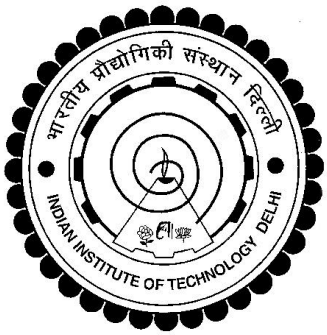
METAL-ORGANIC SOLIDS BASED ON RARE-EARTH MOLYBDATES: SYNTHESIS, CRYSTAL STRUCTURES, OPTICAL AND MAGNETIC PROPERTIES

DINESH KUMAR



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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Metal-Organic Solids Based on Rare-Earth Molybdates: Synthesis, Crystal Structures, Optical and Magnetic Properties

by

DINESH KUMAR

DEPARTMENT OF CHEMISTRY

Submitted

In fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

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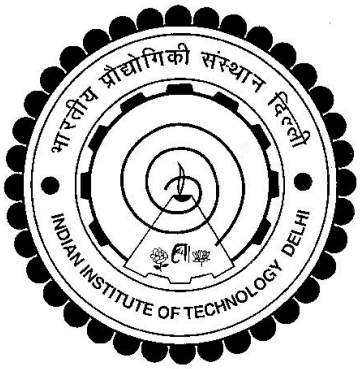

INDIAN INSTITUTE OF TECHNOLOGY DELHI, INDIA

April, 2015

Dedicated
to
my family and teachers

CERTIFICATE

This is to certify that the thesis entitled "**Metal-Organic Solids Based on Rare-Earth Molybdates: Synthesis, Crystal Structures, Optical and Magnetic Properties**" being submitted by **Mr. Dinesh Kumar** to the 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 him. Mr. Dinesh Kumar 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.

29th April, 2015

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Dinesh Kumar

ABSTRACT

Engineering crystals with desirable properties and function is a contemporary research problem. Rationalization of crystal synthesis requires interpretation of nucleation in terms of reacting molecular species as crystallization is perceived as a supramolecular reaction. Crystallization of new metal-organic or hybrid solids with multidimensional networks is currently being explored with an objective to isolate structures with functional properties. Molybdenum oxide based solids have attracted considerable attention for many decades as these exhibit unusual structures and physico-chemical properties. In particular, crystallization of hybrid molybdates is significant. Majority of the groups have exploited the acidic behaviour of molybdates with basic N-containing organic compounds to obtain a variety of molybdates. When molybdates are crystallized from aqueous solution, polyoxomolybdate (POM) cluster anion dominates the supramolecular assembly.

For the past two decades, several groups have been investigating engineering of hybrid crystals based on molybdates assembled in the presence of N-containing organic molecules. In most cases, it was observed that the organic amines exerted a strong influence through N–H···O interactions with cluster oxygens. Under varying acid-base condition, molybdates undergo successive hydrolysis and condensation resulting in polyoxomolybdate cluster anions of varying size and shape.

As demonstrated in many organic and metal-organic solids, we may opt for two strategies to crystallize novel solids: Engineering multidimensional structures between monomeric molybdenum species and/or synthetically reliable *in situ* POM clusters and multidentate organic compounds containing carboxylic acid and/or N- containing bases either through H-bonding or metal coordination. Our group as well as others have earlier demonstrated the use of selected amine, azine and azole in the construction of new polyoxomolybdate based solids exhibiting interesting properties.

The present study is a continuation of the previous methodologies adopted in our laboratory which mostly dealt with transition metals. In this work, we plan to investigate supramolecular assemblies built of reliable and chemically reasonable molybdenum bricks. For this purpose, we opted for two strategies: At first we conducted several crystallization reactions between molybdenum sources and multidentate organic acids/amines to explore the structural landscape of molybdate-N containing organic base-water system for the isolation of new hybrid solids and to rationalize the structure in terms of chemically reasonable building blocks. In the second step, we examined the utility of the well-known molybdenum complexes or clusters to obtain novel structures through H-bonding and metal-cluster interaction. We intended to isolate new solids that exhibit interesting optical and magnetic properties and hence we preferred rare-earth or lanthanide metals. In contrast to transition metals, lanthanides show a higher coordination number with more flexible coordination geometry; this makes crystal engineering more difficult to predict.

