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Synthesis and characterization of novel metal chelates of 2-(8-quinolinol-5-yl) –methyl amino-5-(2- furfural) -1, 3, 4-thiadiazole derivatives

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ABSTRACT

The Synthesis of novel Metal chelates of 5-Chloromethyl-8-quinolinol coupled with 5-(2- furfural)-(1,3,4) thiadiazol-2-yl amine has been carried out in the presence of sodium bicarbonate.The newly synthesised compounds were confirmed on the basis of their spectral characterisation like IR, NMR, Mass and their Elemental analysis. The transition metal chelates viz. Cu^{2+}, Ni^{2+}, Co^{3+}, Mn^{2+} *and* Zn^{2+} *of novel ligand were prepared and characterized by metal-ligand (M:L) ratio, IR and reflectance spectroscopic and magnetic properties.*

Keywords: Metal chelates**,** 5-Chloromethyl-8-quinolinol, 5-(2-furfural-(1,3,4) thiadiazol-2-yl amine

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INTRODUCTION

Co-ordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bound. On the basis of nature of the metal as well as the type of ligand these metal complexes have extensive applications in various fields of human interest [1,2].

Chelation or complexation observes more potent antibacterial effect against some microorganisms than the respective drug [3,4]. Synthesis of Co(II), Ni(II) and Zn(II) complexes with thiazole ring containing Schiff base ligands and their antimicrobial activities were tested against eight different microorganisms [5,6,7]. Earlier we have reported biological importance of metal chelates of 5-Chloromethyl-8-quinolinol (CMQ)derivatives coupled with 5-(4-chloroPhenyl)-1,3,4-thiadiazol-2-yl amine which reveals that the ligand is moderately toxic against fungi, while all the chelates are more toxic than ligand. Among all the chelates the Cu2+ chelate is more toxic against fungi [8]. So here in continuation with our earlier work we wish to report synthesis and characterisation of same class of chelates.

MATERIALS AND METHODS

Synthesis of 2-(8-Quinolinol-5-yl)–methyl amino-5-(2-furfural)-1, 3, 4-thiadiazole:
In a round bottom flask, 5-chloromethyl-8-quinolinol hydrochloride (CMQ), (2.3 gm, 0.01 mole) and 2-amino-5-(2-furfural)-1, 3, 4-thiadiazole (3.24 gm, 0.01 mole) in acetone (50 ml) were suspended. To this suspension sodium bicarbonate (1.68 gm, 0.02 mole) was added and the mixture was warmed on the steam bath for about six hours. End of reaction was monitored by TLC. Finally solution made basic with 5% ammonium hydroxide. Final product was

collected after recovery of solvent (Acetone). The yellow solid was purified by washing with acetone. Yield of the ligand compound is 67% and having melting point 157°C.

ANALYSIS

C% , H% ,N% ,S%

Elemental Analysis	Calculated:	59.25	3.70	17.28	9.87
$C_{16}H_{12}N_4O_2S$ (324)	Found :	59.2	3.6	17.2	9.8

IR Spectral Features: 3400 (NH), 2920 (CH_2), 2850, 1597, 1507, 1450 (aromatic)cm^{-1})

NMR: ppm 7.25-7.72 (m, 8H, Ar-H), 5.76 (OH), 3.35 (CH_2) Signal

Synthesis of metal chelates of novel ligand

The metal chelates of novel ligand with Cu^{2+}, Ni^{2}, Co^{2+}, Mn^{+2}, Zn^{2+} and metal ions were prepared in two steps. All the metal chelates were prepared in an identical procedure. The details are given as follows.

Preparation of compound solution

Ligand (0.05 mol) was taken in 500 mL beaker and formic acid (85% v/v) was added up to slurry formation. To this slurry, water was added till the complete dissolution of compound. It was diluted to 100 mL.

