# Chemistry of Polyoxovanadates and Molybdates: Synthesis, Structure and Magnetic Properties

by
**T. DURAISAMY**
Department of Chemistry

Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy

to the


Indian Institute of Technology, Delhi

December, 1999

## CERTIFICATE

This is to certify that the thesis entitled "**Chemistry of Polyoxovanadates and Molybdates: Synthesis, Structure and Magnetic Properties**" being submitted by **Mr. T. Duraisamy** to the Indian Institute of Technology, New Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. T. Duraisamy has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached requisite standard.

The results contained in the dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

December, 1999

(A. RAMANAN)
Associate Professor)
Department of Chemistry
Indian Institute of Technology
New Delhi 110016

*Dedicated to*

*my grandfather*

## ACKNOWLEDGEMENTS

*I take pleasure in recording my sincere thanks to Dr. A. Ramanan, Associate Professor, Department of Chemistry, Indian Institute of Technology, New Delhi, for his inspiring guidance and constant encouragement throughout the course of this investigation.*

*My sincere thanks are due to Prof. M.N. Gupta, Head of chemistry Department, for providing me necessary facilities in the department. Thanks are also due to all the faculty members (especially to Dr. R. Varadarajan, Dr. Nalin Pant, Prof. A.S.N. Murthy, Dr. N.D. Kurur and Dr.B. Jayaram for valuable discussion) and supporting staff of the department for their kind help and cooperation.*

*My grateful thanks are due to Dr. J.J. Vittal, Associate Professor, Department of Chemistry, National University of Singapore, Singapore for single crystal data collection and structure refinement.*
*My thanks are due to Dr. Ashok Kumar Ganguly, Assistant Professor, Department of Chemistry, IITD for single crystal data collection.*
*Dr. N. Y. Vasanthacharya, SSCU, IISc Bangalore and Dr. K.V. Ramanujachary, Rowan college, New Jersy, USA, for low temperature magnetic susceptibility measurements, Dr. H.N. Vasan, SSCU, IISC, Bangalore, for EDAX and Dr. Yves Piffard, UMR CNRS-Universite de Nantes, France for teaching me the single crystal structure refinement, are also thanked.*

*I am really thankful to IIT-Delhi and CSIR for the research fellowships.*

*I am grateful to all the members of my family for their constant encouragement throughout my academic career which undoubtedly, has added much to my will and vigour to pursue my research work.*

*I thank my colleagues P. Ayyappan and Sanjeev for the support both in the laboratory and outside.*
*I thank Drs. N. Thirupathy, K. Geetha and M. Thangadurai, IISc, Bangalore for their help in solving crystal structures.*

*There are no words to express my feelings of gratitude to Chinnagounder(UIUC, USA) who helped in all the aspects, throughout my Ph.D*

*Finally, I also wish to express my appreciation and warm feelings of gratitude to all my friends Khan, Kittu, Desaka and Desaka, John, Patrick, Charles, Thirumal, Deivaraj, Amburose, Sooriya, Parvesh, Augastin, Pankaj, Kadal, Surjit, Satish, Anupama and Gunjan of the Chemistry Department and Rajagopalan, Bala, Lerua, Srinivasan, Sithu, Rajesh, Murugan, Hari, Guru, Suresh, Elav, Shankar, Ganesan and Puli of Sivalik and Vindy .*

