



Synthesis and Spectroscopic Studies of Co(II), Ni(II) and Cu(II) Complexes of Bidentate Schiff Base having N and Sulphur Containing Donor Site

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ABSTRACT

A series of complexes having the formulae $[M(MTQS)_2X_2]$, where M = Co(II), Ni(II) and Cu(II), MTQS = 2-methyl thioquinazoline – 4 (3H) semicarbazone, X = Cl⁻, Br⁻, I⁻ or NO₃⁻ the ligand as well as metal complexes have been characterized by elemental analysis, magnetic susceptibility, molar conductance, electronic spectra and infrared spectra. On the basis of these studies the complexes of Co(II) and Ni(II) are reported to be octahedral geometry whereas Cu(II) complexes are imposed to be distorted octahedral in geometry. The complexes exhibit enhanced antifungal activity as compared to parent ligand.

Key words : MTQS/ Schiff base/ Complexes/ Antimicrobial/ Antifungal.

INTRODUCTION

Coordination compounds play a vital role in several fields Schiff base plays a central role in the field of coordination chemistry due to their biocidal activities including anticancer, antifungal, herbicidal and antibacterial. The high reactivity specificity and a number of Schiff bases in industry, medicine & agriculture are used in catalytic reaction and as biological models for understanding biomolecules. Schiff base compounds that are

widely studied are attracting wide range of applications in organic synthesis and metal ion complexation⁵⁻⁹. The conventional synthesis of such compounds are still very common along with modern synthetic approaches in continuation of our recent work in synthesizing Schiff bases and their transition metal complexes, we herein report, synthesis and spectroscopic studies of Co(II), Ni(II) and Cu(II) complexes with 2-methyl thioquinazoline – 4(3H) semicarbazone.

EXPERIMENTAL

All the chemicals and reagents used were of AnalR grade. The ligand and complexes were analysed using standard procedure¹⁶. Magnetic susceptibility was measured by using Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. IR spectra were recorded on Perkin Elmer – 577 spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded on a Cary-2390 spectrophotometer.

The molar conductance values were done on systronics conductivity meter using DMF as a solvent.

Preparation of the ligand (MTQS)

Ethanol solution of 2-methylthioquinazoline-4 (3H) one was allowed to react with semicarbazide hydrochloride dissolved in ethanolic solution of sodium acetate. The reaction mixture was refluxed on water bath for about 4 h. The solid thiosemicarbazone started separating after a few minutes. The product was filtered out and washed with ethanol and dried in oven. The compound was crystallised from ethanol and dried in oven with 62% m.p. $214 \pm 1^\circ\text{C}$.

Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) have been prepared by reacting on ethanolic solution of ligand MTQS and ethanolic solution of corresponding metal salts in molar ratio 2:1. The resulting mixture was heated on water bath for 2-3 h when the compounds separated out which were filtered, washed with ethanol followed by tetrahydrofuran and dried in oven. Yield 60-65%.

RESULTS AND DISCUSSION

The IR spectra of ligand compared with that of corresponding metal complexes in order to confirm the coordination sites of the ligand to the metal ion.^{17,18} The IR spectra of the ligand, the carbonyl stretching frequency observed in the region at 1660 cm^{-1} . This band has shifted towards $35\text{-}20\text{ cm}^{-1}$, in the case of complexes, which indicates the coordination of ligand to metal through carbonyl oxygen. A medium and sharp intensity band at 1540 cm^{-1} is observed in the infrared spectra of the ligand which may be attributed due to stretching vibration of $>\text{C}=\text{N}$ group. This band has also shifted towards lower frequency region by cm^{-1} , in the complexes.

