Influence of Organic Diamines in the Crystal Engineering of Hybrid Materials Based on Molybdates

by

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ganic diamines ; Coastal engineering; Molybdates

CERTIFICATE

This is to certify that the thesis entitled **"Influence of Organic Diamines in the Crystal Engineering of Hybrid Materials Based on Molybdates"** being submitted by Mr. Shailesh Upreti to the Indian Institute of Technology, Delhi India for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Shailesh Upreti has worked under my guidance and supervision, and has fulfilled the requirement for the submission of this thesis which, to my knowledge, has reached requisite standard.

The results constrained 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.

February 2007

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To my

Parents and Teachers

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पडङ्गादिवेदो मुखे शास्त्रविद्या
कवित्वादि गद्यं सुपद्यं करोति ।
मनश्चेन्न लग्नं गुरोरङ्घ्रिपद्मे
ततः किं ततः किं ततः किं ततः किम् ॥

The Vedas with their six auxiliaries and knowledge of sciences may be on one's
lips; one may have the gift of poesy; and may compose good prose and poetry;
but if one's mind be not attached to the lotus feet of the *Guru*
what thence, what thence, what thence, what thence?

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Shailesh Upreti

MOTIVATION

There is a rich and long history of gaining inspiration from various self assembled natural and synthetic materials. Essential of the materials science is the availability of high-quality materials which demonstrates explicit properties together with an appropriate tailoring technique. Although there is a sound progress in materials science, there still exists a serious discrepancy in the ability to produce solids with preferred built-in properties by both rational design and synthesis. There the structure of the material plays an important role. Questions relating to the prediction of the crystal structure of a given organic-inorganic or hybrid material may be more gainfully reversed so that a posteriori analysis of a target structure leads to the identification of the molecular precursors. This may ultimately serve as a blue print for the crystal engineering.

The most imperative synthetic techniques that have been recently explored are; synthesis under extreme conditions of temperature and pressure, self-assembly at ambient temperature as well slightly moderated temperature like hydrothermal and flux. Most of these synthetic methods have been fundamental techniques to allow the isolation of various new phases with desired structure. The aim is to establish reliable connections between molecular and supramolecular structures on the basis of intermolecular interaction, especially non-bonding using these traditionally well known synthetic routes.

The major objective of the thesis is to develop a fundamental understanding of the various non-bonding interactions in the crystal engineering of organic-inorganic polyoxomolybdates, with major consequence on the recognition of "*supramolecular synthons*" or "*supramolecular motifs*" and viable molecular precursors that contribute to the formation of novel materials. Emphasis is placed in systematically investigating the effect of solvent medium, reaction condition (ambient room temperature or hydrothermal/solvothermal) and the role of weak interactions exhibited by the organic group in the growth of the final crystal.

ABSTRACT

Chemistry of organic/inorganic hybrid materials is an intense area of contemporary research due to their potential applications in the area of catalysis, sensors, molecular filters, etc. In this context, inorganic-organic hybrid solids based on molybdates are significant as these occur in multidimensional structures and exhibit interesting catalytic and magnetic behaviour. Present report is an attempt towards careful investigations on the formation of novel hybrid molybdates in the presence of dinitrogen organic compounds with varying shape and size. Emphasis is placed in systematically investigating the effect of solvent medium, reaction condition (ambient room temperature or hydrothermal/solvothermal) and the role of weak interactions exhibited by the organic group in the growth of the final crystal. Significance of nonbonding interactions in terms of supramolecular organization have been discussed in details. Wherever possible, we have also made an attempt to rationalize the crystal structures of the solids synthesized in terms of 'molecular recognition'. The results are summarized in six chapters, one appendix and supporting information. All crystallographic information files have been provided in the CD.