T. Dy.
[T. DURAISAMY]

# ABSTRACT

Polyoxovanadates and molybdates are a class of cluster compounds that is unmatched in terms of their molecular and electronic structural versatility, reactivity, and relevance to catalysis, medicine and materials science. There has been extensive research work towards synthesis of novel oxo-anion clusters based on vanadium and molybdenum, since they exhibit variable coordination linkages($MO_4$ tetrahedra, $MO_5$ square pyramids and $MO_6$ octahedra) which are not known for other transition metals. Very recently, Muller and his group have discovered unusual high-nuclearity oxomolybdate clusters (e.g. giant-wheel like $[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]^{(25 \pm 5)-}$ and $[Mo_{176}O_{528}(H_2O)_{80}H_{32}]^{84-}$ and sphere like $[Mo_{248}O_{720}(H_2O)_{128}H_{16}]^{16-}$) with fascinating topology. However, understanding the driving force for the formation of such high-nuclearity clusters is still a formidable challenge. As yet there is no systematic treatment of the formation and topology of the variety of structures. The present study is a attempt to form new polyoxovanadates and molybdates and investigate their crystal structure. Most of the compounds formed belong to $VO_3^-$, $[VO_4 \subset V_{14}O_{38}]^{6-}$, $V_{10}O_{28}^{6-}$, $Mo_8O_{26}^{4-}$, $[MoO_4 \subset Mo_{12}O_{36}]^{6-}$, $[Mo_5O_{15}(PO_4)_2]^{6-}$ or layered vanadium oxide bronzes, $M_xV_2O_5.yH_2O$(M = Na and K) and $V_4O_{10}^{2-}$ incorporating inorganic or organic cations. We have employed both solution evaporation method and hydrothermal techniques to synthesise novel oxovanadate and oxomolybdate compounds. Following are some of the highlights of the thesis: (1) we have demonstrated for the first time, the effect of pH and the role of organic template, morpholine in the formation of metavanadate chain and mixed-valence anion, $[VO_4 \subset V_{14}O_{38}]^{6-}$ encapsulating $VO_4$ tetrahedra. Use of hexamethylenetetramine and 1,3,5-triazine have resulted in the formation of a variety of decavanadate clusters,

from discrete units to 1D molecular chains or 2D molecular arrays. (2) We have shown the formation of β–$Mo_8O_{26}^{4-}$ and $[MoO_4 \subset Mo_{12}O_{36}]^{6-}$ clusters in the presence of tetramethylammonium under different reaction conditions. The anion, $[MoO_4 \subset Mo_{12}O_{36}]^{6-}$ is the first example of a pure Mo/O mixed-valence Keggin anion. An unusual eight-member hydrogen bonded cluster, between two $NH_4^+$ and two water molecules, is formed during the formation of β–$Mo_8O_{26}^{4-}$. (3) We have also discussed the effect of mild hydrothermal conditions in the formation of layered vanadium oxides incorporating organic or inorganic cations. The thesis is divided into four chapters and an appendix with the contents therein detailed below.

Chapter I describes a brief overview of the chemical aspects of polyoxometalates based on transition metals and their syntheses through mild hydrothermal and self-assembly reactions reported in the literature. Unlike other transition metals, vanadium and molybdenum form a variety of oxo-anion clusters in the presence of templating organic molecules or simple inorganic cations from aqueous medium. In recent years, formation of high-nuclearity oxo-anion clusters have been reported with interesting structural features by Pope, Muller, Zubieta and their groups. A brief summary of the structure, synthesis and properties of oxo-anions of vanadium and molybdenum is discussed in this chapter. The effect of reaction parameters such as pH, temperature, molar ratio of the reactants, nature of the templating organic bases, *etc.* are also discussed in terms of nature of the cluster anion formed. In addition to polyoxometalates, a brief review of a few layered vanadium and molybdenum oxides prepared under hydrothermal conditions and their structure and in selected cases, magnetic properties are surveyed.

