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SYNTHESIS AND CHARACTERIZATION OF SOME NEW THIAZOLYL SCHIFF BASE-METAL COMPLEXES

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ABSTRACT:

Our present work focused on the synthesis and characterization of Copper and Nickel metal complexes containing thiazolyl Schiff bases obtained by condensation of the ligands 2-(4-chlorophenyl)-4-methylthiazole-5-carbohydrazide and aromatic aldehyde by refluxing together in alcohol to get new series of thiazolyl Schiff base. The synthesized metal complexes were characterized by various spectroscopic techniques including elemental analysis, UV, FT-IR, ^{1}HNMR and XRD. Geometries of the Cu (II) and Ni (II) complexes were determined by indicated spectroscopic values. X-ray powder diffraction confirms that the complexes are crystalline in nature.

KEY WORDS: Schiff base, Thiazole, XRD.

Article History

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INTRODUCTION:

Schiff's bases and their derivatives have excellent physiochemical and biological properties. They are proven to be a promising industrial material and used in chemical sensors, optics and catalysis (Sahin et al., 2018), (Anacona et al., 2021; Bursal et al., 2021; Chaviara et al., 2004). They are an excellent drug candidate as antibacterial agents, fungicidal, antitumor and anticancer agents (Anacona et al., 2021; Damercheli et al., 2019; Manimohan et al., 2020; Shi et al., 2020; Singh & Barman, 2021). Diverse derivatization of transition metal Schiff's base complexes can be achieved due to the ease of synthesis by condensation of amines and aldehydes. These ligands coordinate with numerous metals and stabilize in several oxidation states. Schiff base ligands with heterocyclic moiety are "privileged ligands" due to their excellent therapeutic utility (Chaviara et al., 2004; Karatepe & Karatas, 2006; Pontiki et al., 2008; Yernale & Bennikallu Hire Mathada, 2014). Especially the ligands with N and S have drowned attention of many researchers due to the excellent chelation properties.

Thiazoles are an important class of heterocyclic compounds contains N and S atoms. Thiazoles are found in many natural products such as Dolastatin 10, Tubulysin, Largazole, Apratoxin [4] and in pharmacophore of many blockbuster drugs for instance sulphathiazole Fentinol (anti-inflammatory), Cambendazole (fungicide), Niridazole (schistozomicial) and Ritonavir (anti-HIV, Covid-19) (Alsharif & Alam, 2017). Since last few decades researchers are attracted towards field of bioinorganic chemistry and coordination chemistry of thiozolyl schiffs base metal complexes. Recently Cozzi nicely reviewed the importance of Schiff base complexes in catalysis (Cozzi, 2004). M.M. Abd-Elzaher reported the synthesis and anticancer activity of Schiff base complex with thiazole moiety (Abd-Elzaher et al., 2016). P. Kavitha et al studied the biological activity and DNA cleavage of Co (II) Schiff's base complexes (Kavitha et al., 2016).

In our pursuit to explore the field of bioinorganic chemistry we have synthesized thiazolyl Schiff bases by condensation of 2-(4-chlorophenyl)-4-methylthiazole-5-carbohydrazide and substituted aromatic aldehydes. Their Cu(II) and Ni(II) complexes were prepared and characterized by sophisticated spectroscopic techniques such as UV, FTIR, ^{1}HNMR and XRD.

EXPERIMENTAL:

The chemicals used were of AR grade. Melting Points were determined by open capillary method and are uncorrected. IR spectra were recorded on a FT-IR spectrophotometer RZX (Perkin Elmer) and Mass spectra were recorded on a Q- TOF MICRO WATER, MS ES+3.79e3. ^{1}H spectra on a BRUKER AVANCE NEO 500 NMR spectrometer with DMSO-d_6 as a solvent and chemical shift (δ) are expressed in ppm using TMS as internal standard. UV-Visible spectra were recorded on Shimadzu UV-1800 instrument.

