

Studies on Mn(II), Co(II), Ni(II) and Cu(II) Complexes of Schiff Bases Derived from Furfurylimine with Benzaldehyde and Phenyl Glyoxal

ADESH KUMAR, SHANU DAS* and RAJESH DHAKAREY

Department of Chemistry, Institute of Basic Sciences

Dr. B.R.A. University, Agra-282 005, India

E-mail: shanu_das@rediffmail.com

All the complexes of Mn(II), Co(II), Ni(II) and Cu(II) with Schiff bases furfurylimine of benzaldehyde (FIB) and furfurylimine of phenyl glyoxal (FIPG) were synthesized and characterized on the basis of elemental analysis, magnetic moment values, NMR, mass, infrared and electronic spectral studies. The infrared spectral data suggests that the ligand coordinates *via* furan and glyoxalic oxygen and azomethine nitrogen. The coordination of chloride ion were also found in the complexes. The magnetic moment values and electronic spectral data indicate six coordinate geometry around the metal ion. In the case of Cu(II) complexes ESR spectral studies have also been taken place. The biological screening was carried out against *P. aeruginosa*, *A. niger* and *A. flavous* suggests strong antimicrobial activities.

Key Words: Furfurylimine, Benzaldehyde, Phenyl glyoxal, Schiff bases, Metal(II) complexes.

INTRODUCTION

In recent years, the complexes of Schiff bases of transition metal have been amongst the widely studied on account of the stereochemical significance as well as agricultural and industrial application of the ligands and their metal complexes¹⁻⁴. Most of the available reports on Schiff base complexes pertain to those involving aromatic Schiff bases have been recently appeared on the complexes of heterocyclic Schiff bases^{5,6}. These complexes possess antimicrobial⁷, antiviral, insecticidal, herbicidal, antitumour⁸ and anticarcinogenic⁹ activities. These complexes have also used as oxygen absorbent, perfumery and in the cosmetic industry. The present work deals with the synthesis and characterization of two new Schiff bases namely furfurylimine of benzaldehyde and furfurylimine of phenyl glyoxal and their Mn(II), Co(II), Ni(II) and Cu(II) complexes.

EXPERIMENTAL

Preparation of Schiff bases

Synthesis of FIB: The Schiff base was prepared by refluxing calculated quantities of furfurylamine (10 mmol in 20 mL ethanol) and benzaldehyde (10 mmol in 20 mL ethanol) for about 4 h. The refluxing material was allowed to cool overnight, when a yellowish red coloured liquid was obtained. It was washed with ethanol and dried under vacuum.

Synthesis of FIPG: The phenyl glyoxal was prepared by reported method¹⁰. The Schiff base was prepared by refluxing a solution of phenyl glyoxal (25 mmol on 50 mL ethanol) on a water bath for 6 h. Excess of solution was removed by distillation. The residue was kept overnight then washed with ethanol and dried in air.

Preparation of metal complexes: To the ethanolic solution of ligand (5 mmol, 20 mL ethanol), a solution of metal(II) chloride (2.5 mmol, 20 mL ethanol) was added. The reaction mixture was refluxed for 5 h. The excess of solvent was removed under vacuum and the residue was washed with ethanol and water mixture and finally with ether then dried over fused CaCl₂.

Physical measurements: The magnetic susceptibility measurements of the synthesized complexes were carried out at room temperature on Guoy's balance using CuSO₄·5H₂O as calibrant and diamagnetic corrections were made using Pascale's constant. The infrared spectra were recorded at Perkin Elmer spectrophotometer at RSIC, IIT, Chennai. The electronic spectra of the complexes were recorded at room temperature. For micro analysis C, H, N, analyzer was used. The measurements were done at RSIC, Chandigarh. The percentage of metal was determined by standard methods and on atomic absorption spectrophotometer at Hindustan Zinc Ltd. Agucha Mines, Bhilwara. The NMR spectra were recorded on Bruker-300 Ultrashield-300 MHz NMR spectrometer.

RESULTS AND DISCUSSION

All the newly synthesized complexes were found soluble in DMF and DMSO. The analytical data were found in support with the calculated values. The Mn(II) complexes shows magnetic moment 5.2-5.4 BM which was found very close to the spin only value for high spin complexes. The Co(II) complexes having magnetic moment of 4.2-4.4 BM which was quite higher than the spin only value for octahedral complexes. The Ni(II) complexes shows the magnetic moment value of 2.7-3.0 BM which suggests a slight distortion in the octahedral symmetry of these complexes. The magnetic moment value of 1.7-1.8 BM in the case of Cu(II) complexes was also suggestive of a slight distortion in octahedral geometry. The analytical data of the complexes are listed in Table-1.

