

Synthesis, Characterization and Antimicrobial Study of Co(II), Ni(II) and Cu(II) Complexes of 2-Phenyl-3-carboxy methyl quinazoline-(3H)-4-semicarbazone[†]

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Complexes of semicarbazone of 2-phenyl-3-carboxy methyl quinazolin-(3H)-4-one with Co(II), Ni(II) and Cu(II) have been prepared and characterized by elemental analyses, spectroscopic data (IR and electronic), magnetic susceptibility, molar conductance measurements. From the analytical and spectral data, the stoichiometry of the complexes has been found to be 1:2 (metal:ligand). The ligand 2-phenyl-3-carboxy methyl quinazoline-(3H)-4-semicarbazone behave as neutral bidentate manner and coordination proposed through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. The remaining coordination positions are satisfied by anions Cl⁻, Br⁻, I⁻ and NO₃⁻. The above mentioned studies suggest the structure for the complexes are monomeric octahedral in geometry.

Key Words: PCMQS, Schiff base, Co(II), Ni(II) and Cu(II), Anti-microbial screening.

INTRODUCTION

The increasing microbial resistance to antibiotics in use now a days necessitate affects against pathogenic bacteria. Many worker studied the synthesis, characterization and structure activity relationship of Schiff bases¹⁻³. Some Schiff bases were reported⁴⁻⁷ to possess antibacterial, antifungal and antiinflammatory activity^{8,9}. Schiff bases are known to be medicinally important and are used to design medicinal compounds^{10,11}. Keeping in mind above biological significance of Schiff base and in continuation of our earlier work¹² we report herein the preparation, characterization and antimicrobial study of complexes of Co(II), Ni(II) and Cu(II) with Schiff base ligand, 2-phenyl-3-carboxy methyl quinazoline-(3H)-4-semicarbazone.

EXPERIMENTAL

All chemicals obtained as reagent grade were used without further purification. The melting points of all the complexes were determined by open capillary method. The metal contents for the complexes were determined using standard method¹³.

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Molar conductance were made on systronics conductivity bridge using DMF as a solvent. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The electronic spectra were recorded on Cary-2390 spectrophotometer. Magnetic susceptibility values were determined by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant.

Preparation of the ligand: Ethanolic solution of 2-phenyl-3-carboxy methyl quinazoline-(3*H*)-4-one (0.01 M) was treated with semicarbazide hydrochloride (0.01 M) in 10 % ethanolic solution of sodium acetate. The resulting mixture was heated on water bath for 3-4 h with frequent stirring. After cooling, the precipitate was collected, washed with ether, treated with dilute sodium carbonate solution and filtered. The solid was washed thoroughly with water and crystallized twice from ethanol to furnish 2-phenyl-3-carboxy methyl quinazoline-(3*H*)-4-semicarbazone (PCMQS) m.p. 183 ± 1 °C, yield 54 %.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) have been formed by reacting ethanolic solution of appropriate metal salts with ethanolic solution of ligand 2-phenyl 3-carboxy methyl quinazoline-(3*H*)-4-semicarbazone (PCMQS) in the molar ratio 1:2. The resulting mixture was heated on water bath for 2-3 h. On cooling solid coloured complexes separated out which was filtered, washed with ethanol, dried and crystallized with tetrahydrofuran. Yield 60-65 %.

RESULTS AND DISCUSSION

The analytical data of all the synthesized metal complexes are given in Table-1. The IR spectra of the free ligand were compared with those of the complexes formed in order to confirm the coordination of the semicarbazone (Table-2). The spectra of the ligand exhibit sharp and strong band in the region $3160\text{-}3150\text{ cm}^{-1}$ assigned^{14,15} to $\nu(\text{N-H})$. This band remain at almost the same positions in the metal complexes suggesting that the terminal amino groups is not involved in chelation¹⁶. IR spectrum of the ligand PCMQS exhibit a strong and broad band at 1480 cm^{-1} assignable^{15,17} to $\nu(\text{C=N})$. In the spectra of the complexes this band show red shift with slightly reduced intensity. The shift of the band and change in intensity coordination of the azomethine nitrogen with metal ion. The linkage with nitrogen is confirmed by the appearance of band in the far ir region at $425\text{-}390\text{ cm}^{-1}$ assigned^{18,19} to $\nu(\text{M-N})$. The next IR spectrum of the ligand exhibit a strong and broad band at 1720 cm^{-1} assigned^{15,20} to $\nu(\text{C=O})$. On complexation this band suffered a downward shift by $20\text{-}30\text{ cm}^{-1}$ in the spectra of the complexes indicate coordination of the metal ion through carbonyl oxygen of semicarbazone moiety. Coordination through oxygen atom of semicarbazone moiety as well as oxygen of nitrate group is supported by the presence of a far IR band at $540\text{-}510\text{ cm}^{-1}$ assigned^{18,19} to $\nu(\text{M-O})$. Coordination through metal-halogen is confirmed by the appearance of a band in the region $320\text{-}270\text{ cm}^{-1}$ which assigned¹⁸ to $\nu(\text{M-X})$ ($\text{X} = \text{Cl}^-, \text{Br}^- \text{ or } \text{I}^-$). The evidence of metal halogen linkage is further confirmed by the low value of molar conductance in the range $4.1\text{-}6.8\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$.

