



SYNTHETIC, STRUCTURAL, MAGNETIC AND TGA STUDIES OF SOME COPPER COMPLEXES OF HETEROCYCLIC LIGANDS

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ABSTRACT

Solid complexes of Cu(II) with substituted Isonicotinamide ligands derived from substituted triazoles have been synthesized and have been characterized by elemental analysis, molar conductance, IR, ¹H-NMR and UV spectra and TG analysis and Probable structures are assigned to the complexes. Physicochemical data suggest octahedral geometry to Cu(II) complexes . The IR spectra of the ligands and their complexes are used to identify the type of bonding. The TG analysis of ligands and their Cu(II) complexes have been carried out.

KEYWORDS: 1, 2, 4- Triazole , Cu(II) complexes, Magnetic, TGA, biological Studies

INTRODUCTION

Heterocyclic compound are very important in field of medicinal Chemistry ¹. Nitrogen based Heterocyclic compound are very important in field of medicinal Chemistry they have very good biological activities ^{2, 3}. Azoles are important five membered heterocyclic rings containing at least one nitrogen atom like Isoxazole, Thiazole, Pyrazole and Triazole ⁴⁻⁶. 1,2,4-triazole is more important because it is the basis of best modern agricultural fungicides as well as drugs for fungal disease in humans ⁷. The importance of metal complexes of 1,2,4- Triazole amide in academic commercial and pharmacological fields provoked our interest in the coordination chemistry of 1,2,4-Triazole. This has led to systematic study of Cu(II) metal complexes of 1,2,4-triazole-4-yl isonicotinamide derived from substituted Oxidiazole and isonicotinic acid hydrazide. The therapeutic effects of 1,2,4-triazole and 1,2,4-triazole 3-one containing compound have been well studied for a no of pathological condition



including cancer, pain, tuberculosis or hypertension ⁸. Copper II ions is a biologically active in chelating ability and biologically transport reaction Cu(II) complex possess wide range of biologically activity and are among the most potent antiviral, antitumor and antiinflammatory agents ^{6, 8}. In the present work, four isonicotinamide ligand and their copper complex have been prepared and characterised.

Method:

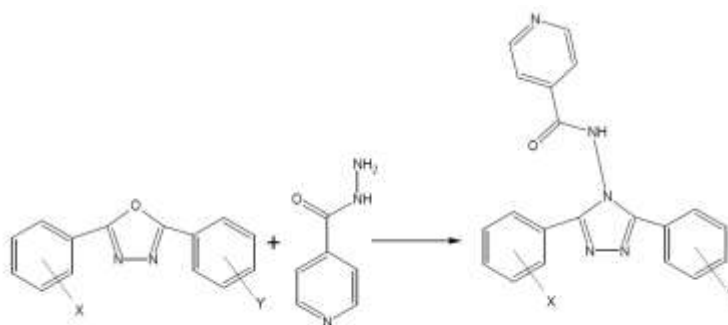
All the chemical use as starting material for synthesis of the ligand and their metal complexes were A.R. grade or chemically pure solvents were purified and dried before use by literature method. The ligand used in the present work were not commercially available hence were synthesized in our laboratory. These newly synthesized ligands were characterised by IR, ¹H NMR. The following four ligands have been synthesized.

Synthesis of ligands.

1. N- (3-phenyl)- 5(4-methoxyphenyl)- 4H-1,2,4-triazole -4 yl) isonicotinamide .L₁
2. N-(3-(2-chloroyphenyl)-5(4-methoxyphenyl)-4H-1,2,4-triazole -4 yl)isonicotinamide. L₂
3. N-(3-(4-methoxyphenyl)-5-(4-nitrophenyl)-4H-1,2,4-triazole-4yl)isonicotinamide. L₃
4. N- (3,5bis (4-methoxyphenyl)-4H-1,2,4-triazole -4 yl) isonicotinamide. L₄

Preparation of L₁, L₂, L₃ and L₄

A mixture of substituted 1,3,4-oxadiazole (0.01 mole) and isoniazid (0.01 mole) in dry pyridine (10ml) was refluxed for 6-8 hr. The reaction mixture was cooled to room temperature and then the contents were poured on to crushed ice and neutralized with dilute HCl solution. The resulting solid was dried and crystallized from glacial acetic acid. The scheme is as shown in fig.



