Oriental Journal of Chemistry Vol. **25**(2), 391-395 (2009)

Physico-chemical and antimicrobial studies on Ni(II), Cu (II) and Ti(III) Schiff base complexes derived from 2- furfuraldehyde

ANANT PRAKASH and SHAMIM AHMAD

Department of Chemistry, Bareilly College, Bareilly (India).

(Received: April 12, 2009; Accepted: June 04, 2009)

ABSTRACT

New complexes of Ti (III) Cu (II) and Ni(II) with Schiff bases obtained by condensation of Furan-2-Carboxaldehyde with L-histidine, L-tryptophan, L-valine, L-methionine & L-glycine have been synthesised and characterised. The complexes of Ti(III) have been found to posses 1:2 while the complexes of Ni(II) and Cu(II) have been found to posses 1:1 (M.L.) Stoichiometry. Coordination of azomethine nitrogen and furan ring oxygen in the schiff base to the metal has been proposed.The ligands and their corresponding complexes were screened for their antimicrobial activities.

Key words: Schiff base, Complexes, Ni, Cu, Ti and Furfuraldehyde

INTRODUCTION

Schiff base metal complexes have been a widely studied subject because of their industrial and biological applicatios1,2. aminoacids are the basic structural material of the proteins and are able to form Schiff bases due to the presence of amino group. Studies of new kind of Schiff bases (chemotherapeutic) are now attracting the attention of biochemists, 3,4. The survey of the literature revealed that a systematic study is further required on this subject5-8. The present study deals with the structural aspects of some Ni(II), Cu (II) and Ti(III) complexes involving bioactive ligands.

EXPERIMENTAL

All the chemicals used were of A.R. & equivalent grade. Amino acids were obtained from *loba-chem,* while aldehyde was purchased from sisco chem industries.

Preparation of metal complexes

The complexes were prepared by stiring aqueous solution of sod. salt of amino acids with hot ethanolic solution of aldehyde in 1:1 molar ratio and then aqueous ethanolic solution of metal salt was added in equimolar ratio with constant stiring.

The products so formed were filtered, washed with ethanol & ether. The samples were dried in vacuum desiccator over anydrous calcium chloride and their purity was checked by TLC. In case of Titanium (III) complexes the whole operation was carried out in a glove bag under the atmosphere of nitrogen in order to avoid oxidation of Ti (III) into Ti (IV).

The elemental analyses for C, H & N were carried out at C.D.R.I., Lucknow. Metals were estimated gravimetrically, IR spectra were recorded on Perkin-Elemer spectrophotometer. The molar conductance at 10^{-3} molar dilution were measured by Elico conductometer bridge. The magnetic susceptibility was determined by Gouy balance using copper sulphate as standard material. Electronic spectra were recorded on Beckman DU spectrophotometer.

RESULTS AND DISCUSSION

The metal complexes were solid and non-hygroscopic. The emperical composition of the complexes has been confirmed on the basis of analytical data (Table 1). The molar conductance values at room temperature and 10^{-3} M dilution in DMF & DMSO showed that all complexes are electrolytic in nature.

The broad band in the 2900-3300 cm^{-1} region in Ni(II) and Cu (II) complexes attributed to the presence of water molecules, which is confirmed by thermal analysis. The IR spectra of these complexes exhibited a new band in the range of 3500-3550 cm^{-1} which may be attributed to uOH vibrations of coordinated water. The appearance of band around 860 cm^{-1} due to wagging and rocking modes of coordinated water molecules[9,10] also supports the above assumption of the presence of coordinated water molecules.

The 15-25 cm^{-1} shift in intense band appearing in the range of 1640-1620 cm^{-1} for all the complexes has indicated the involvement of nitrogen atom of azomethine group in coordination and suggests imine structure[11]. As for as the coordination of the carboxylate ion is concerned the information is drawn from the position of asymmetric and symmetric COO-frequencies occuring at about 1515 and 1530 cm^{-1} respectively in the spectrum of the complexes. This is clear indication of the involvement of the carboxylate ion in the coordination. The presence of a very sharp band in the range 470-510 cm^{-1} indicated the formation of M - O bond involving furan ring oxygen[12,13]. In this way ligands are behaving in tridentate manner coordinating through carboxylate ion, furan ring oxygen and N atom of azomethine group.

