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Synthesis and characterization of novel metal chelates of 2-(8-quinolinol-5-yl) – methyl amino-5 -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-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. Cu^{2+} , Ni^{2+} , Co^{3+} , Mn^{2+} and Zn^{2+} of CTAQ were prepared and characterized by metal-ligand (M:L) ratio, IR and reflectance spectroscopies and magnetic properties.

Keywords: Metal chelates, 5-Chloromethyl-8-quinolinol, 5-phenyl-(1,3,4) thiadiazol-2-ylamine

INTRODUCTION

Derivatives of 8-hydroxyquinoline possess wide spectrum of biological activity in pharmaceutical industry. Due to antibacterial and antifungal activity and it is widely used in creams and ointments for the treatment of skin diseases [1]. Clioquinol is an antifungal drug and antiprotozoal drug [2]. 8-Quinolinol (8Q) or its derivatives have been introduced as chelating groups. [3-5]. The chelating properties of the compounds of the 8Q series are related to its biological activity [6]. Similarly 8-hydroxyquinoline (8Q) and its metalloquinolates have attracted great interest because their high thermal stability and good electroluminescence properties which make them important prototypical electron transport and emitting materials for OLED devices [8-10]. 8-Hydroxyquinoline (8-quinolinol, oxine, 8Q) might be thought to function as a phenol, but of the 7 isomeric hydroxyquinolines only oxine exhibits significant antimicrobial activity, and is the only one to have the capacity to chelate metals [11-13]. 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 [14]. Similarly pyrazoline ligands with Quinolinol shows good activity [15]. Chelation or complexation observes more potent antibacterial effect against some microorganisms than the respective drug [16, 17]. 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-phenyl-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-phenyl-1,3,4-thiadiazole (3.34 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 87% and having melting point- 147°C.

Analysis

C% ,H% ,N% ,S%

Elemental Analysis

Calculated : 64.67 4.19 16.76 9.58

C₁₈H₁₃N₄OS (334)

Found : 64.5 4.20 16.6 9.4

IR Spectral Features: 3400 (NH), 2940 (CH₂), 2850, 1597, 1507, 1450 (aromatic).cm⁻¹)NMR: ppm 6.88-7.58 (m 10H Ar-H), 5.74 (OH) 3.72 (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

