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Synthesis and Characterization of Peroxo Vanadium (V) Complexes with Amino Acids as Ligands

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Abstract

Vanadium is a chemical element with symbol V and atomic no. 23. It is a hard, silvery, grey, ductile, malleable transition metal. The element is found almost exclusively in chemically combined form in nature, but once isolated artificially, the formation of an oxide layer stabilizes the free metal somewhat against further oxidation. In the present paper, synthesis of vanadium (V) complex containing L-phenylalanine and synthesis of vanadium (V) complex with aspartic acid is discussed. The complexes are obtained as coloured microcrystalline products. These newly synthesized complexes are insoluble in aqueous medium and in organic solvents. The complexes are air stable. The presences of ligands such as peroxide (O₂²⁻), phenyl alanine (C₉H₁₁NO₂), aspartic acid (C₄H₇NO₄) are confirmed from qualitative tests in the respective complexes.

Key Words: *Vanadium complexes, Amino acids ligands, Stoichiometric oxidants, Biological relevance, Material sciences.*

Introduction: In 1831, the element vanadium was identified, when N.G. Sefstrom was able to separate and recognize the oxide. The word vanadium was derived from the name of goddess vanedis, in Scandinavian mythology. A. M del Rio had observed the beautiful colours of vanadium compounds as early as 1801 in his experiment with a new element; he called erythronium, because of the red colour after its treatment with acid (1).

A lot of tribulations in the experiment and the various colours observed in the early chemistry were attributed to the formation of different co-ordination compounds which are the signs of a valuable and challenging chemistry.

Appropriate information about the early chemistry of vanadium are available in Mellon's (2) and Sidgwick's (3) account. Vanadium compounds have formal oxidation states from -3 to +5 with the exception of -2. Most stable among them are +4 and +5.

The oxidizing and reducing properties of the metal strongly affects its co-ordination chemistry. The chemistry of vanadium in aqueous solution is restricted to the oxidation states +2, +3, +4 and +5; though V (II) can reduce water.

The VO²⁺ form rather strong bonds mostly with the more electronegative atoms e.g. F, Cl, O, N (and also S and P). Most vanadyl complexes are not air stable and can be easily hydrolysed or oxidized to the +5 oxidation state. The oxo complex of vanadium contains the VO³⁺ (V) or the VO²⁺ (IV) entity and the cis geometry in dioxo complexes has been confirmed by structure determination.

A large number of oxo complexes containing the halides, alkoxides, peroxide, hydronamates and amino carboxylate have been described. Vanadium (V) oxidizes many ligands thus limiting the isolation of a large number of vanadium (V) complexes. Oxidising properties of vanadium are readily exploited in catalysis oxidations. Important example of such catalysis is oxidation of SO_2 to SO_3 in the industrial production of H_2SO_4 , and there is great concern over the presence of small concentrations of vanadium in fuels (coal and petroleum) because of the ability of vanadium to catalysis the oxidation of SO_2 .

The chemistry of vanadium in aqueous medium is complicated owing to (i) multiple oxidation state (ii) extensive hydrolysis (iii) precipitation or polymerization. Vanadium (V) oxidation state is most complicated. At physiological p^{H} , $\text{VO}_2^{(+)}$, exists but in alkaline conditions, mononuclear tetrahedral anionic vanadates (VO_4^{3-}) forms. At physiological p^{H} , vanadium (v) is an efficient oxidizing agent, and it oxidizes aldehydes, ketones, catechols, olefins and sulfhydryls.

In recent years, vanadium phenolate chemistry (4,5) has been shown to possess a great interest, not because of the fact that hard phenolate ligands behave as excellent ancillary ligands (6,7) stabilizing the highest available oxidation state of vanadium incorporating VO^{3+} moiety preferentially (8), but due to their implications in a variety of biomolecules (9). Again vanadium phenolates are used as catalysis in polymerization, oxidation (10) and potential shape selective transformations (11). Although several novel vanadium phenolates are reported to be characterized in the form of multidentate heteroligand chelates (4,12) with special reference in biological systems, yet it is felt that an understanding of the biological significance and physiology of vanadium are based on the knowledge of coordination chemistry of vanadium. Application of vanadium coordination compounds in the field of material sciences for example discovery of novel natural product (amvadin) in the mushroom have attracted the attention of recent workers (13). It is also found that vanadylacetylacetonate and vanadium pentoxide inhibit smoke formation in combustion tests polyvinyl chloride. The former is more active (14). Vanadyl phthalocyanine is effective as a smoke reducer for various styrene polymers. Vanadium (v) has been successfully applied as an oxidant in acidic medium. A vanadium protein has also been proposed to catalyze the oxidation of NADH (15). The similarities between phosphate and vanadate explain the biological activity of metal in the oxidation state +5. The important example is the strong inhibition of Na^+ pump (Na^+ , K^+ - ATPase) and nucleases, where vanadium has trigonal bipyramidal geometry on binding to the active site of enzymes. Vanadium was found to be a cofactor in algal bromoperoxidases, and bacterial nitrogenases (16).