The electronic spectra of all the metal complexes were recorded in DMF solutions. These bands undergo a bathochromic shift and broadening in all the complexes and are located in the range of 26041-20202 cm^{-1}. The broad bands in this range may have d-d transition components in admixture. This is further confirmed by the fact that all complexes are coloured and paramagnetic in nature[14].

Ni (II) Complexes

The electronic spectra of Ni(II) complexes exhibited the bands in the range of 20500-20703 cm^{-1} which may be assigned to 3T1-3T1(P) transition. This support tetrahedral geometry[15] of the complexes.

For Ni (II) complexes, the weight loss corresponding to one molecule of water took place at about 1800C. This is further in the support of the presence of coordinated water molecules.

The magnetic moment of the complexes have the value in the range of 2.80-2.90 BM which is very close to the value expected for two unpaired electrons.

Ti (III) complexes

The titanium (III) complexes gave only one band at 19607-20408 cm^{-1}, which is obviously derived from the transition 2T2g g 2Eg for an OH symmetry.16

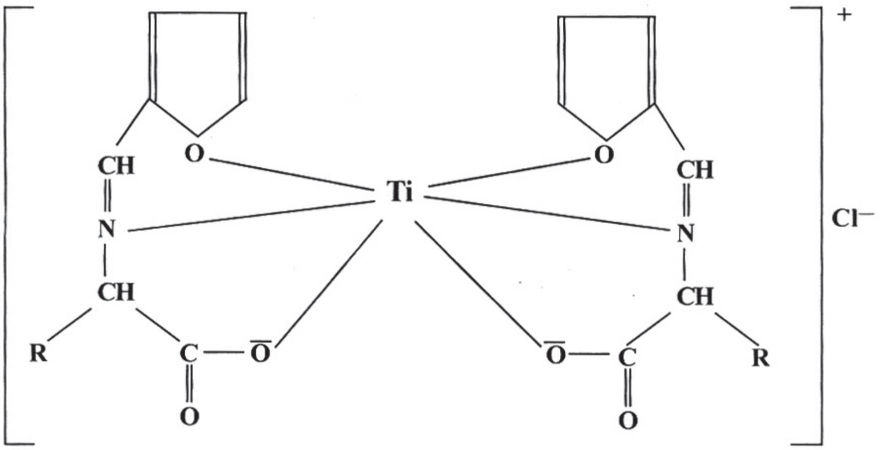
The effective magnetic moment of the Ti (III) complexes was found to be in the range of 1.70 - 1.74 BM which indicates that the metal remains in +3 oxidation state (3d1) even on complexation as the value is very close to 1.73 BM, expected for d1 system.17 This is characteristic of octahedral geometry and indicated paramagnetic nature of the complexes.

Cu (II) Complexes

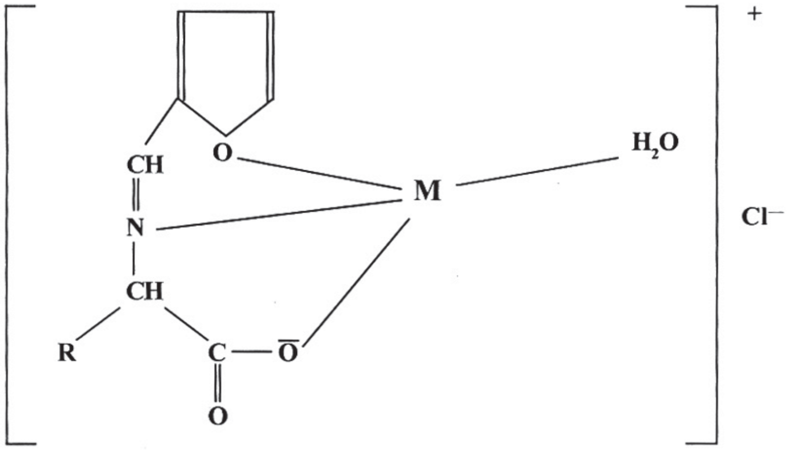
The electronic spectra of the Cu (II) complexes exhibit bands in the range of 13157-19230 cm^{-1} which are attributed to 2B1g g 2B2g and 2B1g g 2Eg transitions and accordingly square-planar geometry has been suggested[18,19]. Where the three corners of the square are occupied by the three donor atoms of the Schiff base and the fourth corner is filled by a solvent water molecule.

