Large Scale Synthesis and uses of a Cobalt based Metal - Organic Framework Compound as Liquid Water Sensor

A

Thesis Submitted

in partial fulfillment of the requirements for the award of the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

BY

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JULY, 2013

Certificate

This is to certify that the project entitled **"Large Scale Synthesis and uses of a Cobalt based Metal – Organic Framework Compound as Liquid Water Sensor"** being submitted by Nayuesh Sharma, Roll no. 301102006 in partial fulfillment of the requirements for the award of degree of Master of Science in School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under my supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other university.

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Candidate's Declaration

I hereby declare that the work which is being presented in the dissertation entitled **"Large Scale Synthesis and uses of a Cobalt based Metal – Organic Framework Compound as Liquid Water Sensor"** in partial fulfillment of the requirements for the award of the degree of master of science in Chemistry, School of Chemistry and Biochemistry, Thapar University, Patiala is an authentic record of my own work during a period of six months from January 2013 to July 2013, under the supervision of Dr. Partha Mahata, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. The report has not been submitted for the award of any other degree or certificate in this or any other university.

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Place: Patiala

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This is to certify that the above statement given by the candidate is correct and true to the best of our knowledge.

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Life at Thapar University would be unforgettable for me throughout my life because I was blessed to spend it with my friends. I thank them all for their great company.

Words fail me to express my thanks to my family for their selfless sacrifice, encouragement and heart full blessings that continue to enlighten my life.

Above all I thank almighty God for blessing me with strength and wisdom to complete this project successfully.

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Contents

Introduction and Review of literature

In 1893, Alfred Werner proposed the structure of octahedral transition metal complexes and presented the basis for assigning coordination number and oxidation state.[1] His theory allows one to understand the difference between coordinated and ionic compounds. The transition metal ions appeared to form bonds not only to anionic ligands with which to neutralize their charge, but also to additional species, which seemed unnecessary since neutrality was already achieved. This work was the origin of modern coordination chemistry and brings revolution in the field of inorganic chemistry. By understanding the preferred coordination geometry about a central metal ion, rational synthetic methodologies to install specific ligands was now possible. The past 120 years have witnessed a tremendous growth in coordination chemistry, leading to enhancing our knowledge in the synthesis, structure, and reactivity of novel complexes and materials from simple metal−ligand complexes to, organo−metallic catalysts and extended inorganic polymers. In recent decades, new branch of coordination chemistry have emerged, metal−organic frameworks (MOFs) which comprised of infinite networks of metal centers or inorganic clusters bridged by simple organic linkers through metal−ligand coordination bonds.

Coordination Polymers and Metal−Organic Frameworks

Metal – Organic Frameworks (MOFs) have a rich history beginning with the development of coordination polymers.[2] Coordination polymers are a subset of inorganic polymers containing metal–ligand bond as the primary design feature. The term coordination polymer has been concerned with polymeric structures comprised of metals and ligands. The motivation behind early interest in inorganic and coordination polymers was application-driven. Inorganic materials were recognized to potentially withstand thermal and oxidative stress better than their organic counter parts.[2] The induction time between the first coordination polymers and modern MOFs chemistry is much greater. The synthetic pigment commonly known as Prussian Blue has been in use since the early 1700s. Its structure was determined by X-ray diffraction in 1977 to reveal a mixed-valent Fe(II)/Fe(III) network with Fe(II)−carbon distances of 1.92 Å and Fe(III)−nitrogen distances of 2.03 Å (Figure 1).[3]

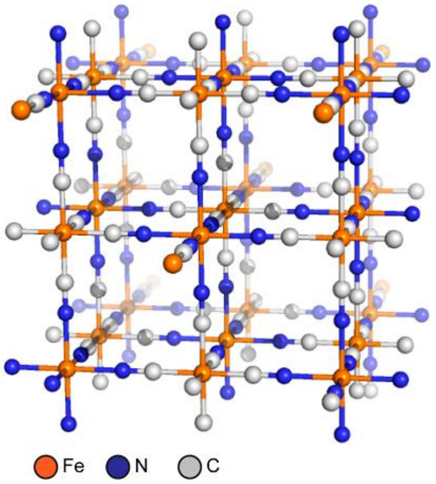


Figure 1: Idealized structure of Prussian Blue, the first synthetic coordination polymer. Alternating octahedral sites of Fe(II) and Fe(III) ions are bridged by cyanide ligands to generate a cubic 3D array.[3]

In 1897, Hoffman and co-workers discovered that the addition of benzene into a solution of $Ni(CN)_2$ in ammonia furnished a coordination network, but early work on these polymers was hindered by a lack of structural characterization techniques. In fact, the structure of the Hoffman complex was not fully understood until X-ray studies by Powell and co- workers over half a century after the initial synthesis was reported.[4] The material, $Ni(CN)_2(NH_3).C_6H_6$, shared similar structural elements with Prussian Blue; the extended structure consisted of metal nodes bridged by cyanide ligands. However, the $Ni(CN)_2$ network did not extend into three dimensions. Instead, parallel 2D sheets with ammine-capped nickel sites were layered to give benzene-containing channels between independent arrays. These exemplary coordination polymers provided the motivation to explore alternative bridging ligands, guests, and capping moieties. As characterization techniques became more refined, efforts to define, classify, and synthesize such materials accelerated throughout the 1960s, cementing coordination polymers as a distinct area of research.[5] Early network materials consisted of Hoffman-type topologies in which the metal centers, capping ligands, and guests were systematically swapped with similar species, for example, by replacing the original benzene guests with biphenyl (Figure 2).[6]