In order to understand the bioinorganic chemistry of vanadium it is necessary to characterize various modes of metal uptake/ elimination, transport and function. These processes generally involve association of vanadium (v) or vanadium (iv) with polypeptides and/ or proteins. The details of these associations such as binding constants, acid base properties and redox potentials are defined by the specific ligands coordinated to, and the geometry of the metal ion. The vanadium coordination chemistry can be probed by ^{51}V NMR for vanadium (v) (d^0 , $S = 0$, $I = 7/2$) or EPR for vanadium (iv) (d^1 , $S = 1/2$).

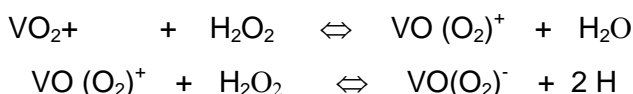
Among the first row transition metal vanadium has been identified as an essential trace element in most living systems. Vanadium is increasingly recognized as being requisite to biological function, dysfunction and therapy. Hence in 1911, discovered the high concentration of vanadium in the blood of ascidians. Vanadium has been identified as an essential element in alternative nitrogenase and in haloperoxidase (17). Vanadium is required for the proper growth of bones and

connective tissues. It also decreases the insulin requirement of diabetic patient. Vanadium also modifies phosphate metabolism.

At present the two most important vanadium enzymes described are vanadium nitrogenase (v-Nase) and haloperoxidase.

Coordination of oxovanadium (v) with N, O – donor ligands is the active site in the vanadium haloperoxidase. The discoveries of the first two naturally occurring vanadium containing enzymes, the bromoperoxidase and nitrogenase, the coordination chemistry and reactivity of vanadium has received considerable attention of various ligands, many carboxylates form anhydrides with vandate in solution, provided carboxylates have additional hydroxyl or amine groups available for chelation (18).

Vanadium peroxo complexes are known to act as catalysis (19, 20) and have been proposed as one of the model system for the biochemistry of vanadium (21, 22). Reagents which can cleave nucleic acids under mild conditions have potential applications as DNA - and RNA - sequencing reagents as well as antitumor and antiviral drugs. A number of redox active transition metal based nucleases cleave DNA and/ or RNA with photoactivation in the presence of cofactors. Transition metal complexes with peroxide as ligands are effective nucleases. Several vanadium (v) peroxo complexes exhibit anti leukemic activities. Using a plasmid DNA relaxation assay, the photo cleavage activities of these vanadium (v) complexes were measured (23). Reactions of hydrogen peroxide with various chemical species is a subject matter of many investigation, because of their biological significance. In analytical chemistry, hydrogen peroxide has been used as reagent for early transition metal ions and in the analysis of trace metal ions using their catalytic effect on the H₂O₂ decomposition. Reaction of vanadium (v) with H₂O₂ in strongly acidic media gives two species of peroxo complex i.e. VO(O₂)⁺ and VO(O₂)⁻ in which coordinated water molecules are omitted for simplicity. Under the experimental conditions, vanadium (v) exists as VO₂⁺. Thus peroxo complexes are produced by the following reactions (24).



Vanadium in presence of H₂O₂ forms several peroxo vandate derivatives including mono, di - and tri peroxo mono vandates and tetra peroxo di vanadate. Some or all of these compounds undergo reaction with additional ligands to give peroxo vandate heteroligands products some of which are characterized by X- ray diffraction studies (25).

Peroxo complexes of vanadium (v) have been largely studied as catalysts or stoichiometric oxidants in hydroxylation or epoxidation of different organic substance.

Peroxo vanadium chemistry has attracted considerable current interest because of the biochemical significance of such compounds. In recent works, the solution chemistry of peroxo vanadium complexes are also addressed (26).

In view of the aforementioned discussion it was considered worthwhile to carry out investigations on synthesis of vanadium (v) peroxo complexes with some chosen ligands. Accordingly in this report I give an account of synthesis of some vanadium peroxo compounds.

Experiment:

Materials: Chemicals used are of reagent grade quality. Vanadium pentoxide, V_2O_5 is obtained from S. d. fine – CHEM LTD; Hydrogen peroxide, H_2O_2 is obtained from Qualigen. Phenylalanine, ($C_9H_{11}NO_2$), Aspartic acid, ($C_4H_7NO_4$) used is obtained from SISCO RESEARCH LABORATORIES PVT. LTD.