Synthesis of thiazolyl Schiff base ligand

Equimolar mixture of 2-(4-chlorophenyl)-4-methylthiazole-5-carbohydrazide (0.01 mole) **3** and aromatic aldehyde **4** (0.01 mole) with 3 drops of Conc.H_2SO_4 were refluxed in alcohol about 1-2 hrs (checked by TLC). After cooling, solid product thus obtained, it was filtered and recrystallized in alcohol to get Schiff base **5**. [Figure 1]

5D: **(*E*)-*N*'-(-2-chlorobenzylidine)-2-(4-chlorophenyl)-4-methylthiazole-5-carbohydrazide.**

IR (KBr): 3245 (N-H), 3058 (C-H), 1653 (C=O), 1090 (Ar-Cl), 832 (disubstituted benzene) cm^{-1}; Mass: *m/z* 390 $(M+1)^+$; ^{1}H NMR (DMSO-d_6): δ 2.77 (s, 3H, CH_3), 7.48 (d, 2H, Ar-H), 7.54 (dd, 1H, Ar-H), 7.62 (d, 2H, Ar-H),

8.03 (m, 3H, Ar-H), 8.55 (s, 1H, N=C-H), 12.08 (s, 1H, NH); Elemental Analysis, Calculated: $C_{18}H_{13}OCl_2N_3S$: C, 55.39; H, 3.36; N, 10.77. Found: C, 55.37; H, 3.34; N, 10.75 %.

5H: **(*E*)-*N*'-(-2-nitrobenzylidine)-2-(4-chlorophenyl)-4-methylthiazole-5-carbohydrazide.**

IR (KBr): 3165 (N-H), 3051(C-H), 1657 (C=O), 1528 (Ar-NO_2), 1092 (Ar-Cl), 832 (disubstituted benzene) cm^{-1}; Mass: *m/z* 401.29 $(M+1)^+$; ^{1}H NMR (DMSO-d_6): δ 2.76 (s, 3H, CH_3), 7.60 (d, 2H, Ar-H), 7.70 (dd, 1H, Ar-H), 7.89 (s, 1H, N=C-H), 8.02 (d, 1H, Ar-H) 8.11 (dd, 1H, Ar-H), 8.14 (d, 1H, Ar-H), 12.18 (s, 1H, NH); Elemental Analysis, Calculated: $C_{18}H_{13}O_3ClN_4S$: C, 53.94; H, 3.27; N, 13.98. Found: C, 53.97; H, 3.29; N, 13.95 %.

Synthesis of Schiff base metal (II) complex

A solution of metal salt (0.01 mole) with 15 ml of ethyl alcohol is added to a solution of (0.01 mole) Schiff base in 10 ml of ethyl alcohol with stirring. The reaction mixture was heated under reflux for 1-1.5 hr. The solid thus obtained was filtered off and then dried, to get Schiff base metal complex. [Figure 2]

RESULTS AND DISCUSSION:

The Schiff base ligand (5) was prepared from the condensation of 2-(4-chlorophenyl)-4-methylthiazole-5-carbohydrazide and substituted aromatic aldehydes in good yield [Table 1]. The ligand and its metal complexes are stable at room temperature.

FTIR analysis showed a strong band a 1657 cm^{-1} was assigned to amide carbonyl group. The band at 1528 cm-1 was attributed to nitro group and bands at 3165 cm^{-1} and 3051 cm^{-1} are allocated to the NH and CH stretching.

^{1}HNMR shown singlet at 2.77 ppm for methyl group, peaks at 7.48, 7.54, 7.62 and 8.03 are for aromatic protons and most down field proton at 8.55 ppm accounts for azomethine (N=C-H) proton. The broad singlet at 12.08 ppm is due to NH group.

Mass spectra of ligand shown the molecular ion peak at 429.1 [M+1]

UV absorption of Cu (II) and Ni (II) metal complexes shown at the bands λmax at 325 and 328 nm respectively. The bands are assigned to n-π* and charge transfer of azomethine group and thiazole ring nitrogen atom. The magnetic moment of Cu and Ni complex are 1.73 B.M. and 2.82 B.M. indicates octahedral geometries for both complexes (Gull & Hashmi, 2017).