TABLE-1
 PHYSICAL PROPERTIES, MAGNETIC MOMENT VALUES AND ANALYTICAL DATA OF
 SCHIFF BASES AND THEIR COMPLEXES

Compound	Physical properties			Analytical data %: Found (Calcd.)					μ_{eff} (BM)
	m.p. (°C)	State	Colour	C	H	N	M	Cl	
$\text{C}_{12}\text{H}_{11}\text{NO}$	185	Solid	Yellowish red	77.84 (77.80)	5.93 (5.98)	7.50 (7.56)	–	–	–
$\text{C}_{13}\text{H}_{11}\text{NO}_2$	213	Solid	Brown	73.15 (73.21)	5.12 (5.20)	6.50 (6.57)	–	–	–
$\text{Mn}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	255	Solid	Chocolate	60.04 (59.86)	4.70 (4.62)	5.92 (5.83)	11.40 (11.44)	14.80 (14.76)	5.43
$\text{Mn}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	125	Solid	Grey	58.20 (58.10)	4.10 (4.13)	5.30 (5.22)	10.20 (10.25)	13.25 (13.20)	5.29
$\text{Co}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	123	Solid	Dark green	60.00 (59.49)	5.62 (5.57)	5.80 (5.78)	12.02 (12.170)	14.70 (14.64)	4.25
$\text{Co}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	198	Solid	Green	57.80 (57.75)	4.15 (4.10)	7.20 (7.18)	10.80 (10.91)	13.16 (13.12)	4.43
$\text{Ni}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	303	Solid	Sandy gray	53.72 (53.60)	4.15 (4.12)	10.50 (10.43)	10.80 (10.92)	–	2.76
$\text{Ni}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	–	Viscous	Yellowish green	52.68 (52.60)	3.80 (3.73)	9.52 (9.45)	10.55 (10.61)	–	2.95
$\text{Cu}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	143	Solid	Yellowish green	59.00 (58.91)	4.60 (4.53)	5.82 (5.73)	12.92 (12.990)	14.62 (14.50)	1.78
$\text{Cu}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	115	Solid	Browinish black	57.30 (57.26)	4.12 (4.03)	5.10 (5.14)	11.56 (11.66)	13.15 (13.01)	1.76

NMR Spectral studies: ^1H NMR: DMSO was used as a denaturated solvent to measure the ^1H NMR spectra of the ligands. The sharp doublet was observed at δ 6.57, δ 6.59 ppm and a singlet at δ 6.89 ppm due to heterocyclic proton of furan ring. A sharp singlet at δ 5.81 ppm is due to the presence of $-\text{CH}_2$ protons attached with the heterocyclic system. In the spectra of Schiff base the aromatic proton multiplet was observed between δ 7.36-7.46 ppm^{10,11}.

^{13}C NMR: DMSO was used as a denaturated solvent to measure ^{13}C NMR spectra of the ligands. The ^{13}C NMR spectra of the ligand FIPG shows a peak at δ 207.9 ppm due to aromatic carbonyl group. This peak is not observed in case of FIB. The spectrum of both the ligands shows a peak at δ 155.8 ppm which may be attribute to the $\text{CH}=\text{N}$ group. The spectrum of the ligands shows a cluster of peaks in the region δ 119.6-132.1 ppm due to five aromatic carbons (C-H).

Infrared spectral studies: The infrared spectral data of the Schiff bases and their complexes are listed in Table-2. The spectra shows a band about 1610 cm^{-1} in the ligands which may be assigned as $\nu(\text{CH}=\text{N})$. This band shifted to lower frequency about 20 cm^{-1} on complexation suggesting the involvement of imino nitrogen in coordination¹². The infrared spectra of ligands shows medium bands at 1230 cm^{-1} due to $\nu(\text{C-O-C})$ group of the furan ring are resolved into a single peak in the lower frequency about 1190 cm^{-1} in all the complexes¹³. The bands observed at 1655 cm^{-1} assignable to glyoxalic $\nu(\text{C}=\text{O})$ in the Schiff base FIP shifted to lower region in the spectra of complexes at 1645 cm^{-1} indicated that carbonyl and furan oxygen atom participate in the chelation¹⁴. Another important feature of the infrared spectrum of these complexes was the appearance of the bands due to $\nu(\text{M-Cl})$ ¹⁵, $\nu(\text{M-O})$ and $\nu(\text{M-N})$ in lower frequency region at about 280, 410 and 600 cm^{-1} in the complexes.