IR Spectra: The IR spectra of the complexes are recorded on a Perkin Elmer model Spectrum RX – 1 FT/ IR spectrophotometer in the form of pressed KBr pellets at Assam University Silchar.

CHN Analysis: Micro analysis of carbon, hydrogen and nitrogen are recorded on RSIC Shillong with the instrument Heracus Crab Erba – 1108.

TGA: Thermo gravimetric analysis is done on TGA – 7, from Department of Chemistry NEHU Shillong.

Procedure for estimation of Vanadium (V): About 0.1 gram of the compound is dissolved in 100 cm^3 of water with about 1 gram boric acid and 30 cm^3 of 5 N H_2SO_4 . The solution mixture was boiled for 10 minutes to get clear light blue solution. About 4 gram of potassium per sulphate, $K_2S_2O_8$ and one drop of silver nitrate, $AgNO_3$ is added and boiled for one hour. The solution is then cooled to room temperature and titrated with sodium thiosulphate, $Na_2S_2O_3$ solution iodometrically.

Procedure for estimation of peroxide: About 0.1 gram of the sample is taken in a 250 cm^3 conical flask with 2-3 spatula of boric acid and 1:4 H_2SO_4 is added. To this 50 cm^3 of water is added. This solution is then titrated against standard $KMnO_4$ solution.

Preparation of complexes:

a) **Synthesis of Vanadium (v) complex containing L- phenylalanine:** About 1 gram (0.005498 m mol) of vanadium pentoxide, V_2O_5 is dissolved in 20 cm^3 of 30% Hydrogen peroxide, H_2O_2 in a 250 cm^3 beaker. Also, 0.9082 gram (0.005497 m mol) of phenyl alanine is dissolved in 20 cm^3 cold water. These two solution are mixed. Reddish brown solution appears having $p^H \sim 2$. The solution is then kept on water bath for concentration. Colour of the solution changes to deep green. It is then cooled at room temperature. And ethanol is added to it. Green precipitate settles down. The solution is then filtered and dried. The compound is isolated as green microcrystalline form.

Yield of the product is found to be 1.036 gram.

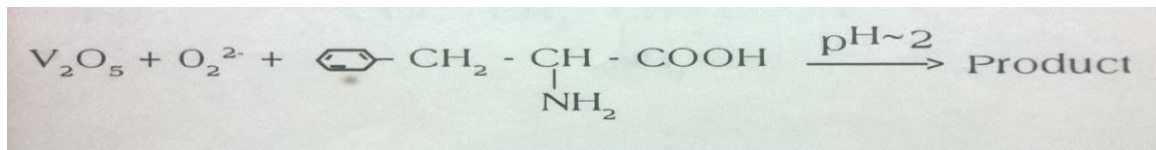
b) **Synthesis of Vanadium (V) complex containing aspartic acid:** Aspartic acid, 2.1613 gram (0.01623 m mol) is dissolved in boiling water. To this then added 3.007 gram (0.01653 m mol) of vanadium pentoxide, V_2O_5 , followed by adding 30 cm^3 of 30% Hydrogen peroxide, H_2O_2 in small lots, which results in wine red colour solution having $p^H \sim 3$. On keeping for overnight, green product appears and it is collected by filtration.

Yield of the product is found to be 1.6579 gram.

Results and Discussion: The complexes are obtained as coloured microcrystalline products. These newly synthesized complexes are insoluble in aqueous medium and in organic solvents. The complexes are air stable. The presence of ligands such as peroxide (O_2^{2-}), phenyl alanine ($C_9H_{11}NO_2$), aspartic acid ($C_4H_7NO_4$) are confirmed from qualitative tests in the respective complexes. Chemical analysis (Table 1) shows the stoichiometric ratio, based on which a empirical

formula has been assigned. Molar conductances are not measured because the complexes are insoluble, and hence do not permit to comment on iconicity.

The complexes are accessed following a strategic route. For the first complex starting material is vanadium pentoxide, V_2O_5 , which is made to react with peroxide (O_2^{2-}), presumably, forming a vanadium peroxide species in solution which on interaction with L- phenyl alanine anticipated to afford the desired mixed ligand complex.



The second complex is made starting from V_2O_5 via direct interaction with aspartic acid in aqueous medium.