TABLE-1
ANALYTICAL, COLOUR, MOLAR MASS, MAGNETIC SUSCEPTIBILITY, MOLAR
CONDUCTIVITY, ELECTRONIC SPECTRA AND DECOMPOSITION TEMPERATURE OF
THE LIGAND PCMQS AND ITS METAL COMPLEXES

Compounds (Colour)	Mol. mass	Elemental analysis (%): Found (calcd.)				Yield (%)	μ_{eff} (BM)	Ω_{m} (ohm ⁻¹ cm ² mol ⁻¹)	λ_{max} electronic (cm ⁻¹)	DT (°C)
		M	C	H	N					
PCMQS (Colourless)	342.00	–	59.42 (59.64)	20.31 (20.46)	5.78 (5.84)	54	–	–	–	–
[Co(PCMQS) ₂ Cl ₂] (Red)	813.93	5.09 (7.24)	49.90 (50.12)	17.04 (17.20)	4.81 (4.91)	65	4.85	6.8	12210, 18410, 23300	197
[Co(PCMQS) ₂ Br ₂] (Rose red)	902.73	6.41 (6.52)	44.89 (45.19)	15.32 (15.50)	4.34 (4.43)	61	4.82	6.6	12330, 18360, 23336	193
[Co(PCMQS) ₂ I ₂] (Light pink)	996.75	5.80 (5.91)	40.63 (40.93)	13.89 (14.04)	3.94 (4.01)	62	4.90	6.1	12260, 18395, 23378	188
[Co(PCMQS) ₂ (NO ₃) ₂] (Pink)	866.93	6.65 (6.70)	46.78 (47.06)	16.01 (16.14)	4.52 (4.61)	63	5.06	6.4	12290, 18320, 23428	193
[Ni(PCMQS) ₂ Cl ₂] (Green)	813.71	7.13 (7.21)	49.73 (50.14)	17.08 (17.20)	4.63 (4.91)	61	3.12	9.7	13240, 9970, 24670	201
[Ni(PCMQS) ₂ Br ₂] (Pale green)	902.58	6.38 (6.50)	44.91 (45.30)	15.38 (15.51)	4.32 (4.43)	60	3.17	4.1	13180, 9960, 24320	204
[Ni(PCMQS) ₂ I ₂] (Light green)	996.53	5.88 (5.83)	40.73 (40.94)	13.92 (14.04)	40.01 (40.13)	61	3.14	4.4	13160, 10090, 24370	209
[Ni(PCMQS) ₂ (NO ₃) ₂] (Yellow)	866.71	6.53 (6.77)	46.89 (47.07)	15.04 (16.15)	4.52 (4.61)	61	318	4.9	13142, 10280, 24400	217
[Cu(PCMQS) ₂ Cl ₂] (Blue)	818.54	7.64 (7.76)	49.69 (49.84)	16.92 (17.10)	4.61 (4.88)	60	1.92	5.3	11100, 25410	187
[Cu(PCMQS) ₂ Br ₂] (Blue)	907.34	6.91 (7.00)	44.81 (44.96)	15.28 (15.42)	4.28 (4.40)	60	1.90	5.7	11170, 25300	186
[Cu(PCMQS) ₂ (NO ₃) ₂] (Deep blue)	871.54	7.15 (7.29)	46.69 (46.81)	15.92 (16.06)	4.51 (4.58)	61	1.88	5.1	11220, 25370	189

DT = Decomposition temperature.

The occurrence of two IR bands in the spectrum of the ligand at 1420 and 1300 cm⁻¹ with a separation of 120 cm⁻¹ indicate monocoordinated nature of nitrate group²¹.

Electronic spectra and magnetic susceptibility of the complexes: The Co(II) complexes display three band in the region 12210-12430, 18320-18410 and 23300-23440 cm⁻¹ assigned to the transitions, ⁴T_{2g}(F)←⁴T_{1g}(F), ⁴A_{2g}(F)←⁴T_{1g}(F) and

TABLE-2
 INFRARED SPECTRAL DATA (cm⁻¹) AND ITS COMPLEXES WITH Co(II), Ni(II) AND Cu(II)