TABLE-2
IMPORTANT IR FREQUENCIES (cm^{-1}) OF SCHIFF BASES
AND THEIR COMPLEXES

Compound	Assignments					
	$\nu(\text{C}=\text{O})$	$\nu(\text{CH}=\text{N})$	$\nu(\text{C-O-C})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$
$\text{C}_{12}\text{H}_{11}\text{NO}$	–	1610 m	1230 w	–	–	–
$\text{C}_{13}\text{H}_{11}\text{NO}_2$	1655 b	1610 s	1230 w	–	–	–
$\text{Mn}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	–	1595 w	1195 w	600 s	410 b	280 w
$\text{Mn}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	1650 b	1570 w	1190 m	600 b	430 w	270 w
$\text{Co}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	–	1600 s	1170 s	600 m	425 w	300 s
$\text{Co}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	1645 b	1560 m	1200 s	600 b	415 w	290 s
$\text{Ni}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	–	1570 m	1200 w	600 w	480 m	–
$\text{Ni}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	1610 s	1585 m	1180 s	605 b	425 s	–
$\text{Cu}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	–	1635 m	1245 m	600 b	450 b	280 s
$\text{Cu}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2\text{Cl}_2$	1680 m	1590 m	1210 s	690 b	425 b	270 s

Electronic spectral studies: The electronic spectral data of all the complexes are listed in Table-3. The electronic spectra of all the complexes were recorded in solution shows a number of bands of the appropriate energy level for octahedral complexes. The various crystal field and ligand field parameters were calculated using Konig's numerical method and Tanabe-Sugano diagram treatment method for octahedral complexes. NSH theory was also applied on Ni(II) complexes. The electronic spectra of Mn(II) complexes shows bands at 19540-19920, 20420-20710, 250203-25525 and 26532-26715 cm^{-1} corresponding to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^6A_{1g} \rightarrow {}^4E_g$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$, respectively suggesting octahedral symmetry in the complexes¹⁶. The Co(II) complexes shows bands at 7800-9760, 16120-16225 and 19525-19910 cm^{-1} due to transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(v_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(v_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)(v_3)$, respectively supports octahedral symmetry, various ligand field parameters 10 Dq, B, C, β , F2, F4, δv %, *etc.* have also been calculated using Konig's method¹⁷. The spectra of both the complexes of Ni(II) shows tetragonal distortion indicates three spin allowed transitions can be assigned as ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(v_3)$, respectively at 8200-8400, 16500-17000 and 25000-26000 cm^{-1} . Besides these three transitions are spin forbidden transitions is often also observed from the ground state 1E_g at 14400 and 14100 cm^{-1} , respectively in both the complexes¹⁸. The various parameters were calculated using Normalized Spherical Harmonic Hamiltonian (NSH) theory for the complexes¹⁹. The electronic spectra of Cu(II) complexes exhibits two bands in the range 9720-19320 cm^{-1} which may be assigned as ${}^2B_{1g} \rightarrow {}^2A_{1g}(v_1)$ and ${}^2B_{1g} \rightarrow {}^2E_{1g}(v_2)$. The electronic spectral bands observed in Cu(II) complexes are of distorted octahedral geometry. The approximate value of 10Dq can be calculated using the mean value of the two peaks. This d^9 system is very sensitive to Jahn-Teller distortion²⁰.

TABLE-3
ELECTRONIC SPECTRAL DATA OF COMPLEXES

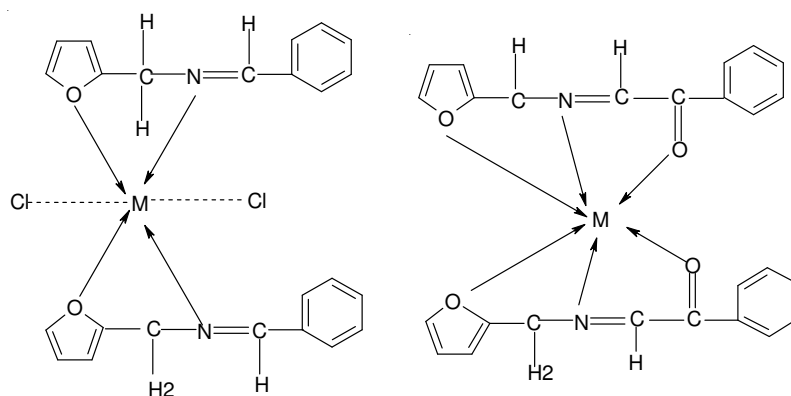
Complexes	v_1	v_2	v_3	v_4	B	C	10Dq	β	F2	F4
Mn(C ₁₂ H ₁₁ NO) ₂ Cl ₂	19540	20420	25023	26532	724	2543	7964	0.84	1087	72.6
Mn(C ₁₃ H ₁₁ NO) ₂ Cl ₂	19920	20710	25525	26715	738	2596	8118	0.85	1109	74.2
Co(C ₁₂ H ₁₁ NO) ₂ Cl ₂	9760	16120	19525	–	873	–	8603	0.89	–	–
Co(C ₁₃ H ₁₁ NO) ₂ Cl ₂	7800	16225	19910	–	897	–	8665	0.92	–	–
Ni(C ₁₂ H ₁₁ NO) ₂ Cl ₂	8400	17000	26000	–	683	–	–	–	–	–
Ni(C ₁₃ H ₁₁ NO) ₂ Cl ₂	8200	16500	25500	–	630	–	–	–	–	–
Cu(C ₁₂ H ₁₁ NO) ₂ Cl ₂	9720	14320	–	–	–	–	1202	–	–	–
Cu(C ₁₃ H ₁₁ NO) ₂ Cl ₂	10820	15950	–	–	–	–	1338	–	–	–

