TRANSITION METAL COMPLEX TEMPLATED POLYOXOMOLYBDATES: SYNTHESIS, STRUCTURE AND MAGNETISM

by

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DEPARTMENT OF CHEMISTRY

Submitted

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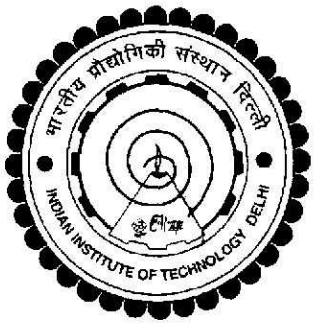

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CERTIFICATE

This is to certify that the thesis entitled "**Transition Metal Complex Templated Polyoxomolybdates: Synthesis, Structure and Magnetism**" being submitted by **Mrs. Katikaneani Pavani** 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 her. Mrs. Katikaneani Pavani 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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Dedicated to my parents and husband

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ABSTRACT

Investigation of structure-property relation of nano-scaled or supra-molecular assemblies such as metal oxide cluster is an important area of contemporary research in the field of solid-state and materials chemistry. In this context, polyoxometalates are versatile candidates as they multi-dimensional structures ranging from nano-scale to giant clusters having metal-oxygen cores. Müller and his group have made significant contributions in this direction. They were able to assemble giant polyoxomolybdates (POM) made of a hundreds of molybdenum atoms, which exhibit unusual magnetic properties. Recently, several groups have synthesized POM based solids having transition metal ions as an integral part of the framework as they can act as oxidative catalysts. For the past few years, our group has been involved in the synthesis and structural characterization of POM based solids in the presence of several organic amines (aliphatic, cyclic, aromatic, long chain). Our results suggest that the soluble molecular precursors formed in the initial stages of the reaction dictate the formation of a particular POM. For example, when a molybdate source is dissolved in aqueous solution in the presence of a suitable organic amine, species such as $[MoO_3(OH)]^-$, $[MoO_2(OH)_3(H_2O)]^-$, $[H_xMo_8O_{26}]^{4-x}$, $[H_xMo_8O_{28}]^{8-x}$ are formed due to change in pH and ionic strength of the medium. In the presence a secondary transition metal, formation of an *in situ* complex is quite facile. Under these conditions, crystallization of a salt or a solid is dominated by the interactions between POM anions and metal complex cations; non-bonding interactions taking place between the hydrated metal ions and the molybdate cluster anions provide additional stability to the structure.

The objective of the present thesis is an attempt towards understanding the influence of transition metal complexes in the formation of POM based solids. We report our results with careful investigations on the crystallization of novel transition metal molybdates, especially copper complex templated POM in the presence of diamines of varying shape and size. The effect of reaction parameters such as metal ion, organic moiety, solvent medium, reaction condition (ambient or hydrothermal) etc. has been systematically investigated. In all the cases, choice of organic species was restricted to diamines as they act as good complexing agents and are stable under hydrothermal condition. In addition, they exhibit non-bonding interactions such as hydrogen bonding, $\pi...\pi$ and $CH...\pi$ etc. We have also studied the magnetic behavior of selected solids. An attempt is made to rationalize the crystal structures of the solids synthesized in this work in terms of 'molecular recognition' recently proposed for the formation of metal organic polymers. We investigated the role of organic amines in dictating the formation of various architectures ranging from discrete polyoxomolybdate clusters to three-dimensional networks of molybdenum oxide based solids. We preferred the aromatic diamine, 2-aminopyridine (*pKa~6.9)* as it forms weak complexes with transition metals and hence readily labile with hydroxyl ligands during hydrolysis and condensation reactions to produce -M-O-Mo-O-M- network. Besides, the amine has good solubility in aqueous solution and show hydrothermal stability. We were successful in synthesizing several metal molybdates using 2-aminopyridine under hydrothermal condition. Among the as-synthesized metal molybdates, Lindgrenite showed interesting meta-magnetic behavior. Reactions of aqueous molybdates with a number of organic amines in the presence of Cu^{2+} was carried out under varying pH and the structures formed were rationalized in

terms of the self-assembling nano-building blocks of POMs. Our results suggest that organic amines are good buffers and play a crucial role controlling the stability of POM clusters in the aqueous medium. Presence of aromatic groups can further act as spacers in the construction of supramolecular motifs. In addition, organic amines can complex with metal and can thus act as a template. Besides, they can act as counter cations. Among the transition metal ions we preferred cupric ion due to its good complexing ability and promising applications in the area of magnetism and catalysis.

Among the POM clusters, the octamolybdate cluster anion is a versatile inorganic building block for the construction of hybrid molybdates. Hydrothermal reaction of aqueous ammonium heptamolybdate solution with cobalt or copper metal salts in the presence of imidazole (*imi*) or pyrazole (*pz*) in the temperature range 120-180°C and autogeneous pressure yielded four fully oxidized metal complex templated octamolybdates. We have also provided plausible mechanisms for the self-assembly of the crystals in terms of supramolecular organization between metal complexes and soluble molybdenum precursors in the initial stages of the reaction.

We have successfully synthesized and structurally characterized five Anderson cluster based solids. The successful synthesis of the solids underlines the potential application of Anderson cluster as a catalyst, which is responsible for the *in situ* generation of oxalate. The formation of all these solids also demonstrates that polyoxometalates act as good building blocks in the design and construction of hybrid porous solid materials.

Metal organic coordination polymers or metal organic frameworks constitute an interesting class of solids due to potential applications in the area of catalysis, gas separation and storage. We present our results on the formation of self-assembled metal

organic hybrid solids from acidified aqueous molybdate solution containing cupric ions and one of the multidentate organic ligands (pyrazine, 2- pyrazine carboxylic acid, isonicotinic acid or piperazine). In addition, we have proposed molecular schemes to rationalize the formation of different structures.

We have also made an attempt to exploit the effect of organic amine on the formation of POM based solids in the absence of a transition metal ion. Here, we have successfully synthesized two new organic-inorganic hybrid solids by hydrothermal route. The extensive non-bonding interactions provide additional stability to the crystal structure.

TABLE OF CONTENTS