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NOTE

Structural Aspects of Schiff Base Metal Complexes of Co(II), Ni(II) and Cu(II) Complexes Derived from 4-Hydroxy-1-ethyl quinoline

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Complexes of Co(II), Ni(II) and Cu(II) with 4-hydroxy-1-ethyl quinolin-2-(1*H*)-one hydrazone [HEQH] have been synthesized and characterized on the basis of their molar mass, elemental analyses, IR, UV, molar conductance and magnetic susceptibility measurements. On the basis of above physico-chemical and spectroscopic measurements it is proposed that the compound 4-hydroxy-1-ethyl quinolin-2-(1*H*)-one hydrazone acts in a bidentate ligand and co-ordination proposes through azomethine N atom and oxygen atom. The remaining valency of metal ions are satisfied by neutral molecules such as ammonia, pyridine, α, β or γ-picolines. Electronic spectral and magnetic susceptibility of the complexes proposes octahedral geometry for Co(II) and Ni(II) complexes. The geometry of the Cu(II) complexes is distorted octahedral in geometry.

Key Words: 4-Hydroxy-1-ethyl quinolin-2-(1*H*)-one hydrazone, Co(II), Ni(II), Cu(II), Complexes.

Schiff bases are most widely used as chelating ligands in coordination chemistry[1,2]. They are also useful in catalysis, in medicine as antibiotics and to treat industrial waste. Semicarbazone Schiff bases are versatile ligands having biological importance as, antitumor agents, plant growth regulators, antibacterial, antineoplastic, antiviral, antileukemic and enzymatic reaction inhibitors. The complexes with such Schiff bases are very important due to their application in medicine, particularly in the chemotherapy of cancer[3-5]. In the view of above importance, we thought of interest to design Schiff bases having, nitrogen and oxygen architecture to bind the metal ions. in this communication, we report the synthesis, spectroscopic characterization of Co(II), Ni(II), Cu(II) complexes with Schiff base, 4-hydroxy-1-ethyl quinolin-2(1*H*)-one hydrazone [HEQH].

All the chemicals were from BDH or SRL. The metal, carbon, hydrogen nitrogen were estimated by standard methods. The magnetic susceptibility measurement were made at room temperature by Gouy method by using $Hg[Co(NCS)_4]$ as a calibrant. Melting point of the complexes were determined by open capillary method, IR spectra of the ligand as well as the metal complexes were recorded on Perkin-Elmer 577 spectrophotometer. The electronic spectra were measured on cary-2390 spectrophotometer. Molar conductance were measured by systronics conductivity meter module 3B in DMF.

Preparation of the ligand: The ligand was synthesized refluxing the mixture of 4-hydroxy-1-ethyl quinolin-2(1*H*)-one (0.001 m) dissolved in acetone and ethanolic solution of hydrazine hydrate (0.01 m). The light yellowish crystalline solid formed during refluxion was cooled, filtered, washed with ethanol and recrystallized from hot ethanol (yield 75 %).

Synthesis of Co(II), Ni(II) and Cu(II) complexes: The metal complexes were synthesized by adding ethanolic solution (20 mL) respective metals acetates of Co(II), Ni(II) and Cu(II) in presence of bases ammonia, puridine, α-, β- or γ- picolines (0.01 m) to Schiff bases with each of metal separately. [HEQH] (2.15 g 0.01 m) in ethanol (30 mL). The reaction mixture was refluxed on a water bath for 3-4 h, on water bath. The partial removal of the solvent and cooling to room temperature gave solid coloured complexes which were filtered, washed thoroughly with ethanol and finally dried. Yield 60-65 %.

The vibrational spectra of the ligand as well as complexes has been recorded in Table-1 in the frequency range 4000-200 cm^{-1}. The elemental analysis shows that all the complexes have 1:2 stoichiometry. The molar conductance values are too low to account for any dissociation of the complexes in DMF, indicating the non-electrolyte complexes (Table-2). The IR brands give valuable information regarding bonding modes of ligand to metal ions in the complexes. The IR spectrum of

TABLE-2
PHYSICOCHEMICAL MEASUREMENT OF LIGAND 4-HYDROXY-1-ETHYL QUINOLIN-2-(1*H*)-ONE HYDRAZONE (HEQH) AND ITS Co(II), Ni(II) AND Cu(II) COMPLEXES