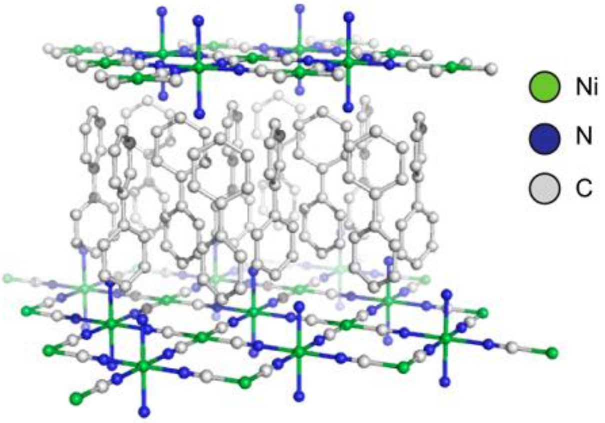


Figure 2: The structure of a Hoffman-type complex, $Ni(CN)_2(NH_3)$-$(C_{12}H_{10})_2$. Hydrogen atoms omitted for clarity.[6]

From the late 1960s into the 1980s, a variety of such species were reported. The final exodus from these early materials occurred when the cyanide ligand was replaced with alternative organic ligands, which rapidly led to the discovery of a myriad of new network materials. A hallmark discovery was made by Robson and co-workers in 1989, in which Cu(I) centers were linked with 4,4′,4″,4‴ - tracyanotetraphenylmethane (tctpm; Figure 3).[7]

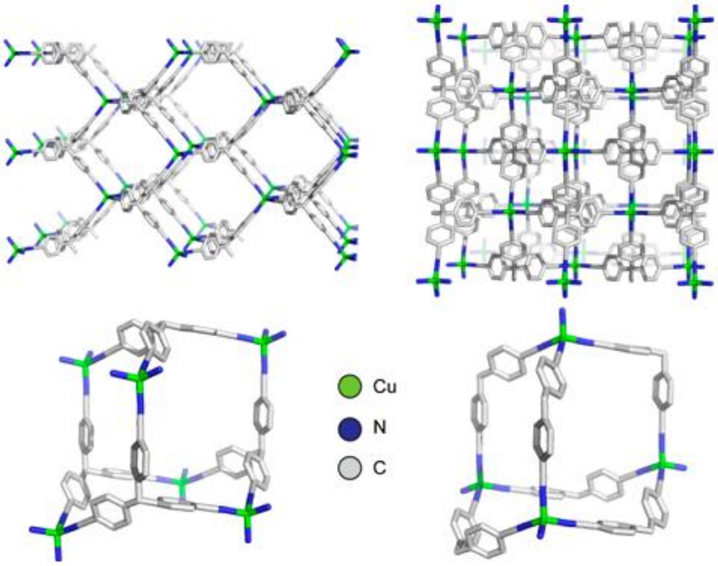


Figure 3: The slow evaporation of a solution of a tetranitrile ligand with a Cu(I) precursor deposits a coordination polymer containing tetrahedral metal nodes with tetrahedral tetratopic spacers. Two views are shown (top) with hydrogen atoms omitted for clarity revealing a diamond-like network comprised of repeating adamantanoid units (bottom).[7]

This tetratopic organic donor adopted a tetrahedral geometry due to the central carbon atom. The four nitrogen atoms each coordinate to a unique Cu(I) center, which are themselves coordinated to three other tctpm ligands. The extended network adopts a diamond-like topology comprised of repeating adamantanoid subunits. This was a key material in that it set the foundation for the use of tunable organic ligands in coordination polymers; such materials were not limited to cyanide bridges. Soon thereafter, ligand diversity continued to increase, from cyanide to organic nitriles to pyridyl-based donors. Of the pyridyl ligands, 4,4′-bipyridine (4,4′-bpy) is the most iconic. The early adoption of 4,4′-bpy as a building block for both MOFs and supramolecular coordination complexes can be attributed to its suitability as a ligand for a variety of metals, its structural rigidity as a linear, ditopic donor, and its ready availability from a number of commercial sources. Fujita and co-workers utilized 4,4′-bpy in the assembly of square grids (Figure 4).[8]

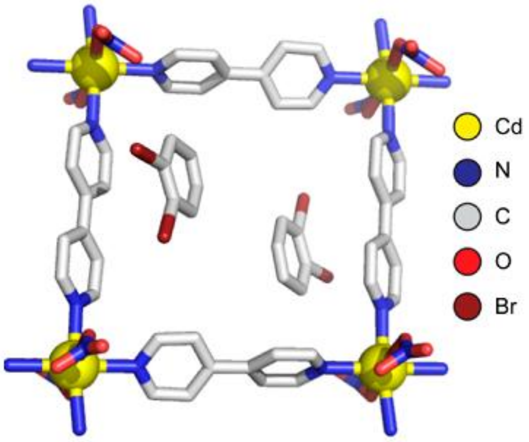


Figure 4: The structure of $[Cd(4,4'\text{-bpy})_2(NO_3)_2]$, a square lattice with channels capable of accommodating guests such as o- dibromobenzene. Hydrogen atoms omitted for clarity.[8]