Synthesis of Ligand-metal-chelates

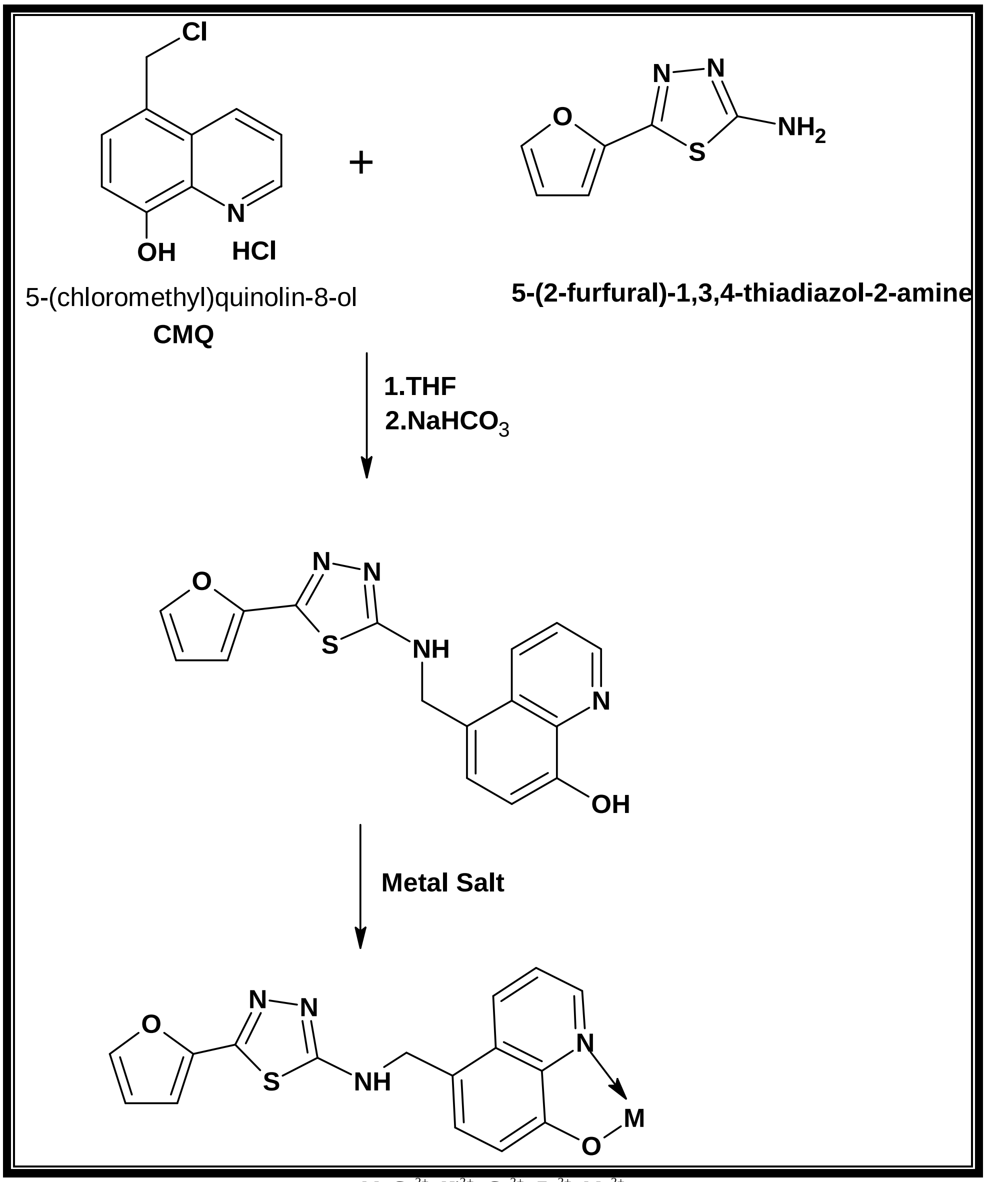
In a solution of metal acetate (0.005 mol) in water (100 mL), 20 ml of above mentioned compound solution (*i.e*. containing 0.01 M compound) was added with vigorous stirring at room temperature. The pH was adjusted around 4.5 to 6 for complete precipitation of metal chelate. The precipitates were digested on a boiling water bath. The precipitates of chelate were filtered off, washed by 1:1 mixture of water: ethanol and finally with acetone and dried at 70°C for 24 hours.

Measurements

The elemental contents were determined by Thermo Finigen Flash1101 EA (Itally), the metals were determined volumetrically by Vogel's method18**.** To 100 mg chelate sample, each 1 mL of HCl, H_2SO_4 and $HClO_4$ were added and then 1 g of $NaClO_4$ was added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to the mark. From this solution the metal content was determined by titration with standard EDTA solution. Infrared spectra of the synthesized compounds were recorded on Nicolet760 FT-IR spectrometer. NMR spectrum of compound was recorded on 400 MHz NMR spectrophotometer. Magnetic susceptibility measurement of the synthesized complexes was carried out on Gouy Balance at room temperature. Mercury tetrathiocynatocobalate(II) $Hg[CO(NCS)_4]$ was used as a calibrant. The electronic spectra of complexes in solid were recorded on at room temperature. MgO was used as reference.

RESULTS AND DISCUSSION

The synthesis of 5-(2-furfural)-1,3,4-thizole-2-yl amino methylene-8-quinolinol was performed by a simple nucleophilic substitution reaction of 5-pyridinyl-1,3,4-thiazole-2-amine and 5-chloromethyl-8-quinolinol hydrochloride (CMQ). The resulted compound was an amorphous yellow powder. The C,H,N,S contents of compound (Table 1) are consistent with the structure predicted (Scheme 1). The IR spectrum of the compound comprises the important bands due to 8-quinolinol. The bands were observed at 1669, 1577, 1509, and 1466 cm^{-1}. The broad band due to -OH group appeared at 3500 cm^{-1}. In this band the inflections are observed at 2850 and 3174 cm^{-1}.While the latter two might be attributed to asymmetric and symmetric vibration of CH_2 of CMQ. The NMR spectrum of compound in DMSO indicates that the singlet of 2 H at 3.35 ppm of N-CH_2-Ar group. While the singlet at 5.76 ppm due to -OH group. The aromatic protons are appeared in multiplicity at 7.25 to 7.72 ppm. The vigorous oxidations of compound yield 8-hydroxy quinoline-5-carboxylic acid. The melting point is 157°C. Thus the structure of compound is confirmed as shown in Scheme 1.



