

Synthesis and Characterization of Novel Metal Chelates of 2-(8-Quinololin-5-Yl) –Methyl Amino-5-(4-Bromo-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-bromo phenyl-(1,3,4) thiadiazol-2-ylamine 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. Cu²⁺, Ni²⁺, Co³⁺, Mn²⁺ and Zn²⁺ 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-bromo 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 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.

EXPERIMENTAL

Synthesis of 2-(8-Quinolinol-5-yl)-methyl amino-5-(4-bromo-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-bromo phenyl)-1,3,4-thiadiazole (4.13 gm, 0.01 mole) in acetone (50 ml) were suspended. To this suspension sodium bicarbonate (1.68 gm, 0.02 mol) 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 compound is 84% and having melting point- 148°C.

ANALYSIS

C% ,H% ,N% ,S%

Elemental Analysis Calculated: 52.30 3.14 13.55 7.74

C₁₈H₁₃N₄OSBr (413) Found : 52.2 3.0 13.4 7.6

IR Spectral Features: 3400 (NH), 2920 (CH₂), 2850, 1599, 1507, 1450 (aromatic).cm⁻¹

NMR: ppm 7.25-7.72 (m 9H Ar-H), 5.76 (OH) 3.35 (CH₂) Signal

Synthesis of metal chelates of compound

The metal chelates of compound with Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺, Zn²⁺ 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

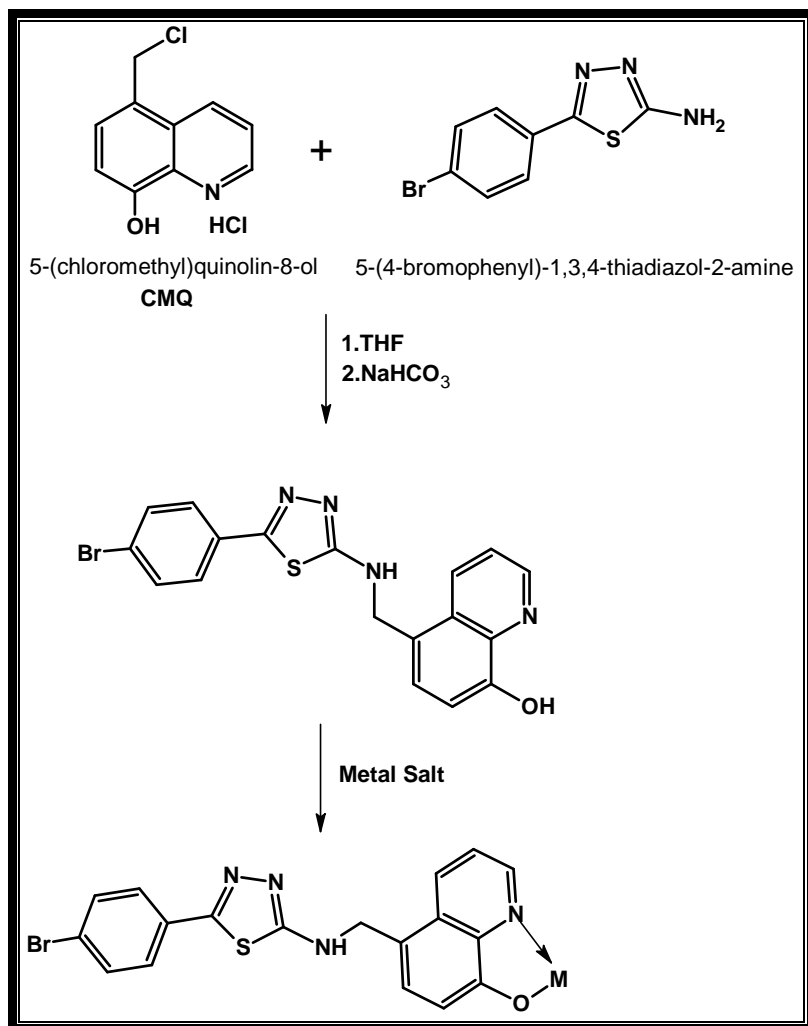
compound (0.05 mol) was taken in 500 mL beaker and formic acid (85% v/v) was added up to slurry formation. To this slurry, water was added till the complete dissolution of compound. It was diluted to 100 mL.

Synthesis of compound-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 (Italy), the metals were determined volumetrically by Vogel's method¹⁸. To 100 mg chelate sample, each 1 mL of HCl, H₂SO₄ and HClO₄ were added and then 1 g of NaClO₄ 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 tetrathiocyanatocobalate(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: Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Mn²⁺

Scheme 1.

