

Studies of Histidine, Phenylalanine Complexes of Oxovanadium(IV) Derived from Acetylacetone

RAJEEV SINGH YADAV

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

dr.rsy@sifv.com

Abstract:

Schiff base complexes of oxovanadium(IV) with amino acids and acetylacetone were synthesized and characterized by elemental analysis, conductivity measurements, spectral and magnetic data. The complexes were found to be non-electrolytes and stoichiometry shown 1:1. The spectral and magnetic data were suggesting the square pyramidal geometry.

Key Words: Schiff base complexes, oxovanadium(IV), amino acids, acetylacetone

Introduction: -

The oxovanadium(IV) complexes with amino acids and acetylacetone have been studied extensively. Comparatively little attention has been given to systems in which the Schiff base is prepared from the condensation of acetylacetone and amino acids¹.

The usefulness of metal complexes in theoretical and applied chemistry and in technology is well established. Complex formation plays an important role in the field of physiological chemistry. The naturally occurring complexes have functions which are vital to organism catalysis or oxidation reduction reaction, oxygen carrying power, hydrolysis, synthesis of protein, the carboxylation and carbon di oxide carrying power².

The coordination and chelation play an important role in electro deposition of metals in leather industries and in textile industries.

Schiff bases can also be prepared by the condensation of amino acids with aldehydes are strong metal coordinating agent.

Experimental:-

The chemicals and reagents used were B.D.H, Analar or E.Merck with extra pure quality. The carbonyl compounds used were acetylacetone (BDH) and amino acids used were L-histidine (BDH), L-phenylalanine (BDH).The metals salts used were oxovanadium(IV) chloride (BDH).

The Schiff bases were prepared by the condensation of acetylacetone with the respective amino acid³. The metal complexes of Schiff bases were prepared by adding ethanolic solution of the Schiff base ligand and aqueous solution (approximate 0.1 M) of

metal salt in round bottom flask. A known amount of metal salt solution (approximate 0.1 M) was taken in a round bottom flask fitted with a mechanical stirrer and the ethanolic solution of Schiff base (approximate 0.1 M) was added drop wise with constant stirring with the help of separating funnel. After the addition was complete, the mixture was allowed to stand on water bath for an hour. The metal complex so obtained as amorphous mass/crystals filtered and washed free of ligand with ethanol. The complex compound was dried in vacuum desiccators⁴.

Result and Discussion:-

(Acetylaceton-histidine/ phenylalanine) oxovanadium(IV) complexes:

The greenish blue coloured complexes resulting from the interaction of oxovanadium(IV) chloride with acetylaceton-histidine and phenylalanine shows 1:1 metal: ligand stoichiometry. On the basis of elemental analysis for C, H and N and gravimetric estimation of the metal ion, the empirical formula of the complexes could be given as- [(VO) (C₁₁H₁₅O₄N₃)] and [(VO) (C₁₄H₁₇O₄N)] respectively⁵. The vast difference between the melting points of the ligand and the complex are also suggestive of the formation of the complexes.

The magnetic moment measurements carried out at room temperature gives a value of 1.80 B.M for histidine and the value of 1.82 B.M⁶. suggest the paramagnetic nature of the phenylalanine complex. This indicates the spin free d¹ configuration for these complexes. The IR spectra of the ligand shows a stretch band for histidine at 1653cm⁻¹ and for phenylalanine at 1648cm⁻¹ shifted to 1620cm⁻¹ in the spectra of the complex, assigned to $\nu(\text{C}=\text{N})$ vibrations⁷. These bands appear in the spectra of the complexes with lowering in frequency. This shift indicates the involvement of azomethine nitrogen in chelation with the metal ion.

The IR spectra of the ligand shows a band for histidine at 3436cm⁻¹ and for phenylalanine at 3432cm⁻¹ which may be assigned to $\nu(\text{OH})$ vibrations⁸. The absence of this band in IR spectra of the complex indicates the deprotonation of enolic (OH) and coordination through O-atom to the metal ion. This is also supported by the downward shift in the $\nu(\text{C}-\text{O})$ vibrations for histidine to 1521cm⁻¹ and for phenylalanine at 1537cm⁻¹ in the IR spectra of the complexes respectively⁹.