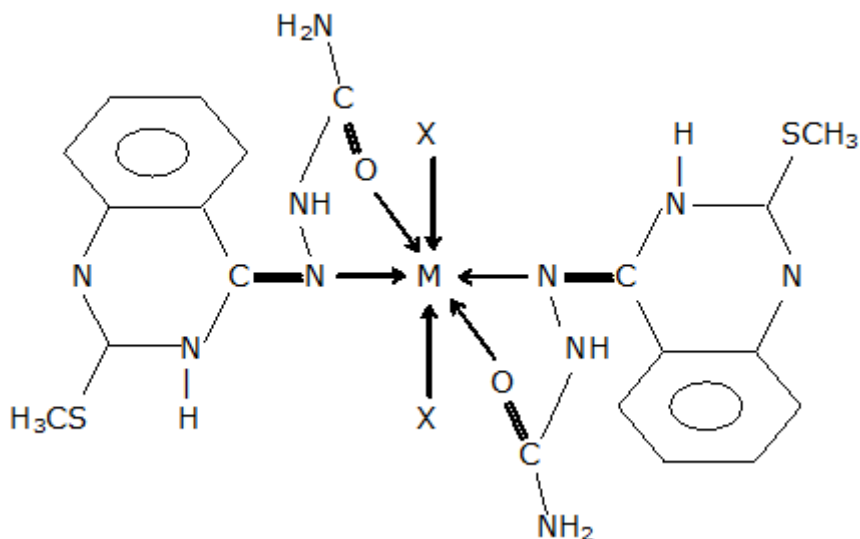


Fig. 1: $[\text{M}(\text{MTQS})_2]\text{X}_2$

$\text{M} = \text{Co(II)}$ 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: Analytical and physical data of schiff base, MTQS and their metal complexes

Compounds	Molar mass	Yield %	Analysis %				μ_{eff} B. M.	Ω_m ohm $^{-1}$ cm 2 mol $^{-1}$	DT °C	λ_{max} electronic cm $^{-1}$
			M	C	N	H				
MTQS	237	62	50.40 (50.63)	29.39 (29.53)	4.58 (4.64)					
Brown [Co(MTQS) $_2$ Cl $_2$]	603.9	63	9.68 (9.75)	39.56 (39.73)	23.09 (23.18)	3.59 (3.64)	4.87	17.1	217	9622, 19270, 21700
Brown [Co(MTQS) $_2$ Br $_2$]	692.74	62	8.41 (8.50)	34.50 (34.64)	20.02 (20.20)	3.12 (3.17)	4.80	17.7	206	9263, 19347, 22217
Brown [Co(MTQS) $_2$ I $_2$]	786.73	65	7.36 (7.49)	30.29 (30.50)	17.60 (17.79)	2.73 (2.79)	4.89	16.9	211	9336, 19510, 22280
Brown [Co(MTQS) $_2$ (NO $_3$) $_2$]	656.93	62	8.89 (8.97)	36.41 (36.53)	21.18 (21.31)	3.28 (3.34)	4.82	16.2	214	9433, 19470, 21940
Dark brown [Ni(MTQS) $_2$ Cl $_2$]	603.71	60	9.63 (9.72)	39.58 (39.75)	23.04 (23.18)	3.59 (3.64)	3.20	18.2	231	10620, 18340, 25317
Orange [Ni(MTQS) $_2$ Br $_2$]	692.52	60	8.40 (8.47)	34.48 (34.65)	20.04 (20.21)	3.12 (3.17)	3.22	18.9	227	10540, 18260, 24736
Yellowish orange [Ni(MTQS) $_2$ I $_2$]	786.31	61	7.38 (7.46)	30.33 (30.51)	17.62 (17.80)	2.71 (2.79)	3.18	18.7	222	10917, 18245, 24930
Deep orange [Ni(MTQS) $_2$ (NO $_3$) $_2$]	656.71	62	8.86 (8.94)	36.30 (36.54)	21.20 (21.31)	3.17 (3.35)	3.12	18.4	229	10970, 18330, 25271
Orange [Cu(MTQS) $_2$ Cl $_2$]	608.54	64	10.35 (10.44)	39.27 (39.43)	22.84 (23.00)	3.53 (3.61)	1.94	14.4	194	15327, 29280
Green [Cu(MTQS) $_2$ Br $_2$]	697.35	64	9.02 (9.11)	34.28 (34.41)	19.92 (20.07)	3.09 (3.15)	1.99	14.1	199	15270, 24360
Greenish yellow [Cu(MTQS) $_2$ (NO $_3$) $_2$]	661.54	64	9.52 (9.60)	36.14 (36.37)	211.01 (21.16)	3.24 (3.32)	1.91	14.7	192	15380, 24440

