting orange colored solid was collected, washed with dil. HCl (200 mL), and crystallized from water. The yield was found to be 80%, and the melting point was found to be 144°C. Scheme 1, represents its synthesis.



Synthesis of N,N'-1,4-Phenylene Bis(2,4-Dihydroxy Acetophenonylidene Imine)

2,4-dihydroxy acetophenone (0.05 M, 7.6 g) and p-phenylene diamine (0.025 M, 2.7 g) were placed in round bottomed flask in distilled ethanolic medium, and few drops of acetic acid were added as a catalyst. The reaction mixture was refluxed on sand bath for 1 hr and then poured on crushed ice to get yellow-orange crystals of Schiff base ligand N,N'-1,4-phenylene bis(2,4-dihydroxy acetophenonylidene imine). The precipitated crystals of Schiff base were filtered and recrystallised with aqueous ethanol and dried. The yield was found to be 65%, and the melting point was found to be 125°C. Scheme 2, represents synthesis of ligand.



Synthesis of Polymeric Complexes

N,N'-1,4-Phenylene bis (2,4-dihydroxy acetophenonylidene imine) (1 mol) was dissolved in distilled methanol and then added to the metal acetate (1 mol) in distilled methanol. The reaction mixture was then refluxed on water bath for 2 hr and kept at room temperature for overnight. The precipitated complex was then filtered under suction and washed successively with hot water and methanol to remove unreacted ligand and metal acetate if any present and then dried.

III. RESULT AND DISCUSSION

The stoichiometry of the ligand and its polymeric complexes were confirmed by their elemental analysis.- The elemental analysis of the ligand and its metal complexes show good support with the proposed structures of the ligand8 and its complexes and have been reported in Table 1.

Table 1. Analytical and physical data of the compound studied

Compound	Colour	Empirical formula	Mol. Wt	C Cal. (found)	H Cal. (found)	N Cal. (found)
L	Orange	$C_{22}H_{20}N_2O_4$	376.41	70.13 (70.15)	5.31 (5.35)	7.43 (7.39)
Mn(II)L $2H_2O$	Brown	$C_{22}H_{18}N_2O_4Mn\cdot 2H_2O$	465.34	56.73 (56.80)	4.72 (4.80)	6.01 (6.14)
Co(II)L $2H_2O$	Bluish black	$C_{22}H_{18}N_2O_4Co\cdot 2H_2O$	469.34	56.24 (56.33)	3.68 (3.92)	5.96 (5.98)
Ni(II)L $2H_2O$	Grey	$C_{22}H_{18}N_2O_4Ni\cdot 2H_2O$	469.10	56.27 (56.40)	4.68 (4.99)	5.96 (5.99)
Cu(II)L	Shining black	$C_{22}H_{18}N_2O_4Cu$	437.95	60.28 (60.35)	4.11 (4.20)	6.39 (6.46)
Zn(II)L	Whitish	$C_{22}H_{18}N_2O_4Zn$	439.81	60.02 (60.08)	4.09 (4.16)	6.36 (6.39)

Infrared Spectral Analysis of Schiff Base Ligand

IR spectra of ligand L show an intense band at 3299 cm^{-1} indicating the presence of phenolic OH group. This sharp band is absent in the spectra of complexes indicting that the phenolic OH group is deprotonated and involved in coordination with metal[9] .

The ligand shows an intense band due to ν (C=N) of azomethine group at around 1608 cm^{-1} consistent with the iminic absorption of free Schiff base.[10] The band for phenolic C–O stretching is seen at 1516 cm^{-1}. The medium intense band at 3302–3362 cm^{-1} which is the characteristic of strong hydrogen bonded O–H vibration shows existence of intramolecular H bonding between phenolic oxygen and azomethine nitrogen.[11]

Infrared Spectral Analysis of Schiff Base Complexes

The band for the azomethine group shifts to a lower energy in all complexes, showing that the metal ion and azomethine nitrogen are coordinated[12]. This finding is further reinforced by the emergence of a few additional bands in the spectra of complexes, notably (M-N) at 630-667 cm-1 and (M-O) at 410-491 cm-1 [13]. Lattice water may be present in the complex broad band between 3200 and 3600 cm1. The IR bands caused by phenyl ring systems between 1520 and 1566 cm1, which are essentially unaffected in the compound, have also been classified as aromatic (C=C) in addition to the bands mentioned above. The establishment of the C-O-M bond causes the band for phenolic (C-O) stretching to move noticeably (17–25 cm−1) to a higher wave number in all complexes.[14] In complexes, the band for intramolecular H bonding is absent, indicating that the phenolic -OH group has been deprotonated and is in coordination with the metal.[15] Bands at 745-780 cm1 may be due to the coordinated water's wagging and rocking motions. The absence of this band in the spectra of CuL and ZnL indicates that coordinated water is not present.[16]

The significant shift of the free ligand's (C=N) stretching band to the side with lower wave number and the increased wave number of the phenolic ligand's (C-O) stretching band in complexes lead to the conclusion that the ligand's bond to the metal ion is formed by azomethine nitrogen and phenolic oxygen. Table 2 is a table of IR data.[17]

