



Antimicrobial Screening of Co(ii), Ni(ii) and Cu(ii) Complexes with Nitrogen and Oxygen Containing Schiff Base

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(Received: January 12, 2012; Accepted: February 29, 2012)

ABSTRACT

This study reports the preparation and spectroscopic evaluation of a series of transition metal complexes of Co(II), Ni(II), and Cu(II) with schiff base ligand 1-ethyl, 1, 2, 3, 5, tetrahydroimidazo (2, 1-b) quinazolin 5-one semicarbazone (ETQS). The ligand and its Co(II), Ni(II) and Cu(II) complexes were formulated by elemental analysis, molar mass, infrared spectra, electronic spectra, molar conductivity and magnetic susceptibility measurements. In the light of above studies it is proposed that the compound ETQS behaves a bidentate ligand and coordination takes place through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. The remaining positions of metal ions are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ and NO₃⁻. The complexes were proposed octahedral geometry. All the synthesized ligand and complexes have been screened for antimicrobial activity.

Key words: Schiff Base/ ETQS/ Co(II), Ni(II) and Cu(II) complexes/ Antimicrobial Screening.

INTRODUCTION

Schiff Base ligands and their application have aroused considerable interest mainly due to preparative accessibility, diverse reactivity and structural variability. Metal complexes of Schiff base have played a vital role in the development of coordination chemistry and many applications in

various fields³. Schiff base ligands and their coordination compounds have several applications in biology and industry due to their role in catalysis and organic synthesis. They are also useful in catalysis in medicine as antibiotics and to treat industrial wastes. Schiff bases are versatile ligands having several biocidal importance as plant growth regulators antibacterial, antiviral, antileukemic and

enzymatic reaction inhibitors. The coordination compounds containing Schiff base ligand can be utilized to unfold the mechanism of various biocidal activities occurring in nature. In view of above importance of Schiff and their biocidal activity and our earlier recent work in this field we have taken up antimicrobial screening of Co(II), Ni(II) and Cu(II) complexes.

EXPERIMENTAL

All the chemicals used were of Analytical grade and used as without further purification. The ligand and complexes were analysed for metal contents by standards procedures¹². IR spectra of the ligand as well as complexes were recorded on perkin Elmer 577 spectrophotometer using KBr disc. Electronic spectra of the complexes were recorded on a Cary 2390 spectrophotometer. Magnetic susceptibility of the complexes were measured by Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. The molar conductivity were measured by Systronics conductivitymeter using DMF as a solvent.

Preparation of the ligand (ETQS)

A mixture of 1-ethyl 1, 2, 3, 5 tetrahydroimidazo (2, 1-b) quinazolin 5-one (0.02 mol) and semicarbazide hydrochloride dissolved in ethanol was refluxed for 3 h using air condensor with frequent shaking. After cooling the precipitate was collected, washed with tetrahydrofuran, treated with dilute sodium carbonate solution and filtered. The solid was washed throughly with water and crystallised with ethanol to give 1-ethyl-1, 2, 3, 5-tetrahydroimidazo. (2-1, b) quinazolin- 5- one semicarbazone as light yellow needles m. p 209± 1°C yield – 60%.

Preparation of the complexes

Metal complexes were synthesized by the reaction of 20ml ethanolic solution of ligand ETQS with ethanolic solution of respective metal halides/nitrate in the molar ration 2:1. This mixture was then refluxed for 2-3 h on water bath. The procedure carried out in each case of similar nature with slight variation of timing of reflux. On cooling, coloured precipitates were obtained. Products were filtered and washed with ethanol followed by ether and dried in oven. Yield in all cases 60-65%.

RESULT AND DISCUSSION

I.R.Spectra

It is established from the literature¹³ that semicarbazone ligand can coordinate in a bidentate manner in most cases through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety.

IR spectrum of the ligand ETQS exhibits a medium broad band at 3220 cm^{-1} assigned^{14,15} to $\nu_{\text{N-H}}$. In the spectra of the complexes this band appears without any change indicating that either primary amino or secondary amino groups has not taken part in the coordination with metal ion.

