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Synthesis, IR, UV Studies of Schiff's Base Ligand Dichloro bis (p-methoxy phenyl carbonyl azomethine benzene sulphanilamide and p-methoxy phenyl carbonyl azomethine thiocarbamide and their Mn(II),Co(II),Ni(II) and Cu(II)Complexes

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ABSTRACT

A novel Schiff's base ligand p-methoxy phenyl carbonyl azomthine benzene sulphanilamide was isolated from refluxing p-methoxy phenyl glyoxal (10 mmol) and p-amino benzene sulphonamide (10 mmol) in acetonic medium in 1:1 ratio for 4 hours. The configuration of resulting ligand was illustrated by elemental analysis, melting-point analysis, electronic spectra and IR studies. Schiff's base metal complexes of Mn(II), Co(II), Ni(II), Cu(II) with ligand were also analyzed by molar-conductance studies and magnetic-moment studies. Bsed on the analytical studies, transition-metal complexes have been designated with the composition, $[ML_2]Cl_2$ where M = Mn(II), Co(II), Ni(II), Cu(II) and L = p-methoxy phenyl carbonyl azomethine benzene sulphanilamide.

The values of molar-conductance indicated an electrolytic character of metal-complexes. As per the spectroscopic analysis, the synthesized complexes have been assigned with six-coordinated octahedral and/or tetragonal geometry. All of the synthesized products were also assessed for antibacterial behavior against the bacterias *S. typhi and E. coli*. Based on the result of antimicrobial studies, the higher inhibition potential of metal-complexes, as compared to individual Schiff's base ligand was recognized.

1. Introduction

Transition metal-complexes derived from the Schiffs base ligand having biological-activity are extensively being studied (Keri et al.2015: Keypour et al.2015:). Countless complexes of Schiff bases with transition-metals have shown strong pharmacological and therapeutic activities (Bootwala and Aruna 2012: Jadhav et al.2014: Joginder et al.2017) Schiff bases have received renewed attention in recent years because of their proven antitumor and carcinostatic activities (Brodowska and Chruscinska 2014: Kathiresan et al.2015). Schiff bases and their complexes with Azomethine group derived from glyoxalic aldehydes with various aromatic amines have broad biological (Bruijnincx and Sadler 2008: Joseph and Janaki 2016) and industrial applications. Sulphanilamides are organic compounds derived from aniline, condensed with sulfonamide group and have the S(=O2)-NH2 group linked with an amine-group(Heffern et al.2013: Hill and Sadler 2016). The general-formula of these compounds is RSO2NH2 where R is an organic group(Sharma and Chandra 2011: Vamsikrishna et al.2016). Sulphonamides are one of the very first antibacterial drugs to be discovered by the scientists. The antibacterial nature of sulphonamides makes them important in chemotherapeutic applications, unaccompanied or, in amalgamation with supplementary drugs[2-4]. Schiff-bases and metal complexes extracted from sulphonamides have proved to be effective for hypo-glycemic, anti-bacterial, and anti-inflammatory treatments (Tyagi and Chandra 2014: Tyagi et al.2014: Zaki et al.2016).

2. Materials and methods

2.1 Raw-material

All of the chemical substances and solvents being utilized are of analytical (AR) grade and solvents in use, were 99% pure or were purified by identified laboratory measures. All of the metal-salts were obtained fron E.Merk and chemical compounds used were purchased from Sigma-Aldrich.

2.2. Synthesis of Schiff-Base Ligand

2.2.1Preparation of p-methoxy phenylglyoxal

p-methoxy phenyl glyoxal was prepared by the oxidation of p-methoxy acetophenone with selenium dioxide (50 mmol) and 30 ml of absolute ethanol were placed in 200ml two necked flask fitted with a reflux condenser. The mixture was heated with continuous stirring, until the solid dissolved. To this solution 7.5gm of (50mmol) of p-methoxy acetophenone dissolved in absolute alcohol was added and the mixture was refluxed for 7 hours. It was then distilled and kept overnight. Then the liquid was filtered and solvent (ethanol) was removed. The residual contents were distilled until yellow oily p-methoxy phenyl glyoxal was obtained.

2.2.2 Preparation of p-methoxy phenyl carbonyl azomethine benzene sulphanilamide (L1)

An alcoholic solution of 1.6ml (10mmol) p-methoxy phenyl glyoxal was mixed with 1.72gm (10mmol) p-amino benzene sulphonamide which was dissolved in acetone (10ml). The mixture was refluxed for 4 hours, the solvent of this mixture was evaporated by heating on a water bath. The mixture was kept in the porcelain dish for overnight, then recrystallised and dried. Light yellow coloured powder of p-methoxy phenyl carbonyl azomethine benzene sulphanilamide was obtained.

2.2.3 Preparation of p-methoxy phenyl carbonyl azomethine thiocarbamide (L2)

An alcoholic solution of 1.6ml (10mmol) p-methoxy phenyl glyoxal was mixed with 0.76gm (10mmol) thiocarbamide which was dissolved in acetone (10ml). The mixture was refluxed for 3 hours, the solvent of this mixture was evaporated by heating on a water bath. The mixture was kept in the porcelain dish for overnight, dissolved in acetone, then recrystallised and dried. Light green coloured powder of p-methoxy phenyl carbonyl azomethine thiocarbamide was obtained.

2.3. Preparation of Metal Complexes

2.3.1 Metal complexes of Mn(II), Co(II), Ni(II), Cu(II) with L1 (dichloro bis(p-methoxy phenyl carbonyl azomethine benzene sulphanilamide)

A solution of manganese chloride(II) tetrahydrate (0.99gm, 5mmol) , cobalt(II)chloride hexaahydrate (1.18gm, 5mmol), nickel(II) nitrate (1.45gm, 5mmol) and copper(II) chloride (0.85gm, 5mmol) in ethanol was mixed with the solution of ligand (3.18gm, 10mmol) in the same volume of ethanol and refluxed for four hours. After distillation, the contents were cooled at room temperature. The precipitates were first filtered, then washed with ethanol and dried in air.

