Transition Metal Complexes of Oxygen and Nitrogen Containing Schiff Base Derived from 4-Methyl-1,2-dihydro-2-oxoquinazoline

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Co(II), Ni(II) and Cu(II) complexes of 4-methyl-1,2-dihydro-2-oxoquinazoline were synthesized and characterized by molar mass, elemental analyses, infrared spectra, electronic spectra, conductivity and magnetic measurements. The analytical data proposes the composition of the metal complexes to be ML_2X_2 ; where $M = Co(II), Ni(II)$; $X = Cl^-, Br^-, I^-$ and NO_3^- and $M = Cu(II)$, $X = Cl^-, Br^-$ and NO_3^- ; $L = 4\text{-methyl-1,2-dihydro-2-oxoquinazoline hydrazone}$. IR results demonstrate the bidentate binding of the Schiff base involving azomethine nitrogen and carbonyl oxygen. The electronic spectral measurements proposes Co(II), Ni(II) have octahedral geometry, where Cu(II) complexes have distorted octahedral geometry.

Key Words: Schiff base, 4-Methyl-1,2-dihydrooxoquinazoline hydrazone, Co(II), Ni(II), Cu(II), Complexes.

INTRODUCTION

Schiff base metal complexes are being studied extensively due to their various applications such as anticonvulsion, pharmaceutical agents, antibacterial, antiviral and corrosion inhibitors¹⁻³. Metal complexes with nitrogen and oxygen containing Schiff base play an important role in several biological applications⁴ and represent interesting models for metalloenzyme, which efficiently catalyze the reduction of dioxygen⁵ and dinitrogen. Recently^{6,7}, we have synthesized and characterized some Schiff base metal complexes and their *in vitro* antimicrobial activities have been investigated. In the present work we report synthesis, characterization of metal complexes Co(II), Ni(II) and Cu(II) complexes with Schiff base, 4-methyl-1,2-dihydrooxoquinazoline hydrazone (MDOQH).

EXPERIMENTAL

All the used chemicals and solvents were of AnalR grade. All the chemicals and solvents were used as such without further purification.

Elemental analyses were performed by standard technique⁸. The IR spectra of ligand and complexes were recorded on Perkin Elmer 577 spectrophotometer. Electronic spectra were recorded on Cary-2390 spectrophotometer. Magnetic susceptibility were measured by Guoy balance using $Hg[Co(NCS)_4]$ as a calibrant. The molar conductance was

measured on systronics conductivity meter model 303 using DMF as a solvent.

Preparation of ligand MDOQH: The ligand 4-methyl-1,2-dihydro-2-oxoquinazoline hydrazone was prepared by condensation of 4-methyl-1,2-dihydro-2-oxoquinazoline (0.001 m) with hydrazone hydrate [0.001 m] dissolved in 10 % ethanolic solution. The mixture was heated on water bath for 2 h, upon cooling and slow evaporation, the compound MDOQH was formed. m.p. $203 \pm 1^\circ C$. Yield 65 %.

Preparation of the complexes: The Co(II), Ni(II) and Cu(II) complexes were prepared by the treatment of ethanolic solution of 4-methyl-1,2-dihydro-2-oxoquinazoline hydrazone (MDOQH) (0.002 m) with ethanolic solution of respective metal chloride/nitrate (0.001 m) and refluxed for 3-4 h. The complexes obtained were washed with water, ethanol and diethyl ether, dried in desiccator and stored in air tight bottles. Yield 61-65 %.

RESULTS AND DISCUSSION

The important IR spectral bands of the ligand and their complexes along with their probable assignments are given in Table-1. The IR spectrum of the ligand MDOQH show a strong band of broad intensity at 3300 cm^{-1} assigned^{9,10} quinazoline nitrogen. The spectra of all the complexes exhibits this band shifted to lower wave number. The Schiff base of the band and change in intensity proposes linkage with nitrogen atom of quinazoline ring. The spectrum of the ligand exhibit another

band at 1470 cm^{-1} assigned^{9,11} to $\nu(\text{C}=\text{N})$. This band also suffered downward shift by $20\text{--}35\text{ cm}^{-1}$ proposes linkage of azomethine N with metal ions. The coordination with nitrogen of quinazoline ring as well as through azomethine nitrogen are further supported by the presence of a band in far ir region at $490\text{--}465\text{ cm}^{-1}$ assigned⁹ to $\nu(\text{M}-\text{N})$. The evidence of metal halogen linkage are proposed by the appearance of band in far ir region at $320\text{--}260\text{ cm}^{-1}$ assigned⁹ to $\nu(\text{M}-\text{X})$ ($\text{X}=\text{Cl}^-$, Br^- or I^-). This argument is supported by the low value of molar conductance of the complexes in the range $2.1\text{--}4.9\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ which proposes non-electrolytic nature of the complexes. The evidence of mono coordinated linkage of nitrate ion with metal ions are supported by the appearance of a significant IR band at 1340 cm^{-1} and 1220 cm^{-1} with a separation of 120 cm^{-1} .

The electronic spectral¹² and magnetic susceptibility measurements^{13,14} (Table-2) proposes octahedral geometry for the complexes.

Conclusion

On the basis of physicochemical and spectral measurements the ligand, MDOQH acts as a neutral bidentate ligand and coordination proposes through quinazoline ring nitrogen, azomethine nitrogen. The remaining coordination centres are satisfied by negative ions such as Cl^- , Br^- , I^- or NO_3^- . The geometry of the complexes of Co(II) and Ni(II) proposes octahedral in nature whereas the geometry of Cu(II) complexes are distorted octahedral in nature as shown in Fig. 1.