Motivated by materials utilizing the ditopic 4,4′- bpy, the field then moved toward polytopic donors with varying geometries. In the mid-1990s, the exploration of carboxylate-based materials garnered significant interest, building upon the milestone discovery of permanently microporous pyridyl based network compounds by Kitagawa and co-workers [9] with an example of carboxylate based porosity by Yaghi and co-workers.[10] These coordination networks distinguished themselves by possessing reversible gas adsorption and adopted the name metal−organic frameworks. These names are technically suitable for any extended array comprised of metal nodes (either mono- or polynuclear); however it is not uncommon for the term MOF to be reserved for materials that are characterized as microcrystalline, well-defined materials containing polynuclear clusters and often showing permanent porosity. The clusters themselves are stabilized by bridging ligands, and the networks of clusters are supported by the strong covalent bonds found within the organic components of MOFs.[11]

Modern MOFs synthesis is driven in part by a goal to generate extremely porous materials often accompanied by very large internal surface areas. This is accomplished by a careful selection of molecular precursors and reaction conditions, which dictate the thermodynamically favored architecture. In addition to ongoing synthetically focused research, a major hallmark of MOF chemistry results from the properties afforded by the aforementioned surface area and porosities. MOFs are increasingly applied toward applications that require efficient uptake of substrates, such as energy storage,[12] chemical purification,[13] sensing,[14] and more.[15]

Metal Organic Framework Materials as Chemical Sensors

Recently MOFs have been emerged as new types of chemo-sensory materials. The majority of MOF sensors that have been reported are based on luminescence quenching of lanthanide ions or aromatic fluorophores used as corners and struts, respectively. But few MOFs show sensing ability as a visible change in a material's color. As an example, a copper MOF containing the ligand 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz), which shows a blue shift with increasing solvent polarity (Shown in Figure 5).[16]

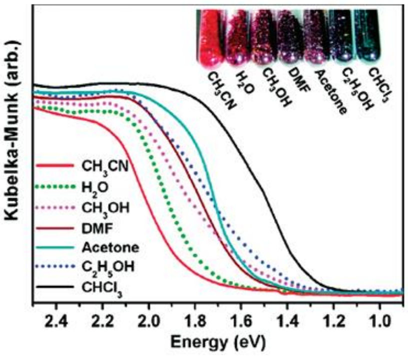


Figure 5: Visible spectra and photograph of MOF crystals containing solvents (condensed vapors). A negative vapochromic effect is observed for both hydroxylic and nonhydroxylic vapors (solvents).[16]

As MOFs contain metal ions in addition to their organic components, they have characteristic similar to discrete coordination complexes, and changes in the coordination sphere of these metal centers can play a role in MOF sensing. Early in the MOF literature, Long and coworkers proposed that exposing Co^{2+} MOFs to various vapors could shift the optical absorption across the visible region.[17] The explanation was a change in coordination environment from the as synthesized octahedral to a tetrahedral geometry. A similar mechanism of color change is proposed in a recent paper by Lee et al. reporting on a MOF that senses chloride ions derived from chlorine-containing vapors or gases. The MOF contains Co^{2+} nodes coordinated to 1,2,4,5-tetra(2H-tetrazole- 5-yl)-benzene (TTB) struts as well as Br^- anions.[18] It is obtained as an amorphous gel (via standard solgel chemistry), rather than as crystalline compound, and so, strictly speaking, may not fit the definition of a MOF. As synthesized, the material is characterized by a visible absorption peak at 475 nm, suggesting octahedral coordination of the Co^{2+} centers. Interestingly, when the coordination polymer is exposed to chlorine-containing gases, including HCl, $SOCl_2$, $(COCl)_2$, and $COCl_2$ (phosgene), its color changes from red to blue (see Figure 6). A new absorption feature appears at 670 nm, creating the blue color. The authors attribute this absorption peak to tetrahedrally coordinated Co^{2+}. To explain the change in metal coordination geometry, they hypothesize that the Br^- is replaced with Cl^- originating from the reactive gases.

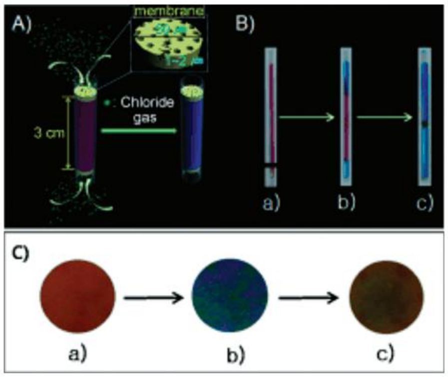


Figure 6: (A) Cartoon of MOF-coated capillary for sensing chloride gas. (B) Photo of capillary as made (a), after 10 s (b), and after 30 s (c) exposure to 100 mM chloride-containing vapor or gas. (C) Photo of MOF pellet as made (a), after exposure to phosgene gas (b), and after rinsing with 100 mM HBr to regenerate original structure (c).[18]