Compounds	v(N-H)	v(C=O)	v(C=N)	v(M-O)	v(M-N)	v(M-X)
PCMQS	3160 s,b	1730 s,b	1480 s,b	–	–	–
[Co(PCMQS) ₂ Cl ₂]	3160 s,b	1690 s,b	1460 s,b	530 m	420 m	303 m
[Co(PCMQS) ₂ Br ₂]	3160 s,b	1690 m,b	1655 m,b	540 m	410 m	280 m
[Co(PCMQS) ₂ I ₂]	3160 s,b	1690 m,b	1455 m,b	535 m	410 m	275 m
[Co(PCMQS) ₂ (NO ₃) ₂]	3160 s,b	1695 m,b	1460 m,b	535 m	410 m	–
[Ni(PCMQS) ₂ Cl ₂]	3160 s,b	1695 m,b	1455 m,b	525 m	395 m	320 m
[Ni(PCMQS) ₂ Br ₂]	3160 s,b	1690 m,b	1450 m,b	520 m	390 m	295 m
[Ni(PCMQS) ₂ I ₂]	3160 s,b	1695 m,b	1455 m,b	520 m	390 m	270 m
[Ni(PCMQS) ₂ (NO ₃) ₂]	3160 s,b	1695 m,b	1660 m,b	525 m	390 m	–
[Cu(PCMQS) ₂ Cl ₂]	3160 s,b	1695 m,b	1460 m,b	540 m	420 m	315 m
[Cu(PCMQS) ₂ Br ₂]	3160 s,b	1695 m,b	1460 m,b	540 m	425 m	285 m
[Cu(PCMQS) ₂ (NO ₃) ₂]	3160 s,b	1690 m,b	1465 m,b	540 m	425	–

⁴T_{1g}(P)←⁴T_{1g}(F), respectively which indicate octahedral^{22,23} geometry of Co(II) complex which further supported²⁴⁻²⁶ by high μ_{eff} value in the range 4.81-5.10 BM. The Ni(II) complexes exhibits three bands in the region 10000-10300, 13220-14100 and 24200-24410 cm⁻¹ assigned to ³T_{2g}(F)←³A_{2g}(F), ³T_{1g}(F)←³A_{2g}(F) and ³T_{1g}(P)←³T_{2g}(F), respectively, suggesting octahedral^{23,27} geometry for Ni(II) complexes. The proposed geometry of Ni(II) complexes are further supported^{24,25,28} by μ_{eff} value of Ni(II) complexes in the range 3.09-3.18 BM. The Cu(II) complexes exhibit two ligand field bands in the region at 11000-11290 and 25300-25430 cm⁻¹ assigned to the transitions ²T_{2g}(F)←²E_g and charge transfer band which suggest octahedral^{23,29} geometry for the Cu(II) complexes. The magnetic susceptibility value of Cu(II) complexes lie in the range 1.87-1.92 BM^{24,25,30}.

Molar conductance of the complexes: Molar conductance values of the complexes are measured in the solvent DMF and the complexes were found to be non-electrolytic³¹ in nature. The molar conductance value of the complexes are lies in the range 4.1-9.7 ohm⁻¹ cm² mol⁻¹.

Antimicrobial activity: The ligand PCMQS and its complexes of Co(II), Ni(II) and Cu(II) complexes were screened for their antibacterial activity against bacteria, *Escherichia coli* and antifungal activity against *Aspergillus niger* by disc diffusion method³² using DMF as solvent at concentration of 50 μg³². The activity was compared with known standard drugs, tetracycline and diethane Z-78, respectively at same concentration³³ 50 μg. The ligand were found biologically active and their metal complexes showed significantly enhanced antibacterial activity and antifungal activity. It is established that chelation tends to make the ligand act as more potent bacterial agents, than the parent ligand. The antimicrobial activity of the compound increases after metal chelation. Chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donar groups³⁴ increasing lipophilic nature of the central metal ion which in turn favours its permeation to the lipid layer of the membrane.

Conclusion

On the basis of above observations it proposes that PCMQS behaves as neutral bidentate ligand and coordination takes place through azomethine nitrogen and carbonyl oxygen atoms of semicarbazone moiety. The remaining positions of the metal ions are satisfied by negative ions such as Cl^- , Br^- , I^- and NO_3^- . The geometry of the complexes are proposed to be monomeric octahedral in geometry as shown in Fig. 1.

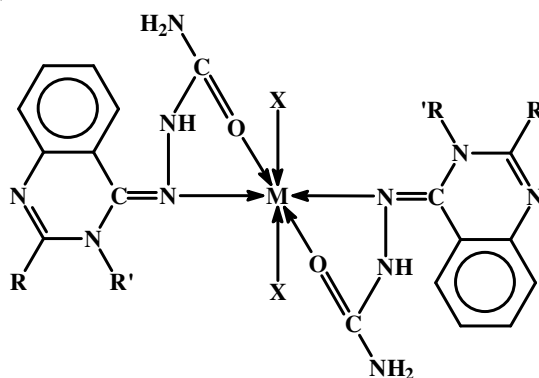


Fig. 1. $[\text{M}(\text{PCMQS})_2\text{X}_2]$; M = Co(II), Ni(II) and Cu(II); X = Cl^- , Br^- , I^- and NO_3^- ; R = Phenyl; R' = Carboxy methyl

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