Ti, V, Nb Metalloporphyrin Chemistry

Jong-Hee Hwang Literature Seminar November 21, 1985

In recent years, much interest has been shown in synthetic analogs of various biological systems. The bioinorganic approach to the understanding and utilizing of hemoproteins has led to numerous studies of synthesis and reactivity of dioxygen adduct of metal complexes. Relatively few studies of Ti, V, Nb porphyrins have been published [1-20], however, Nb, V and Ti show appropriate characteristics for the study of O_2 binding [1].

The first peroxoporphyrin metal complex with symmetrically bonded dioxygen was reported in 1976 [2]. The dihalide complexes, which are precursors of low valent titanium complexes which will bind dioxygen, were prepared in 1977 [3-6]. Low valent titanium complexes show various types of autoxidation, which are determined by characteristics of axial ligands [7,8,10]. Recently, it was reported that titanium porphyrin compounds are catalysts for the epoxidation of olefins by alkylperoxides [9].

In 1934, the first oxovanadium(IV) porphyrin complex was found in petroleum and shale. However, the inertness of V=O moiety limited the study of vanadium porphyrin chemistry. Low valent vanadium(II) can be prepared from vanadium(IV) porphyrin halides [11,12], but vanadium(III) complexes have not been reported yet.

A French group succeeded in the preparation of acetato-oxo niobium(V) and trioxo niobium(V) complexes [13]. The crystal structures of these complexes were determined, and the complexes were found to be seven-coordinate [14-16]. The porphyrin complex of a tri-μ-oxo niobium dimer ($Nb_2TPP_2O_3$) has two different structures from different solvents, which means that the complex ($Nb_2TPP_2O_3$) has several stable configurations, depending on the nature of the crystallization solvent. Niobium(IV) porphyrin complexes of O_2 have been reported [18]. Using the O_2 complex, catalytic activity of niobium porphyrins for photochemical induced epoxidation was reported in 1985 [19].

References

1. Marchon, J.; Latour, J.; Boreham, C. J., "Dioxygen Adducts of Low-Valent Titanium Porphyrins. Prospects for the Selective Binding and Activation of Molecular Oxygen," J. Mol. Catal. **1980**, 7, 227-33.

2. Guilard, R.; Fontess, M.; Fournari, P., "The First Peroxometalloporphyrin with Dioxygen Symmetrically Bonded by Both Atoms; Synthesis and X-Ray Crystal Structure of Peroxotitaniumoctaethylporphyrin," J. Chem. Soc., Chem. Commun. **1976**, 161-62.

3. Ellinge, Y.; Latour, J. M.; Marchon, J.; Subra, R., "Conformation of Triangular Peroxo d° Metalloporphyrins," Inorg. Chem. **1978**, 17, 2024-26.

4. Guilard, R.; Latour, J.; Lecomte, C.; Marchon, J.; Protas, J.; Ripoll, D., "Peroxotitanium(IV) Porphyrins, Synthesis, Stereochemistry, and Properties," Inorg. Chem. **1978**, 17, 1228-1237.

5. Nakajima, M.; Latour, J.; Marchon, J., "Dihalide Complexes of Titanium(IV) Tetraphenylporphyrin. Precursors to Low-Valent Porphyrins," J. Chem. Soc., Chem. Commun. **1977**, 763-64.

6. Latour, J.; Marchon, J.; Nakajima, M., "Titanium(III) Porphyrins and Their Dioxygen Adducts," J. Am. Chem. Soc. **1979**, 101, 3974-76.

7. Latour, J.; Boreham, C. J.; Marchon, J., "Novel Titanium(III) Porphyrins with Aryl Axial Ligands. Redox Stoichiometry Tuned by Axial Ligation," J. Organomet. Chem. **1980**, 190, C61-63.

8. Boreham, C. J.; Buisson, G.; Duee, E.; Jordanov, J.; Latour, J.; Marchon, J., "Molecular Structure of Methoxotitanium(III) Tetraphenylporphyrin, A Slightly Bent Methoxo Complex," Inorg. Chim. Acta **1983**, 70, 77-82.