Several aspects make this chemosensory material promising. First, the color change is rapid and easily visible by eye. The calculated limit of detection for phosgene is as low as 1 ppb. In addition, the sensor can be regenerated by washing with HBr to reform the original compound, (as shown in Figure 6). Perhaps most intriguing is the hypothesis that chloride from these harmful gases is being incorporated into the MOF structure, implying that the hazardous analyte is being destroyed (albeit, likely only stoichiometrically rather than catalytically). Few MOFs are frequently air/moisture-sensitive. In particular, IRMOF-1 degrades in the presence of small amounts of water at room temperature. Studies on metal analogues have unraveled the ability of metals different than Zn to stand higher water concentrations at high temperatures.[19] To compensate for this, specially constructed storage containers are required, which can be costly. Strong metal-ligand bonds, such as in metal-imidazolate, -triazolate, and -pyrazolate frameworks, are known to decrease a MOF's sensitivity to air, reducing the expense of storage.[20]

Other Properties of MOF compounds

Magnetic properties

The transition metal based MOF compounds are important due to their interesting magnetic behavior. The magnetic behavior of these compounds would depend on many factors including the site symmetry of the magnetic ions and the nature of the bridging modes/angles of the connectors (carboxylate group or carboxylate oxygen atoms/OH) etc. A variety of magnetic properties have been found with MOF compounds. Of particular interest being those with ferromagnetic (FM) properties. For example, a chiral three-dimensional nickel glutarate, $[Ni_{20}(H_2O)_8(C_5H_6O_4)_{20}\cdot 40H_2O]$ shows a cooperative ferromagnetic behavior ($T_c \approx 4K$), without any spin frustration,[21] Magnetic studies of three-dimensional cobalt terephthalate $[Co_2(OH)_2(C_8H_4O_4)]$ show that the intralayer exchanges between the Co(II) ions are ferromagnetic,[22] but the whole system orders antiferromagnetically at 48 K with a metamagnetic (MM) transition above a threshold field of 0.2 T and three-dimensional manganese trimesate, $[Mn_3(C_9H_3O_6)]$ exhibits antiferromagnetic behavior.[23] A 3D porous magnet, $[KCo_7(OH)_3(ip)_6(H_2O)_4]\cdot 12H_2O$ (H_2ip = isophthalic acid) undergoes a reversible single-crystal-to-single-crystal transformation, concomitant with reversible magnetic property change upon desorption/adsorption of guest molecules (Figure 7).[24] This compound lose all the water molecules at 120 °C (both bonded and non-bonded) to form dehydrated structure along with change of coordination environment around the Co^{2+} ions. Both the compounds (hydrated and dehydrated) show ferrimagnetic behavior, the strength of ferromagnetic exchange is stronger in the hydrated state.

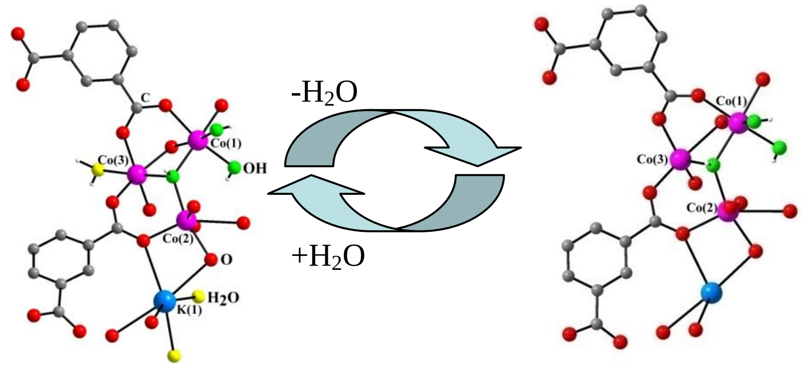


Figure 7: Coordination environment Co^{2+} ions in $[KCo_7(OH)_3(ip)_6(H_2O)_4]\cdot 12H_2O$ (1) and its dehydrated state (1′).[24]

Photoluminescent properties

The lanthanide based MOF compounds shows interesting photoluminescence behavior.[25] Direct excitation of lanthanides produces only weak emission spectra due to their low molar absorptivity. But when metals are complexed or chelated with organic moieties then there emission increases.[26] In general, in most cases, direct excitation of the ligand to a singlet state followed by an intersystem crossing to a triplet state with the emission from the metal results when a nonradiative energy transfer occurs from the ligand triplet state to the lanthanide ion.[27] The newly excited lanthanide ion can, then, emit a photon or relax via a series of nonradiative processes. This effect is commonly known as the ‘antenna effect’.[28] The efficiency of the emission depends on energy level difference between the ligand and the rare earth ion. Early work on a rare-earth glutarate, $[Gd_{1-x}Eu_x\ (glu)].4H_2O$, illustrated the potential of this area.[29] The as-synthesized material has water molecules in the channels between the chains which can be removed reversibly. It has been shown that the photoluminescent lifetime of the Eu^{3+}-dopant depends upon the degree of dehydration because the coordinating water molecules could act as relaxation agents. Such materials clearly have the potential to be used as sensors. The 3-D pyridine-2,5-dicarboxylate of lanthanide, $[Ln_3(OH)_4(2,5\text{-pydc})(2,5\text{-Hpydc})_3(H_2O)_4]$ (Ln= Dy, Eu) also exhibits characteristic emission corresponding to the lanthanide ion.[30] The Eu^{3+}/Tb^{3+} doped sample in place of La^{3+} in $[La(NO_3)M_2(C_{12}H_8N_2)_2][(C_8H_4O_4)_4]\cdot H_2O$ shows interesting red/pink or green luminescence using 252 nm excitation energy through ligand-sensitized metalcentered emission .[31] It can be noted that the intensity of the intra-ligand emission bands (~ 400 nm) decrease with the increase of the amount of dopant, which suggests that more energy gets transformed from the ligands to the dopant (Eu^{3+}, Tb^{3+}).