Chapter II describes the formation of novel polyoxovanadates from aqueous solution in the presence of organic bases such as hexamethylenetetramine(HMTA), 1,3,5-triazine(Tz) and morpholine(morph). Crystal structure analyses of oxo-vanadate clusters have been extensively carried out by single crystal X-ray diffraction data. The inorganic-organic hybrid structures discussed in this chapter are: $[Morp]_6[V^{V}O_4 \subset V^{IV}_3V^{V}_{11}O_{32}(OH)_6].2H_2O$, $[Morp]VO_3$, $[HMTA\text{-}CH_3]_4[H_2V_{10}O_{28}].5H_2O$, [HMTA-H] $[HMTA\text{-}CH_2OH]_2[H_5V_{10}O_{28}].6H_2O$, $[HMTA\text{-}H\cdots H_2O][HMTA\text{-}CH_2OH][H_3V_{10}O_{28}\{Na(H_2O)_4\}].4H_2O$ and $[Na_2(H_2O)_{10}][H_3V_{10}O_{28}\{Na(H_2O)_2\}].3H_2O$. These polyoxo-vanadates exhibit a range of solids from compact zero dimensional clusters $[V_{10}O_{28}]^{6-}$ and $[VO_4 \subset V_{14}O_{32}(OH)_6]^{6-}$ to infinite metavanadate chains and 1D and 2D networks. Effect of pH and the role of morpholine in the formation of metavanadate and discrete mixed-valence anion, $[VO_4 \subset V_{14}O_{32}(OH)_6]^{6-}$ are reported. The bi-capped Keggin anion which is constructed from four $V_3O_{13}$ groups and capped by two $VO_5$ square pyramids, encapsulates $VO_4$ tetrahedra. Use of hexamethylenetetramine and 1,3,5-triazine has resulted in the formation of a variety of decavanadate clusters under different reaction conditions. In addition to discrete units, decavanadate clusters form 1D molecular chains and 2D molecular arrays interlinked through hydrated sodium cations. All these oxo-vanadate clusters are built up from the elementary building blocks $VO_6$ octahedron, $VO_5$ square pyramid and $VO_4$ tetrahedron, through hydrolysis and condensation of V(IV/V) in aqueous media under given reaction condition. Effect of pH, molarity of the reactants, temperature and geometry of structure directing organic molecules is also discussed in this chapter in terms of their role in the formation of different oxo-vanadate clusters and their packing arrangements. In all the cases, we also noticed significant non-bonding interactions between the anionic clusters, cations and water of crystallization.

Chapter III discusses the formation of isopolymolybdates, containing β-Keggin and β-$Mo_8O_{26}$ anions and heteropolymolybdates containing phosphomolybdate ring, $Mo_5O_{15}(PO_4)_2$, from aqueous solution in the presence of organic bases tetramethylammonium(TMA), morpholine(morph) and hexamethylenetetramine (HMTA). Two novel inorganic-organic hybrid materials, $[Me_2NH_2]_4[Me_4N]_2$ $[Mo_{0.5}O_4\subset(Mo_{12}O_{36})].1.5H_2O$(**$Mo_{12}$**) and $[NMe_4]_2[NH_4]_2[Mo_8O_{26}].2H_2O$(**$Mo_8$**) are crystallized along with TMA cations as structure directing organic molecules under slightly different reaction conditions. **$Mo_{12}$** contains layers of disordered dimethyl ammonium ions alternating with mixed-valence Keggin clusters surrounded by tetramethylammonium cations. The first example of a pure Mo/O mixed-valent β-Keggin metal oxo-anion frame work core, $[Mo_{0.5}O_4\subset(Mo_{12}O_{36})]^{6-}$ encapsulating $MoO_4$ tetrahedra and its structural aspects are discussed. **$Mo_8$** possesses a unique structure with alternate layers containing tetramethylammonium cations and β-$Mo_8O_{26}$ anions; the cavity formed between the anionic clusters is occupied by an unusual eight-membered hydrogen bonded cluster formed between two ammonium ions and two water molecules. In addition to the formation of isomolybdate clusters, this chapter also discusses the use of morpholine and HMTA in the isolation of two novel heterophosphomolybdates, $[Morp]_5][Mo_5O_{15}(PO_4)(HPO_4)].5H_2O$(**$HMo_5P_2$**) and $[HMTA\text{-}Me]_2[H_2Mo_5O_{15}(HPO_4)_2].6H_2O$(**$H_4Mo_5P_2$**) containing molecular ion $[Mo_5O_{15}(PO_4)_2]^{n-}$ built of $Mo_5$ oxo-anion ring capped by two $PO_4$ tetrahedra linked by means of edge and corner-sharing. The structures also showed interesting non-bonding interactions between the anionic clusters, cations and water of crystallization.

