

Synthesis and Characterization of some Metal Complexes prepared from Schiff Base Ligand having Heterocyclic unit

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Abstract: New series of co-ordination compounds of some transition metal ions [Zr(IV), Co(II), Cu(II)] of synthesized ligand (4-[2{5-[4-Nitrobenzylidene)-amino]-[1,3,4]thiadiazole-2yl}phenylimino)-methyl]-phenol. These new prepared metal complexes and Schiff base ligand were characterised by elemental microanalysis (CHNSO), FTIR, UV-Vis, ¹H-NMR, thermal analysis (TGA-DTA), magnetic susceptibility and molar conductance. Accordance to the obtained data all the prepared complexes were non-electrolytic. On the basis of the instrumental results, structures of metal complexes have been proposed. From the spectral data it is revealed that all prepared complexes exhibit 2:1 (ligand: metal) ratio. Thermal data shows degradation of these complexes.

Keywords: Schiff base, synthesis, thermal analysis, 1,3,4 thidiazole, transition metal.

I. INTRODUCTION

Schiff bases prepared from amino and carbonyl compounds which act as important ligands, co-ordinate with metal through (>C=N-) group is having a wide range of study (Bader et al., 2019). Compounds containing azomethine group have a broad spectrum of biological importance (Mishra et al., 2013). Metal complexes derived from Schiff base are studied due to the interesting feature like biochemical properties enzymatic reaction, catalysis, electrochemical studies (Giri et al., 2015). Schiff base containing compounds shows flexibility with natural biological substance due to presence of imines group which is used for the transformation and racemisation reaction in biological system (Salimon et al., 2010). Also metal complexes prepared from schiff base ligands have found to be oxygen carriers (Henri et al 2010). Co (II), Cu (II) metal complexes are prepared from Schiff base used in current science because of DNA binding and cleavage properties under physiological condition (Xavier et al., 2010). Schiff base metal

complexes extensively studied because of the versatility in field of industries, biological activities like antitumor, antifungal, antiviral, anticonvulsant, anti-inflammatory, antimicrobial (Mohapatra et al., 2012). Copper (II) complexes effectively used in treating inflammatory diseases like rheumatic arthritis (Donald et al 2014). Transition metal complexes with ligands containing N, S and N, O donors are widely studied due to stereo chemical, electrochemical and electronic properties (Leelavathy et al., 2013). Transition metal ion prepared from Schiff base study focus on the reactivity of metal ion in transmethylation reaction (Boghaei et al., 2001). Silver complexes which possess I oxidation state gives effective inhibition against mosaic virus (Lashanzadegan et al., 2000). In this paper, we proposed the synthesis and characterisation of newly prepared metal complexes having oxidation number (II), (IV) with Schiff base containing heterocyclic moiety.

II. MATERIAL

Solvents used were of A.R. grade which used without further purification. Cobalt chloride procured from Burgoyne. Zirconium oxychloride purchase from Hi-media. Potassium hydroxide, Copper chloride, phosphorus oxychloride, salicyldehyde were purchased from Loba chemie. Agilent Cary 5000 used to record uv-visible spectra and infrared spectra were recorded on Perkin Elmer FTIR 400, While ¹H NMR in Bruker Avance III, melting point were determine in electrical melting point measurement apparatus. Digital conductivity meter (model no. EQ 660A) was used to evaluate conductivity of prepared ligand and complexes in DMSO. Elemental analyses such as C, H, N, S was determined on ELEMENTARY Vario EL III. TGA, DTA were done on Perkin Elmer 600. The magnetic susceptibility was measured at room temperature using Gouy method (SSA-1305B).

III. EXPERIMENTAL

A. Synthesis of Schiff base ligand (L)

1. (4-[2{5-[4-Nitrobenzylidene)-amino]-[1,3,4] thiadiazole-2-yl} phenylimino)-methyl]-phenol.