Porous behavior of MOFs

Porosity of MOF compounds have been investigated extensively due to their potential applications in catalysis, gas storage, guest exchange, sorption, separation, sensing and other areas.[32] Not all the interesting properties are to be found in systems with large pores. A highly robust three-dimensional erbium 1,4-phenylendiacetate, $[Er_2(PDA)_3(H_2O)]\cdot 2H_2O$ reversibly undergoes dehydration of both the coordinated and lattice water molecules to form $[Er_2(PDA)_3]$.[33] Thermogravimetric analysis show that $[Er_2(PDA)_3]$ remains stable up to 450 °C. An effective pore window size of 3.4 Å allows the adsorption of CO_2 into the pores and exhibits nonporous behavior towards Ar or N_2. The selectivity of CO_2 over Ar may be due to the differences in the size as well as host-guest interactions.

Synthesis of MOFs

The main goal in MOF synthesis is to establish the synthesis conditions that lead to defined inorganic building blocks without decomposition of the organic linker. At the same time, kinetics of crystallizing must be appropriate to allow nucleation and growth of the desired phase to take place. In conventional synthesis, reactions are carried out by conventional electric heating without any parallelization of reactions. The reactions can be further classified as the ones at room temperature or one taking place at elevated temperatures. As exemplified by the work of Hoskins and Robson,[34] early has mainly relied on low-temperatures routes. Thus, a precipitation reaction followed by recrystallization or the slow evaporation of the solvent was reported. To grow crystals from clear solutions, the concentration of the reactant has to be adjusted in a way that critical nucleation concentration is exceeded. This is commonly achieved by changing the temperature or by evaporating the solvent.

Although a large number of MOFs as well as many potential applications have reported in the literature, the synthesis up-scale to the gram-scale or larger and the larger scale production of these materials have surprisingly been neglected. Most of the reports on scaled-up reactions can be found in patents,[35-39] but some have been published, with varying amounts of details, in the scientific literature.[40-41] The first successful scale up was demonstrated for HKUST-1 on the 80 g scale,[42] and subsequently MOF-5 was synthesized on a 50 g scale.[43] The challenges for the use of MOFs in industrial applications lie in their inherent properties as well as their production. Requirements of the MOFs that must be fulfilled include high porosity, thermal and chemical stability, as well as sustainability. The reported scale-up procedures do not comply with most of the criteria for industrial-scale syntheses.

Characterization techniques

Powder X-ray diffraction

The powder X-ray diffraction (XRD) is used as a very important tool in the characterization of porous materials. Powder diffraction is used as a fingerprint in identification of a material; however, other information can also be obtained from a powder diffraction pattern. To index the powder pattern the important parameters are the peak position (2θ) and full-width half maximum (FWHM). The FWHM value of 0.01 or less would be an ideal value (standardized using the Si [111] reflection; $2\theta = 28.44^{o}$ with Cu-Kα_1 radiation). The measured 2θ values for the peaks in Si XRD pattern should agree with the literature values to within 0.01^{o}. In case of MOF compounds, powder diffraction data are most commonly used to identify a newly synthesized material or to monitor the phase changes that take place as a function of changes in the reaction conditions or to monitor the effect of post-synthesis treatment.

Thermogravimetric analysis (TGA)

Thermogarvimetric analysis (TGA) is one of the techniques which is used frequently for the characterization of MOF compounds. In this process, the sample is heated under a constant flow of oxygen or air. The mass loss occurring due to the step wise decomposition of the various species present in the compounds is measured as a function of temperature. The temperature at which the weight loss occurs and the amount of weight loss give a quantitative determination of the specific moiety present in the structure and the information can be used to verify the structural formulations.

UV-Visible spectroscopy

UV-Visible spectroscopy provides useful information regarding the various electronic transitions within the MOF compounds. The electronic transitions in the UV region (200-400 nm) are mainly due to the various transitions of the organic ligand such as $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ and ligand to metal change transfer (LMCT). The visible region (400-1100 nm) is useful for the identification of various d-d transitions of transition metal ions and f-f transitions of lanthanide metal ions.

Results and Discussion

To explore the properties and applications of metal-organic framework compounds, we have selected a cobalt based MOF, [Co(OBA)(H_2O)$_2$] [OBA = 4,4'-oxybis(benzoate)]. This MOF has been synthesized earlier in small scale by Mahata and coworkers.[44] We have synthesized this compound in large scale (gram scale) using very simple procedure. We have used 4,4'-oxybis(benzoic acid), cobalt salt, sodium hydroxide and water to prepare this MOF. The details of the large scale synthesis have been presented in experimental section. This part of the thesis describes the properties and applications of the synthesized cobalt based MOF, [Co(OBA)(H_2O)$_2$], **I**.