The coordination through carbonyl oxygen and azomethine nitrogen atom of semicarbazone moiety are further supported by the appearance of bands in the far IR region at 547-520 cm^{-1} and 470-450 cm^{-1} assigned to $\nu_{\text{M=O}}$ and $\nu_{\text{M-N}}$ ^{18,21} respectively. The linkage with halogen is indicated by the appearance of another band in the far infrared region 330-275 cm^{-1} . assigned $\nu_{\text{M-x}}$ ($\text{x}=\text{Cl, Br or I}$).

The linkage with halogen with metal ion supported by the low molar conductance of the complexes in the range 18.9-14.1 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. The significant band at 1460 cm^{-1} and 1340 cm^{-1} with a separation of 120 cm^{-1} indicates mono-coordinate nature of nitrate group²³.

The electronic spectral²⁴ and magnetic susceptibility measurements^{25,26} proposes

Table 2: Infra RED and FAR infra red spectral data (Cm^{-1}) of the ligand mtqs and its complexes

Compounds	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-x}}$
MTQS	1660 s,b	1540 s,b			
[Co(MTQS) ₂ Cl ₂]	1625 m,b	1515 m,b	525 m	450 m	310 m
[Co(MTQS) ₂ Br ₂]	1625 m,b	1510 m,b	540 m	446 m	283 m
[Co(MTQS) ₂ I ₂]	1635 m,b	1510 m,b	528 m	448 m	275 m
[Co(MTQS) ₂ (NO ₃) ₂]	1635 m,b	1505 m,b	520 m	442 m	
[Ni(MTQS) ₂ Cl ₂]	1635 m,b	1520 m,b	537 m	452 m	330 m
[Ni(MTQS) ₂ Br ₂]	1625 m,b	1520 m,b	535 m	456 m	300 m
[Ni(MTQS) ₂ I ₂]	1625 m,b	1520 m,b	545 m	460 m	280 m
[Ni(MTQS) ₂ (NO ₃) ₂]	1625 m,b	1505 m,b	540 m	462 m	
[Cu(MTQS) ₂ Cl ₂]	1640 m,b	1505 m,b	541 m	455 m	320 m
[Cu(MTQS) ₂ Br ₂]	1640 m,b	1515 m,b	547 m	464 m	290 m
[Cu(MTQS) ₂ (NO ₃) ₂]	1635 m,b	1520 m,b	537 m	460 m	

m = medium, b = broad, s = strong, s b = strong and broad

octahedral geometry for the complexes which is justified by other physicochemical as well as infrared spectral data.

Molar Conductance

Molar conductance measurements of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 18.9 -14.1 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMF which proposes their non-electrolytic nature²⁷. The molar conductance values also supported the structure assigned on the basis of physicochemical and spectroscopic measurements.

Antifungal Study

The ligand MTQS and its Co(II), Ni(II) and Cu(II) complexes have been screened for their antifungal activity against *Apergillus niger* and *Penicillium expansum*. The susceptibility of fungi

towards ligand and its metal complexes was tested by disc plate method²⁸. The observed results revealed an enhancement of the antifungal activity of metal complexes with free ligands which can be explained on the basis of chelation theory.

CONCLUSION

Thus on the basis of elemental analysis, IR, electronic spectra, molar conductance and magnetic susceptibility measurements it may be proposed that the ligand MTQS acts in a bidentated manner and coordination is proposed through azomethine N and carbonyl oxygen of semi carbazone moiety. The remaining positions of metal ions are satisfied by negative ions such as Cl^- , Br^- , I^- that proposes it to be octahedral in nature as shown in Fig-1.

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