Mixture of 2-(4 hydroxybenzylideneamino) benzoic acid (0.01 molar), thiosemicarbazide (0.01 molar) and 5 ml phosphorus oxychloride as a solvent were reflux for about 3 hour in water bath. After cooling 50ml distilled water was added to the reaction mixture and heating was carried for 4 hour. After that filtrate was neutralised with potassium hydroxide solution to obtain 4-[(2-5-Amino-[1, 3, 4] thiadiazole-2-yl) phenylimino]-methyl]-phenol. Afterward, 4-[(2-5-Amino-[1,3,4] thiadiazole-2-yl) phenylimino]-methyl]-phenol (0.02 molar) was added drop-wise in 20 mL ethanolic solution of salicylaldehyde in (0.02 molar) solution. The reaction mixture was refluxed for about 3 hour. The yellow coloured precipitate was filtered, recrystallized with ethanol and dried in vacuum.

2. Synthesis of Metal Complex (C)

An ethanol solution of the metal ions [ZrOCl₂.8H₂O, CoCl₂.6H₂O, CuCl₂.2H₂O] was added to ethanolic solution of (4-[2{5-[4-Nitrobenzylidene)-amino]-[1, 3, 4] thiadiazole-2-yl}phenylimino)-methyl]-phenol(SB) in 1:2 (metal : ligand) molar ratio. Then the

mixture was heated under reflux for half an hour and coloured precipitates were obtained. Later, the precipitate were filtered and recrystallised with ethanol.

IV. RESULT AND DISCUSSION

A. Physical properties and elemental analysis

The data of CHNSO and other physical properties of the ligand and their metal complexes are shown in table 1. Prepared compounds were coloured, non-hygroscopic and stable at room temperature. All above metal complexes were insoluble in water, partly soluble in ethanol and generously soluble in DMSO and DMF. Molar conductance of the complexes was measured in DMSO at room temperature whose value is in the range 10-20 ohm⁻¹cm³mol⁻¹ which indicate that the complexes are non-electrolytic in nature.

B. Elemental analysis

The analytical data suggested that ligand co-ordinated with central metal ion in all the complexes. All complexes were mononuclear. The data indicate that the formation of complexes having 1:2 (metal:ligand) ratio. Their empirical formula have been computed and given in table 1.

Table I. Analytical data of Schiff base and their metal complexes

Comp.	Micro analysis					
	C	H	N	S	O	M
L	66.13 (65.87)	14.13 (14.84)	14.03 (14.84)	8.16 (8.10)	7.82 (7.31)	-
C1	60.56 (60.42)	2.86 (2.53)	13.25 (13.48)	7.23 (7.65)	7.22 (6.80)	9.86 (9.40)
C2	61.60 (61.53)	3.52 (3.30)	13.06 (12.93)	7.48 (7.36)	7.46 (7.23)	6.87 (5.93)
C3	61.28 (60.83)	3.51 (3.02)	12.99 (12.76)	7.44 (7.20)	7.22 (7.18)	7.37 (6.83)

Calculated values are given in parentheses.

C. Magnetic susceptibility

Magnetic properties give value because of presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements. Magnetic susceptibility measurements were used for the structure determination of complex. Measurement gives

information of strength of ligand field of complex and number of unpaired electrons. Magnetic moments of metal complexes are listed in table below.

Table II. Magnetic susceptibility

Compound	Magnetic susceptibility (B.M.)	
	Cal	Found
C1	Diamagnetic	
C2	1.61	1.73
C3	1.46	1.73

D. IR Analysis

The spectral study data of the schiff base ligand and their metal complexes are given in table 3. Ir spectra of ligand (L) showed band at 3063cm^{-1} indicating $\nu(\text{C-H})$ stretching. A broad band was observed in the region 3728 reveal $\nu(\text{O-H})$ stretching. The azomethine (C=N) band observed in 1635cm^{-1} region, the shifting