Table 1:

S.	Name and Molecular formula	Molecular	Colour	m.p.	% Elemental Analyses					Magnetic
No.		Weight				C	H	N	of S	Metals
1.	Furfuraldehyde-L-histindine Ti (III) chloride $(C_{11}H_{10}N_3O_3)_2$ TiCl	547.40	Yellow	270°C	47.890 (48.227)	3.175 (3.653)	14.700 (15.340)	-	7.988 (8.750)	1.73
2.	Furfuraldehyde-L-tryptophan Ti (III) chloride $(c_{16}H_{13}N_3O_3N_2)_2$ TiCl	645.40	Light Green	300°C	59.040 (59.497)	3.898 (4.028)	10.251 (10.459)	- -	7.000 (7.421)	1.71
3.	Furfuraldehyde-L-Methionine Ti (III) chloride $(c_{10}H_{12}N_3O_3NS)_2$ TiCl	535.40	Light Pink	210°C	44.165 (44.826)	4.050 (4.482)	5.021 (5.229)	5.175 (5.946)	8.210 (8.946)	1.74
4.	Furfuraldehyde-L-Valine Ti (III) chloride $(C_{10}H_{12}O_3N_2)_2$ TiCl	471.40	Orange	245°C	50.687 (50.912)	4.865 (5.091)	5.230 (5.939)	-	9.805 (10.161)	1.77
5.	Furfuraldehyde-L-Glycine Ti (II) chloride $(C_7H_6O_3H_2N)$ TiCl	387.40	Pale Yellow	280°C	42.731 (43.366)	2.865 (3.097)	7.100 *7.227)	-	12.050 (12.364)	1.75
6.	Furfuraldehyde-L-histidine Ni (II) chloride $C_{11}H_{13}O_2H_2O$. NiCl	344.21	Pink	285°C	37.508 (38.348)	5.3231 (5.810)	24.100 (24.403)	-	16.325 (17.056)	2.85
7.	Furfuraldehyde-L-Tryptophan Ni (II) chloride $(C_{16}H_{13}N_3O_3N_2)_2$ TiCl	393.21	Green	301°C	48.531 (48.828)	13.121 (3.306)	6.865 (7.120)	-	14.565 (14.930)	2.86
8.	Furfuraldehyde-L-Methionine Ni (II) chloride $C_{10}H_{12}O_3NSH_2O$. NiCl	338.21	Yellow	291°C	35.225 (35.480)	3.445 (3.548)	4.040 (4.135)	9.205 (9.461)	17.088 (17.359)	2.80
9.	Furfuraldehyde-L-Valine Ti (III) chloride $C_{10}H_{12}O_3N.H_2O$. NiCl	306.21	Orange	265°C	38.265 (39.188)	3.765 (3.918)	4.321 (4.572)	-	18.855 (19.173)	2.90
10.	Furfuraldehyde-L-Glycine Ni (II) chloride $(C_7H_6O_3H_2N)$ TiCl	264.21	Light Blue	209°C	31.261 (31.792)	2.080 (2.270)	5.177 (5.298)	-	21.875 (22.220)	2.87
11.	Furfuraldehyde-L-Histidine Cu (II) chloride $(C_7H_6O_3H_2N)$ TiCl	349	Blue	210°	37.161 (37.792)	2.110 (2.865)	11.285 (12.034)	-	17.560 (18.209)	1.75
12.	Furfuraldehyde-L-Tryptophan Ni (II) chloride $(C_{16}H_{13}O_3N_2H_2$. CuCl	398	Brown	260°C	48.050 (48.241)	3.200 (3.266)	6.525 (7.035)		15.210 (15.967)	1.77
13.	Furfuraldehyde-L-Tryptophan Cu (II) chloride $C_{10}H_{12}O_3NSH_2O$. NiCl	343	Light Blue	240°C	34.210 (34.585)	2.950 (3.498)	3.825 (4.081)	9.201 (9.329)	18.205 (18.527)	1.73
14.	Furfuraldehdye-L-Valine Cu (II) chloride $C_{10}H_{12}O_3N.H_2O$. CuCl	311	Sky Blue	210°C	38.325 (38.585)	3.885 (3.858)	4.000 (4.501)	-	19.565 (23.624)	1.80
15.	Furfuraldehyde-L-Glycine Cu (II) chlrodie $C_7H_6O_3N.H_2O$. CuCl	269	Brown	270°C	30.758 (31.226)	2.110 (2.230)	4.385 (5.204)	-	23.255 (23.624)	1.84



Complexes of Ti(III)



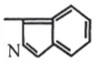
Complexes of Ni(II) & Cu (II)

Where

M = Ni(II) & Cu (II)

R = -CH$_2$ (In complexes of L-histidine)

= -CH$_2$ (In complexes of L-tryptophan)



= -CH$_2$ - CH$_2$S CH$_3$ (In complexes of L-methionine)

= -CH - CH$_3$ (In complexes of L-valine)
CH$_3$

= H (In complexes of L-glycine)

Scheme 1

The complexes showed weight loss corresponding to one molecule of water at about 185°C. This further indicates that water molecules are coordinated with the metal.