2.3.2 Metal complexes of Mn(II), Co(II), Ni(II), Cu(II) with L2 (dichloro bis(p-methoxy phenyl carbonyl azomethine benzene thiourea)

An ethanolic solution of Mn(II) chloride tetrahydrate (0.99gm, 5mmol), Co(II)chloride hexahydrate(1.18gm,5mmol), Nickel(II)nitrate (1.45gm,5mmol), copper(II)chloride (0.85gm, 5mmol) was added to ligand solution (2.22gm, 10mmol) in ethanol and the solution mixture was refluxed for four hours and then distilled. The contents were cooled and the solvent was slowly evaporated. The precipitates were first filtered then washed with ethanol and then dried in air.

3. Physical Measurements

The elemental-analysis for H, C and N was performed on the Carlo-Erba 1106 analyser and the molar-conductance of the samples was calculated on ELICO (CM82T) conductivity-bridge. Their magnetic-susceptibility was calculated through Gouy-balance with $CuSO_4.5H_2O$ calibrant. The IR-spectra of the compounds were traced by using Perkin-Elmer FTIR Spectrum BX-II spectro-photometer. The electronic-spectra of the compounds were recorded by using DMSO on Shimadzu-UV mini-1240 spectro-photometer.

Table: 1 Physical properties, analytical data and magnetic moment values of metal complexes

Compounds	**Mp^{0}C**	**Color/State**	**Analysis % Found (Calc.)**						**μeff (B.M.)**
			C	**H**	**N**	**S**	**Cl**	**Metal**	
$[Mn(C_{15}H_{14}N_2SO_4)_2Cl_2]$	108	Coffee Crystalline	47.28 (47.34)	3.67 (3.25)	7.21 (7.35)	8.22 (8.40)	9.56 (9.31)	7.48 (7.21)	5.12
$[Co(C_{15}H_{14}N_2SO_4)_2Cl_2]$	80	Light Brown Crystalline	46.68 (47.03)	3.72 (3.65)	7.12 (7.31)	8.04 (8.35)	9.38 (9.26)	7.78 (7.70)	3.95
$[Ni(C_{15}H_{14}N_2SO_4)_2(NO_3)_2]$	110	Dark Brown Crystalline	43.21 (43.98)	3.23 (3.42)	10.01 (10.26)	7.34 (7.81)	-	7.02 (7.16)	2.95
$[Cu(C_{15}H_{14}N_2SO_4)_2Cl_2]$	116	Blakish Brown Crystalline	46.88 (46.76)	3.46 (3.63)	7.29 (7.27)	8.34 (8.30)	9.07 (9.21)	8.66 (8.24)	1.78
$[Mn(C_{10}H_{10}N_2SO_2)_2Cl_2]$	155	Grey Crystalline	42.01 (42.09)	3.24 (3.53)	9.12 (9.08)	11.12 (11.20)	12.62 (12.44)	9.14 (9.62)	6.04
$[Co(C_{10}H_{10}N_2SO_4)_2Cl_2]$	154	Brown Crystalline	41.56 (41.79)	3.42 (3.50)	9.78 (9.81)	11.34 (11.12)	12.51 (12.35)	10.15 (10.24)	3.86
$[Ni(C_{10}H_{10}N_2SO_2)_2(NO_3)_2]$	130	Dark Green Crystalline	38.23 (38.30)	3.14 (3.21)	10.25 (10.20)	13.51 (13.39)	-	9.14 (9.36)	2.84
$[Cu(C_{10}H_{10}N_2SO_2)_2Cl_2]$	221	Grey Crystalline	41.23 (41.47)	3.71 (3.48)	11.01 (11.85)	11.12 (11.05)	12.13 (12.25)	19.56 (10.94)	1.95

4. Results and Discussion

4.1 Structure of Schiff Base Ligands (L1 and L2)

The Physical properties, analytical data , IR analysis and magnetic moment values of ligands L1 and L2 are depicted in table 2 and 3 and IR spectra in Fig 1.

Table: 2 Important IR Bands and their tentative assignments of the ligands

Compound	νNH (asy)	νNH (sy)	νC=O	νC=N	νC=S	νSO_2 (asy)	νSO_2 (sy)
$C_{15}H_{14}N_2SO_4$	3380	3240	1710	1590	-	1300	1140
$C_{10}H10N_2SO_2$	3400	3210	1720	1590	1120	-	-

Table; 3 Physical properties, analytical data and magnetic moment values of ligands

Compounds	Mp^{0}C	Color/State	Analysis % Found (Calc.)			
			C	H	N	S
$C_9H_8O_3$	122^0	Liquid /Yellow	65.40 (65.85)	4.70 (4.87)	-	-
$C_{15}H_{14}N_2SO_4$ (L1)	130^0	Solid /Yellow	57.20 (56.76)	4.94 (4.41)	9.16 (8.76)	9.45 (10.06)
C_{10}H10N_2SO_2 (L2)	137^0	Solid /Light Green	52.64 (52.28)	4.42 (4,51)	12.49 (12.68)	14.27 (14.38)