9. Ledon, H. J.; Varescon, F., "Role of Peroxo vs. Akylperoxo Titanium Porphyrin Complexes in the Epoxidation of Olefins," Inorg. Chem. **1984**, 23, 2735-37.

10. Deronzier, A.; Latour, J. M., "Oxygen and Sulfur Chelates of Titanium(VI) Tetraphenylporphyrin. A New Autoxidation Reaction of a Titanium(III) Porphyrin," Nouv. J. Chim. **1984**, 8, 393-99.

11. Richard, P.; Poncet, J. L.; Barbe, J. M.; Guilard, R.; Goulon, J.; Rinaldi, D.; Cartier, A.; Tola, P., "Vanadium(IV) Porphyrins: Synthesis and Spectrochemical Characterization of Dihalogenovanadium(IV) Porphyrins. Extended X-Ray Absorption Fine Structural Study of Dibromo(OEP)vanadium(IV)," J. Chem. Soc., Dalton Trans. **1982**, 1451-56.

12. Oumous, H.; Lecomte, C.; Protas, J.; Poncet, J. L.; Barbe, J. M.; Guilard, R., "Vanadium(II) Porphyrins: Synthesis and Physicochemical Properties. Crystal Structure of Bis(dimethylphenylphosphine)- and Bis(tetrahydrofuran)-(OEP)-Vanadium(II)," J. Chem. Soc., Dalton Tran. **1984**, 2677-82.

13. Guilard, R.; Fliniaux, B.; Maume, B.; Fournari, P., "Sur la synthése et l'étude de quelques niobioporphyrines," C. R. Acad. Sc. Serie C **1975**, 281, 461-63.

14. Lecomte, C.; Protas, J.; Guilard, R.; Fliniaux, B.; Fournari, P., "X-Ray Crystal Structure of Tetraphenylporphyrinatoniobium Oxide Acetate; Demonstration of the Presence of Seven-Coordinated Niobium," J. Chem. Soc., Chem. Commun. **1976**, 434-35.

15. Lecomte, C.; Protas, J.; Guilard, R.; Fliniaux, B.; Fournari, P., "Synthesis of Niobium(V) Porphyrinates. Crystal Structures of Tri-μ-oxo-bis [5,10,15,20-tetraphenylporphyrinatoniobium(V)] and Acetato-oxo-(5,10,15,20-tetraphenylporphyrinato)niobium(V)-Acetic Acid (1/1)," J. Chem. Soc., Dalton Trans. **1979**, 1306-13.

16. Johnson, J. F.; Scheidt, W. R., "Remarkably Different Structures of Two Metalloporphyrins Containing $M_2O_3^{4+}$ Units," J. Am. Chem. Soc. **1977**, 99, 294-95.

17. Guilard, R.; Richard, P.; Borai, M.; Laviron, E., "Chemical and Electrochemical Preparation of Low Oxidation State Niobium Porphyrinates," J. Chem. Soc., Chem. Commun. **1980**, 516-19.

18. Richard, R.; Guilard, R. "Synthesis and Characterization of Niobium(IV) Porphyrins. Formation and Spectroscopic Properties of Dioxygen Adducts of Niobium(IV) Porphyrins," J. Chem. Soc., Chem. Commun. **1983**, 1454-55.

19. Matsuda, Y.; Sakamoto, S.; Koshima, H.; Murakami, Y., "Photochemical Epoxidation of Olefins with Molecular Oxygen Activated by Niobium Porphyrin: A Functional Model of Cytochrome P-450," J. Am. Chem. Soc. **1985**, 107, 6415-16.

20. Guilard, R.; Lecomte, C., "Recent Developments in the Studies of Titanium and Vanadium Porphyrins with a Special Emphasis on Oxygen Adducts, Low Valent Metalloporphyrins, and Related Systems with Sulfur and Selenium," Coord. Chem. Rev. **1985**, 65, 87-113.