IR spectrum of the ligand exhibits sharp and strong band at 1690 cm^{-1} assigned^{14,16} to $\nu_{\text{C=O}}$. In the spectra of the complexes this band is shifted to lower frequency region and appear at 1660 cm^{-1} with slightly reduced intensity. The shift of the band and change in intensity suggests coordination through carbonyl oxygen of semicarbazone moiety. The linkage with oxygen atom is further supported by the appearance of a new band in the far ir region at 540-500 cm^{-1} in the complexes assignable^{14,17} to $\nu_{\text{M-O}}$. The IR spectrum of the ligand exhibit a band at 1450 cm^{-1} assigned^{14,18} to $\nu_{\text{C=N}}$. In the spectra of the complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity proposes coordination of azomethine N with metal ion. The linkage with nitrogen atom is further supported by the appearance of a band in the far ir region at 475-440 cm^{-1} assigned¹⁴ to $\nu_{\text{M-N}}$. The evidence of metal halogen is confirmed by the low molar conductance of the complexes in the range 6.9-4.1 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. This statement is further confirmed by the appearance of a band in far ir region at 320-260 cm^{-1} which assigned to $\nu_{\text{M-X}}$. Nitrate complexes shows characteristic medium intensity bands at 1375 and 1255 cm^{-1} with a separation of about 120 cm^{-1} due to monodentately coordinated nitrate group^{19,20}.

Electronic spectra and magnetic susceptibility of the complexes

The electronic spectra of all the complexes have been recorded in the region 10,000-25,000 cm^{-1} . The copper complexes exhibits two broad bands in the region 11500-11100 cm^{-1} and 14800-14400 cm^{-1} assigned to ${}^2T_{2g} (F) \leftarrow {}^4E_g$ and charge

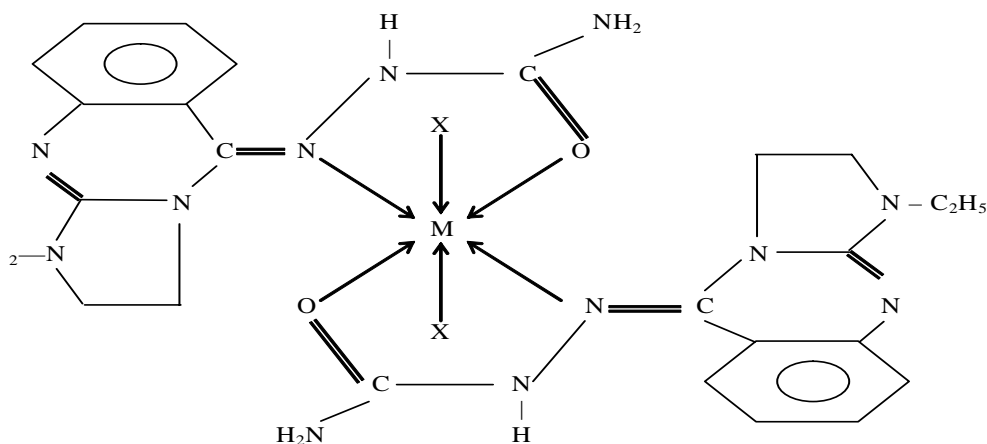
Table .1: Analytical and Physical Data of Schiff Base, Etqs and their Metal Complexes