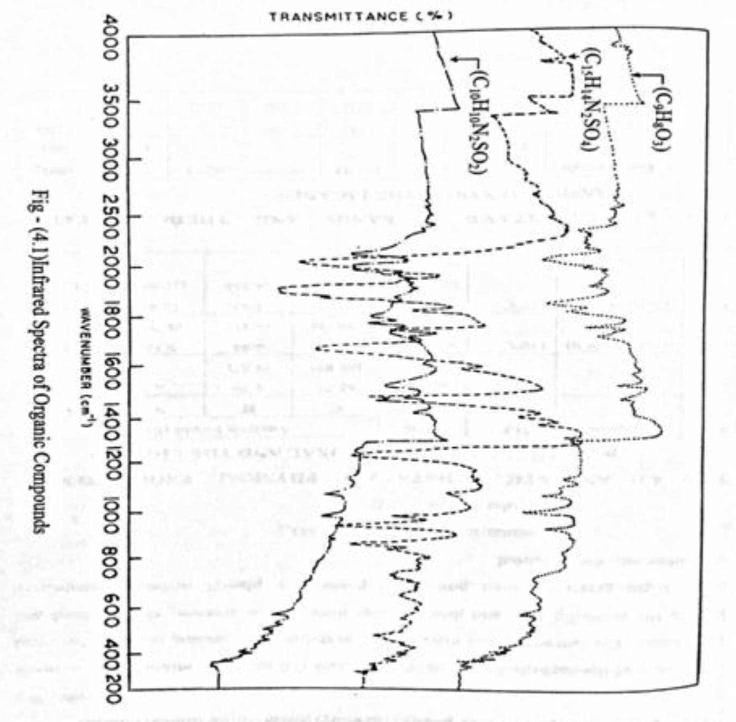

Fig: 1 IR Spectra of ligands (starting material, L1 and L2)

4.2 Structure of metal complexes

The complexes are soluble in acetone, alcohol, DMSO and DMF. All complexes are solids with high melting points. Elemental analysis suggests 1:2 (metal:ligand) stoichiometry for all the complexes (El-halim et al. 2011a, b: More et al.2016).. Physical data of these complexes are given in table 3.

4.2.1Magnetic Moment

Mn(II) complexes are generally spin free complexes. In the present course of study the value of magnetic moment was found to be in the range 5.32-6.04 B.M. which shows the presence of five unpaired electrons in complexes which was independent of temperature. Magnetic studies reveal that the complexes possess octahedral stereochemistry. Due to five unpaired electrons, complexes are of high spin (Prakash and Adhikari 2011:Nagesh and Mruthyunjayaswamy 2015).The magnetic moment data of Co(II) complexes, obtained from calibrated magnetic-susceptibilities estimated at the room-temperature are specified in table 1. They lie in the range 3.86-3.95BM. The μeff values, reported indicate the octahedral environment around the metal ions. The room-temperature magnetic value of Ni (II) complexes fall in the range 2.85-2.95B.M. indicating the magnetically normal, six coordinated, spin free, octahedral nature of these complexes (Reddy et al.2013:Al-Hamdani and Zoubi 2015).The magnetic moment values of Cu(II) complexes lies in the range 1.78-1.95B.M which suggests the spin free octahedral geometry for these complexes due to presence of unpaired electrons.(table 1)

4.2.2Electronic Spetra

The electronic spectra of manganese (II) complexes show a number of bands of weak intensity. The bands observed are assigned to the transitions and energies in terms of Rach parameter and are as follows:

$$^6A_{1g} \longrightarrow {}^4T_{1g}\ (4D),\ (10B+5C) \qquad {}^6A_{1g} \longrightarrow zE_{1g}\ ,\ {}^4A_{1g}\ (4G),\ (10B+5C)$$

$$^6A_{1g} \longrightarrow {}^4E_g\ (4D),\ (17B+5C) \qquad {}^6A_{1g} \longrightarrow {}^4T_{1g}\ (14P),\ (7B+7C)$$

The experimentally observed transition energies and calculated values for various parameters B,C, Dq and β are summarized in table 4. The transition $^6A_{1g} \longrightarrow {}^4T_{1g}$ (4D) and $^6A_{1g} \longrightarrow {}^4E_{1g}$, $^4A_{1g}$ (4G) have been used to calculate the values of B and C because these transitions depend only on B and C.Parameter Dq has been calculated by the following equation

$Dq/B = 1:1$

The slator condon shortley parameter F_2 and F_4 have been calculated by using the values of Racah interelectronic repulsion parameters B and C as follows-

$B = F_2 – 5F_4$

$C = 35F_4$

Value of B has been obtained from the nephelauxetic parameter for ligand (h_x) and nephelauxetic parameters of the metal (K_M) as follows-

$(1\text{-}B) = h_x.\ K_M$

All the values of different ligand field parameters are found to be in good agreement with those of known octahedral Mn(II) complexes (Ammar et al.2014:Chandra and Ruchi (2013).

Co(II) complexes table 5 and 6) show three d-d bands which may be attributed to the following transitions-

$^4T_{1g}(F) \longrightarrow {}^4T_{2g}\ (F)\nu_1$; $^4T_{1g}(F) \longrightarrow {}^4A_{2g}\ (F)\nu_2$; $^4T_{1g}(F) \longrightarrow {}^4T_{1g}\ (P)\nu_3$

The Racah parameter (B) and the crystal field splitting energy(10Dq) have been calculated by using the following equations-

(a) $B=(2\nu_1 - \nu_1\nu_2) / (12\nu_2 - 27\nu_1)$
$10Dq = (\nu_2 - \nu_1)$
(b) $B= 1/30[(-2\nu_1 - \nu_3)+- (\nu_2^2 +\nu_3^2+\nu_2\nu_3)^{1/2}]$
$10Dq = (2\nu_1 - \nu_3+15B)$
(c) $B= 1/510[7(\nu_3 - 2\nu_2)+- 3(81\nu_3 -16\nu_2)(\nu_2\text{-}\nu_3)^{1/2}]$
$10Dq = 1/3\ (2\nu_2 - \nu_3)+5B)$
(d) $B= ((\nu_2 +\nu_3\text{-}3\nu_1)/15$
$10Dq = (\nu_2 - \nu_1)$