Structure

To describe and discuss the properties of the compound **I**, it is important to discuss briefly about the structure. The compound has been crystallized in monoclinic systems with $P2_1/c$ space group. In this structure, the Co^{2+} ions have a distorted octahedral geometry formed by four carboxylate oxygen atoms and two water molecules (Figure 8). There is one OBA anion present in the structure. The two carboxylate groups of OBA show differences in the connectivity: one carboxylate has both the oxygens bonded with the same Co^{2+} ion and the other carboxylate has the oxygens bonded with two different Co^{2+} ions. The Co^{2+} ions are linked to the carboxylate units forming a one dimensional wire-like structure, which are connected by the OBA unit forming a two-dimensional layer structure (Figure 9). Hydrogen bond interactions between the coordinated water of one layer and carboxylate oxygens of another layer gives rise to a supra-molecularly organized three-dimensional structure (Figure 10).

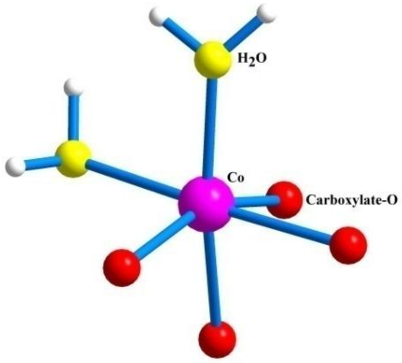


Figure 8: Coordination environment Co^{2+} ions in **I**.

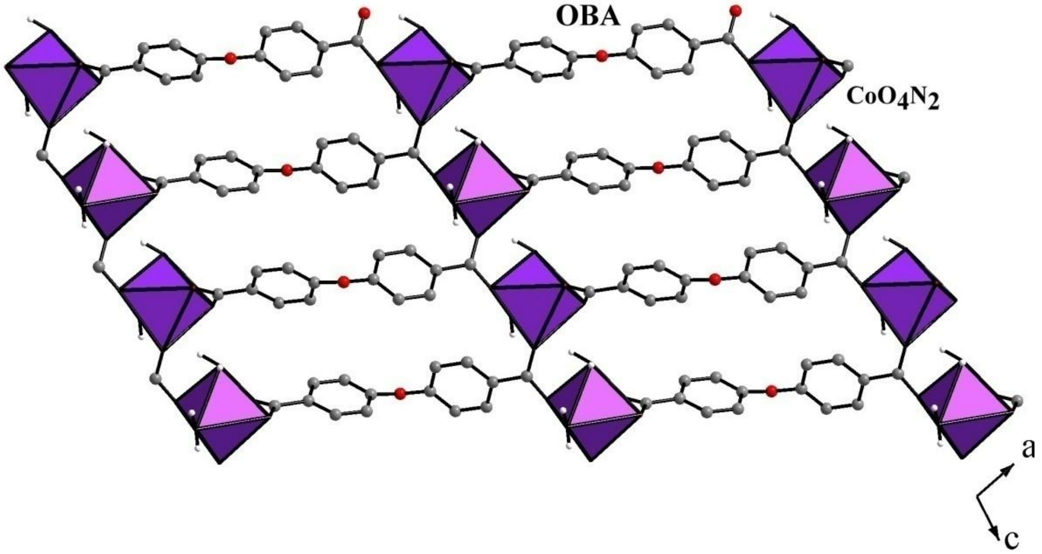


Figure 9: View of the connectivity between the Co^{2+} ions and the OBA units to form two-dimensional structure in **I**.

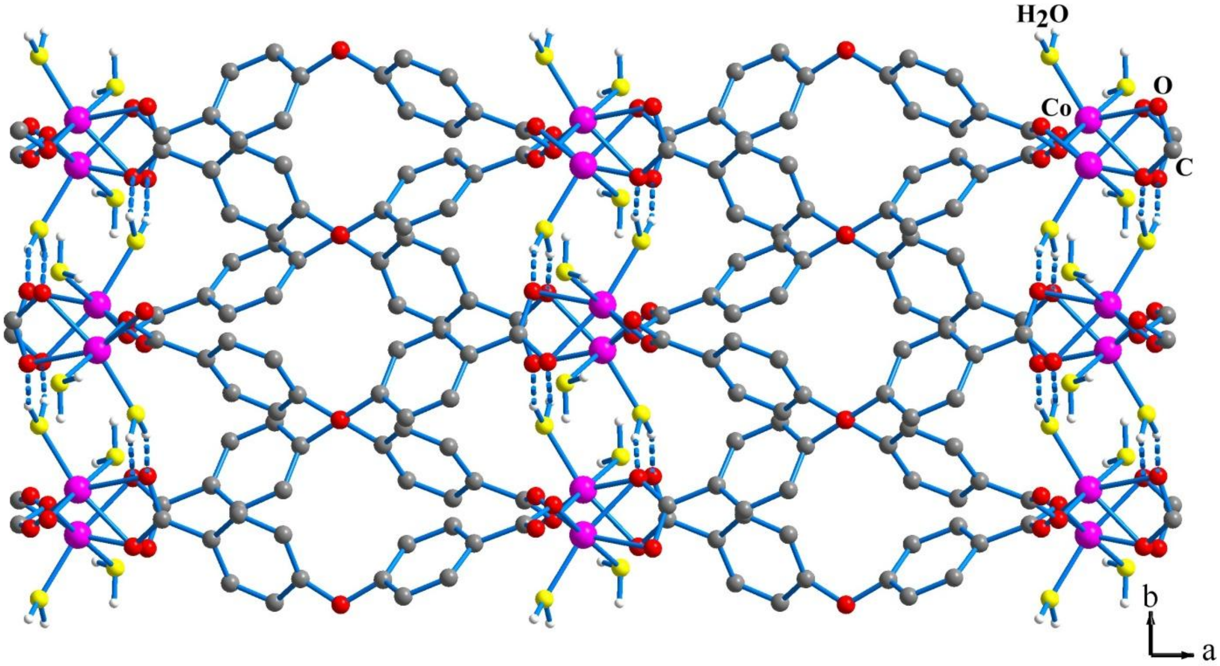


Figure 10: Arrangement of layers in **I**. Dotted lines represent the hydrogen bond interactions.

