STRUCTURE-SYNTHESIS CORRELATION OF PHOSPHOMOLYBDATE BASED SOLIDS: LINKING MOLECULAR UNITS AND THEIR SOLID-STATE COUNTERPARTS

by

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Submitted

In fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

July, 2009

Dedicated to

My Family

We often take for granted the very things that most deserve our gratitude.

~ Cynthia Ozick

CERTIFICATE

This is to certify that the thesis entitled "**Structure-synthesis correlation of phosphomolybdate based solids: Linking molecular units and their solid-state counterparts**" being submitted by **Ms. Jency Thomas** to Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Ms. Jency Thomas 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 full, to any other university or institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

The task of the excellent teacher is to stimulate "apparently ordinary" people to unusual effort. The tough problem is not in identifying winners: it is in making winners out of ordinary people.

~ K. Patricia Cross

I express my sincere gratitude to my supervisor Prof. A. Ramanan for his constant support, encouragement and guidance. Without his valuable suggestions this thesis would not have taken the following shape. As a teacher, he has always motivated me to realize my potential to pursue and accomplish goals that I alone could only imagine. Working under his supervision has been a truly enriching experience.

I extend my sincere thanks to the heads of the Department of Chemistry, Late Prof. U. K. Nadir and Prof. B. Jayaram for providing the necessary facilities to carry out my Ph. D. work at IIT Delhi. I would also like to thank all the staff associated with the Department of Chemistry, IIT, Delhi. I am highly obliged to Prof. K. V. Ramanujachary, Rowan University, New Jersey, for carrying out magnetic susceptibility measurements.

I thank Department of Physics for providing TEM facility and Mr. Khanna, operator of TEM facility, for his patience and perseverance. I also thank Mr. K. R. Kannan at S.S.C.U., IISc, Bangalore for SEM and EDAX.

I also express my sincere thanks to my labmates Dr. Sanjeev Sharma, Dr. Minakshi Asnani, Dr. Purnendu Parhi, Dr. Shailesh Upreti, Dr. Katikaneani Pavani, Dr. Sudarshan Mahapatra, Dr. Monika Agarwal, Dr. Kalawati Saini, Monika Singh, Dinesh Kumar and Florence Joseph. A special note of thanks is due to Dr. Sanjeev Sharma and Dr. Katikaneani Pavani for all their help especially during my initial days as a research scholar. I thank Dr. Sudarshan Mahapatra for all the help, in particular during the workshops at IISc. My labmates Monika, Anupam and Kaustubh have been really motivating and made the last two years really memorable. Among my colleagues, I thank Vivek Bagchi and Saroj Samal for helpful discussions. I also thank Dr. Shalabh Gupta, Dr. Senthil Kumar and Nem Singh for their help in operating the single crystal XRD facility.

I would also like to thank my M. Sc. classmates especially Vandana, Nahren, Priya, Alex, Lekha and Tathagata for being there with me through my difficult times. I really thank them for the great time we had in IIT. I thank my room mates Dr. Gunjan Prakash and Manisha for their love and affection. My dearest friend, Rachna who has not only proof-read all my papers and thesis but has also been a patient listener to my queries and anxieties. I am really fortunate that I have a friend like her. I thank Sameena for motivating me to aim higher whenever I failed. I will always cherish the great time I had at Kailash Hostel with Sunita, Meenal, Pallavi, Chetna, Shruti, Reshmi, Unnati, Nimrita and Priyanka. Dipti, Ananya, Bindu and Ruchi have always been more like close friends than seniors.

Words are no measure to describe the forbearance and fortitude with which my family has encouraged me. I thank my grandparents for their blessings and prayers. I express my sincere gratitude towards my parents for their unconditional love and support. My brother, Joby has always brought cheer and joy especially when I needed it the most. My aunts, Mrs. Lucy Philipose and Mrs. Catherine Thomas, my uncle Mr. Dominic Thomas and my cousin Dain have specially been very supportive.

My special thanks to Mrs. Goel, my chemistry teacher at Convent of Jesus and Mary School, without whom I would have never pursued a career in chemistry. I appreciate my teachers at Maitreyi College for their persistence to bring out the best in their students. I thank Dr. Konar for her help and guidance.

I also thank IIT Delhi, CSIR and Honeywell International Private Limited for providing the research fellowship.

Above all, I thank The Almighty for giving me the strength, patience and perseverance to achieve and accomplish my desires and aspirations always.