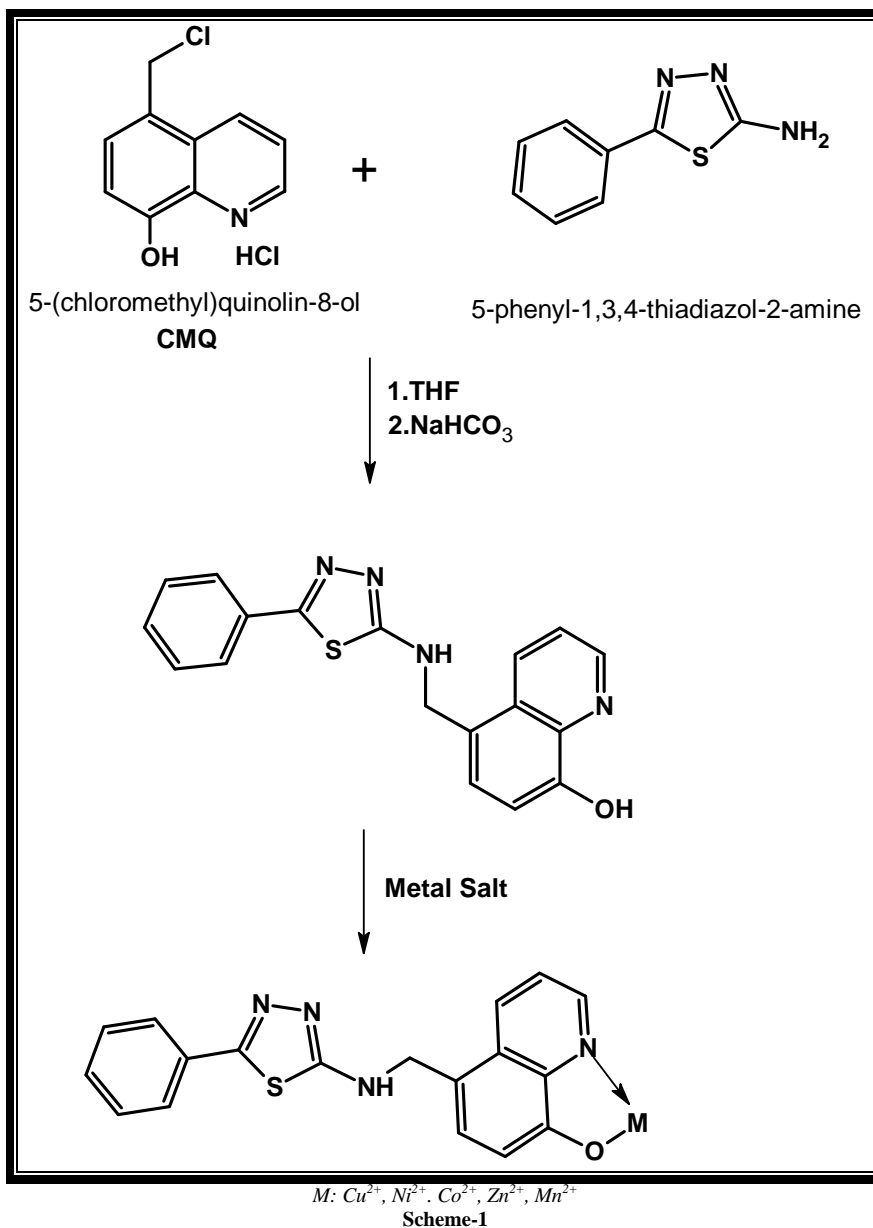
compound (0.05 mol) was taken in 500 mL beaker and formic acid (85% v/v) was added up to slurry formation. To this slurry, water was added till the complete dissolution of compound. It was diluted to 100 mL.

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.



RESULTS AND DISCUSSION

The synthesis of 5-phenyl-1,3,4-thiazol-2-yl amino methylene-8-quinolinol was performed by a simple nucleophilic substitution reaction of 5-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 1624, 1578, 1507, and 1470 cm^{-1} . The broad band due to -OH group appeared at 3800 cm^{-1} . In this band the inflections are observed at 2850 and 2940 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 2H at 3.72 ppm of N- CH_2 -Ar group. While the singlet at 5.74 ppm due to -OH group. The aromatic protons are appeared in multiplicity at 6.88 to 7.52 ppm. The vigorous oxidations of compound yield 8-hydroxy quinoline-5-carboxylic acid. The melting point is 147°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 the entire 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 Cu²⁺ chelates shows two broad bands at 15656 and 23372 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. 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 24655 and 19980 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. The spectrum of Mn²⁺ polymeric chelate comprised two bands at 18658 cm⁻¹ and 24042 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 Ni²⁺ show two distinct bands at 24122 and 15191 cm⁻¹ are assigned as 3 A2g(F)_ 3T1g(F) and 3 A2g(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.

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 ₁₈ H ₁₄ N ₄ OS	334	78	--	--	64.67	64.5	4.19	4.2	16.76	16.6	9.58	9.4
C ₃₆ H ₂₆ N ₈ O ₂ S ₂ Cu ⁺² 2H ₂ O	765.5	67	8.30	8.3	56.43	56.3	3.39	3.3	14.63	14.5	8.36	8.2
C ₃₆ H ₂₆ N ₈ O ₂ S ₂ Ni ⁺² 2H ₂ O	761	70	7.71	7.6	56.76	56.6	3.41	3.3	14.71	14.7	8.40	8.4
C ₃₆ H ₂₆ N ₈ O ₂ S ₂ Mn ⁺² 2H ₂ O	757	71	7.25	7.2	57.06	57.0	3.43	3.4	14.80	14.8	8.45	8.5
C ₃₆ H ₂₆ N ₈ O ₂ S ₂ Co ⁺² 2H ₂ O	761	67	7.74	7.7	56.76	56.6	3.41	3.4	14.71	14.7	8.40	8.4
C ₃₆ H ₂₆ N ₈ O ₂ S ₂ Zn ⁺² 2H ₂ O	767	70	8.52	8.5	56.32	56.2	3.38	3.2	14.60	14.6	8.34	8.3