Powder X-ray diffraction

The powder X-ray diffraction (XRD) patterns were recorded on crushed single crystals in the 2θ range 5- 50° by using CuKα radiation. The XRD patterns of the as-synthesized compounds were entirely constituted with the simulated XRD generated from the CIF file of the single-crystal studies of compound **I**. Simulated and experimental PXRD patterns of compound **I** are given in Figure 11.

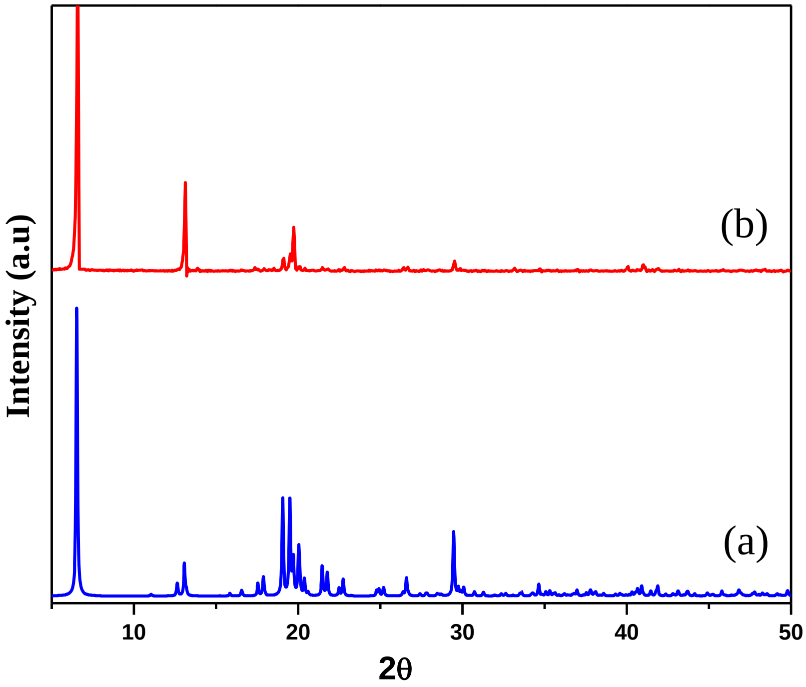


Figure 11: Powder XRD pattern for **I**: (a) simulated and (b) experimental.

Thermogravimetric Analysis

The TGA studies (in air) of **I** indicate that the coordinated water molecules are removed in the temperature range of 150-170 °C (obsd. 11%, calc. 10.25%) followed by the decomposition of the framework in the range of 250-370 °C in two steps (Figure 12). The total observed weight loss of 78% corresponds well with the loss of the water molecules and the OBA units (calc. 77.14%).