Chapter IV deals with the effect of mild hydrothermal reactions in the formation of novel layered vanadium oxides. Use of reducing agents such as alkali metal borohydrides and $SnCl_2.2H_2O$ have resulted in the formation of crystalline

alkali metal and tin intercalated layered structures of vanadium oxide bronzes, $M_xV_2O_5.yH_2O$ (M = Na, K and Sn). Low temperature magnetic behaviour of the reduced alkali vanadium oxide is reported. A novel inorganic-organic hybrid material, $[H_3N(CH_2)_2NH_3]V_4O_{10}$ containing V-O layer isolated in the presence of ethylenediamine under hydrothermal conditions at 180 °C and autogenous pressure from a reaction mixture containing $V_2O_5$, $V_2O_4$, ethylenediamine and $H_2O$, is also discussed. The anionic cluster, $V_4O_{10}$ is made from $VO_5$ square pyramids and $VO_4$ tetrahedra and incorporates protonated ethylenediammonium cations in between the layers.

In the Appendix, two new Scheelite-related solid solutions of the compositions $Na_{x/2}Bi_{1-x/2}Mo_xV_{1-x}O_4$ ($0 \leq x \leq 1$) and $Bi_{1-x/3}\ Mo_xV_{1-x}O_4$($0 \leq x \leq 0.2$) are discussed. These two phases are synthesized by the substitution of Na and Mo at the A and B sites respectively of the $ABO_4$ type ferroelastic $BiVO_4$. The phases were characterised using chemical analysis, powder X-ray diffraction, scanning electron microscopy, EDAX, and Raman spectroscopy. While almost a continuous solid solution is obtained for the series $Na_{x/2}Bi_{1-x/2}Mo_xV_{1-x}O_4$, the absence of Na at the A-site results only in a narrow stability region for the other series, $Bi_{1-x/3}\ Mo_xV_{1-x}O_4$ where $0 \leq x \leq 0.2$. Raman spectra of selected samples at room temperature also suggest that vanadium and molybdenum atoms are disordered at the tetrahedral sites.

## TABLE OF CONTENTS

CHAPTER II

# FORMATION OF NOVEL POLYOXOVANADATE CLUSTERS IN THE PRESENCE OF ORGANIC BASES : ISOLATION AND SINGLE CRYSTAL X-RAY STRUCTURES OF $[Morp]_6[V^{V}O_4 \subset V^{IV}_3V^{V}_{11}O_{32}(OH)_6].2H_2O$, $[Morp]VO_3$, $[HMTA\text{-}CH_3]_4[H_2V_{10}O_{28}].5H_2O$, $[HMTA\text{-}H][HMTA\text{-}CH_2OH]_2[H_5V_{10}O_{28}].6H_2O$, $[HMTA\text{-}H\cdots H_2O][HMTA\text{-}H_2OH][H_3V_{10}O_{28}\{Na(H_2O)_4\}].4H_2O$ and $[Na_2(H_2O)_{10}][H_3V_{10}O_{28}\{Na(H_2O)_2\}].3H_2O$

## CHAPTER III

# FORMATION OF NOVEL POLYOXOMOLYBDATE CLUSTERS IN THE PRESENCE OF ORGANIC BASES : ISOLATION AND SINGLE CRYSTAL X-RAY STRUCTURES OF $[Me_2NH_2]_4[Me_4N]_2[Mo_{0.5}O_4\subset(Mo_{12}O_{36})]$. $1.5H_2O$, $[NMe_4]_2[NH_4]_2[Mo_8O_{26}].2H_2O$, $[(C_4H_{10}NO)_5][(Mo_5O_{15})(PO_4)(HPO_4)]$. $5H_2O$ and $[(HMTA\text{-}Me)_2][(H_2Mo_5O_{15})(HPO_4)_2]$. $6H_2O$

## CHAPTER IV

### HYDROTHERMAL SYNTHESIS AND MAGNETIC PROPERTIES OF LAYERED VANADIUM OXIDES



## APPENDIX

### NEW SCHEELITE-RELATED PHASES: $Na_{x/2}Bi_{1-x/2}Mo_xV_{1-x}O_4$ and $Bi_{1-x/3}Mo_xV_{1-x}O_4$