Table 2. Spectral features and magnetic moment of Novel metal chelates.

Metal Chelates	μ_{eff}	Electronic spectral data cm ⁻¹	Transition	IR spectral features common for all cm ⁻¹	
CTAQ-Cu ²⁺	2.12	23372	Charge transfer	1610	Quinoline Moiety
		15656	2B1g_2A1g	1576	
				1509	
				1459	
CTAQ-Ni ²⁺	3.37	24122	3A1g_3T1g(P)	2990	CH ₂
		15191	3A1g_3T1g(F)	2929	
CTAQ-Co ²⁺	5.15	24655	4T1g(F)_4T2g(F)	1289	C-N bands and -NH
		19980	4T1g(F)_4T2g	3400	
		8788	4T1g(F)_4T2g(P)	--	
CTAQ-Mn ²⁺	5.95	24042	6A1g_6A2g 4Eg	--	
		18658	6A1g_4T2g (4G)	--	
		16222	6A1g_4T1g(PG)	--	
CTAQ-Zn ²⁺	-				

REFERENCES

- [1]. J. Giménez-Izquierdo, J. Guiteras, A. Izquierdo and M. D. Prat, *Fres. J. Anal.Chem.*, 341, 638, (1991)
- [2]. W. Rohde, P. Mikelens, J. Jackson, J. Blackman, J. Witcher and W. Levinson, *Antimicrob.Agents Chemother*, 10(2), 234, (1976)

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- [3] Geckeler, K. E. and Rongnong, Z., .DE 4227019 (Cl. C08F8/00), 1994; *Chem.Abstr.* 121,10302f, (1994)
- [4] Purohit R and Devi S. *Analyst*, 116, 825, (1991)
- [5] Pittman C U Jr, Ramachandran K S and Lawyer K R *J. Coat.Technol.* 1982, 54, 27.
- [6] Albert E *Selective Toxicity*. Chapman and Hall, London, (1979)
- [7] W. Rohde, P. Mikelens, J. Jackson, J. Blackman, J. Witcher and W. Levinson, *Antmicrob.Agents Chemother.* 10(2), 234, (1976)
- [8] Shen Z L, Burrows P E, Bulovic V, Forrest S R, Thompson M E. *Science* 2009, 1997, 276.
- [9] Aziz H, Popovic Z D, Hu N X, Hor A M, Xu G. *Science*. 283, 1900, (1999)
- [10] Barth S, M€uller P, Riel H, Seidler P F, RießW, Vestweber H, *Journal of Applied Physics*, 89, 3711, (2001)
- [11] Albert, A and co-workers, *Br. J. Exp. Pathol.* 28, 69, (1947)
- [12] Albert A, Gibson M I and Rubbo S D *J. Exp. Pathol.* 34, 119, (1953)
- [13] Rubbo S D, Albert A and Gibson M I *J. Exp. Pathol.*, 31, 425, (1950)
- [14] Patel D K, Arun Singh. *E-Journal of Chemistry*, 6(4), 1017-1022, (2009)
- [15] B. N. Patel, P. S. Patel and V. G.Patel, *Der Chemica Sinica*, 2 (2): 194-198, (2011)
- [16] H. Kumar, R. Chaudhary, *Der Chemica Sinica*, 1(2), 55, (2010)
- [17] S.I. Habib, M.A. Baseer, P.A. Kulkarni, *Der Chemica Sinica*, 2(1), 27,(2011)