Fig. 1. $[\text{M}(\text{MDOQH})_2\text{X}_2]$; $\text{M} = \text{Co(II)}$ and Ni(II) ; $\text{X} = \text{Cl}^-$, Br^- , I^- and NO_3^- ; $\text{M} = \text{Cu(II)}$, $\text{X} = \text{Cl}^-$, Br^- and NO_3^-

TABLE-1
IR SPECTRAL BAND (cm^{-1}) OF THE LIGAND
MDOQH AND ITS COMPLEXES

Compounds	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{X})$
MDOQH	3300 s,b	1470 s,b		
$[\text{Co}(\text{MDOQH})_2\text{Cl}_2]$	3270 m,b	1455 m,b	485 m	270 m
$[\text{Co}(\text{MDOQH})_2\text{Br}_2]$	3270 m,b	1450 m,b	480 m	275 m
$[\text{Co}(\text{MDOQH})_2\text{I}_2]$	3275 m,b	1450 m,b	490 m	280 m
$[\text{Co}(\text{MDOQH})_2(\text{NO}_3)_2]$	3265 m,b	1440 m,b	490 m	285 m
$[\text{Ni}(\text{MDOQH})_2\text{Cl}_2]$	3265 m,b	1440 m,b	475 m	300 m
$[\text{Ni}(\text{MDOQH})_2\text{Br}_2]$	3270 m,b	1450 m,b	475 m	310 m
$[\text{Ni}(\text{MDOQH})_2\text{I}_2]$	3270 m,b	1450 m,b	470 m	325 m
$[\text{Ni}(\text{MDOQH})_2(\text{NO}_3)_2]$	3270 m,b	1450 m,b	475 m	325 m
$[\text{Cu}(\text{MDOQH})_2\text{Cl}_2]$	3275 m,b	1455 m,b	465 m	290 m
$[\text{Cu}(\text{MDOQH})_2\text{Br}_2]$	3275 m,b	1450 m,b	470 m	295 m
$[\text{Cu}(\text{MDOQH})_2(\text{NO}_3)_2]$	3270 m,b	1450 m,b	465 m	200 m

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TABLE-2
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES OF THE LIGAND MDOQH

Compounds (colour)	Molar mass	Yield (%)	Analysis found (calculated) (%)				λ_{max} Electronic (cm^{-1})	$\Omega_m\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$	DT ($^{\circ}\text{C}$)	μ_{eff} (BM)
			M	C	H	N				
MDOQH (Colourless)	174	65			5.11 (5.17)	32.06 (32.18)				
$[\text{Co}(\text{MDOQH})_2\text{Cl}_2]$ (Brownish red)	477.93	61	12.26 (12.33)	45.49 (45.61)	3.69 (3.76)	23.32 (23.43)	10000, 14300, 21500	3.1	272	5.16
$[\text{Co}(\text{MDOQH})_2\text{Br}_2]$ (Brown)	566.75	65	10.30 (10.39)	38.32 (38.45)	3.07 (3.17)	19.68 (19.76)	10300, 14700, 22100	3.03	2.78	5.11
$[\text{Co}(\text{MDOQH})_2\text{I}_2]$ (Brown)	660.73	64	8.83 (8.91)	32.86 (32.99)	2.64 (2.72)	16.88 (16.95)	10200, 14600, 21700	3.04	2.69	4.93
$[\text{Co}(\text{MDOQH})_2(\text{NO}_3)_2]$ (Dark brown)	530.93	64	10.94 (11.09)	40.89 (41.06)	3.311 (3.39)	20.94 (21.09)	10400, 14100, 21900	3.7	286	4.89
$[\text{Ni}(\text{MDOQH})_2\text{Cl}_2]$ (Green)	477.71	64	12.19 (12.28)	45.52 (45.63)	3.68 (3.76)	23.32 (23.44)	12600, 17900, 23700	4.1	301	3.11
$[\text{Ni}(\text{MDOQH})_2\text{Br}_2]$ (Brownish green)	566.53	64	10.32 (10.40)	38.33 (38.47)	3.11 (3.17)	19.66 (19.76)	12100, 18300, 24100	4.3	311	3.07
$[\text{Ni}(\text{MDOQH})_2\text{I}_2]$ (Deep green)	660.52	64	8.80 (8.88)	32.90 (33.00)	2.66 (2.72)	16.89 (16.95)	12000, 18100, 24200	4.7	290	3.04
$[\text{Ni}(\text{MDOQH})_2(\text{NO}_3)_2]$ (Greenish brown)	530.71	63	10.92 (11.08)	40.86 (41.07)	3.30 (3.39)	20.89 (21.10)	12840, 18200, 23800	4.9	288	3.7
$[\text{Cu}(\text{MDOQH})_2\text{Cl}_2]$ (Blue)	482.54	65	13.03 (13.16)	45.01 (45.11)	3.68 (3.73)	23.10 (23.21)	13700, 14900	2.7	272	1.89
$[\text{Cu}(\text{MDOQH})_2\text{Br}_2]$ (Blue)	571.36	65	10.01 (11.12)	37.99 (38.15)	3.09 (3.15)	19.49 (19.60)	13900, 16100	2.1	263	1.92
$[\text{Cu}(\text{MDOQH})_2(\text{NO}_3)_2]$ (Deep blue)	535.54	65	11.78 (11.86)	40.58 (40.70)	3.27 (3.36)	20.80 (20.91)	13300, 16300	3.00	280	1.96

DT = Decomposition temperature

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