The values of transitions ν_1,ν_2 and ν_3 may be obtained by using Konig's equations-

$\nu_1 = 1/2[(10Dq\text{-}15B)] + 1/2[(10Dq + 15B)]^2 – 10Dq.12B]^{1/2}$
$\nu_2 = 1/2[(30Dq\text{-}15B)] + 1/2[(10Dq + 15B)]^2 – 10Dq.12B]^{1/2}$
$\nu_3 = [(10Dq + 15B)]^2 – 10Dq.12B]^{1/2}$

In case on Ni(II) complexes splitting of 3F Russel Saunders term takes place into three components $^3A_{2g}$ $^3T_{2g}$ $^3T_{1g}$ in order of increasing energies. Following are the three spin allowed transitions table7 and 8-

$^3A_{2g} \longrightarrow {}^3T_{2g}\ (F)\nu_1$; $^3A_{2g} \longrightarrow {}^3T_{1g}\ (F)\nu_2$; $^3A_{2g} \longrightarrow {}^3T_{1g}\ (P)\nu_3$

The occurrence of these spin allowed transitions supported the octahedral geometry for Ni(II) complexes. The calculations of the inter-electronic parameter (B) were made by the following equations-

(a) $B = (2\nu_1^2 + \nu_2^2\text{-}\ 3\nu_1\nu_2) / (15\nu_2 - 27\nu_1)$
(b) $B = (2\nu_1^2 + \nu_3^2\text{-}\ 3\nu_1\nu_3) / (15\nu_3 - 27\nu_1)$
(c) $B = (\nu_2 + \nu_1\text{-}\ 3\nu_1) / 15$
(d) $B = 1/75[3\nu_1 +\text{-}25(\ \nu_3\text{-}\ \nu_2)^2 - 16\nu_1^2]$
(e) $\nu_{2,3} = 1/2(15B+30Dq) +\text{-}1/2(15B\text{-}10Dq)^2+(12B.10Dq)^{1/2}$
(f)

Generally the Cu(II) complexes have square planar geometry because the CFSE for Cu(II) ion in square planar configuration is much higher than in octahedral and tetrahedral ones. The electronic spectra of prepared Cu(II) complexes exhibited bands which may be assigned to following transitions-

$^3B_{1g} \longrightarrow {}^3B_{2g}(\nu_1)$; $^2B_{1g} \longrightarrow {}^2E_g(\nu_2)$; $^3B_{1g} \longrightarrow {}^2A_{1g}(\nu_3)$

10Dq value can be calculated using the following equation-

$$10Dq = \nu_3 – 1/2\nu_1\text{-}\ 1/3(\nu_3\text{-}\nu_2)$$

On the basis of CFSE, electronic spectra, octahedral geometry was assumed for Cu(II) complexes.

Table; 4 Electronic Spectral data and various Ligand Field Parameters of Mn(II) Complexes

Complexes	ν1	ν2	ν3	B	C	F2	F4	10Dq	β	λ	$Fx10^{-3}\ cm^{-1}$	hx
$[Mn(L1)_2Cl_2]$	30303	23256	17241	1007	2637	1383	75.33	11073	1.04	247.2	1.302	1.68
$[Mn(L2)_2Cl_2]$	26315	22727	21976	512.5	4238	1117.5	121.0	5637	533	125.80	.663	6.67

Table; 5 Experimental and Calculated Transition Energies and some Parameters in cm^{-1} of Co (II) complexes

Method of Calculation	Observed and calculated transition energies in cm^{-1}			β	10Dq	β_{35}	$\nu_2 - \nu_1$	ν_2/ν_1	$\delta\nu$
	ν_1	ν_2	ν_3						
$[Co(C_{15}H_{14}N_2SO_4)_2Cl_2]$									
Experimental	11346	15848	20999	-	-	-	-	-	-
(a)	Fitted	Fitted	25877	-688	4502	-	-	-	-
(b)	Fitted	29369	Fitted	898	15163	0.92	-	-	45.08
(c)	7488	Fitted	Fitted	996	8545	1.02	8360	2.11	55.27
(d)	7488	15848	20999	958	8360	0.98	-	-	-
$[Co(C_{10}H_{10}N_2SO_2)_2Cl_2]$									
Experimental	11905	16667	22727	-	-	-	-	-	-
(a)	Fitted	Fitted	13889	-700	4762	-	-	-	-
(b)	Fitted	29959	Fitted	980	15783	1.01	-	-	44,36
(c)	7634	Fitted	Fitted	1058	8825	1.09	9033	2.18	55.94
(d)	7634	16667	22727	1096	9033	-	-	-	-

Table; 6 Electronic Spectral Data and Various Ligand Field Parameters of Co(II) Complexes

Spectral data and different ligand field parameters from fitting		$[Co(C_{15}H_{14}N_2SO_4)_2Cl_2]$	$[Co(C_{10}H_{10}N_2SO_2)_2Cl_2]$
Experiment spin allowed bands (in cm^{-1})	ν_1 ν_2 ν_3	11346 15848 20999	11905 16667 22727
Racah parameters (in cm^{-1})	B C	996 4611.4	1058 4898.5
Slater-Condon Shortley parameters (in cm^{-1})	F_2 F_4	1654.5 131.7	1757.7 139.95
Crystal field stabilization energy (in cm^{-1})	E	-	-
Crystal field splitting energy (in cm^{-1})	10Dq	8545	8225
Oscillator strength of transition	f	92	95
Nephelauxetic ratio	β_{35}	92	1.01
Ratio between ν_1, ν_2 and ν_3	ν_3/ν_1 ν_3/ν_2	1.85 1.12	1.90 1.36

Table; 7 Experimental and Calculated Transition Energies and some Parameters in cm^{-1} of Ni(II) complexes

