Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(10):70-72

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Complexes of P-Chlorobenzylidene-2-Aminothiazole with Titanium (III) and Oxovanadium (IV)

Mahe Safia

Rajkiya Engineering College, Bijnor, Uttar Pradesh, India

ABSTRACT

The preparation and characterization of a new research series of metal complex of Titanium (III) and Oxovanadium (IV). In which titanium (III) a Oxovanadium (IV) as a metal ion and p-chlorobenzylidene-2-aminothiazole as a ligand are studied. The complexes $[C_{20}H_{18}N_4S_2O_2.TiCl_2]$ *and* $[C_{20}H_{16}N_4S_2Cl_2O.VOSO_4]$ *have been characterized by elemental analysis, infrared, electronic absorptional spectral and magnetic susceptibility measurements. An octahedral geometry is predicted for Ti (III) and VO (IV) complexes.*

Keywords: Schiffbase ligand; Oxovanadium (IV) complexes; Titanium (III) complex

---

INTRODUCTION

Metal complex of Schiff bases have played a central role in the development of coordination chemistry. Schiff bases offer a versatile and flexible serves of ligands capable to bind with various metal ion to give complexes with suitable properties of theoretical and practical applications during the past two decades. In recent year Vanadium complexes have attracted much attention for their potential utility as catalyst for various oxidation reaction *viz.* hydroxylation of phenols [1,2], oxidation of sulfides to sulfoxides [3,4], hydroxylation of benzene to mono and dihydroxy benzene [1,5,6] including reactions such as the coupling of 2-naphthols as well as Mannich type reaction [7,8]. Most recently, the application of various oxovanadium complexes as catalyst in different oxidation reaction has been reviewed [9,10]. The IR spectra of the ligands and their complexes were compared to determine any changes during complexation and to confirm their structure. The IR spectra of the ligands showed a broad absorption band at 3230-3117 cm^{-1} attributed to the stretching vibration of intra molecular hydrogen bonded OH group [11]. This band disappeared on complexation indicating the coordination of vanadium metal through OH group after deprotonation. A new medium intensity band near 3400-3500 cm^{-1} is attributed to V_{OH} stretching vibration of the coordinated water molecule to the central metal ion [12]. A strong band at 1648-1626 cm^{-1} of the spectra of the ligand was assigned to the azomethene (C=N) stretching vibration.

EXPERIMENTAL SECTION

Material

The chemicals and reagents used were of A.R. or equivalent grade. The aldehyde used was p-chloro benzaldehyde and o-amino phenol (BDH). The metal salt used titanium (III) Chloride (BDH, England) and oxovanadium (IV) sulphate (Fluka).

Method for Preparation of P-Chlorobenzylidene -2-Aminothiazole as a Schiff Base Ligand

The pure crystal of 2–aminothiazole (1.09 gm) in 25 ml of ethanol were mixed with p-chlorobenzadehyde (1.40 gm) and the mixture was refluxed for about 6 hours.

Characterization of Ligand

The colour of the prepared ligand (p-chlorobenzylidene-o-aminophenol) is dark brown. The melting point of the ligand was determined by open capillary method and is uncorrected. The ligand subjected to elemental analysis for C, H, N and Cl. The IR spectra of the ligand were regarded as 1626 cm^{-1} in order to show the presence of azomethine linkage.

Method of Preparation of Complexes

Diaquobis (p-chlorobenzylidene-2-aminothiazole) titanium (III) chloride:

Ethanolic solution of $TiCl_3$ was gradually added with stirring to a solution of the ligand in molar ratio 1:2. The solid complex Diaquobis (p-chloroben zylidene-2-aminothiazole) titanium (III) Chloride formed which washed and dried over P_4O_{10} in Vacuum desiccator.

Monoaquobis (p-chlorobenzylidene-2-aminothiazole) oxovanadium (IV):

The aqueous methanolic solution of vanadyl sulphate and the ligand was reflux on water bath for about 5-6 hr. The pH of the solution was adjusted to 7 by dropwise addition of 10% methanolic sodium acetate solution. The metal chelates separated out on cooling. The product was washed repeatedly with methanol and finally with petroleum ether (60-80°C) dried in vacuuo.

