

## Synthesis and Characterization of Schiff Base Complexes of Molybdenum(VI), Tungsten(VI) and Chromium(III) with Vanillin and Aspartic Acid

A. JEPA MALAR<sup>†</sup> and M. SANKARANARAYANA PILLAI\*  
*Department of Chemistry, S.T. Hindu College, Nagercoil-629 002, India*

Metal chelates of Mo(VI), W(VI) and Cr(III) with Schiff bases have been synthesized by the condensation of *o*-vanillin with aspartic acid and characterized by spectroscopic method. Coordination of azomethine nitrogen in the Schiff base of the metal has been proposed.

**Key Words:** Molybdenum(VI), Tungsten(VI), Chromium(III), Complexes, Schiff bases.

### INTRODUCTION

The coordination compounds with Schiff base ligands have gained importance in recent past<sup>1-5</sup>, due to their industrial<sup>6</sup>, antimicrobial<sup>7</sup>, fungicidal<sup>8</sup>, anticancer<sup>9</sup> and antiinflammatory<sup>10</sup> activities. The complexing behaviour of vanillin derived Schiff bases with transition metals and their biological studies have been reported<sup>11-14</sup>. Schiff base metal complexes derived from different anilines have also been reported<sup>15,16</sup>. The survey of literature reveals that no attempt has been made to study the chelating behaviour of the Schiff bases derived from the condensation of *o*-vanillin and substituted anilines. The present communication describes the synthesis and characterization of complexes of Mo(VI), W(VI) and Cr(III) with Schiff base vanillidene-L-aspartate.

### EXPERIMENTAL

Chemicals used were either of BDH or E. Merck quality. Metal salts and solvents were used without further purification.

**Preparation of the Schiff base:** The Schiff bases were synthesized by refluxing a mixture of an equimolar amount of *o*-vanillin with aspartic acid in ethanolic solution on a water bath for 3-4 h. The resulting products were crystallized from methanol.

**Preparation of the complexes:** The metal complexes were prepared by adding the methanolic solution of the appropriate metal salt to methanolic solution of Schiff base in 1:1 metal-ligand ratio. The resulting mixture was refluxed on a water bath for about 4-5 h. The coloured precipitate that appeared on cooling the solution was

<sup>†</sup>Department of Chemistry, Nesamony Memorial Christian College, Marthandam-629 301, India.

washed with methanol and petroleum ether. It was crystallized and dried over anhydrous  $\text{CaCl}_2$  under reduced pressure and then in an electric oven at  $60^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The analytical data of the metal-complexes show that the complexes have metal to ligand stoichiometry of 1:1.

**Mo(VI)-Vanillin-L-aspartate system:** IR spectrum of the complex shows a band centered around  $3575\text{ cm}^{-1}$  which has been assigned to the presence of coordinated water molecules. The absorption band at  $1666\text{ cm}^{-1}$  corresponds to the absorption of imino group ( $-\text{CH}=\text{N}$ )<sup>17</sup>. The normal absorption frequency of the imino group appears around  $1640\text{--}1600\text{ cm}^{-1}$ . The blue shift of  $-\text{CH}=\text{N}$  stretching vibration suggests chelation of the azomethine nitrogen with the central metal ion. The absorption bands at  $1301\text{ cm}^{-1}$  is due to  $\alpha$ -carboxylato group. This decrease in frequency than expected is due to the effect of the nearby substituents. The band at  $1414\text{ cm}^{-1}$  corresponds to  $\beta$ -carboxylato group. The absorption band at  $1275\text{ cm}^{-1}$  corresponds to the stretching frequency of phenolic oxygen. An intense band at  $1240\text{ cm}^{-1}$  in the ligand due to the phenolic C-O vibration shifts higher to  $1280 \pm 10\text{ cm}^{-1}$  in the complexes. The blue shift of C-O stretching vibration and the disappearance of -OH band suggest the deprotonation of the phenolic -OH after its chelation with the metal ion. Thus the Schiff base ligand tetradentately coordinate with  $\text{Mo}^{6+}$  ion through phenolic oxygen, imino nitrogen and two carboxylato groups forming one five, one six and one seven membered chelates.

The characteristic absorption frequencies of the complex are given in Table-1. It is obvious that Mo(VI) is octahedrally coordinated. The analytical data indicates a composition of  $\text{Mo}\cdot\text{SB}\cdot 2\text{H}_2\text{O}$  with a total number of six coordination sites.

TABLE-1  
Mo(VI)-VAN-ASP SYSTEM

Groups	Frequencies ( $\text{cm}^{-1}$ )
C-O	1275
$\alpha$ -COO <sup>-</sup>	1301
$\beta$ -COO <sup>-</sup>	1414
CH=N	1666
O-H	3575

**W(VI)-Vanillin-L-aspartate system:** The absorption band at  $3323\text{ cm}^{-1}$  corresponds to the absorption of coordinated water molecule. The absorption band at  $1666\text{ cm}^{-1}$  is assigned to the absorption of imino group  $\nu(-\text{CH}=\text{N})$ <sup>17</sup>. The normal absorption frequency of the imino group appears around  $1640\text{--}1600\text{ cm}^{-1}$ . The blue shift of  $\text{CH}=\text{N}$  stretching vibration suggests chelation with the central metal ion. The absorption bands at  $1394$  and  $1348\text{ cm}^{-1}$  corresponds to the stretching frequency of the carboxyl groups. As aspartic acid contains two -COOH groups ( $\alpha$  and  $\beta$ ) the band at  $1348\text{ cm}^{-1}$  corresponds to  $\alpha$ -carboxylato group. This decrease in frequency

than expected is due to the effect of the nearby substituents. The band at  $1275\text{ cm}^{-1}$  corresponds to the stretching frequency of phenolic oxygen. This demonstrates that all the four possible donor atoms of the Schiff base ligand *viz.*, imino nitrogen, phenolic oxygen and two carboxylato oxygen atoms participate in complexation with W(VI). This would result in the formation of a stable complex with one five, one six and one seven membered chelates.