Method of Calculation	Observed and calculated transition energies in cm^{-1}			B	$\delta\nu$	β_{35}	λ	ν_2/ν_1	ν_3/ν_1	10Dq/B
	ν_1	ν_2	ν_3							
$[Ni(C_{15}H_{14}N_2SO_4)_2Cl_2]$										
Experimental	10770	16030	24901	-	-	-	-	-	-	-
(a)	10Dq	Fitted	24972	-573	71	53	-	1.48	2.31	18.79
(b)	10Dq	16074	Fitted	565	44	0.52	-	-	-	19.06
(c)	10Dq	16103	24905	574	73	0.53	-	-	-	18.76
(d)	10Dq	15909	24979	552	-121	0.51	80.31	-	-	19.51
$[Ni(C_{10}H_{10}N_2SO_2)_2Cl_2]$										
Experimental	11111	15385	27777	-	-	-	-	-	-	-
(a)	10Dq	Fitted	24279	422	-3498	0.39	-	1.38	2.50	26.33
(b)	10Dq	17458	Fitted	793	2073	0.73	-	-	-	14.01
(c)	10Dq	16863	26926	655	1478	0.60	-	-	-	16.96
(d)	10Dq	18121	10512	1020	2716	94	126.8	-	-	10.89

Table; 8 Electronic Spectral Data and Various Ligand Field Parameters of Ni(II) Complexes

Spectral data and different ligand field parameters from fitting		$[Ni(C_{15}H_{14}N_2SO_4)_2Cl_2]$	$[Ni(C_{10}H_{10}N_2SO_2)_2Cl_2]$
Experiment spin allowed bands (in cm^{-1})	ν_1 ν_2 ν_3	10770 16030 24901	11111 15385 27777
Racah parameters (in cm^{-1})	B C	574 2703.5	655 3085.0
Slater-Condon Shortley parameters (in cm^{-1})	F_2 F_4	960.2 77.24	1095.7 88.14
Crystal field stabilization energy (in cm^{-1})	E	-	-

Crystal field splitting energy (in cm^{-1})	10Dq	10770	11111
Oscillator strength of transition	f	1.24	1.27
Nephelauxetic ratio	β_{35}	53	60
Ratio between ν_1, ν_2 and ν_3	ν_3/ν_1 ν_3/ν_2	2.31 1.48	2.50 1.38
Spin-orbit coupling constant	λ	80.31	126.80

Table; 9 Electronic Spectral data and various Ligand Field Parameters of Cu(II) Complexes

Compounds	Band position	Dq cm^{-1}	CFSE(KJ/Mole)	f
$[Cu(C_{15}H_{14}N_2SO_4)_2Cl_2]$	15625	1562.5	111.96	0.65
$[Cu(C_{10}H_{10}N_2SO_2)_2Cl_2]$	16129	1612.9	115.57	0.67

4.2.3 Infra Red Spectral Studies

Table 10 indicates the important IR frequencies and their tentative assignments for Mn(II), Co(II), Ni(II) and Cu(II) complexes. The main features of IR spectra are as follows-

No remarkable shift is observed in the IR frequencies of $\nu NH_{(asy)}$ stretching and $\nu NH_{(ay)}$ stretching of the complexes and ligands. These bands are observed at 3380 cm^{-1} and 3400 cm^{-1} and 3240 cm^{-1}, 3210 cm^{-1} for $\nu NH_{(asy)}$ and $\nu NH_{(sy)}$ groups respectively. Thus it is concluded that these groups are not involved in complex formation in with any of the metal involoved.

The free carbonyl group frequencies and azomethine group frequencies occur at 1710 cm^{-1}, 1590 cm^{-1} and 1720 cm^{-1}, 1580 cm^{-1} and 1710 cm^{-1}, 1600 cm^{-1} in the spectra of complexes respectively. Shifting of ν(C=O) and ν(C=N) band to lower frequencies indicates the involvement of carbonyl oxygen and azomethine nitrogen in complexation.

The bands at 1140 cm^{-1} and 1300 cm^{-1} are observed due to νSO_2(sy) and νSO_2(asy) groups respectively. On complexation, no shift is observed in any of these two bands which show the non-involvement of these groups with metal ion. The three new bands at 510 cm^{-1}, 570 cm^{-1} and 370 cm^{-1}, 390 cm^{-1} and 320 cm^{-1}, 340 cm^{-1} which appeared in the spectra of complexes may be assigned due to νM-N, νM-O and νM-Cl stretching modes respectively.

The IR spectra of these ligands exhibit two strong bands in the region 1710cm^{-1}, 1720cm^{-1} and 1590cm^{-1}, due to νC=O and νC=N groups respectively. These bands are found to be shifted to 1690cm^{-1}, 1700cm^{-1} and 1610cm^{-1},1580cm^{-1} frequencies in the spectra of Co(II) complexes indicating the involvement of νC=O and νC=N groups in complexation.

Two bands appeared in the region 1140cm^{-1} and 1300cm^{-1} due to νSO_2(sy) and νSO_2(asy) groups. No shift is observed during chelation which shows the non-involvement of these groups in bond formation.

Three new bands appear in the spectra of the complexes at 540-550cm^{-1},460-480cm^{-1} and 360-370cm^{-1} due to νM-N, νM-O and νM-Cl stretching modes respectively.

The νC=N frequency of the free Schiff bases occurs at 1590cm^{-1}. In our complexes thesr bands is shifted to 1580cm^{-1} and 1610cm^{-1} indicating coordination through the nitrogen atom of the Schiff base. The νC=O frequency which was observed at 1710cm^{-1} and 1720cm^{-1} in the spectrum of the ligands, shifted towards lower frequency at 1680cm^{-1} and 1710cm^{-1} indicating the coordination through carbonyl oxygen.