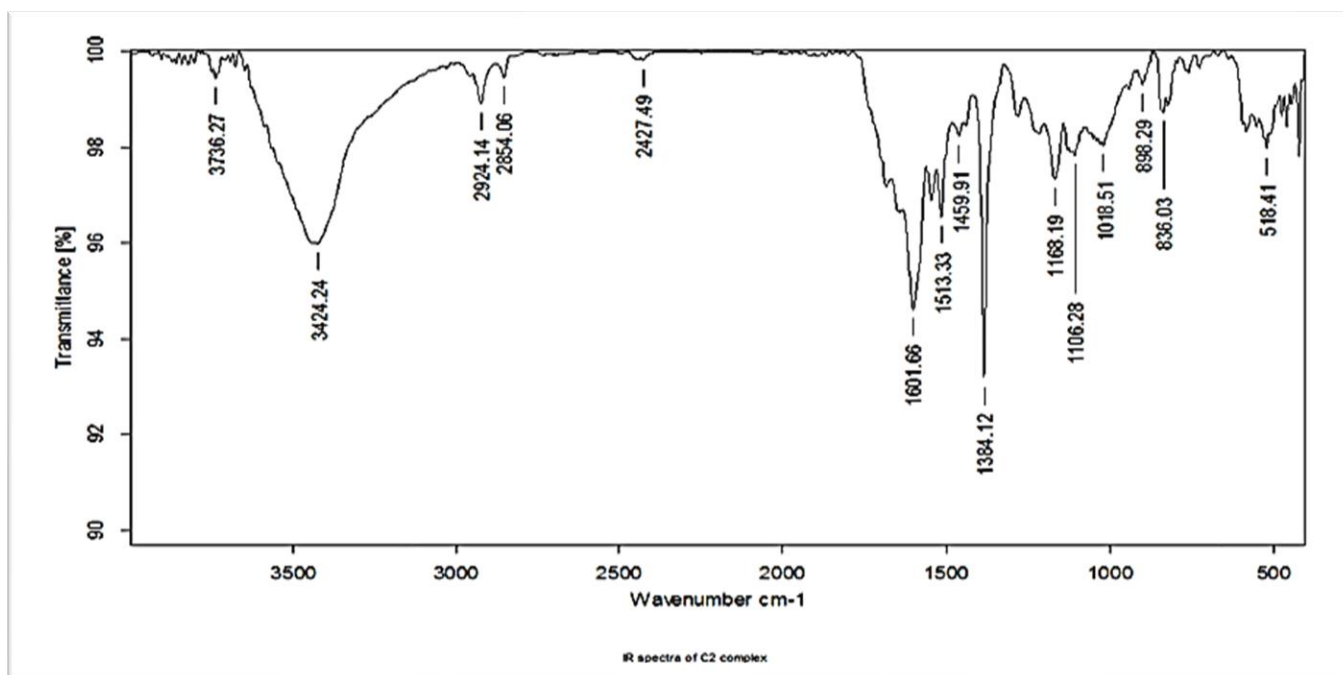
of band from ligand to metal ion region by $10\text{-}15\text{cm}^{-1}$ which indicates complexes were formed. The spectrum band at 1072cm^{-1} assign for C-S-C in heterocyclic ring. Complexes showed new bands at $(400\text{-}525)\text{cm}^{-1}$. These new bands observe in metal complexes while absent in ligand may be enclosed due to vibration of (M-O) and (M-N). These gives confirmation of bonding of metal

Table III. IR Analysis

Symbol	$\nu(\text{O-H})$	$\nu(\text{C=N})$	C-S-C	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L	3727	1635	1072	-	-
C1	3386	1601	1013	491	486
C2	3424	1601	1018	518	482
C3	3430	1602	1014	507	482