ESR Spectral studies of Cu(II) complexes: The ESR spectra of Cu(II) complexes have been recorded at room temperature exhibit an axial type of signal with two 'g' values computed by Piesach and Blumberg's methods. The trend $g_{\perp\perp} > g_{\perp} > g_{\parallel}$ observed for these complexes shows that the unpaired electron is localized in dx^2-y^2 orbital of Cu(II), characteristic of tetragonally elongated structure for Cu(II) complexes. The g_{\parallel} value was found 2.28 which is a measure of covalent character of the metal-ligand bond. The value of G was found 2.96. The covalent nature can also be ascertain from the value of λ 108.18 cm^{-1} which is comparable for the Cu(II) complexes to that of free ion also suggests a considerable overlap²¹. Various ESR parameters are listed in Table-4.

TABLE-4
ESR VALUE OF Cu(II) COMPLEXES

Parameters	$\text{Cu}(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{Cl}_2$	$\text{Cu}(\text{C}_{13}\text{H}_{11}\text{NO}_{2/2})_2\text{Cl}_2$
g	2.04	2.04
g_{\perp}	1.98	2.08
$g_{\perp\perp}$	2.28	2.24
g_{av}	2.03	2.13
G	15.30	2.96
A_{\perp}	82.50	264.00
$A_{\perp\perp}$	264.00	610.50
A_{av}	143.00	379.50
μ_{eff}	1.73	1.79
λ	-108.18	-458.59

From the above studies it is concluded that the ligand FIB is bidentate with ON donor system and ligand FIPG is tridentate with OON donor system. The complexes having the octahedral symmetry. The proposed structure of the complex on the basis of the above studies is as follows-



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

Antimicrobial studies: Biological screening is done by filter paper disk method using different concentrations of the solutions. All the results of antibacterial and antifungal screening of Schiff bases and their metal complexes are shown in Table-5.

TABLE-5
ANTIBACTERIAL SCREENING OF SCHIFF BASE AND
ITS COMPLEXES AGAINST *P. aeruginosa*

Compound	Concentration (ppm)	Inhibition of radial growth (mm)	
$C_{12}H_{11}NO$	100	–	
	250	0.20	
	500	0.50	
$C_{13}H_{11}NO_2$	100	–	
	250	–	
	500	–	
$Ni(C_{12}H_{11}NO)_2Cl_2$	100	1.70	
	250	2.20	
	500	2.70	
$Cu(C_{12}H_{11}NO)_2Cl_2$	100	1.00	
	250	1.80	
	500	3.20	
$Mn(C_{13}H_{11}NO_2)_2Cl_2$	100	–	
	250	–	
	500	–	
$Cu(C_{13}H_{11}NO_2)_2Cl_2$	100	–	
	250	0.50	
	500	1.70	
Antifungal Screening Against <i>A. niger</i> and <i>A. flavous</i>			
Compound	Concentration (ppm)	Inhibition zone (mm)	
		<i>A. niger</i>	<i>A. flavous</i>
$C_{12}H_{11}NO$	–	2.00	2.00
$Cu(C_{12}H_{11}NO)_2C_{12}$	100	6.00	4.00
	250	4.00	3.00
	500	2.00	2.00
$Ni(C_{12}H_{11}NO)_2Cl_2$	100	7.00	5.00
	250	5.00	4.00
	500	4.00	3.00

Antibacterial activities: It is observed that the Schiff bases FIB is inactive at all concentrations but FIPG is toxic at higher concentrations specially against those of *P. aeruginosa*. The Cu(II) complexes of FIB are also more active against the bacteria only at 500 ppm. But Mn(II) FIPG complex is inactive in all concentrations against bacteria. It is also observed that Ni(II) complex of FIB is more active against bacteria.

Antifungal activities: From the experimental data it is observed that Schiff bases FIB is used as control against fungi *A. niger* and found to be more toxic than its Cu(II) complexes²². Their Ni(II) complexes were also found to be active at all concentrations. These complexes were also found to be active against *A. flavous* at all concentrations

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