Powder X-ray analysis of Cu (II) and Ni (II) metal complexes shown that the complexes are crystalline in nature. X-Ray diffractogram shows 25 reflections with maxima at 25.58 A and 26.17 A for Cu (II) and Ni (II) metal complexes respectively (Gull & Hashmi, 2017). [Figure 3 and 4]

CONCLUSION:

We have synthesized Schiff base ligand in good yield. Spectroscopic techniques FTIR, mass and ^{1}HNMR confirms its formation whereas UV and XRD revels that the Cu (II) and Ni (II) metal complexes are crystalline in nature and geometries are octahedral for both the complexes. In conclusion, the versatile Cu (II) and Ni (II) metal complexes have excellent properties and worth for further studies on its biological activities.

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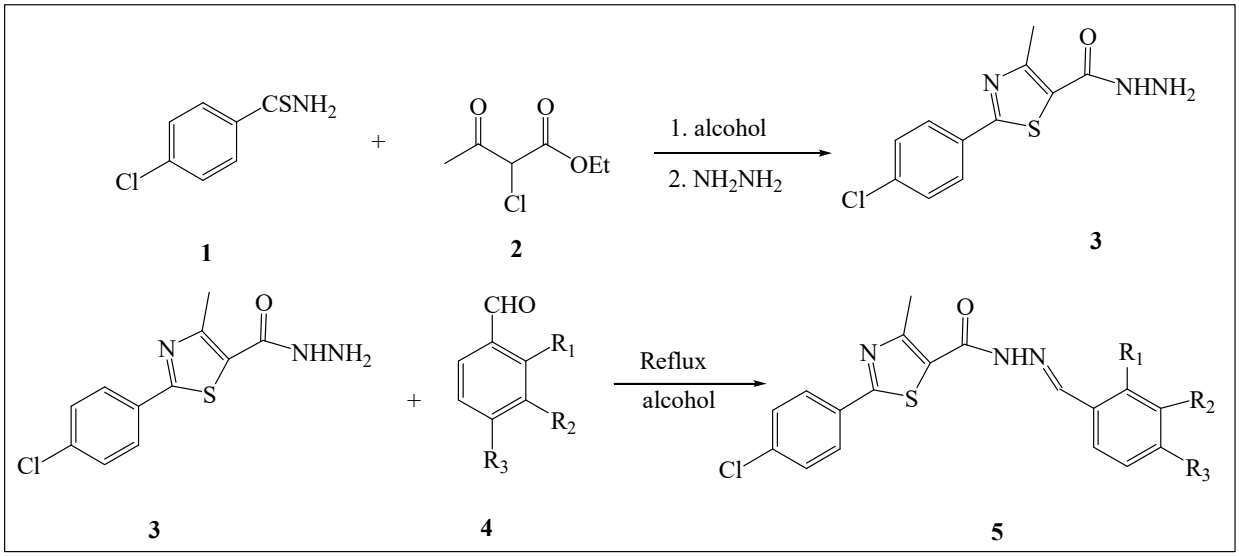