IR Spectra of C2 complex

IR Spectra of C2 complex



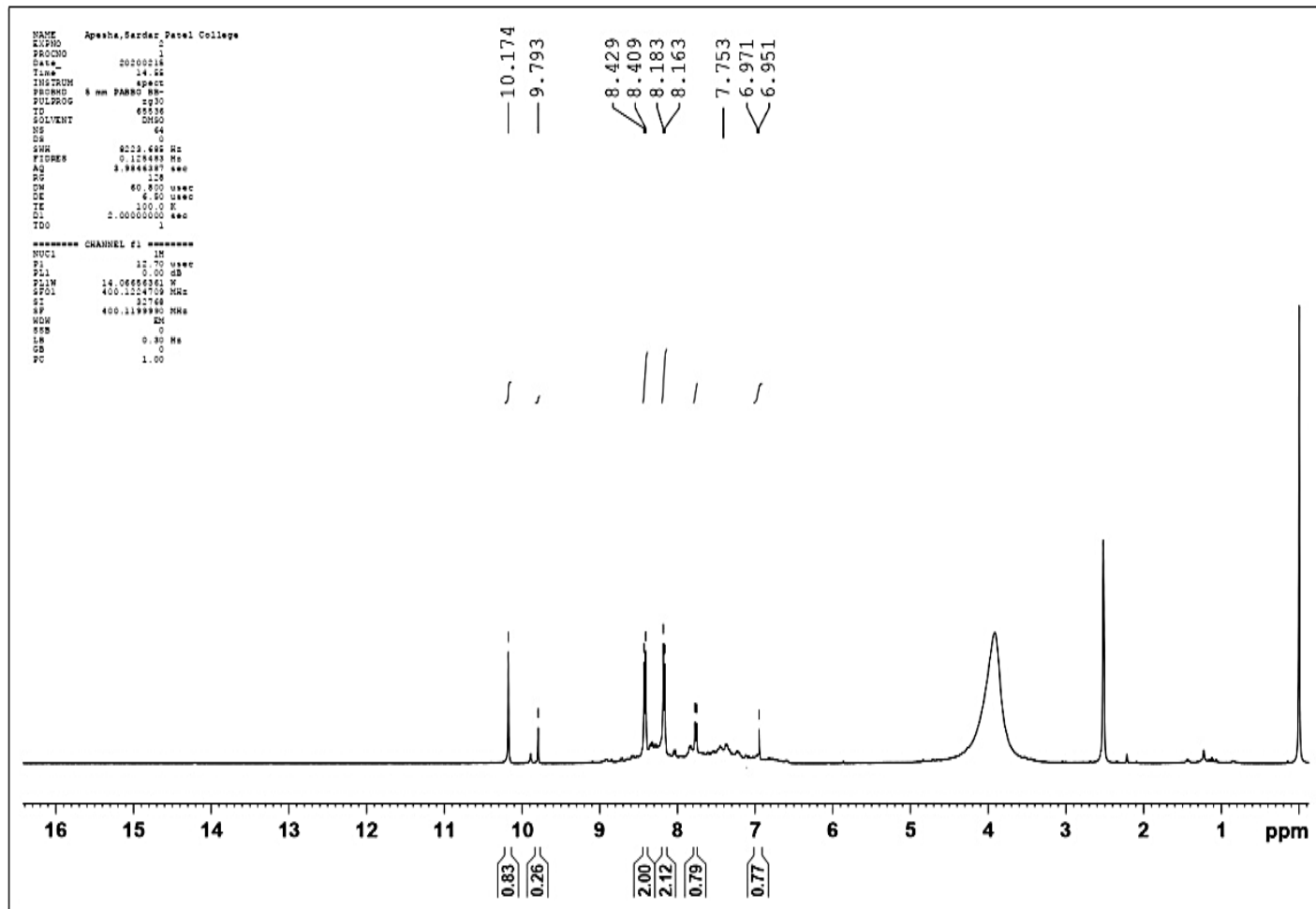
E. $^1\text{H NMR}$

In $^1\text{H NMR}$ spectrum a strong peak observes in ligand at 9.79 peaks in the range of $\delta(8.16\text{-}8.42)$ and $\delta(7.75)$ for aromatic (C=C) ppm shows Ar-OH shown in table 4. The $^1\text{H-NMR}$ data showed and azomethine for ligand which lower down in metal complexes.