Chapter I describes a brief review on the chemistry of hybrid molybdates templated in the presence of N-containing organic molecules. We have broadly classified these hybrid molybdates into four types: (i) Hybrid salts based on discrete oxomolybdate clusters with organic groups as counter cations; (ii) Extended molybdenum oxides with varying dimensionality (one dimensional chain, two dimensional layer or three dimensional framework) with organic groups as intercalated cations; (iii) molybdenum oxide chains or layers pillared by neutral organic amines and (iv) Organically derivatised

molybdates (either discrete clusters or extended solids) wherein organic molecule is an integral part of the hybrid architecture. Major focus of the discussion *will be to* understand the structure directing role of organic amines and the influence of reaction condition especially when crystallisation is carried out under at room temperature or hydrothermal/solvothermal condition.

Chapter II includes a detailed description of synthesis, characterization and structural analysis of the role of weak interactions in the stabilization of phenylenediammonium octamolybdates. In this study, we have systematically explored the role of nonbonding interactions occurring between water and organic groups and how it influences the structure of the hybrid salts based on octamolybdate.

Chapter III describes the isolation and structural characterization of organic diamines based hybrid phosphomolybdates ($P_2Mo_5O_{23}$). The chapter is divided into two parts: While Part A deals with the study of weak interactions existing between isomeric phenylenediamines and water along with $P_2Mo_5O_{23}$ cluster, in Part B we have discussed the synthesis and structures of $P_2Mo_5O_{23}$ cluster based solids crystallized with a different molybdenum source and other organic amines.

In Chapter IV we have investigated the formation of hybrid molybdates in the presence of a few planar and non-planar diamines. Hydrothermal reactions were carried out between α-MoO_3 and an organic diamine (4,4'-diaminobiphenyl, 2,2'-dipyridyl, 4,4'-dipyridyl and 4,4'-bipiperidine). A detailed crystal structure study of all compounds revealed the occurrence of different molecular building blocks in the formation of molybdates wherein amines occur as pillars or ligands or counter cations.

Chapter V is divided into two parts: Part A reports synthesis and characterisation of alkali metal intercalated hexagonal molybdates whereas part B describes the crystallization of $(NH_4)_2Mo_2O_7$ under solvothermal condition and its phase transition to other molybdates. In Part A we present our results on direct hydrothermal reaction between α-MoO_3 and alkali metal salts mixed in stoichiometric ratio. Crystal structures and phase homogeneity were established using powder X-ray diffraction (XRD) analysis. We obtained four single phasic hexagonal molybdates $M^{+}{}_{x}Mo^{6+}{}_{6-x/3}O_{18-x}(OH)_{x}.yH_2O$ (a) M=Li, (b) M = Rb, (c) M=Cs and (d) M= NH_4 under our reaction condition. In Part B role of solvent has been studied to understand the role of precursors in nonaqueous solvents. Solvothermal treatment of ammonium heptamolybdate in DMF led to the crystallisation of $(NH_4)_2Mo_2O_7$.

In Chapter VI we have attempted a controlled growth of organic crystals from aqueous solution (without any acidification), we succeeded in isolating two new solids: a new organic hydrate, 2,3-phenazinediamine tetrahydrate and a known anhydrous $C_{18}N_6H_{18}$ (Bandrowski's base) from o-phenylenediamine and p-phenylenediamine solutions respectively. In this chapter we have presented their crystal structures along with a detailed analysis of nonbonding interactions. Presence of 2D water layers made of hexameric clusters that are exclusively in chair conformation similar to that found in hexagonal ice (Ih) on the {0001} were observed.

Appendix I describe the synthesis and characterization of a copper phenylenediamine complex derivatised by heptamolybdate cluster. An attempts to exploit the complexing ability of phenylenediamines with a metal ion such as copper, was carried out via hydrothermal synthesis

Supporting information has been provided for detailed crystallographic and other characterization techniques used through out the work.

Due acknowledgement has been made to other investigations wherever the work described is based on their findings. The author apologizes for any omission or mistakes, which might have occurred due to oversight.

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Copper Phenylenediamine Complex Derivatised Heptamolybdate Cluster