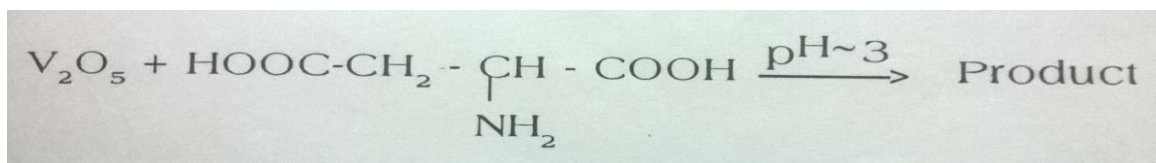
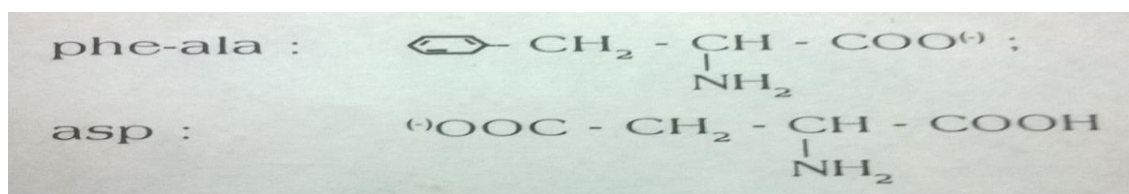


Table – 1: Analytical Data of the Complex

Compound	Colour	Analysis %				
		Found (Calculated)				
		V	O_2^{2-}	C	H	N
$(VO_2)_3(O_2)(\text{phe-ala}) \cdot H_2O$ phe-ala = phenyl alanine	Green	32 (33)	6.8 (7.0)	23 (22)	2.3 (2.2)	3.0 (4.7)
$(VO_2)_2(\text{asp})_2 \cdot 2 H_2O$ asp = aspartate	Green	21.7 (22)	-----	20.5 (22)	2.9 (3.5)	6.0 (8.2)



The vanadium content is determined by redox titration using standardized this sulphate solution iodometrically.

The characteristic IR absorption peak of the complexes is displayed in Table 2.

The phenyl alaninate complex of vanadium exhibits absorption peak at 990 cm^{-1} owing to $V = O$ stretch characteristic of vanadyl moiety. The band at 1384 cm^{-1} is due to H-N-H bending mode (δ H-N-H). The occurrence of bands at 2343 cm^{-1} and 2360 cm^{-1} are assigned to N-H stretching. The observance of band at 1630 cm^{-1} is due to δ H-O-H. This band shows the presence of water in the complex.

The aspartate complex of vanadium shows absorption band at 535 cm⁻¹ due to (V-O₂) symmetric stretching. The band at 1600 cm⁻¹ is due to ^vCOO stretching. δ H-N-H bending mode occurs at 1385 cm⁻¹. The band at 760 cm⁻¹ is assigned to P_r(H-O-H) mode. Water is suggestive of co-ordinated water group.

Table – 2: I.R. Spectral Data of the Complex

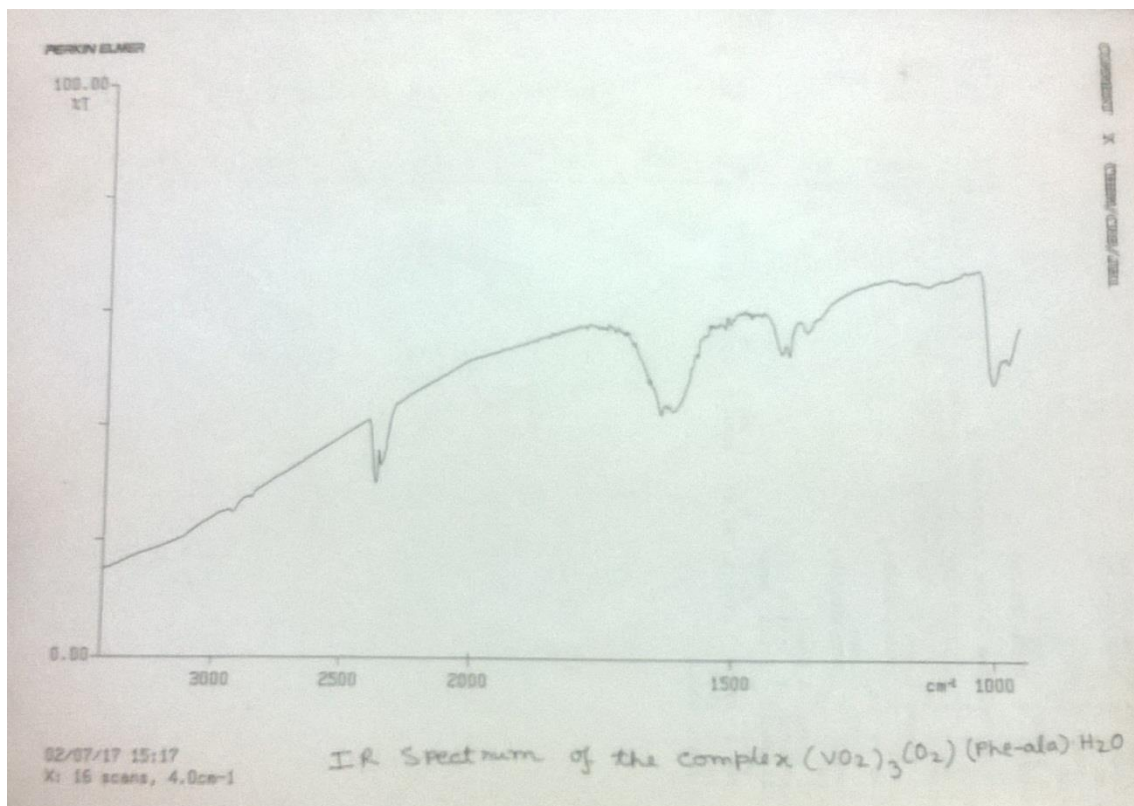
Compound	Colour	I. R. Bands (Cm ⁻¹)	Assignment
(VO ₂) ₃ (O ₂) (phe-ala). H ₂ O phe-ala = phenyl alanine	Green	990	^v V = O
		1384	δ H-N-H
		1630	δ H-O-H
		2343	^v N-H
		2360	^v N-H
(VO ₂) ₂ (asp) ₂ . 2 H ₂ O asp = aspartate	Green	535	^v _s (V-O ₂)
		1385	δ H-N-H
		1600	^v COO
		760	P _r (H-O-H)