M: Cu^{2+}, Ni^{2+}. Co^{2+}, Zn^{2+}, Mn^{2+}

Scheme 1

The metal and C,H,N contents of metal chelates of compound Table 1 are also consistent with the predicted structure. The results show that the metal: ligand (M:L) ratio for all divalent metal chelate is 1:2.

The infrared spectra of all the chelates are identical and suggest the formation of all the metal cyclic compound by the absence of band characteristic of free -OH group of parent compound. The other bands are almost at their respectable positions as appeared in the spectrum of parent-compound ligand. However, the band due to (M-O) band could not be detected as it may appear below the range of instrument used. The important IR spectral data are shown in Table 2.

Magnetic moments of metal chelates are given in Table 2. The diffuse electronic spectrum of Cu^{2+} chelates shows two broad bands 15521 and 23992 cm^{-1}. The first band may be due to a 2B1g _ 1A1g transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} metal chelates. The higher value of the magnetic moment of the Cu^{2+} chelate supports the same. The Co^{2+} metal chelate gives rise to two absorption bands at 24118 and 19888 cm^{-1}, which can be assigned 4T1g_ 2T2g, 4T1g_ 4T1g(P) transitions, respectively. These absorption bands and the μeff value indicate an octahedral configuration of the Co^{2+} metal chelate. The spectrum of Mn^{2+} polymeric chelate comprised two bands at 18537 cm^{-1} and 22124 cm^{-1}. The latter does not have a very long tail. These bands may be assigned to 6 A1g_ 4T2g (G) and 6 A1g_ 4A2g(G) transitions, respectively. The high intensity of the bands suggests that they may have some charge transfer character.

The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment it is difficult to attach any significance to this. As the spectrum of the metal chelate of Ni^{2+} show two distinct bands at 24960 and 14148 cm^{-1} are assigned as 3 A2g(F)_ 3T1g(F) and 3 A2g(F)_ 3T1g(F) transition, respectively suggested the octahedral environment for Ni^{2+} ion. The observed μeff values in the range 3.01-3.2 B.M are consistent with the above moiety.

Table 1. Analysis of novel ligand and its metal chelates

Molecular Formula	M. Wt Gm/mole	Yield %	Elemental analysis									
			%Metal		%C		%H		%N		%S	
			Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
$C_{16}H_{12}N_4O_2S$	324	76	--	--	59.25	59.2	3.70	3.6	17.28	17.2	9.87	9.8
$C_{32}H_{22}N_8O_4S_2Cu^{+2}.2H_2O$	745.5	75	8.52	8.5	51.50	51.5	3.48	3.4	15.02	15.0	8.58	8.5
$C_{32}H_{22}N_8O_4S_2Ni^{+2}.2H_2O$	741	76	7.92	7.8	51.82	51.7	3.50	3.5	15.11	15.0	8.63	8.6
$C_{32}H_{22}N_8O_4S_2Mn^{+2}.2H_2O$	737	70	7.45	7.4	52.10	52.0	3.52	3.4	15.19	15.1	8.68	8.6
$C_{32}H_{22}N_8O_4S_2Co^{+2}.2H_2O$	741	82	7.95	7.8	51.82	51.7	3.50	3.5	15.11	15.0	8.63	8.6
$C_{32}H_{22}N_8O_4S_2Zn^{+2}.2H_2O$	747	79	8.75	8.7	51.40	51.4	3.48	3.4	14.99	14.9	8.56	8.5

Table 2. Spectral data and magnetic moment of compound metal chelates

Metal Chelates	μ_{eff}	Electronic spectral data cm^{-1}	Transition	IR spectral features common for all cm^{-1}	
Compound-Cu^{2+}	2.17	23992	Charge transfer	1669	Quinoline Moiety
		15521	2B1g_2A1g	1577	
				1509	
				1466	
Compound-Ni^{2+}	3.37	24960	3A1g_3T1g(P)	1466	CH_2
		14148	3A1g_3T1g(F)	2850	
				3174	
Compound-Co^{2+}	5.15	24118	4T1g(F) _4T2g(F)	1289	C-N bands and -NH
		19888	4T1g(F) _4T2g	3400	
		9824	4T1g(F) _4T2g(P)	--	
Compound-Mn^{2+}	5.96	22124	6A1g _6A2g 4Eg	--	
		18537	6A1g_4T2g (4G)	--	
		16107	6A1g 4T1g(PG)	--	
Compound-Zn^{2+}	--	--	--	--	

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