Jency Thomas

ABSTRACT

Understanding nucleation of a crystal from its reacting molecular units in solution is crucial for engineering materials with desirable properties and function. However, rational design of solids is still far fetched. Although nucleation is considered as a self-assembly process, no hypothesis or postulates are being proposed in terms of chemical events that precede the organization of a structure. Factors like low solubility of heterogeneous reactants in a solvent medium, inability to control pH during the reaction due to hydrolysis of metal and organic amines, redox coupling and complexation between metal and organic moieties complicate the chemistry of formation. Recently, Davey *et. al.* have highlighted the necessity to understand the link between molecular assemblies (crystal growth units) found in the liquid phase and their solid state counterparts, the *supramolecular synthons* to understand the nucleation of solids. In this context, the mechanistic approach by Ramanan and Whittingham is significant as it provides chemical insights into self-assembly of solids in terms of supramolecular interactions.

Phosphomolybdates (PMOs) provide excellent opportunity to explore these issues as one can tune the architectures from simple cluster based solids to nanostructured materials by suitable choice of organic amine(s). A careful analysis of the PMOs synthesized from solution routes suggested the following structural features: (i) Extended PMOs having -O-P-O-Mo-O- connectivity are invariably obtained under hydrothermal condition in acidic medium. (ii) Occurrence of solids based on well-known PMO cluster anions like fully oxidized Strandberg-type cluster $\{P_2Mo^{VI}_5O_{23}\}^{6-}$, fully reduced $\{P_4Mo^{V}_6O_{31}\}^{12-}$, Keggin cluster $\{PMo^{VI}_{12}O_{40}\}^{3-}$ and Wells-Dawson cluster $\{P_2Mo^{VI}_{18}O_{68}\}^{18-}$ is more facile as compared to extended PMOs under ambient or hydrothermal condition. However, pH

of the reaction medium appears to be crucial in dictating the formation of a particular cluster anion. While the cluster anion $\{P_2Mo^{VI}_5O_{23}\}^{6-}$ (henceforth referred as $\{P_2Mo_5\}$) is quite stable over a wide pH range (1-7), higher pH (4-7) favors $\{P_4Mo^{V}_6O_{31}\}$ under reducing condition, Keggin or Wells-Dawson are stable over narrow pH range but also depend on selected organic cations.

Earlier our group has reported synthesis and structure of several PMOs in the presence of different organic amines. Significantly, structural features of pheneylenediamine incorporated PMO solids could be analyzed in terms of *supramolecular synthons* between organic and water along with $\{P_2Mo_5\}$. The non-bonding interactions dictated the self-assembly of molecules and in selected cases facilitated the aggregation of water clusters resulting in crystal hydrates. However, self-assembly of metal complex based PMOs in terms of supramolecular interactions between their molecular units has rarely been investigated. Incorporation of transition metal complexes formed *in-situ* can invariably result in structurally diverse metal complex linked PMO solids of varying dimentionality. Therefore, our objective was two fold: (i) To understand the nucleation of PMO based solids in terms of interactions between metal amine complexes and molybdenum as well as phosphate precursors in aqueous solution. (ii) To understand the effect of reaction parameters on the growth of solids in order to establish structure-synthesis correlation.

To achieve our goal of structure-synthesis correlation, initially the reactivity of cupric ions, pyrazole and molybdate species in aqueous solution was investigated under ambient condition. During the course of investigation it was observed that pH of the reaction medium and the concentrations of reactants were the major structural determinants

influencing the self assembly. The crystallization of PMOs was further investigated using its isomer imidazole under ambient as well as hydrothermal condition. It was realized that unlike pyrazole, imidazole could cause the reduction of both copper and molybdate centers. The influence of other 3d transition metal ions *viz.* Ni^{2+}, Co^{2+} and Zn^{2+} was further examined. Since unambiguous *ab initio* structural characterization of hybrid PMOs in powder form was found to be difficult, we tuned the reaction condition to obtain suitable single crystals for X-ray diffraction analysis. In all the cases, single phasic nature of the solids was established by powder and single crystal XRD. *Á posteriori* analysis of the crystal structures has been interpreted in terms of the mechanistic approach recently proposed by Ramanan and Whittingham. Our recent analysis on the growth of copper chloride based organic frameworks suggested that supramolecular aggregation between molecular units is influenced by non-bonding interactions during the initial stages of the reaction. Therefore, growth and nucleation of the synthesized metal azole based PMOs has been discussed herein by inducing supramolecular interactions prior to crystallization. During our investigation it was observed that the weakly basic 5-membered azoles can get protonated and hence involve in the supramolecular assembly during aggregation. This prompted us to examine the formation of PMO solids in the presence of isomeric six-membered diazine ligands (pyridazine, pyrimidine and pyrazine). Interestingly, copper halide based solids rather than hybrid PMO solids were precipitated under ambient as well as hydrothermal condition.

In recent times, nanoscience and nanotechnology have become an important area of research. In this context, an attempt was made to explore nanostructures of PMOs. A

simple bottom-up approach using dodecylpyridinium chloride as templating agent resulted in nanostructures of PMOs.

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APPENDIX I: PYRAZINE MEDIATED COPPER HALIDE FRAMEWORKS