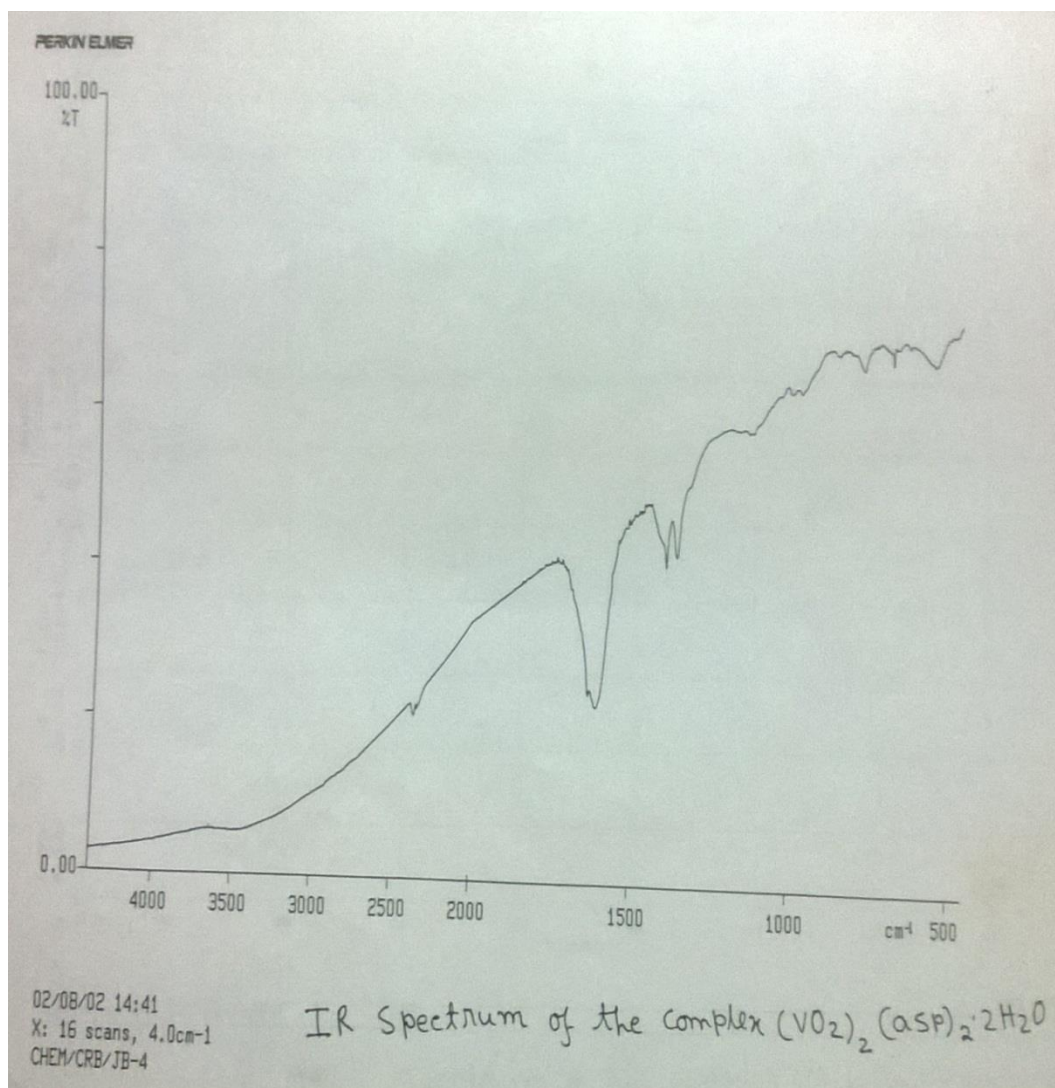
On the basis of analytical data and spectral features, the compounds are tentatively formulated as: (VO₂)₃(O₂) (phe-ala). H₂O and (VO₂)₂(asp)₂ . 2 H₂O