Compounds	Molar Mass	Yield %	Analyses % found (calculated)			DT °C	Ω_m cm ² mol ⁻¹	μ_{eff} B. M	λ_{max} electronic cm ⁻¹
			Metal	C	N				
ETQS	72	60		57.26 (57.35)	30.79 (30.88)	5.80 (5.88)			
Light yellow [Co(ETQS) ₂ Cl ₂]	673.93	64	8.66 (8.74)	46.12 (46.29)	24.82 (24.92)	4.69 (4.74)	4.5	13600, 19680, 22400	
Brown [Co(ETQS) ₂ Br ₂]	762.75	62	7.64 (7.72)	40.77 (40.90)	21.89 (22.02)	4.13 (4.19)	4.7	13800, 19320, 22100	
Brownish red [Co(ETQS) ₂ I ₂]	856.73	61	6.79 (6.87)	34.28 (36.41)	19.51 (19.60)	3.67 (3.75)	4.1	12400, 19200, 22640	
Deep brown [Co(ETQS) ₂ (NO ₃) ₂]	726.93	62	8.01 (8.10)	42.80 (42.9)	22.98 (23.11)	4.33 (4.40)	4.9	12600, 19700, 22580	
Deep brown [Ni(ETQS) ₂ Cl ₂]	673.71	65	8.62 (8.71)	46.20 (46.31)	24.81 (24.23)	4.69 (4.74)	5.9	11900, 15400, 24200	
Green [Ni(ETQS) ₂ Br ₂]	762.52	64	7.60 (7.69)	40.79 (40.91)	21.86 (22.03)	4.12 (4.19)	5.4	11700, 15100, 24360	
Green [Ni(ETQS) ₂ I ₂]	856.52	60	6.79 (6.85)	36.30 (36.42)	19.49 (19.61)	3.67 (3.73)	5.6	12000, 15700, 24780	
Deep green [Ni(ETQS) ₂ (NO ₃) ₂]	726.71	60	7.98 (8.07)	42.86 (42.93)	23.01 (23.11)	4.32 (4.40)	5.4	11980, 16000, 24800	
Greenish red [Cu(ETQS) ₂ Cl ₂]	678.54	62	9.27 (9.36)	45.84 (45.98)	24.64 (24.75)	4.63 (4.71)	6.9	10700, 14670	
Blue [Cu(ETQS) ₂ Br ₂]	767.36	63	8.19 (8.28)	40.53 (40.65)	21.78 (21.89)	4.09 (4.17)	6.7	10500, 14460	
Blue [Cu(ETQS) ₂ (NO ₃) ₂]	731.54	64	8.59 (8.68)	42.52 (42.64)	22.88 (22.96)	4.32 (4.37)	6.5	11100, 14680	

Table.2 : IR Spectral Measurement of ligand ETQS and its metal complexes

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	ν_{M-O}	ν_{M-N}	ν_{M-X}
ETQS	1690 s,b	1450 s,m			
[Co(ETQS) ₂ Cl ₂]	1660 m,b	1420 m,b	505 m	455 m	310 m
[Co(ETQS) ₂ Br ₂]	1660 m,b	1430 m,b	500 m	445 m	280 m
[Co(ETQS) ₂ I ₂]	1655 m,b	1425 m,b	515 m	440 m	260 m
[Co(ETQS) ₂ (NO ₃) ₂]	1650 m,b	1425 m,b	510 m	455 m	
[Ni(ETQS) ₂ Cl ₂]	1650 m,b	1430 m,b	515 m	460 m	320 m
[Ni(ETQS) ₂ Br ₂]	1655 m,b	1420 m,b	525 m	465 m	300 m
[Ni(ETQS) ₂ I ₂]	1650 m,b	1415 m,b	520 m	475 m	295 m
[Ni(ETQS) ₂ (NO ₃) ₂]	1650 m,b	1410 m,b	530 m	470 m	
[Cu(ETQS) ₂ Cl ₂]	1650 m,b	1410 m,b	540 m	455 m	310 m
[Cu(ETQS) ₂ Br ₂]	1650 m,b	1410 m,b	535 m	450 m	290 m
[Cu(ETQS) ₂ (NO ₃) ₂]	1650 m,b	1410 m,b	540 m	445 m	285 m

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

Fig.1 [M(ETQS)₂X₂]