RESULTS AND DISCUSSION

The synthesis of 5-(4-bromo-phenyl)-1,3,4-thiazole-2-yl amino methylene-8-quinolinol was performed by a simple nucleophilic substitution reaction of 5-(4-bromo-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 1609, 1577, 1509, and 1459 cm⁻¹. The broad band due to -OH group appeared at 3500 cm⁻¹. In this band the inflections are observed at 2839 and 2901 and cm⁻¹. While the latter two might be attributed to asymmetric and symmetric vibration of CH₂ of CMQ. The NMR spectrum of compound in DMSO indicates that the singlet of 2 H at 3.35 ppm of N-CH₂-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 148°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.

Table 1. Analysis of novel ligand and its metal chelates.

Molecular formula	M.Wt Gm/mole	Yield %	Elemental analysis											
			%Metal		%C		%H		%N		%Br		%S	
			Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
C ₁₈ H ₁₃ N ₄ OSBr	413	78	--	--	52.30	52.2	3.14	3.0	16.76	16.6	--	--	7.74	7.6
C ₃₆ H ₂₄ N ₈ O ₂ S ₂ Br ₂ Cu ⁺² .2H ₂ O	923.5	67	6.88	6.7	46.77	46.6	3.03	3.0	14.63	14.5	17.32	17.2	6.93	6.8
C ₃₆ H ₂₄ N ₈ O ₂ S ₂ Br ₂ Ni ⁺² .2H ₂ O	919	70	6.40	6.4	47.00	47.0	3.04	3.0	14.71	14.7	17.41	17.3	6.96	6.9
C ₃₆ H ₂₄ N ₈ O ₂ S ₂ Br ₂ Mn ⁺² .2H ₂ O	915	71	6.00	6.0	47.21	47.2	3.06	3.0	14.80	14.8	17.48	17.4	6.99	6.9
C ₃₆ H ₂₄ N ₈ O ₂ S ₂ Br ₂ Co ⁺² .2H ₂ O	919	67	6.41	6.3	47.00	47.0	3.04	3.0	14.71	14.7	17.41	17.3	6.96	6.9
C ₃₆ H ₂₄ N ₈ O ₂ S ₂ Br ₂ Zn ⁺² .2H ₂ O	925	70	7.06	7.0	46.70	46.6	3.02	3.0	14.60	14.6	17.29	17.2	6.91	6.9

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⁺	2.12	24388	Charge transfer	1609	Quinoline Moiety
		15620	2B1g_2A1g	1577	
				1509	
				1459	
Compound-Ni ²⁺	3.34	24194	3A1g_3T1g(P)	1459	CH ₂
		14122	3A1g_3T1g(F)	2839	
				2901	
Compound-Co ²⁺	5.16	24116	4T1g(F)_4T2g(F)	1269	C-N bands and -NH
		19720	4T1g(F)_4T2g	3400	
		8668	4T1g(F)_4T2g(P)	--	
Compound-Mn ²⁺	5.97	23984	6A1g_6A2g_4Eg	--	
		17645	6A1g_4T2g(4G)	--	
		15465	6A1g_4T1g(PG)	--	
Compound-Zn ²⁺	--	--	--	--	

The infrared spectra of all the chelates are identical and suggest the formation of all the metalocyclic 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 Cu²⁺ chelates shows two broad bands 15620 and 24388 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 Cu²⁺ metal chelates^{21,22}. The higher value of the magnetic moment of the Cu²⁺ chelate supports the same. The Co²⁺ metal chelate gives rise to two absorption bands at 24116 and 19720 cm^{-1} , which can be assigned 4T1g_2T2g, 4T1g_4T1g(P) transitions, respectively. These absorption bands and the μ_{eff} value indicate an octahedral configuration of the Co²⁺ metal chelate^{23,24}. The spectrum of Mn²⁺ polymeric chelate comprised two bands at 17645 cm^{-1} and 23984 cm^{-1} . The latter does not have a very long tail. These bands may be assigned to 6A1g_4T2g(G) and 6A1g_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 Ni²⁺ show two distinct bands at 24194 and 14122 cm^{-1} are assigned as 3A2g(F)_3T1g(F) and 3A2g(F)_3T1g(F) transition, respectively suggested the octahedral environment for Ni²⁺ ion. The observed μ_{eff} values in the range 3.01-3.2 B.M are consistent with the above moiety.

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