The presence of $\nu(\text{V}=\text{O})$ vibrations in the IR spectra of the complex shows a stretch

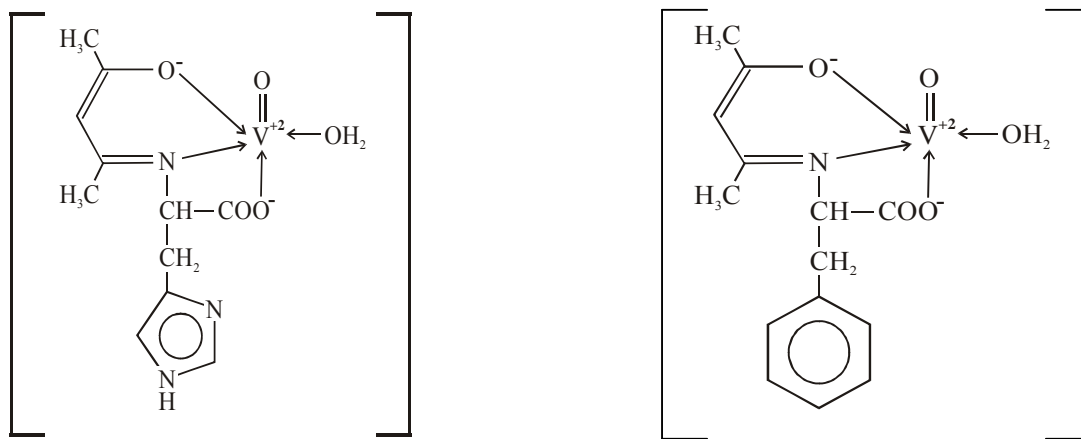
band for the histidine at 995cm^{-1} and also for phenylalanine at 1002cm^{-1} which indicates the non chained structures for both the histidine and phenylalanine complexes respectively¹⁰.

The IR spectra of the ligand shows a symmetrical stretch band for histidine at 1445cm^{-1} and for phenylalanine at 1450cm^{-1} assignable to $\nu(\text{COO}^-)$ vibrations which is shifted to 1405cm^{-1} and 1410cm^{-1} in the complexes¹¹. This downward shift in $\nu(\text{COO}^-)$ vibrations is suggestive of the involvement of carboxylate O-atom in chelation with the metal ion.

A medium broad band at 3400cm^{-1} and at 3403cm^{-1} in the IR spectra of both the complexes only, assignable to coordinated $\nu(\text{OH})$ vibrations, is suggestive of the involvement of water molecule in coordination with the metal ion. The presence of water molecule is further indicated by TGA¹².

The non-electrolytic nature of the complex is indicated by molar conductivity measurements carried out in CH_3OH , DMF, and DMSO at 10^{-3} molar concentration¹³.

On the basis of above facts the following square pyramidal geometries has been assigned for these (Acetylacetonate-histidine/phenylalanine) oxovanadium(IV) Complexes-



The Proposed Structures of the complexes:

Acknowledgement: The author is grateful to Dr. N.K. Agarwal head, Deptt. Of Chem. And Principal, Bareilly College, Bareilly to provide extending facilities.