M = Co(II) and Ni(II); X = Cl⁻, Br⁻, I⁻ or NO₃⁻; M = Cu(II); X = Cl⁻, Br⁻ or NO₃⁻

transfer bands respectively indicating distorted octahedral^{21,22} geometry for the copper(II) complexes. The magnetic moment^{23,24} values for copper(II) complexes i.e. in the range 1.81 to 1.94 B.M. The cobalt(II) complexes exhibit three bands in the regions 13800-12400 cm⁻¹, 19700-19200 cm⁻¹ and 22640-22100 cm⁻¹ assignable to the transitions ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, respectively. The above mentioned spectral bands indicate octahedral^{21,25} geometry for the cobalt(II) complexes. The octahedral geometry of cobalt(II) complexes is also

supported^{23,24} by magnetic susceptibility values in the range 4.90 to 5.09 B.M. The nickel(II) complexes exhibits three absorption bands in the region 11700-12,000 cm⁻¹, 16000-15100 cm⁻¹ and 24800-24200 cm⁻¹ respectively assignable to ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions respectively. The suggesting octahedral^{21,26} geometry for Ni(II) complexes is further supported^{23,24} by magnetic susceptibility values of the complexes in the range 3.10 B.M. to 3.16 B.M.

Conductivity measurement

Molar conductance values of the complexes of cobalt(II), nickel(II) and copper(II) were found to be in the range 6.9-4.1 $\text{ohm}^{-1} \text{mol}^{-1}$ in DMF indicating their non electrolytic³⁰ nature. The values of conductance also support the structure assigned on the basis of elemental analysis, IR spectra and magnetic susceptibility values.

Biocidal screening

Schiff base ETQS and their metal complexes have been evaluated for their antimicrobial activity against *E. coli* and *B. subtilis* by disc diffusion method²⁸ at concentrations 50 and 25 $\text{m}_g \text{ml}^{-1}$ using streptomycin as a control. On comparison with reference to antibiotic, the complexes were found to be more effective than free ligand. Further it is also observed that the order

of activity for complexes are $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$ and also nitrate complexes were effective biocidal effect than metal-halide complexes, which is supported by literature²⁹⁻³¹.

CONCLUSIONS

Based on the stoichiometrics and spectroscopic studies it is proposed that ETQS behaves as neutral bidentate ligand and coordination takes place through azomethine N and carbonyl oxygen. The remaining position of metal ions are satisfied by negative ions such as Cl^- , Br^- , I^- or NO_3^- . Hence on the basis of above studies the geometry of the complexes of Co(II), Ni(II) and Cu(II) of the type $(\text{M}(\text{ETQS})_2\text{X}_2)$ may be proposed to have octahedral geometry as shown in Fig 1.

REFERENCES

- N. Raman, S. Ravichandran and C Thangraja, *Indian Acad, Sci*; **116**, 215 (2004).
- S. G. Shirodkar, P.S. Mane and T. K. Chondhekar, *Indian J. Chem; Sect. A* **40**, 114(2001).
- M. A. Neelkantan, S.S. Mariappan J. Dharmraja, T. Jeyakumar and K. Muthukumar, *Spectrochim. Acta*, **71 A**, 628(2008).
- G. Wilkison, *Comprehensive coordination chemistry*, Pergamon press, oxford, P. 166 (1987).
- T. M. Sielecki, J. Liu, S. A Mousa, A. L. Racanelli, E. A. Hausner, R. R. Wexler and R. E. Olson, *Biorg med. chem. Lett*; **11**, 2201(2001).
- M. Verma, S.N. Pandeya, K.N. Singh and J.P. Stables, *Acta. Pharma*, **54**, 49 (2004).
- P. Sienkiewicz, K. Bielawski, A. Bielwaska and J. Palka, *Environ, Toxicol, Pharmacol.*, **10**, 118(2005).
- M.R. Maurya, S. Agarwal, M. Abid, A. Azam, C. Badur, M. Ebel and D. Rehdar, *Dalton Trans*, **7**, 937(2006).
- C.L. Eichhorn (ed.), *Inorganic Biochemistry*, Elsevier, Amsterdam, **1,2** (1973).
- B.K. Rai, *Asian J. Chem.*, **22**, 2761(2010), B.K. Rai and Chandan Kumar, *Asian J. Chem.*, **22**, 5613 (2010); B.K. Rai and Satydeo Singh, *Asian J. Chem.*, **22** 5619 (2010); B.K. Rai and K.K. Sharma, *Asian J. Chem.* **22**, 5625 (2010); B.K. Rai, Hitesh Kumar, Minaxi Sharma, and V.K. Rastogi, *J. Indian Chem. Soc.*, **87** 11241 (2010), B.K. Rai, *J. Ind. Council Chem.* **27**, 68 (2010).
- Rai B.K and K.K. Sharma, *Orient J. Chem* **27**, 143 (2011). Rai B.K and Kumari Rachna, *Asian J. Chem* **23**, 4625 (2011) Rai B.K, Sinha P, Vidyarthi S.N and Singh Vineta; *Orient J. Chem.* **23**, 4629 (2011), Rai B.K and Kumar Bimal, *Asian J. Chem*, **23**, 4635(2011). Rai B.K, Singh V, Vidyarthi S.N and Sinha Puja, *Asian J. Chem*; **23**, 4638 (2011).
- A. I. Vogel, *Textbook of quantitative chemical analysis* revised by J. Mendhan, R.C. Denny, J.D. Barnes and M. Thomas, *Person education*, 7th ed. (2008).
- Gingros; B.A. Samarjal R.L, Bayley C.S *Can J. Chem.* **29**, 974 (1961).
- William Kemp, *Organic spectroscopy* Palgrave, New York 3rd edn. (2008), R.M.