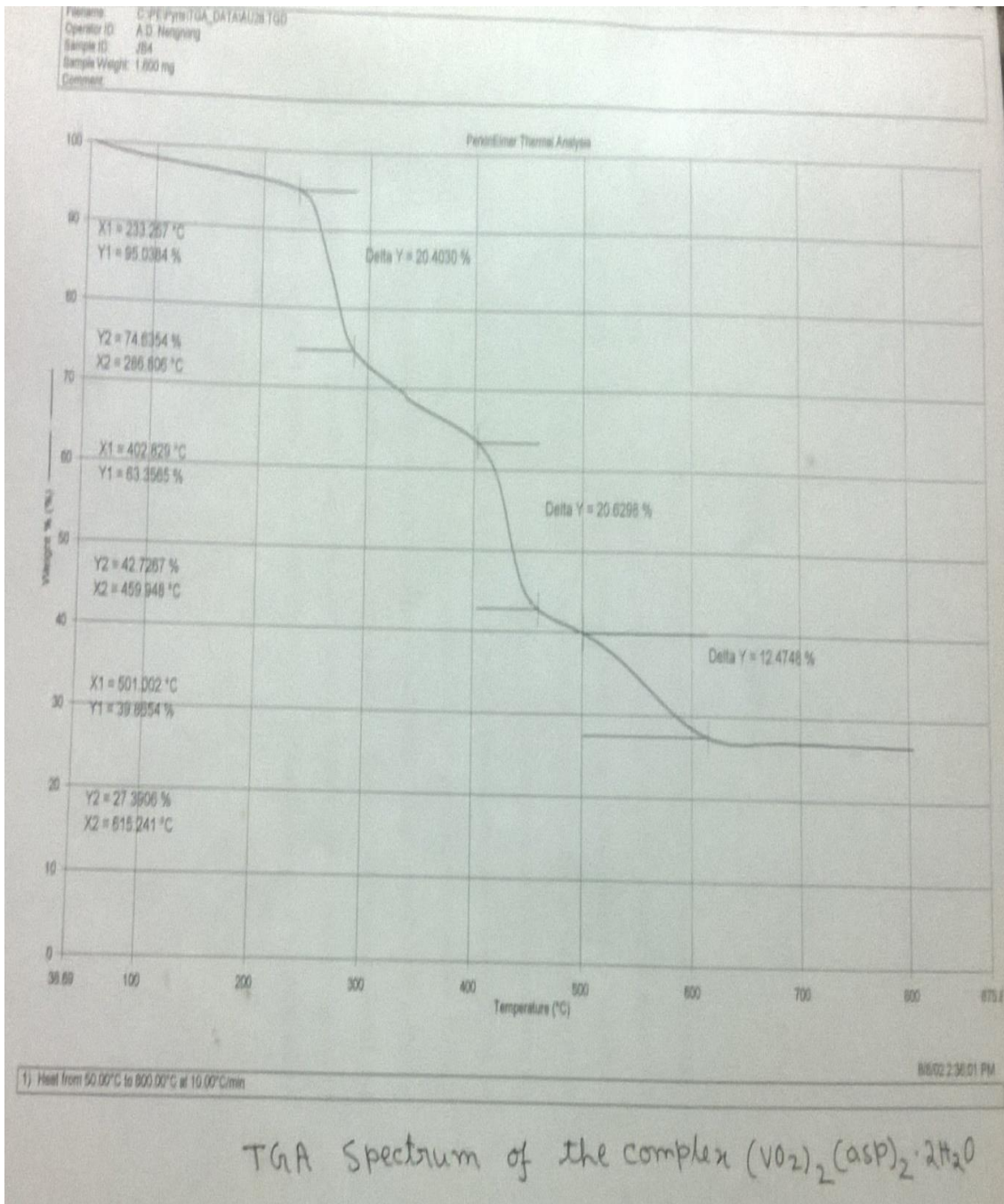
It is evident that under the chosen reaction condition (p^H ~ 3) formation of polynuclear complexes of dioxovanadyl moiety predominates. Interestingly, under rather similar condition peroxide did not coordinate to VO₂⁺ centre and only the amino acid complex was accessed. Noteworthy in this context is the presence of VO₂⁺ moiety. This however would require more evidence, although such species formation is not unprecedented (27).