The characteristic absorption frequencies of the complex are given in the Table-2. It is obvious that W(VI) is octahedrally co-ordinated. The analytical data indicates a composition of  $\text{W}\cdot\text{SB}\cdot 2\text{H}_2\text{O}$  with a total number of six co-ordination sites.

TABLE-2  
W(VI)-VAN-ASP SYSTEM

Groups	Frequencies ( $\text{cm}^{-1}$ )
C-O	1275
$\alpha\text{-COO}^-$	1348
$\beta\text{-COO}^-$	1394
CH=N	1666
O-H	3323

**Cr(III)-Vanillin-L-aspartate system:** The IR spectrum of the complex gives a band at  $3171\text{ cm}^{-1}$  corresponds to the coordinated water molecule. The absorption bands at  $1679\text{ cm}^{-1}$  is due to imino nitrogen<sup>17</sup>. The absorption bands at 1308 and  $1367\text{ cm}^{-1}$  corresponds to the stretching frequency of the carboxylato groups. As aspartic acid contains two -COOH groups ( $\alpha$  and  $\beta$ ) the band at  $1367\text{ cm}^{-1}$  corresponds to the  $\beta$ -carboxylato group. The band at  $1308\text{ cm}^{-1}$  corresponds to  $\alpha$ -carboxylato group. This decrease in frequency than the  $\beta$ -carboxylato groups is due to the effect of nearby substituents. The band at  $1268\text{ cm}^{-1}$  corresponds to the stretching frequency of phenolic oxygen. This demonstrates that all the four possible donor atoms of the Schiff base ligand *viz.*, imino nitrogen, phenolic oxygen and two carboxylato oxygen participate in complexation with Cr(III). This would result in the formation of a stable complex with one five, one six and one seven membered chelates.

The characteristic absorption frequencies of the complex are given in the Table-3. It is obvious that Cr(III) is octahedrally coordinated. The analytical data indicates a composition of  $\text{Cr}\cdot\text{SB}\cdot 2\text{H}_2\text{O}$  with a total number of six coordination sites.

TABLE-3  
Cr(III)-VAN-ASP SYSTEM

Groups	Frequencies ( $\text{cm}^{-1}$ )
C-O	1268
$\alpha\text{-COO}^-$	1308
$\beta\text{-COO}^-$	1367
CH=N	1679
O-H	3171

## REFERENCES

1. R.K. Choudhary, R.N. Pathak and L.K. Mishra, *J. Indian Chem. Soc.*, **77**, 32 (2000).
2. K.C. Satpathy, A.K. Panda, R. Mishra, A. Mahapatra and A. Patel, *Synth. React. Inorg. Met-Org.*, **22**, 201 (1992).
3. P.A. Vigato, S. Tampurini and D.E. Fenton, *Coord. Chem. Rev.*, **10**, 25 (1974).
4. P. Guerriero, P.A. Vigato, D.E. Fenton and P.C. Hellier, *Acta Chem. Scand.*, **46**, 1025 (1992).
5. F.S. Watanabe and S.R. Olsen, *Soil Sci. Soc. Am. Proc.*, **29**, 672 (1995).
6. A.K. Dey, *J. Indian Chem. Soc.*, **63**, 339 (1966).
7. R.D. Jones, D.A. Summerville and F. Basolo, *Chem. Rev.*, **79**, 130 (1979).
8. S. Goyal and K. Lal, *J. Indian Chem. Soc.*, **66**, 477 (1989).
9. W. Zishen, G. Ziqi and Y. Zhenhuan, *Synth. React. Inorg. Met-Org. Chem.*, **20**, 335 (1990).
10. R.K. Parashar, R.C. Sharma, A. Kumar and G. Mohan, *Inorg. Chem. Acta*, **151**, 201 (1988).
11. N.S. Biradar, M.A. Pujar and V.R. Marathe, *Indian J. Chem.*, **9**, 712 (1971).
12. M.L. Dhar, V.R. Gupta and O. Singh, *Indian J. Chem.*, **27A**, 739 (1988).
13. L. Guofa, N. Chang and L. Bin, *Synth. React. Inorg. Met-Org. Chem.*, **20**, 1387 (1990).
14. L.K.W. Henri, J. Tagenine and B.M. Gupta, *Indian J. Chem.*, **40A**, 999 (2001).
15. A.P. Mishra, *J. Indian Chem. Soc.*, **75**, 251 (1998).
16. K.M. Reddy, M.B. Halli and A.C. Hiremath, *J. Indian Chem. Soc.*, **71**, 751 (1994).
17. K.K. Aravindrakshan, *Indian J. Chem.*, **26A**, 291 (1987).

(Received: 10 November 2009;

Accepted: 30 March 2010)

AJC-8588