Three new bands which appear at 570-520cm^{-1}, 410-420cm^{-1} and 270-260cm^{-1} are due to νM-N, νM-O and νM-Cl stretching modes respectively.

The IR discussion is confined to important bands of the ligands and their complexes. The important IR bands and their tentative assignments are given in table 10.

The IR spectra of the ligands show two strong bands in the region 1710-1720cm^{-1} and 1590cm^{-1}. These bands are shifted to lower frequencies in the spectra of the complexes to 1690cm^{-1} and 1580cm^{-1}, 1600cm^{-1} indicating the involvement of νC=O and νC=N groups in complexation.

The new bands appear in the spectra of the complexes in the region 550-540cm^{-1}, 440-430cm^{-1} and 320-310cm^{-1} due to νM-N, νM-O and νM-Cl stretching modes respectively table 10.

Table; 10 IR spectral data (in cm-1) of divalent metal complexes of Schiff bases

Compound	νasyNH	νsyNH	νC=O	νC=N	$\nu asySO_2$	$\nu sySO_2$	νC=S	νM-N	νM-O	νM-Cl
$[Mn(C_{15}H_{14}N_2SO_4)_2Cl_2]$	3380	3240	1700	1580	1300	1140	-	510	370	320
$[Co(C_{15}H_{14}N_2SO_4)_2Cl_2]$	3380	3240	1690	1610	1300	1140	-	540	460	370
$[Ni(C_{15}H_{14}N_2SO_4)_2(NO_3)_2]$	3380	3240	1680	1580	1300	1140	-	570	410	270
$[Cu(C_{15}H_{14}N_2SO_4)_2Cl_2]$	3380	3240	1690	1580	1300	1140	-	550	440	320
$[Mn(C_{10}H_{10}N_2SO_2)_2Cl_2]$	3400	1210	1710	1600	-	-	1120	670	390	340
$[Co(C_{10}H_{10}N_2SO_4)_2Cl_2]$	3400	3210	1700	1580	-	-	1120	550	480	360
$[Ni(C_{10}H_{10}N_2SO_2)_2(NO_3)_2]$	3400	3210	1710	1610	-	-	1120	520	420	260
$[Cu(C_{10}H_{10}N_2SO_2)_2Cl_2]$	3400	3210	1690	1600	-	-	1120	540	430	310