Compound	X	Y
L1	-H	4- OMe
L2	2-Cl	4- OMe
L3	4- OMe	4-NO ₂
L4	4- OMe	4- OMe

¹H NMR spectra of data of ligands

The value following by the number of protons nature of peak and group cantoning protons in parenthesis are given for each ligand

Ligand (L₁):-N- (3-phenyl)- 5(4-methoxyphenyl)- 4H-1,2,4-triazole -4 yl) isonicotinamide show the following pick

1. δ 7.3 (s ,1H ,NH)
2. δ 7.6-7.8(m, 9H, aromatic)
3. δ 8.1-8.8 (m, 4H ,hetero-aromatic)
4. δ 3.9 (s ,3H ,OCH₃)

Ligand (L₂):- N-(3-(2-chloroyphenyl)-5(4-methoxyphenyl)-4H-1,2,4-triazole-4 yl)isonicotinamide.

1. 7.34 (s ,1H ,NH)
2. δ 7.1-8.0 (m, 8H,aromatic)
3. δ 7.8 – 8.88 (m, 4H ,hetero-aromatic)
4. δ 3.9 (s ,3H ,OCH₃)



Ligand(L₃):-N-(3-(4-methoxyphenyl)-5-(4-nitrophenyl)-4H-1,2,4-triazole-4yl)isonicotinamide.

1. δ 7.34 (s ,1H ,NH)
2. δ 7.1-8.2 (m, 8H, aromatic)
3. δ 8.2-8.8 (m ,4H ,hetero-aromatic)
4. δ 3.9 (s ,3H ,OCH₃)

Ligand (L₄):- N- (3,5bis (4-methoxyphenyl)-4H-1,2,4-triazole -4 yl) isonicotinamide

1. δ 7.2 (s ,1H ,NH)
2. δ 7.5 –8.12 (m, 8H, aromatic)
3. δ 8.41-8.8 (m ,4H ,hetero-aromatic)
4. δ 3.9 (s ,6H ,OCH₃)

Synthesis of complexes

Metal salts cupric nitrate (0.01mole) and the ligands (0.02mole) of the dissolved separately in ethanol (25 ml) and DMF–ethanol (1:4 v/v, 25 ml) respectively. Both the solution were filtered and mixed in hot condition. The reaction mixture was refluxed for 4-6 hr in a water bath. The coloured product obtained was filtered, washed several times with hot water followed by ethanol and diethyl ether and finally dried over fused calcium chloride.

PHYSICAL MEASUREMENTS

The estimation of carbon, hydrogen and nitrogen were obtained on a Carlo-Erba 1108 C-H-N-analyser at micro analytical unit SAIF, CDRI, Luknow. The IR spectra were recorded in KBr pellets on a Perkin-Elmer-1600 FT-IR spectrophotometer. The reflectance spectra of the complexes were recorded on a Carry-2390 spectrophotometer using BaSO₄ as a dilutant and MgO as a reference in the range 200-1500 nm at SAIF, IIT



Chennai. $^1\text{H-NMR}$ spectrum of the ligand was recorded in a mixed solvent ($\text{CDCl}_3 + \text{DMSO}$) on a Bruker AC-200F, 300MHz, NMR spectrometer using TMS as an internal standard at RSIC- Punjab university, Chandigarh. Magnetic measurements were carried out at room temperature using Gouy's method using $\text{Hg} [\text{Co} (\text{SCN})_4]$ as calibrant and values were corrected for diamagnetism by using Pascal's constant. Thermogravimetric analyses of the complexes were carried out using a TGS-2Perkin Elmer thermal analyzer in the temperature range 50-700 °C at a heating rate of 10 °C min^{-1} . Antibacterial and antifungal activities of the ligand and their complexes were carried out against the bacteria *E. coli* and *S. aureus* by cup plate method.

RESULTS AND DISCUSSION

The required 1,3,4-oxadiazoles prepared by refluxing a mixture of substituted benzohydrazide and substituted benzoic acid in phosphorus oxychloride for 4-6 hours. Then these oxadiazoles were refluxed with isoniazide in dry pyridine. The ligands were confirmed on the basis of IR, NMR and nitrogen analysis. The physical characterization and micro analytical data of ligands and its coordination complexes are given in (Table 1).

IR Spectra

The IR spectra of the ligand were recorded for the identification of their donor sites in frequencies after their complexation with metal ion. The Partial listing of the IR spectra of the ligand is given in Table 2 the entire ligand exhibit following assignment.

1. A medium sharp absorption band around at 3290-3180 cm^{-1} is assigned to N-H stretching vibration of NH group of the ligands⁹
2. A strong absorption band at 1685-1665 cm^{-1} is due to C=O (amide) stretching frequency^{10, 11}
3. A strong absorption band at 1617-1603 cm^{-1} is assigned to C=N (imine) stretching vibration^{10, 11}.