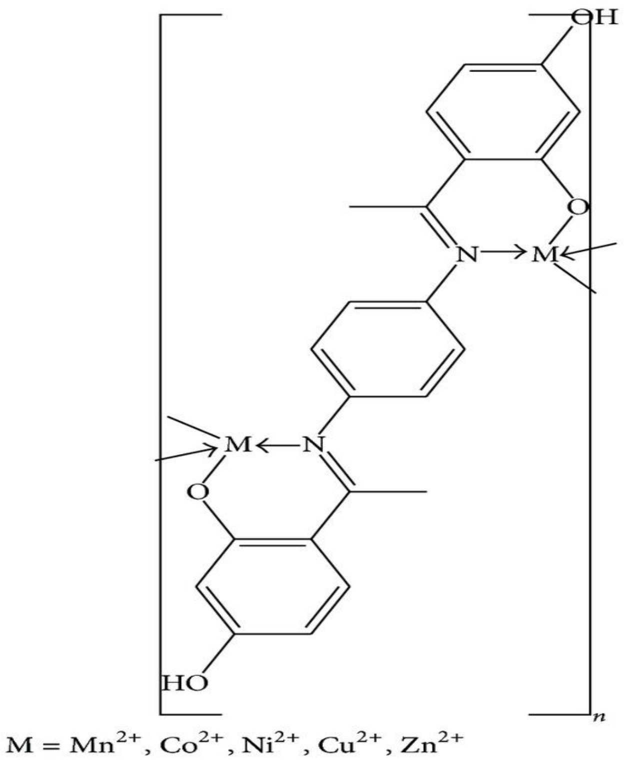
Table 2. Infrared absorption frequencies (cm^{-1}) of ligand and its polymeric complexes.

S. number	Compound code	(Ar–OH)	(C=N)	(M–N)	(M–O)	(C–O)
1	L	3302, 3362	1608	—	—	1516
2	MnL	—	1605	630	410	1560
3	CoL	—	1590	565	412	1520
4	NiL	—	1585	667	428	1566
5	CuL	—	1604	650	422	1532
6	ZnL	—	1603	667	491	1522

H NMR Analysis of Ligand and Its Polymeric Complexes

1H NMR spectra of ligand at 400 MHz in DMSO exhibit a singlet at ppm for phenolic –OH and multiplets in the aromatic region to 7.5 ppm, corresponding to benzene rings.[18] The NMR signal at ppm as a sharp and singlet peak is due to –CH_3 proton.[19]

1H NMR spectra of complexes at 400 MHz in DMSO show no peak corresponding to the presence of phenolic –OH, thus indicating removal of hydrogen and coordination of metal to ligand through phenolic oxygen.[20] Peaks corresponding to benzene rings are also present in spectra of complexes without any change. Retention of peaks in aromatic region without any formal change indicates the preservation of the formal structure of ligand without any deformation. The structure of polymeric compounds has been shown in Figure 1.



Antimicrobial Activity of Ligand and Its Polymeric Complexes.

Synthesized Schiff bases and their corresponding mixed ligand metal complexes were screened against E. coli, S. aureus, B. subtilis, and P. aeruginosa to assess their potential as antimicrobial agent by well-diffusion method also called as agar ditch method. The zones of inhibition based upon zone size were measured. The measured zones of inhibition against the growth of various microorganisms have been listed in Table 3.[21]

Table 3
Minimum inhibitory zones for ligand and complexes.

Sample	Conc. (g)	Zone of inhibition in mm against			
		S. aureus	E. coli	B. subtilis	P. aeruginosa
L	0.25	12	11	10	11
	0.5	14	12	12	13
	0.75	15	13	15	15
	1.0	16	15	20	18
MnL	0.25	19	19	22	18
	0.5	23	21	25	22
	0.75	25	24	27	26
	1.0	28	25	30	31
CoL	0.25	14	—	12	13
	0.5	17	—	14	21
	0.75	19	15	17	25
	1.0	22	20	19	27
NiL	0.25	12	19	12	16
	0.5	15	21	16	21
	0.75	18	23	21	23
	1.0	20	24	24	26
CuL	0.25	14	20	14	18
	0.5	16	23	17	20
	0.75	19	25	19	22
	1.0	22	27	24	24
ZnL	0.25	13	11	23	11
	0.5	16	12	27	22
	0.75	—	14	31	33
	1.0	25	17	36	33

From Table 3 it has been found that all complexes show greater antibacterial activity than that of ligand.[17] CuL and MnL show very good results against all bacterial strains. Furthermore ZnL shows very good antibacterial activity against B. subtilis.

IV. CONCLUSION

From the characterization of ligand and complexes using CHN analysis, IR and NMR structures of ligand and complexes were proposed. Measurements of inhibition zones of ligand and complexes at different concentrations show that all complexes have enhanced bactericidal activity more than ligand.

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