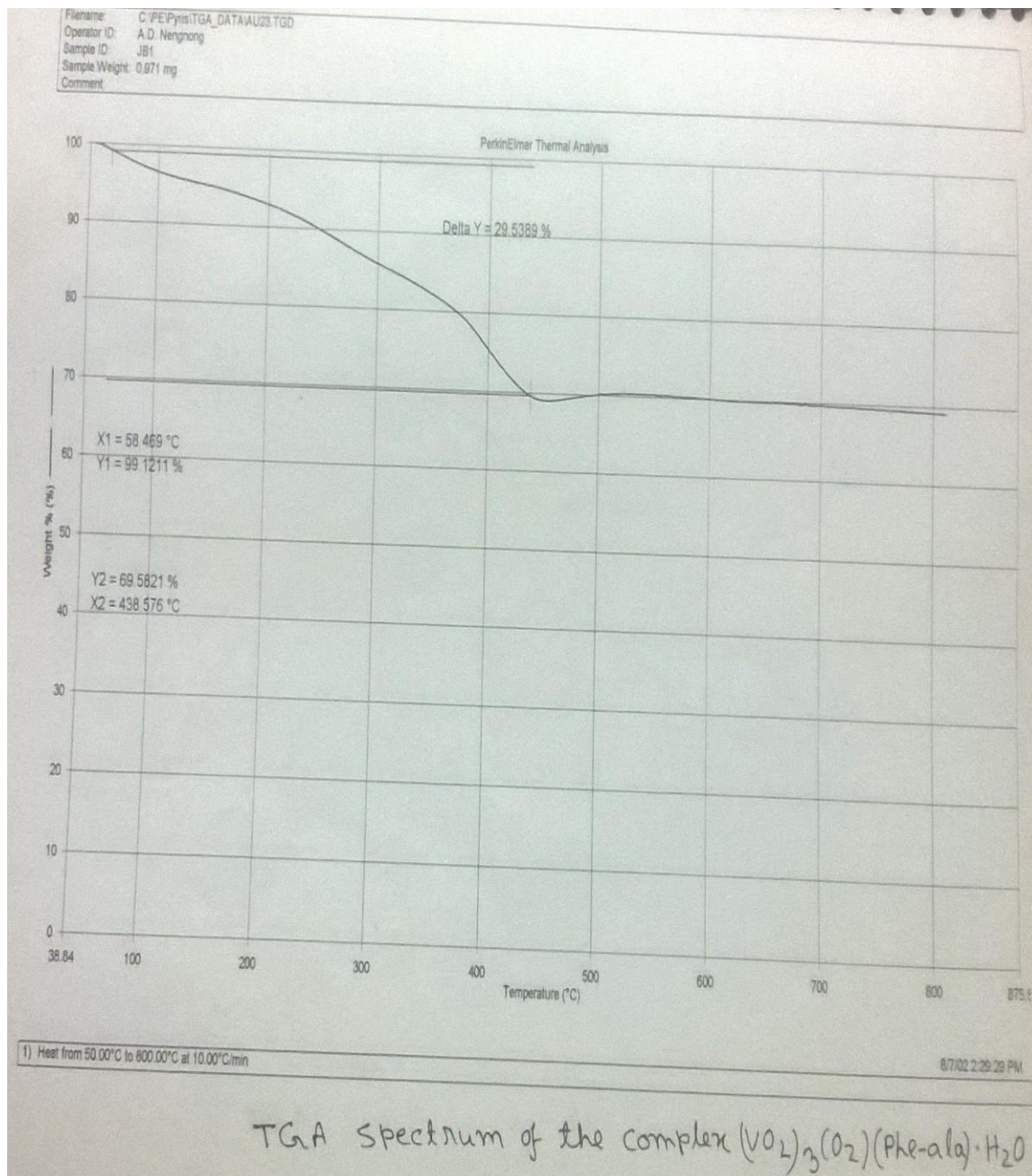
The TGA was run for both the complexes characteristic pattern. The phenyl - alaninate complex exhibited 30% loss corresponding to molecular weight 140, indicating loss of almost all the ligands. Simultaneously forming some sub oxide of vanadium. For example with aspartic acid as ligand, the decomposition continued till 72% corresponding to 337, suggesting the loss of water and aspartic acid ligand.