Compound	Molar mass	Yield (%)	Elemental analysis (%): Found (calcd.)				λ_{max} electronic (cm^{-1})	DT (ºC)	μ_{eff} (BM)	Ω_m (ohm^{-1} cm^2 mol^{-1})
			M	C	H	N				
HEQH	215	75		66.80	5.92	19.45	–	–	–	–
				(66.97)	(8.84)	(19.53)				
$[Co(HEQH)_2(NH_3)_2]$	554.93	63	10.50	51.72	4.59	20.03	13300	223	4.96	3.4
			10.61	51.89	(4.68)	(20.18)	19400			
$[Co(HEQH)_2(C_6H_5N)_2]$	664.93	65	8.48	43.20	3.87	16.73	13360	217	4.90	3.1
			8.86	43.31	(3.91)	(16.84)	18600			
$[Co(HEQH)_2(\alpha\text{-pic})_2]$	672.93	65	8.68	42.64	2.89	16.52	13500	242	4.92	2.8
			8.75	42.79	(2.97)	(16.64)	19100			
$[Co(HEQH)_2(\beta\text{-pic})_2]$	672.93	65	8.69	42.65	2.92	16.53	13700	254	4.96	2.6
			8.75	42.79	(2.97)	(16.64)	18800			
$[Co(HEQH)_2(\gamma\text{-pic})_2]$	672.93	65	8.67	42.67	2.93	16.57	13900	220	4.94	2.1
			8.75	42.79	(2.97)	(16.64)	18700			
$[Ni(HEQH)_2(NH_3)_2]$	554.71	64	10.49	51.80	4.62	20.06	11300,16000	210	3.18	1.8
			10.58	51.91	(4.68)	(.20.19)	23900			
$[Ni(HEQH)_2(C_6H_5N)_2]$	664.71	65	8.75	43.21	3.87	16.76	11260, 15900	218	3.20	1.9
			8.83	43.32	(3.91)	(16.84)	23960			
$[Ni(HEQH)_2(\alpha\text{-pic})_2]$	672.71	62	8.64	42.70	3.89	16.58	11200, 15800	202	3.22	2.2
			8.72	42.81	(3.95)	(16.64)	23990			
$[Ni(HEQH)_2(\beta\text{-pic})_2]$	672.71	60	8.66	42.69	3.90	16.56	11100, 16100	213	3.17	2.4
			8.72	42.81	(3.95)	(16.64)	24020			
$[Ni(HEQH)_2(\gamma\text{-pic})_2]$	672.71	60	8.67	42.67	3.91	16.50	11220, 15980	217	3.21	2.5
			8.72	42.81	(3.95)	(16.64)	24000			
$[Cu(HEQH)_2(NH_3)_2]$	555.54	61	11.27	51.35	4.58	20.07	13620-16770	202	1.90	1.8
			11.35	51.17	(4.64)	(20.16)				
$[Cu(HEQH)_2(C_6H_5N)_2]$	669.54	61	9.40	42.80	3.81	16.61	13620-16770	201	1.92	1.7
			9.49	43.01	(3.88)	(1.72)				
$[Cu(HEQH)_2(\alpha\text{-pic})_2]$	677.54	61	9.31	42.33	3.78	16.47	13620-16770	213	1.89	1.6
			9.37	42.50	(3.83)	(16.53)				
$[Cu(HEQH)_2(\beta\text{-pic})_2]$	677.54	65	9.30	42.35	3.79	16.44	13620-16770	212	1.93	1.4
			9.37	42.50	(3.83)	(16.53)				
$[Cu(HEQH)_2(\beta\text{-pic})_2]$	677.54	65	9.28	42.37	3.77	16.40	13620-16770	211	1.91	1.3
			9.37	42.50	(3.83)	(16.53)				

DT = Decomposition temperature.

TABLE-1
IR SPECTRAL BANDS OF LIGAND 4-HYDROXY-1-ETHYL QUINOLIN-2-(1*H*)-ONE HYDRAZONE (HEQH) AND ITS METAL COMPLEXES

Compounds	ν(O-H)	ν(C=N)	ν(M-O)	ν(M-N)
HEQH	3260s,b	1560s	–	–
$[Co(HEQH)_2(NH_3)_2]$	3230m,b	1535mb	515m	460m
$[Co(HEQH)_2(C_6H_5N)_2]$	3230m,b	1535m,b	510m	465m
$[Co(HEQH)_2(\alpha\text{-pic})_2]$	3235m,b	1530m,b	525m	465m
$[Co(HEQH)_2(\beta\text{-pic})_2]$	3235m,b	1525m,b	530m	465m
$[Co(HEQH)_2(\gamma\text{-pic})_2]$	3235m,b	1535m,b	535m	465m
$[Ni(HEQH)_2(NH_3)_2]$	3230m,b	1530m,,b	495m	470m
$[Ni(HEQH)_2(C_6H_5N)_2]$	3225m,b	1535mb	495m	460m
$[Ni(HEQH)_2(\alpha\text{-pic})_2]$	3230m,b	1530m,b	495m	465m
$[Ni(HEQH)_2(\beta\text{-pic})_2]$	3230m,b	1525m,b	495m	470m
$[Ni(HEQH)_2(\gamma\text{-pic})_2]$	3230m,b	1535mb	495m	470m
$[Cu(HEQH)_2(NH_3)_2]$	3230mb	1530m,b	510m	475m
$[Cu(HEQH)_2(C_6H_5N)_2]$	3225mb	1525mb	505m	475m
$[Cu(HEQH)_2(\alpha\text{-pic})_2]$	3230m	1530mb	510m	475m
$[Cu(HEQH)_2(\beta\text{-pic})_2]$	3225m	1535mb	510m	475m
$[Cu(HEQH)_2(\gamma\text{-pic})_2]$	3225m	1530m,b	515m	475m

the free ligand was compared with the spectra of the metal complexes. The IR spectrum of the Schiff bases strong[6] and broad band at 3260 cm^{-1} assigned to no-N stretching. The shifting of this band to $^{-1}$ lower wave number by 20-30 cm^{-1} indicates involvement of 0 atom of hydroxyl group in banding. The strong band observed at 1560 cm^{-1}, indicating participation of azomethine nitrogen in coordination. The intense band at 1100-1020 cm^{-1} in the complexes have been taken to be characteristic vibration of coordination pyridines and picolines molecules. The proposal coordination through oxygen atom of hydroxyl group is further supported by the appearance of a far ir band at 535-495 cm^{-1} assigned[7] to ν(M-O). The linkage with azomethine nitrogen is further confirmed by the appearance of another band in far[14] IR region at 470-450 cm^{-1} assigned to ν(M-N). The medium intensity band at 690-650 cm^{-1} in the complexes suggesting assign due to pyridine and picolines molecules.

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