- Silverstein and Francis, P.X Webster, Spectrometric identification of organic compound 6th edn, John Wiley and sons (2008).
15. M.S Patil and J. R. Shah, *J. Indian Chem. Soc.*, **58**, 944(1981).
 16. BalaSubramaniam, K.P, Karvember R, Chinniswami V and Natrajan K., *Indian J. Chem*; **44****13**, 2450(2005).
 17. Mahapatra B.B and Saraf S.K, *J. Indian Chem. Soc.* **80**, 696 (2003).
 18. A Syamal and K.S Kale, *Inorg.* **4**, 867(1965).
 19. C.C. Addison, N. Lugin, S.C Wall Work and D.C Barner, *Quart. Rev.* (1971).
 20. R.A Nyquist, C.L Putzig, M.A Leugers, *Infrared and Raman Spectral Atlas of Inorganic compound and organic salts*, Academic Press New York(1995).
 21. A.B.P. Lever, *Inorganic Electronic Spectroscopic Elsevier*, Amsterdam **395** (1968); C.K. Jorgenson, *Acta Chem: Scand*, **19**, 887, (1966). J.R Allen. *Inorg. Nucl. Chem*; **26**, 1895 (1964).
 22. A.P Mishra, M. Khare and S.K Gautam, *Synth. React. Inorg. Met. Org. Chem*; **32**, 1485 (2002).
 23. B.N Figgis, *Introduction to Ligand Field*, Wiley eastern Ltd., New Delhi, 279 (1976).
 24. R.L Carlin and A.J Van Dyneveledi, *Magnetic property of transition metal*.
 25. P.S Mane, S.G Sirodhar and B.S Arbad and T.K Chandekar *Indian J. Chem*; **40 A**, 648, (2000).
 26. A.K Tahir, H.S Shivanjnal, J. Nalees, K. Shoukat, *Indian J. Chem.*; **SectA. 39** 450(2000)
 27. J. A Wolmesly and S.V Tayree, *Inorg. Chem*; **2**, 312, 1963; P.N Sathyanarayan and C.C Patel, *Indian J. Chem.*; **5**, 360, (1967)
 28. Mukharjee P.K, Saha K, Giri, S.N., Palm and Sohay B.P *Indian J microbiology*, **35** (1995).
 29. Parasher R.K and Sharma R.C. , *J Inorg. Biochem* ; 225 (1987).
 30. Rainsford K.D and White house and M.W, *J. Pharmacol*, **28**, 83 (1976).
 31. Nishant N, Ahmad S and Ahmad R.T, *J. Appl, Polym. Sci.*, **100**, 928(2006).