In this context when we employed aminocarboxylic acids as potential organic ligands in place of simple N-containing organics with different molybdenum source. These have potential sites to interact with acid or base groups and metals through H-bonding and metal-ligand coordination to assemble into multidimensional solid state structures. In this regard, we used multidentating ligands based on aminocarboxylic acids like ethylenediaminetetraacetic acid (H_4*edta*), Pyridine-2,6-dicarboxylic acid (H_2*pda*) and benzene-1,3-dicarboxylic acid (*m*-H_2*bdc*) as organic acid/base and commonly available molybdate source for our crystallization reaction. H_4*edta* is a well-known multidentated aminocarboxylic acid. Whenever H_4*edta* molecules are crystallized in the presence of a metal ion, then the dominating tectons are *edta* anions and metal hydrates.

A similar situation arises when crystallization is carried out from solution containing both molybdate and *edta* ions. Most of the thirty plus crystals reported in the CSD are based on 2:1 Mo-*edta* complex. Like molybdates, Mo-*edta* complex is also susceptible for reduction whenever the medium contains suitable reducing agents; slightly higher temperatures also favour reduction.

POMs are versatile molecular anions made of nano-size oxomolybdate clusters as building blocks that contain a few to several hundred molybdenum atoms. In the context of hybrid solids, Anderson-Evans cluster anion, $\{CrMo_6O_{24}\}^{n-}$ is a well-known cluster that occurs as a building block in several polyoxomolybdate based solids. An important feature of this cluster is that it could be considered as molecular equivalent of the much studied fluorophore namely ruby (chromium doped alumina). During the investigation of Anderson–Evans cluster based solids, our group observed that single crystals made of chromium molybdate clusters appeared light to dark purple in color. Our preliminary investigation of its optical properties revealed that in most cases the color of the solids was dominated by a red emission reminiscent of ruby. All our earlier studies involved only transition metal ions. This prompted us to investigate the photophysical properties of chromium molybdates coordinated with rare-earth ions that are potential emitters.

The aluminium analogue of chromium cluster, $\{AlMo_6O_{24}\}$ is also well-known building block and crystallizes with several metal ions. We attempted to prepare rare-earth coordinated aluminium molybdate cluster with an objective to study the photoluminescence properties of rare-earth ions in solids structurally analogous to chromium members. By default we obtained 0-D solids made of lanthanide dipicolinate complex and aluminium hexahydrate: $[\{Al(H_2O)_6\}\{Ln(pda)_3\}].10H_2O$. The results are described in six chapters and one appendix.

TABLE OF CONTENTS

List of abbreviations

CP	coordination polymer
POM	polyoxomolybdate
MOF	metal-organic framework
H_4*edta*	ethylenediaminetetraacetic acid
H_2*pda*	pyridine-2,6-dicarboxylic acid
dab	butane-1,4-diamine
tmeda	tetramethylethylenediamine
H4-*pyc*	pyridine-4- carboxylic acid
pym	pyrimidine
bpee	1,2-bis(4-pyridyl)-ethylene
bp	benzidine
(*m*–H_2*bdc*)	benzene-1,3-dicarboxylic acid
dipy-pra	1,3-bis(4-pyridyl)propane
H_2*ppmdc*	2-phenylpyrimidine-4,6-dicarboxylic acid
phen	phenanthroline
CSD	Cambridge Structural Database
BEDT-TTF	bis(ethylenedithio) tetrathiafulvalene
2,2′-*bpy*	2,2′-bipyridine
4,4′-*bpy*	4,4′-bipyridine
pz	pyrazole
pyz	pyrazine
pdz	pyridazine
H2-*pyc*	pyridine-2-carboxylic acid
H3-*pyc*	pyridine-3-carboxylate

pip	piperazine
ox	oxalate
imi	imidazole
HMTA	hexamethylenetetramine
inpa	isonipecotamide
inca	isonicotinamide
H*dpa*	2,2-dipyridylammonium
py	pyridine
dfe	desferrioxamine E
en	ethylene diamine
H_2*azdc*	4,4'-azobenzoic acid