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RESEARCH ARTICLE

Synthesis and Characterization of Novel Metal Chelates of 2-(8-Quinolinol-5-yl) – methyl amino-5-(4-methyl-phenyl)-1, 3, 4-thiadiazole derivatives

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ABSTRACT

The Synthesis of novel Metal chelates of 5-Chloromethyl-8-quinolinol coupled with 5-(4-methyl phenyl-(1,3,4) thiadiazol-2-ylamine has been carried out in the presence of sodium bicarbonate. The newly synthesized compounds were confirmed on the basis of their spectral characterization like IR, NMR 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-(4-methyl phenyl-(1,3,4) thiadiazol-2-ylamine**.**

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 Cu^{2+} chelate is more toxic against fungi[8]. So here in continuation with our earlier work we wish to report synthesis and characterization of same class of chelates.

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EXPERIMENTAL

Synthesis of 2-(8-Quinolinol-5-yl)–methyl amino-5-(4-methyl-phenyl)-1, 3, 4-thiadiazole

In a round bottom flask, to a suspension of 5-chloromethyl-8-quinolinol (CMQ) hydrochloride (2.3 g, 0.01 mol) and 2-amino-5-(4-methyl phenyl)-1,3,4-thiadiazole (3.48 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 83% and having melting point 155°C.

Analysis

C%, H%, N%, S%

Elemental Analysis

Calculated: 65.51 4.60 16.10 9.19

$C_{19}H_{16}N_4OS$ (348)

Found: 65.4 4.5 16.0 9.0

IR Spectral Features: 3400 (NH), 2920 (CH_2), 2849, 1598, 1507, 1450 (aromatic).cm^{-1})

NMR: ppm 7.25-7.72 (m 9H 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

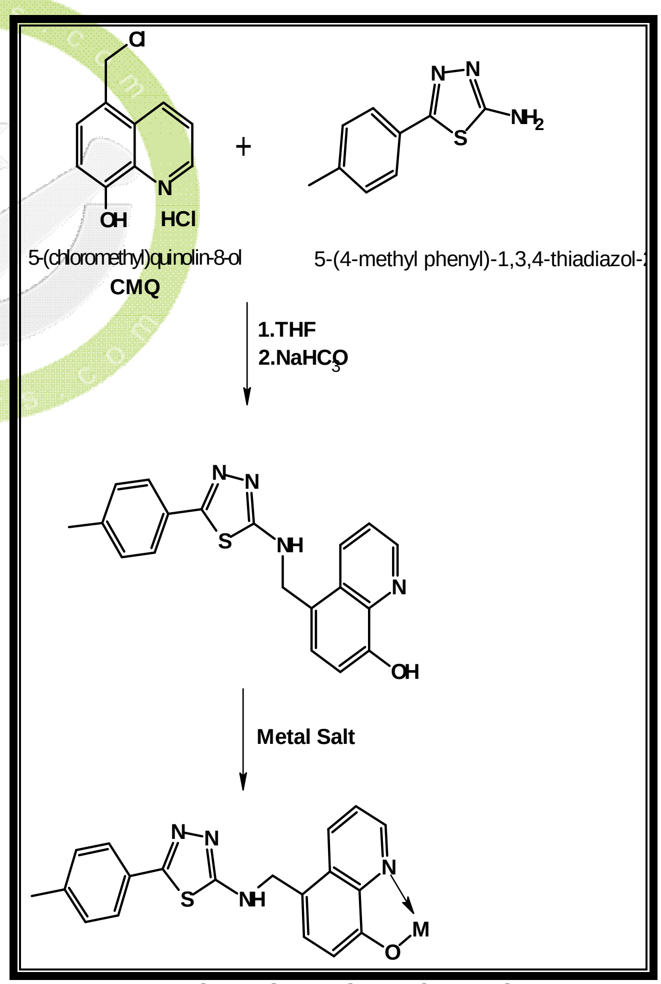
Ligand (0.05 mol) was taken in 500 mL beaker and formic acid (85% v/v) was added up to slurry formation. To this slurry, water was added till the complete dissolution of compound. It was diluted to 100 mL.

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.



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

Scheme 1

RESULTS AND DISCUSSION

The synthesis of 5-(4-methyl-phenyl)-1,3,4-thizole-2-yl amino methylene-8-quinolinol was performed by a simple nucleophilic substitution reaction of 5-(4-methyl-phenyl)-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 1610, 1578, 1509, and 1478 cm^{-1}. The broad band due to -OH group appeared at 3500 cm^{-1}. In this band the inflections are observed at 2888 and 2969 and 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 point20 is 155°C. Thus the structure of compound is confirmed as shown in 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 15762 and 24503 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 chelates21, 22. 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 22978 and 19042 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 18593 cm^{-1} and 23415 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 22496 and 13124 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.

CONCLUSION

A series of novel metal chelates of 2-(8-quinolinol-5-yl) –methyl amino-5-(4-methyl-phenyl)-1, 3, 4-thiadiazole derivatives were designed and synthesized, and their structures were confirmed by IR, ^{1}H NMR and their elemental analysis. The modification of the active Quinolinol moiety offers a promising and useful intermediate for the formation of new chemical entities.

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
$C_{19}H_{16}N_4OS$	348	85	--	--	65.5	65.4	4.60	4.5	16.1	16.0	9.19	9.0
$C_{38}H_{30}N_8O_2S_2$ $Cu^{+2}.2H_2O$	793.5	73	8.00	8.0	57.4	57.3	4.28	4.2	14.1	14.0	8.06	8.0
$C_{38}H_{30}N_8O_2S_2$ $Ni^{+2}.2H_2O$	789	76	7.44	7.3	57.7	57.7	4.30	4.3	14.2	14.2	8.11	8.0
$C_{38}H_{30}N_8O_2S_2$ $Mn^{+2}.2H_2O$	785	74	7.00	7.0	58.0	58.0	4.33	4.2	14.2	14.1	8.15	8.1
$C_{38}H_{30}N_8O_2S_2$ $Co^{+2}.2H_2O$	789	81	7.46	7.3	57.7	57.7	4.30	4.2	14.2	14.2	8.11	8.0
$C_{38}H_{30}N_8O_2S_2$ $Zn^{+2}.2H_2O$	795	78	8.22	8.2	57.3	57.2	4.27	4.2	14.0	14.0	8.05	8.0

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	24503	Charge transfer	610	Quinoline Moity
		15762	2B1g_2A1g	1578	
				1509	
				1478	
Compound-Ni^{2+}	3.33	22496	3A1g_3T1g(P)	1409	CH_2
		13124	3A1g_3T1g(F)	2888	
				2969	
Compound-Co^{2+}	5.15	22978	4T1g(F)_4T2g(F)	1299	C-N bands and -NH
		19042	4T1g(F) _4T2g	3400	
		8535	4T1g(F)_4T2g(P)	--	
Compound-Mn^{2+}	5.94	23415	6A1g _6A2g 4Eg	--	
		18593	6A1g_4T2g (4G)	--	
		16125	6A1g 4T1g(PG)	--	
Compound-Zn^{2+}	--	--	--	--	

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