Table IV. $^1\text{H NMR}$

Comp.	Ar-OH	Ar(C=C)	-(C=N)
L	7.79(S)	8.16-8.42(M)	7.75(S)
C1	9.72(S)	8.05-8.73(M)	7.05(S)
C2	9.70(S)	8.13-8.93(M)	7.14(S)
C3	9.73(S)	8.11(M)	7.11(S)

¹H NMR Spectra of L



¹H NMR Spectra of L

F. Electronic Spectra

The uv-vis spectra were used to evaluate the results given by other methods of structural elucidation. The uv spectra of complex shows band at 375 nm which is due to charge transfer from (M→L). The complex exhibit a peak in the region at 556 nm region because of d-d transition.

G. Thermal Analysis

The thermal decomposition of metal complexes was carried in the thermal range of 40 to 830°C at 20.00°C/min under Nitrogen flow. The TGA, DTA curves undergoes decomposition in three - four steps. There is no mass loss up to 200°C indicates absence of water molecule. The thermal analysis was performed to suggest the structure and studied the thermal stability of prepared metal complexes. Results are shown in table 5.

Table V. Elemental analysis

Compound	Temp range °C	Loss of moiety	Mass loss	
C1	330-440	2C ₇ H ₆ O	23.85	23.55
	450-650	2C ₈ H ₄ N ₃ S	39.14	30.00
	650-750	2C ₇ H ₅ N	23.16	20.05
C2	320-450	2C ₆ H ₅ N	21.26	21.32
	450-670	2C ₃ HN ₃ S	25.90	25.51
	670-750	2C ₁₃ H ₁₀ N	42.01	41.84
C3	340-450	2C ₇ H ₆ O	32.05	31.92
	450-650	2C ₈ H ₄ N ₃ S	40.39	40.21
	650-700	2C ₇ H ₅ N	23.91	23.72

H. Molar Conductance

Molar conductance of all the above complexes was taken at room

Table VI. Molar Conductance

Compound	Molar conductance $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
L	46
C1	55
C2	50
C3	52

CONCLUSION

All above prepared complexes were coloured, stable at room temperature. Prepared schiff base and complexes were characterised using UV, FTIR, elemental analysis, thermal analysis, ^1H NMR and molar conductance. Infra-red spectroscopy support that Schiff base is bi-dentate, O, N donor and co-ordinated via phenolic oxygen and azomethine nitrogen. Molar conductance of Schiff base and metal complexes suggests that, they are non-electrolytic in nature. From the analytical and spectroscopic values we can say that all the prepared complexes were square planar in structure.

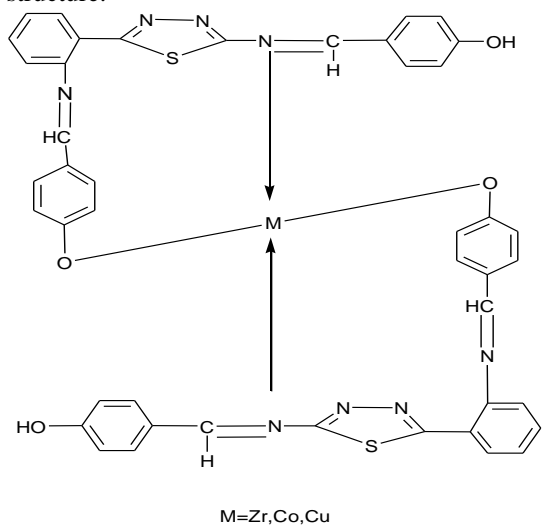


Fig. Proposed structure of metal complex

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temperature. DMSO is used as solvent for conductance measurement. All the complexes were found to be non-electrolytic in nature suggested that all the complexes are neutral which is shown in table 6.

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