Fig- 2 Infrared Spectra of Complexes

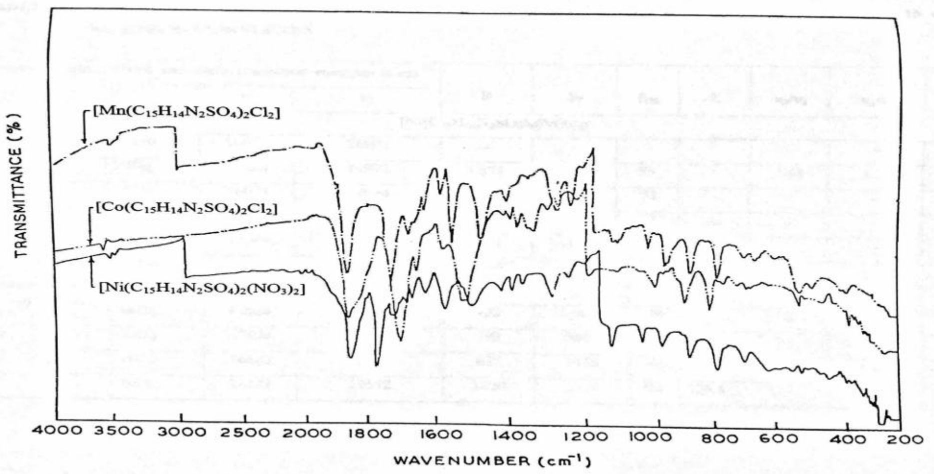

Fig - (5.1) Infrared Spectra of Complexes

Fig- 3 Infrared Spectra of Complexes

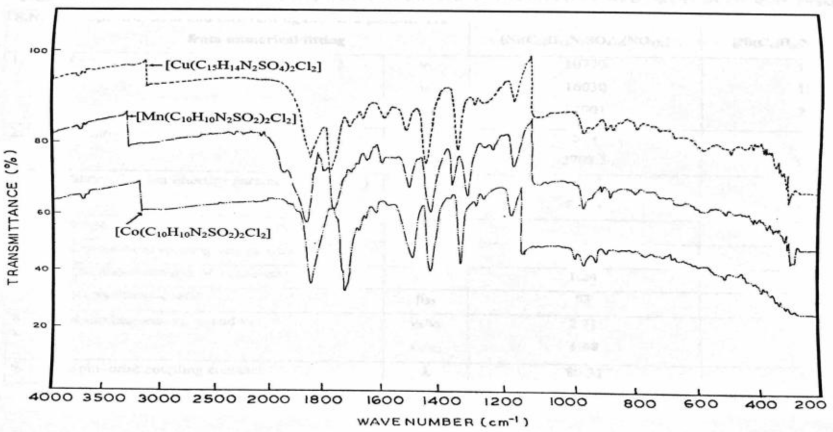

Fig - (5.2) Infrared Spectra of Complexes

Fig- 4 Infrared Spectra of Complexes

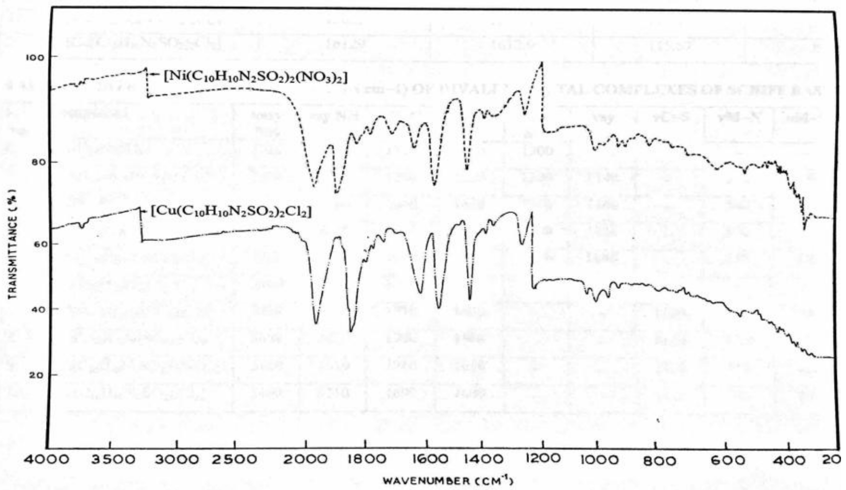

Fig - (5.3) Infrared Spectra of Complexes

4.2.4 Biocidal Activity

4.2.4.1 Test organisms

24 hours old culture of Bacillus subtilis and Escherichia coli were used as the test organisms for bactericidal screenings and seven days old culture of

Candida albicans and Alternaria alternate for fungicidal screenings.

4.2.4.2 Bactericidal Screenings

Agar disc diffusion method was employed for assessing bactericidal activity of ligands and complexes against these bacteria (Chandra and Gautam 2014, Dhanaraj and Johnson 2014). Sterile filter paper(Whatman No. 41) discs of 5mm diameter saturated with solution of different concentrations of test compounds (250,500,1000ppm) were kept on nutrient agar plates (Beef extract 1gm, NaCl 1gm, Agar 4gm, peptone 1gm and distilled water 200ml). Plates were incubated at 28+- 1^{0}C for 48-hours and the zones of inhibition, depending on the zone-size around the disc were measured (Chang et al.2010: Kuklkarni et al.2015). Observations of experiments and bio-assay data are recorded in table.

4.2.4.3 Fungicidal Screening

Seven days old culture of Candida albicans and Alternaria alternate, the metal complexes alongwith the ligands were screened for their funicidal activity by agar plate technique. The screening was made at 250,500 and 1000ppm and the number of replications in all the cases was three. The linear-growth of fungus was recorded by assessing the colony-diameter after five days and average of replications of growth in nm was recorded (Sharma and Chandra 2013: Base 2015). The percentage inhibition was calculated by the following equation-

Percentage of inhibition = $X - \frac{Y}{X} \text{ x } 100$ where X is the diameter of fungus colony in control plate, Y is the diameter of fungus colony in test plate.

Compound	Bacteria						Fungi					
	B.subtilis			E.coli			C.albicans			A.alternata		
	1000 ppm	500 ppm	250 ppm	1000 ppm	500 ppm	250 ppm	1000 ppm	500 ppm	250 ppm	1000 ppm	500 ppm	250 ppm
($C_{15}H_{14}N_2SO_4$)	2	1	1	1	1	-	2	1	-	2	1.5	1
[$Mn(C_{15}H_{14}N_2SO_4)_2Cl_2$]	1	5	-	1	-	-	2	1	-	1	1	-
[$Co(C_{15}H_{14}N_2SO_4)_2Cl_2$]	2	1	2	2	1	-	1	0.5	-	-	-	-
[$Ni(C_{15}H_{14}N_2SO_4)_2(NO_3)_2$]	2	1	1	2	1	0.5	2	1	-	2	-	-
[$Cu(C_{15}H_{14}N_2SO_4)_2Cl_2$]	2	1	0.5	3	1	1	1	1	-	1	1	-

References

1. Al-Hamdani AAS, Zoubi WA (2015) New metal complexes of N3 tridentate ligand: synthesis, spectral studies and biological activity. Spectrochim Acta Part A Mol Biomol Spectrosc 137: 75–89
2. Ammar RAA, Alaghaz AMA, Elhenawy AA (2014) characterization and investigation of vibrational spectroscopy of 4-(4-hydroxy)-3-(2-pyrazine-2-carbonyl) hydrazonomethylphenyl- diazen-ylbenzenesulfonamide and its copper(II) complex. J Mol Struct 1067:94-103
3. Base TS (2015) Potential antimicrobial properties of two new synthetic metal complexes containing a materials and methods. Int. J. of Advanced Res 3:1230–1238
4. Bootwala S, Aruna K (2012) Synthesis, spectroscopic and biological characterization of the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)complexes with a new macrocylic tridentate[ONO] ligand, AsianJ. Chem. 24 (5) :2125–2131
5. Brodowska K, Chruscinska E (2014) Schiff bases – interesting range of applications in various fields of science. CHEMIK 68(2):129–134
6. Bruijnincx PC, Sadler PJ (2008)New trends for metal complexes with anticancer activity, Curr. Opin. Chem. Biol. 12 (2):197–206
7. Chandra S, Gautam S (2014) Antibacterial and antifungal activity of Schiff base ligands and their metal complexes-A Review. Int J Chem Pharm Sci 5:27–41
8. Chandra S, Ruchi (2013) Synthesis, spectroscopic characterization, molecular modeling and antimicrobial activities of Mn(II), Co(II), Ni(II), Cu(II) complexes containing the tetradentate aza Schiff base ligand. Spectrochim Acta Part A Mol Biomol Spectrosc 103:338–348
9. Chang EL, Simmers C, Knight DA (2010) Cobalt complexes as antiviral and antibacterial agents. Pharmaceuticals 3 (6):1711–1728
10. Dhanaraj CJ, Johnson J (2014) Synthesis, characterization, electrochemical and biological studies on some metal(II) Schiff base complexes containing quinoxaline moiety. Spectrochim Acta Part A Mol Biomol Spectrosc 118:624–631
11. El-halim HFA, Omar MM, Mohamed GG (2011a) Synthesis, structural, thermal studies and biological activity of a tridentate Schiff base ligand and their transition metal complexes. Spectrochim Acta Part A Mol Biomol Spectrosc 78:36–44
12. El-halim HFA, Omar MM, Mohamed GG, Sayed MAE (2011b) Spectroscopic and biological activity studies on tridentate Schiff base ligands and their transition metal complexes. Eur J Chem 2:178–188
13. G. More, D. Raut, K. Aruna, S. Bootwala (2016), Synthesis, spectroscopic characterization and antimicrobial activity evaluation of new tridentate Schiff bases and their Co(II) complexes. J Saudi Chem Soc 20 (1): 69-80
14. Heffern MC, Yamamoto N, Holbrook RJ, Eckermann AL, Meade TJ (2013) Cobalt derivatives as promising therapeutic agents.Curr Opin Chem Biol 17 (2):189–196.