4. A medium band at 1535-1480 cm^{-1} may be assigned to C-O phenolic stretching vibration ¹²⁻¹⁴
5. A weak band appearing at 1070-1060 cm^{-1} is attributed to pyridine ring breathing vibration ¹⁵.
6. A weak band at 1000-990 cm^{-1} is assigned to N-N stretching vibration ¹⁵.
7. **Table 1: The Proposed composition, formula weight, colour, Thermal data and Magnetic moment of Ligands and its Cu(II) Complexes**

Sr.no	Ligand	M.P./ Half DecompTemp °C	Yield (%)	Molecular Formula	Formula Weight	Colour	C%	H%	N%	M %	Magnetic Moment in B.M.
1.	L ₁	158	65	C ₂₁ H ₁₇ N ₅ O ₂	371.36	Creamish	69.22 (67.90)	4.48 (4.69)	19.36 (18.86)	--	--
2.	L ₂	218	60	C ₂₁ H ₁₆ ClN ₅ O ₂	405.36	Creamish	61.26 (62.64)	3.49 (3.97)	17.98 (17.27)	--	--
3.	L ₃	235	58	C ₂₁ H ₁₆ N ₆ O ₄	416.390	Yellow	61.38 (60.52)	3.96 (3.84)	20.79 (20.17)	--	--
4.	L ₄	222	62	C ₂₂ H ₁₉ N ₅ O ₃	401.361	Pale yellow	66.02 (65.06)	4.12 (4.74)	18.06 (17.70)	--	--
5.	Cu L ₁ Complex	378	58	Cu[C ₄₂ H ₃₆ N ₁₀ O ₆]	839.92	Blue	59.23 (60.32)	4.12 (4.73)	15.25 (16.67)	7.25 (7.69)	1.87
6.	Cu L ₂ Complex	392	62	Cu[C ₄₂ H ₃₄ Cl ₂ N ₁₀ O ₆]	909.92	Green	53.92 (55.55)	4.06 (3.77)	14.26 (15.03)	5.52 (6.93)	1.86
7.	Cu L ₃ Complex	400	54	Cu[C ₄₂ H ₃₄ N ₁₂ O ₁₀]	930.34	Green	54.93 (54.22)	3.64 (3.68)	18.25 (18.07)	6.68 (6.83)	1.81
8.	Cu L ₄ Complex	294	64	Cu[C ₄₄ H ₄₀ N ₁₀ O ₈]	900.05	Green	57.26 (58.53)	3.26 (4.44)	16.46 (15.51)	6.89 (7.03)	1.82

Table 2: IR Spectral data (cm^{-1}) of the Ligands and Cu(II) metal complexes.

Sr.no	Ligand	ν (N-H)	ν (C=O)	ν (C=N)	ν (M-N)	ν (H ₂ O)	ν (C-O)
1.	L ₁	3215	1719	1585	--	--	1220
2.	L ₂	3211	1722	1569	--	--	1232
3.	L ₃	3209	1732	1576	--	--	1305
4.	L ₄	3214	1735	1557	--	--	1292
5.	Cu L ₁ Complex	--	--	1596	425	3360,789	1221
6.	Cu L ₂ Complex	--	--	1588	436	3446,860	1295
7.	Cu L ₃ Complex	--	--	1578	466	3376,834	1292
8.	Cu L ₄ Complex	--	--	1566	467	3387,898	1236



Electronic spectra and magnetic studies

The magnetic moments for Cu (II) complexes are given in Table 1. at room temperature corresponding to one unpaired electron. The electronic spectrum of Cu (II) complex displayed band at 16478-16562cm⁻¹ as signed for the ${}^2T_{2g} \rightarrow {}^2E_g$ transition. The electronic transitions and magnetic moment value suggests pseudo octahedral geometry around Cu (II) ion ¹⁶⁻¹⁸. A detailed interpretation of the electronic spectra of Cu (II) complexes is rather complicated owing to distorted octahedral which is very common in Cu (II) complexes which give strong charge transfer bands telling off in the blue end of the visible spectrum.

Thermogravimetric analysis

In the present investigation, analysis of TG curves of ligands and its Cu complexes reveals a two stage decomposition pattern. All the Cu complexes are almost stable upto 70-80°C. The Cu complexes loss their weight in the range 180-230 °C corresponding to two coordinated water molecules. The Cu (II) complexes show a gradual but continuous weight loss between 265-645°C due to oxidative thermal degradation of ligand. The final stage ends with the arial oxidation of the complexes and formation of respective stable metal oxide. The thermal decomposition temperature is as shown in Table 1.

Conclusion:

All the complexes are coloured solids, air stable and are having line solubility in polar solvents DMF and DMSO. The elemental analyses shown in Table 1 indicate that all these complexes have 1:2 metal: ligand stoichiometry and were in good agreement with the values calculated from proposed formula.



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