RESULTS AND DISCUSSION

Diaquobis(p-Chlorobenzylidene-2-Aminothiazole) Titanium(III) Chloride

The yellow coloured complex was subjected to elemental analysis which indicated that the ligand has reacted with metal in 2:1 molar ratio. On this basis, the molecular formula of the complex comes out to be $C_{20}H_{18}N_4S_2O_{2.}TiCl_2$. The melting point of the ligand was found to be 105°C and that of the complex was 209°C. This vast difference between the melting points of the ligand and the complex indicate that the complex may have been formed.

The IR spectrum of the ligand and the complex were recorded in KBr phase and compared. The IR spectrum of the ligand shows an important absorption band at 1626 cm^{-1} which may be assigned to the azomethine group (I). This band undergoes a negative shift of 26 cm^{-1} and appeared at 1600 cm^{-1} in the IR spectrum of the complex. This shift indicated the involvement of nitrogen atom of azomethine group in coordination with the metal.

The thermogravimetric analysis also confirms the presence of two coordinated water molecules. The percent weight less at 180°C in the thermogram corresponds to the loss of two water molecule. The electronic spectrum of the complex shows a band at 17850 cm^{-1} which may be assigned to d-d transition. The value of d-d transition corresponds to crystal field splitting energy. This is due to ^2T_2g-^2Eg transition and characteristic of octahedral geometry.

Monoaquobis(p-Chlorobenzyliden-2-Aminothiazoleoxovanadium (IV) Sulphate

The analytical data of the complex suggested 1:2 metal ligand stoichiometry for the complex. On the basis the molecular formula comes out to be $C_{20}H_{16}N_4S_2Cl_2O.VOSO_4$. The much higher melting point of the complex as compared to that of ligand indicated the formation of the adduct. The IR spectrum of the complex show an important band at 1570 cm^{-1}, which may be assigned $V_{(C=N)}$ azomethinelinkage.

The TGA also confirim the presence of one coordinated water molecule. The percent weight loss at 180° in the thermogram corresponds to the loss of one water molecule. The electronic spectrum of the complex exhibit three bands of 10867, 19424 and 26109 cm^{-1} assignable to dxy (b_2) → dxz, dyz (e^*), dxy (b_2) → $d_2 - y_2$ (b_1^*) and dxy (b_2) → dz_2 (a_1^*) transitions respectively, for octahedral stereochemistry. On the basis of the studies performance, the complex may be assigned an octahedral geometry with possible distortion due to V=0 group.

CONCLUSION

On the basis of studies performed octahedral geometry has been proposed for both prepared metal complexes.

Elemental analysis and spectral data of the free ligand and metal complexes Titanium (iii) oxovanadium (Iv) were found to be in good agreement with their structure.

REFERENCES

[1] MK Maurya; SJJ Titinchi; HS Abbo; S Chand. *Catal Lett*. **2003**, 86, 97-105.
[2] TA Alsalim; JS Hadi; EA Al-Nasir; Hs Abbo; SJJ Titinchi. *Catal Lett*. **2010**, 136, 228-233.
[3] AP de Azevedo Marques; ER Dockal; FC Skrobot; IL Viana Rosa. *Inorg Chem Commun*. **2007**, 10, 255-261.
[4] S Bunce; RJ Cross; LJ Farrugia; S Kunchandy; LL Meason; KW Muir; MO Donnell; RD Peacorck; D Stirling; SJ Teat. *Polyhedron*. **1998**, 17, 4179-4187.
[5] MR Maury; S Agrwal; C Bader; M Ebel; D Rehder. *Dalton Trans*. **2005**, 537-544.
[6] PM Reis; JAL Silva; JJRFD Silva; AJL Pombeiro. *J Mol Catal A Chem*. **2004**, 224, 189-195.
[7] P Reddy; CY Chu; DR Hwang; SK Wang; BJ Uang. *Coord Chem Rev*. **2003**, 237, 257-269.
[8] Z Luo; Q Liu; L Gong; X Cui; A Mi; Y Jiang. *Angew Chem Int Ed*. **2003**.
[9] G Licini; V Conte; A Coletti; M Mba; Zonta. *Coord Chem Rev*. **2011**, 255, 2232-2248.
[10] H Petik; C Albayrak; M Odabasoglu; I Senel; O Buyukgunor. *J Chem Crystalligr*. **2008**, 38, 901-905.
[11] K Nakamoto. Infrared and Raman Spectra of Inorganic Coordination compounds. New York Wiley and sons, **1978**, 229.
[12] HL Yang; Lanchen; WW Jing; XW Ming; WZ Ya; B Wang. *Inorganica Chimica Acta*. **2016**, 450, 8-11.