In the absence of any other physical studies, it is too premature to suggest any tentative structures for the complexes.









Conclusion: Within the ambit of present project work it has been possible to synthesize and characterize mixed ligand complexes of vanadium (v) with peroxide and amino acids. Interaction of vanadium (v) with peroxide has a biological relevance. Application of vanadium coordination compounds in the field of material sciences e.g. discovery of a novel natural product (amvadin) in the mushroom have attracted the attention of recent workers. The study of newly synthesized compounds would aid in the understanding of this aspect. The methods adopted here are simple and convenient and may be extended to afford newer vanadium complexes.

References

1. M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, 7th edn.; Chemical Education Publishing, Eastern, PA, 1968, *P* 351.
2. J. W. Mellor, 'Comprehensive Treatise on Inorganic and Theoretical Chemistry', Vol. IX, Longmans, Green and co., Newyork, 1929.
3. N. V. Sidgwick, 'The Chemical Elements and Their Compounds', Oxford University Press, London, 1950.
4. J. A. Bonadies and C. J. Carrano, *J. Am. Chem. SOC.*; 1986, *108*, 4088.
5. A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, 1991, *109*, 61.
6. M. Mazzanti, C. Floriani, A. Chiesi - Villa and C. Guastini; *Angew Chem. Int. Ed. Engl.*, 1988, *27*, 576.
7. R. A. Henderson, G. J. Leigh and C. J. Pickett; *Adv. Inorg. Chem. Radiochem.*, 1983, *27*, 576.
8. S. R. Copper, Y. Baikoh and K. N. Raymond, *J. Am. Chem. SOC.*, 1982, *104*, 5092.
9. I. R. Cornman, G. J. Colpas, J. D. Hoeschele, J. Kampf and V. L. Pecorao., *J. Am. Chem. SOC.*, 1992, *114*, 9925.
10. W. Priebsch and D. Rehder., *Inorg. Chem.*, 1990, *29*, 3013.
11. W. C. A. Wilisch, M. J. Scott and W. J. Armstrong., *Inorg Chem.*, 1988, *27*, 4333.
12. V. Pecorino, J. A. Bonadies, C. A. Marrese and C. J. Carrano. *J. Am. Chem. SOC.*, 1984, *106*, 3360.
13. Xiao - Min Zhang, Xiao - Zeng, and Xin Wong, *Polyhedron*, 1996, *15*, 1793.
14. G. Wilkinson, R. D. Gillard and Jon A. McCleverty, 'Comprehensive Coordination Chemistry.' Vol - 6. *P*. 665.
15. R. A. Coulomb, D. P. Briskin, R. J. Keller, W. R. Thornley, R. P. Sharma, *Anch. Biochem. Biophys.* 1987, 225.
16. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 1999, 6 th edn. *P*. 714.
17. C. R. Cornman, E. P. Zovinka, Y. D. Boyajian, K. M. Geiser - Bush, P. D. Boyle and P.. Singh, *Inorg. Chem.* 1995, *34*, *P*. 4213.
18. Man - Holey, Nam Ho Heo, and S. Hayashi, *Polyhedron*, 1998, *17*, 55.
19. H. Mimoun, L. Saussine, E. Daire, M. Postal, J. Fischer, R. Weiss, *J. Am. Chem. SOC.* 1983, *105*, 3101.
20. S. Patai, "The Chemistry of Peroxides"; Wiley: Newwork 1983.
21. C. Djordjevie, S. A. Craig, M. Lee, 186th National Meeting of the Am. Chem. SOC., D. Washington, 1983.
22. C. Djordjevie, G. L. J. Wampler; *Inorg. Biochem* in press.
23. D.W.J. Kwong, O. Y. Chan, R.N.S. Wong, S. M. Musser, Luisvaca, and S .I. Chan, *Inorg. Chem.* 1997, *36*, 1276.
24. S. Funahashi, K. Ishihara, M. Inamo and M. Tanaka, *Inorganic Chimica Acta*, 157 (1989) 65, 71.
25. A. S. Tracey and J. S. Jaswal, *Inorg. Chem.* 1993, *32*, 4235.
26. M. Sivak, J. Tyrseova and F. Pavelcik, *Polyhedron*, 1996, *15*, 1057.
27. N .N. Greenwood and A. Earnshaw, in *Chemistry of Elements*, 1989, *P*. 1156.