The magnetic moment of the complexes have the value in the range 1.73-1.84 B.M. which is very close to the value expected for 1 unpaired electron.

Antimicrobial activity

Antibacterial and antifungal activities of complexes and the schiff bases were studied against *B. subtilis. E.coli, A. fumigatus* and *A. niger* at 50 mg/ml^{-1} concentration by single disc method[20,21] using streptomycine as control. Against all the organism ligands did not exhibit any remarkable activity whereas all the complexes showed moderate activities. The activity was found to increase in the order Cu(II) > Ni (II)> Ti (III). It is suggested that the compounds having antimicrobial activity may act either by killing the microbe or by inhibiting multiplicaion of the microbe by blocking their active sites[3, 20, 21].

ACKNOWLEDGEMENTS

The authors are thankful to Dr. R.P. Singh Principal, Bareilly College, Bareilly for providing laboratories facilities to carry out this research work.

REFERENCES

1. T. Hitoshi, N. Tamao, A. Hideyuki, F. Manabu and M. Takayuki, *Polyhedron*, **16**: 3787 (1997).
2. T. Punniyamurthy, S. J.S. Kalra and J. Iqbal, *Tetrahedron Lett.*, **36**: 8497 (1995).
3. Y.K. Choi, K.H. Chjo, S.M. Park and N. Doddapaneni. *J. Electrochem. Soc.,* **142**: 4107 (1995).
4. B. Katia, L. Simon, R. Anne, C. Gerard, D. Francoise and M. Bernard, *Inorg. Chem.*, **35**: 387 (1996).
5. A. P Mishra, V. Srivastava and S.K. Srivastava, *Synth. React. Inorg. Metal-Org. Chem.* **25**: 21 (1995).
6. G. Sarkar, R.R P. Kumar and S.K. Ramalingam, *Polyhedron*, **5**: 991 (1986).
7. N.K. Jha and D.M. Joshi, *Synth. React Inorg. Metal Org. Chem.,* **16**: 947 (1986).
8. R. Thomas and G. Parmesharan, *J. Indian Chem. Soc.,* **69**: 117 (1992).
9. R.C. Das, M.K. Mishra and S.K. Mohanty, *J. Indian Chem. Soc*. (Communicated).
10. J. Fujita, A.E. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**: 324,331 (1962).
11. P.K. Sharma, A.K. Sen & S.N. Dubey. *Indian Journal of Chemistry* **33**A: 1031-1033 (1994).
12. C.R. Panda, v. Chakravorty and K.C.. Dash. *Thermo-chem, Acta*., **125**: 17 (1988).
13. C. L. Jain, P.N. Mundley, Y. Kumar and P.D. Sethi, *J. Indian Chem. Soc.,* **66**: 43 (1989).
14. D. Sandhya Rani, P.V. Ananthalaksmi & V.. Jayatyagaraju. *Indian Journal of Chemistry,* **38**A: 843-846 (1999).
15. Lever A.B.P., Inorganic electronic spectroscopy 2nd Edn (Elsevier, Amsterdam). (1984) .
16. M.S. Islam, M.Q. Islam and T. Hossain, Pak. *J. Soc. Ind. Res.*, **33**: 205 (1990).
17. J. Selbir, *Chem, Rev.,* **65**: 153 (1965). *Coord. Chem. Rev.* **7**: 293 (1966). B.N. Finggis and J. Lewis, *Prog. Inorg. Chem.* **6**: 37 (1964).
18. A.B.P. Lever, “Electronic Spectroscopy”, 2nd ed. ELsevier, Amsterdum, (1984).
19. B.N. Figgis in “Comprehensive Coordination Chemistry”, ed. G. Wilkinson, Pergamon, **5** (2): 214 (1987).
20. D.S. Rao and M.C. Ganorkar, *J. Indian Chem. Soc.,* **58**: 217 (1981).
21. M.Athar, N. Ahmad, A.A. Gupta and A.K. Sengupta. Indian Drugs, 225 (1983).