Figure 1: Synthesis of Schiff base ligand

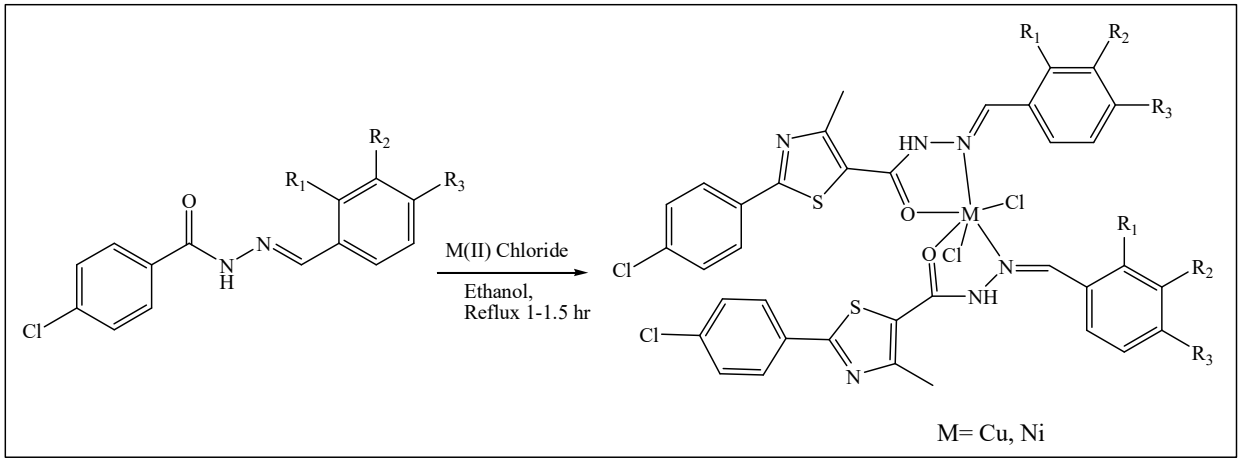

Figure 2: Synthesis of Schiff base metal complexes

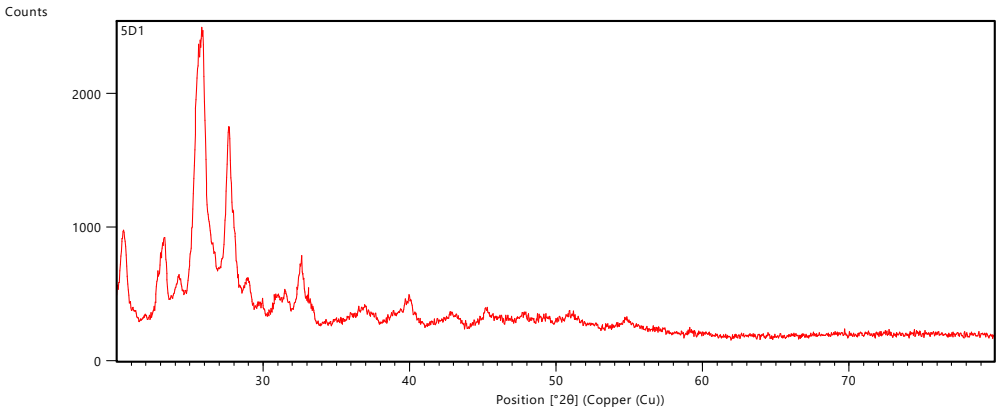

Figure 3: X-Ray diffractogram of Cu (II) complex

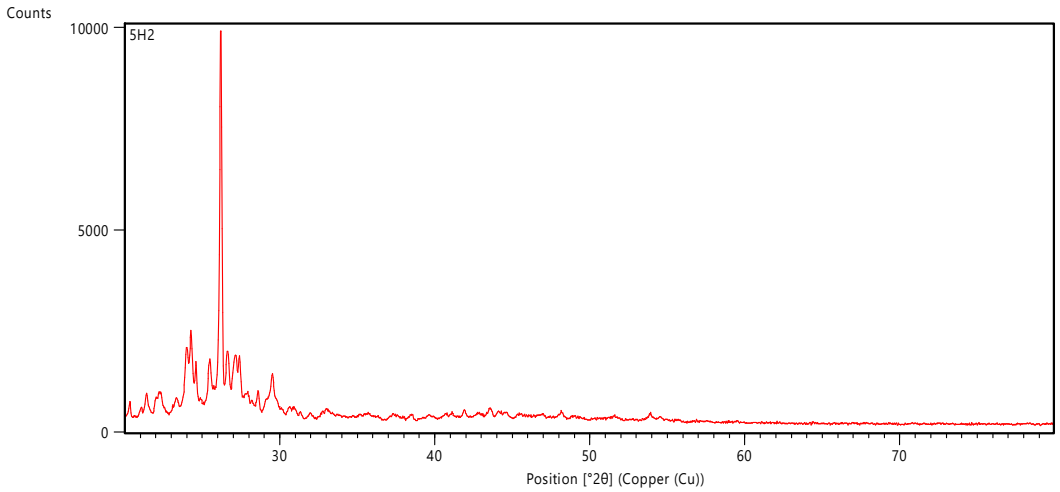

Figure 4: X-Ray diffractogram of Ni (II) complex

Table- 1:

Compds	R_1	R_2	R_3	M.P. (^oC)	Time (min.)	Yield (%)
5A	H	H	Cl	278-280	80	66
5B	H	H	Br	286-288	80	63
5C	H	H	OH	266-268	90	68
5D	Cl	H	H	280-282	80	65
5E	H	H	H	250-252	85	70
5F	H	H	OCH_3	260-262	90	61
5G	H	H	NO_2	288-290	75	77
5H	NO_2	H	H	282-284	75	75

Physical data of synthesized Schiff bases