15. Hill HAO, Sadler PJ (2016) Bringing inorganic chemistry to life with inspiration from R. J. P Williams. J Biol Inorg Chem 21:5–12 Holm RH, Kennepohl P, Solomon EI (1996) Structural and functional aspects of metal sites in biology. Chem Rev 96:2239–2314
16. Jadhav SM, Shelke VA, Shankarwar SG, Munde AS, Chondhekar TK (2014) Synthesis, spectral, thermal, potentiometric and antimicrobial studies of transition metal complexes of tridentate ligand. J Saudi Chem Soc 18:27–34
17. Joginder K, Amit Rai, Vinit R (2017)A Comprehensive Review on the Pharmacological Activity of Schiff Base Containing Derivatives. Organic & Medicinal Chem I J 1(3): 555564. DOI: 10.19080/OMCIJ.2017.01.555564
18. Joseph J, Janaki GB (2016) Copper complexes bearing 2-aminobenzothiazole derivatives as potential antioxidant: Synthesis, characterization. J of Photochem and Photobio B: Biology162:86–92,
19. Kathiresan S, Anand T, Mugesh S, Annaraj J (2015) Synthesis, Spectral Characterization and DNA bindings of Tridentate N2O donor Schiff base Metal (II) Complexes. J Photochem Photobiol B 148:290–301
20. Keri RS, Patil MR, Patil SA, Budagupi S (2015) A comprehensive review in current developments of benzothiazole-based molecules in medicinal chemistry. Eur J of Med Chem 89: 207–251
21. Keypour H, Shayesteh M, Rezaeivala M, Chalabian F, Elerman Y, Buyukgungor O (2013) Synthesis, spectral characterization, structural investigation and antimicrobial studies of mononuclear Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes of a new potentially hexadentate N2O4 Schiff base ligand derived from salicylaldehyde. J Mol Struct1032:62-68
22. Kuklkarni D, Patil SA, Badami PS (2009) Electrochemical Properties of some Transition Metal Complexes: Synthesis, Characterization and In-vitro antimicrobial studies of Co(II), Ni(II), Cu(II), Mn(II) and Fe(III) Complexes. Int J Electrochem Sci 4: 717-729
23. Nagesh GY, Mruthyunjayaswamy BHM (2015) Synthesis, characterization and biological relevance of some metal (II) complexes with oxygen, nitrogen and oxygen (ONO) donor Schiff base ligand derived from thiazole and 2-hydroxy-1-naphthaldehyde. J Mol Struct 1085:198–206
24. Prakash, D. Adhikari, Application of Schiff bases and their metal complexes-a review,Int. J. Chem. Techol. Res., 3 (4) (2011), pp. 1891-1896
25. Reddy NS, Shankara BS, Murali Krishana P, Basavaraj C, Mahesh B (2013) Synthesis, characterization, and antibacterial activity of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes of Schiff's Base type ligands containing benzofuran moiety. Int J Inorg Chem 2013:1–10
26. Sharma AK, Chandra S (2011) Complexation of nitrogen and sulphur donor Schiff's base ligand to Cr(III) and Ni(II) metal ions: synthesis, spectroscopic and antipathogenic studies. Spectrochim Acta Part A Mol Biomol Spectrosc 78:337–342
27. Sharma AK, Chandra S (2013) Synthesis, structural and fungicidal studies of hydrazone based coordination compounds. Spectrochim Acta Part A Mol Biomol Spectrosc 103:96–100
28. Tyagi M, Chandra S (2014) Synthesis and spectroscopic studies of biologically active tetraazamacrocyclic complexes of Mn(II), Co(II), Ni(II), Pd(II) and Pt(II). J Saudi Chem Soc 18:53–58
29. Tyagi M, Chandra S, Tyagi P (2014) Mn(II) and Cu(II) complexes of a bidentate Schiff's base ligand: Spectral, thermal, molecular modelling and mycological studies. Spectrochim. Acta A Mol Biomol Spectrosc 117:1–8.
30. Tyagi M, Chandra S, Tyagi P (2014) Mn(II) and Cu(II) complexes of a bidentate Schiff's base ligand: spectral, thermal, molecular modeling and mycological studies. Spectrochim Acta Part A Mol Biomol Spectrosc 117:1–8
31. Vamsikrishna N, Kumar MP, Tejaswi S, Rambabu A, Shivaraj (2016) DNA Binding, Cleavage and Antibacterial Activity of Mononuclear Cu(II), Ni(II) and Co(II) Complexes Derived from Novel Benzothiazole Schiff Bases. Journal of Fluorescence 26(4)1317–1329
32. Zaki M, Arjmand F, Tabassum S (2016) Current and future potential of metallo drugs: Revisiting DNA-binding of metal containing molecules and their diverse mechanism of action. Inorganica Chimica Acta 444:1–22