References

1. H. Schiff. Ann, 131, 118, (1864).
2. L. J Nunez and G.L.Eichhorn. J. Amer. Chem. 84, 901(1962).
3. A.Nakahara;H.Yamamoto.and H.Matsumoto Bull.chem. soc. Jpn, 37, 3457, (1970).
4. Y.Nakao; H.Ishibashi. and A. Nakahara Bull. Chem. Soc. 43, 3457, (1970).
5. Singh,RajendraP,and Khan, A.A J. Inorg. Nucl. Chem. 34 (5),1663-3 (Eng).(1972).
6. Amar Srivastava and A.K Shrimal. Indian J. Chem. Vol. 41A,pp.785-790. (2002).
7. T.Daniel;Thangadurai,IndianJ.Chem.Vol.41A,pp.741-745.(2002).
8. N.S.Bhavi; P.J. Bahad; J. Indian Chem. Soc., Vol. 79, pp. 342-344. (2002).
9. Debabrata Chatterjee Indian J. Chem. Vol. 41A, pp.1406-1409. (2002).
10. Syamal, D.Kumar, A.K. Singh,Indian J. Chem. Vol. 41A, pp. 1385-1390. (2002).
11. Deoghoria, soma; Sain,J. Indian Chem. Soc., Vol. 79, pp, 857-859. (2002).
12. B. S. Jhaumur-Laulloo .Indian J. Chem. Vol. 42A, pp, 2536-2540. (2003).
13. S.R.Aswale, P.R.Mandlik,Indian J. Chem. Vol. 42A, pp, 322-326. (2003).
14. P.S. Mane; S.G. Shirodkar,J. Indian Chem. Soc., Vol. 70,pp, 176-178. (2003).
15. Soma Deoghoria, W.T Wong Indian J. Chem. Vol. 42A, pp, 1004-1007. (2003).
16. G. Indira Devi; Geetha, Asian J. Chem. Vol. 16, No. 1
17. Parameswaran ; V. Veena pp, 493-500. (2004).
18. D.Kumar, A.K.Singh Asian J. Chem. Vol. 16, No. 2, pp, 679-687, (2004).
19. Xin- Wen Liu; Ning Tetrahedron: Asymmetry, 15, pp, 1269-1273, (2004).
20. Min-Yu Tan.Asian J. Chem. Vol. 16, No. 1 501-507. (2004).
21. Kugalur P. Balasubramanian,Transition Metal Chemistry.29, 644-648, (2004).
22. Abdou S. El-Tabl. Transition Metal Chemistry.29, 543-549. (2004).
23. Dalma Gyepesova,Budapest, Hungary, Acta Cryst.A60, pp, 266, (2004).
24. Hassaan Keypour, Hamid Inorg. Chim. Acta, Vol. J-58-pp, 247-56. (2005).
25. Sumana Sarkar, Amrita Inorganica Chimica Acta Vol. J-58,pp, 641-649. (2005).
26. ShantaDhar,Munirathianam,InorganicaChimicaActaVol.358,pp,2437-2444.(2005).
27. Aysegul Golcu, Mehmet Tumer Inorganica Chimica Acta Vol. 358pp, 1785-1797. (2005).
28. Subhendu Biswas; Kamala Mitra; Inorg. Chim. Acta, Vol. 358,pp, 2473-2481. (2005).

Table 1

CHARACTERISATION OF COMPLEXES
Oxovanadium (IV) Complexes (Elemental Analysis)

Observed (Calculated)

S.No	Name and mole formula of the complexes/Mol.wt	Colour	M.P.	%C	%H	%N	%M	(Molar conductance) Methanol DMF DMSO	Mag. moment (in B.M.)
1.	(Acetylaceton-histidine) Oxovanadium (IV) [(VO) (C ₁₁ H ₁₃ O ₃ N ₃).H ₂ O] Mol.wt. = 319.95	Greenish blue	270°C	42.45 (41.26)	5.78 (4.69)	14.36 (13.13)	16.98 (15.93)	(Non-electrolyte)	1.80
2.	(Acetylaceton-phenylalanine) Oxovanadium (IV) [(VO) (C ₁₄ H ₁₅ O ₃ N)H ₂ O] Mol.wt. = 328.95	Green	253°C	52.23 (51.08)	6.35 (5.17)	5.38 (4.26)	16.63 (15.49)	(Non-electrolyte)	1.82

Table 2

Infra Red Spectral Data
Bands (in cm⁻¹)

S.No.	Name of Ligand/Complex	ν (C=N)	ν (COO ⁻)	ν (OH)	ν (C-O)	ν (V=O)	ν (M-N)	ν (M-O)
Ligand								
1.	Acetylaceton-histidine	1653	1445	3436	1547	-	-	-
Complex								
2.	(Acetylaceton-histidine) Oxovanadium (IV)	1625	1405	3400	1521	995	-	-
Ligand								
1.	Acetylaceton-phenylalanine	1648	1450	3432	1537	-	-	-
Complex								
2.	(Acetylaceton-phenylalanine) Oxovanadium (IV)	1620	1410	3403	1506	1002	-	-