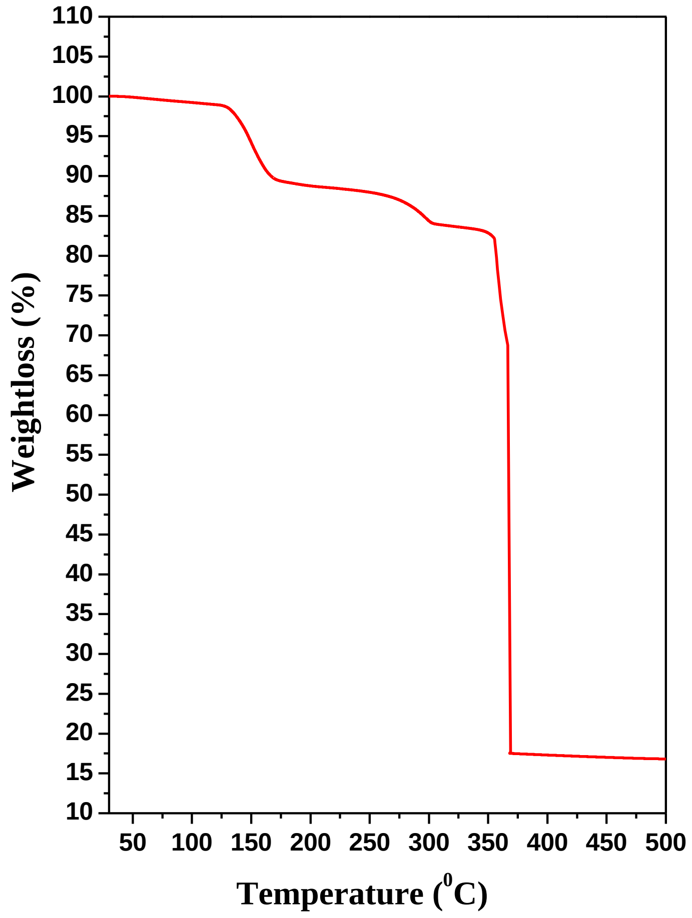
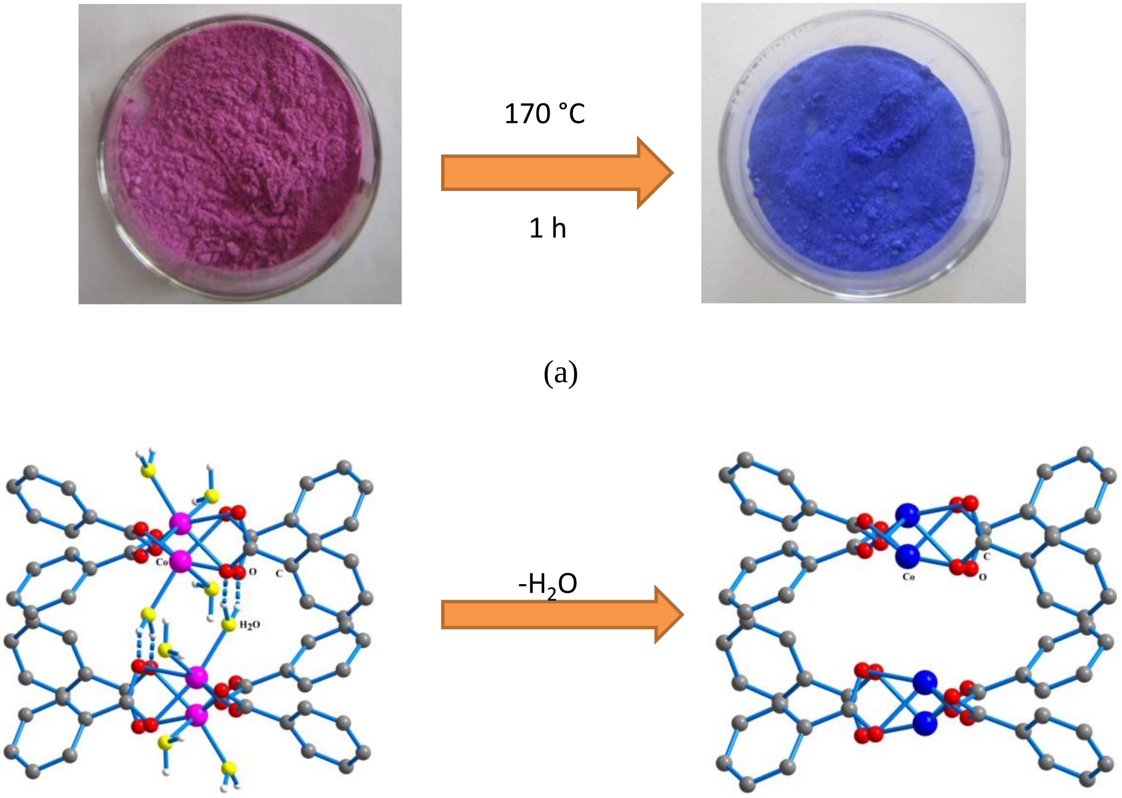


Figure 12: TGA studies of **I** in air in the temperature range of 30-600 °C.

Thermal studies

From TGA, it was established that the initial weight loss in **I** below 170 °C corresponded to the loss of the coordinated water molecules and also suggested to examine the possible reversible nature of the water sorption in the sample. To understand the dynamics of the water molecules, we have first heated the compound at 170 °C for 1h in an oven. The dehydration/removal of the water molecules also brings about a change in the color of the sample. Thus, the compound changes from pink to dark blue after dehydration (Figure 13). It has also been observed that the dehydrated compound (blue) changed to pink in presence of liquid water. (Figure 14)



(a)

(b

Figure 13: (a) View of color of compound **I** (original) and after heating at 170 °C for 1 h. (b) View of possible changes in the coordination environment around Co^{2+} ions in original compound and dehydrated compound.

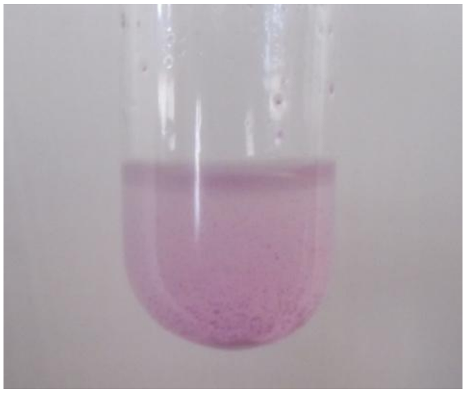


Figure 14: View of color of compound **I** in water.

Sensors based studies

Based on structure of the compound and the changes of color in dehydration and rehydration, it was occurred to us that this compound might be a water sensor. To investigate that behavior, we have carried out detail investigations using this compound. It is well known that $CoCl_2.6H_2O$ show visible color changes on dehydration and rehydration state. To compare the water sensing behavior of the present compound and the $CoCl_2.6H_2O$, we have heated both the compound at 170 °C for 1h. The compound **I** changed to dark blue color and the $CoCl_2.6H_2O$ changed to light blue color. Both the dehydrated compound kept in open air for about 1h. The images of both the dehydrated compounds taken in regular time intervals are presented in Figure 15.

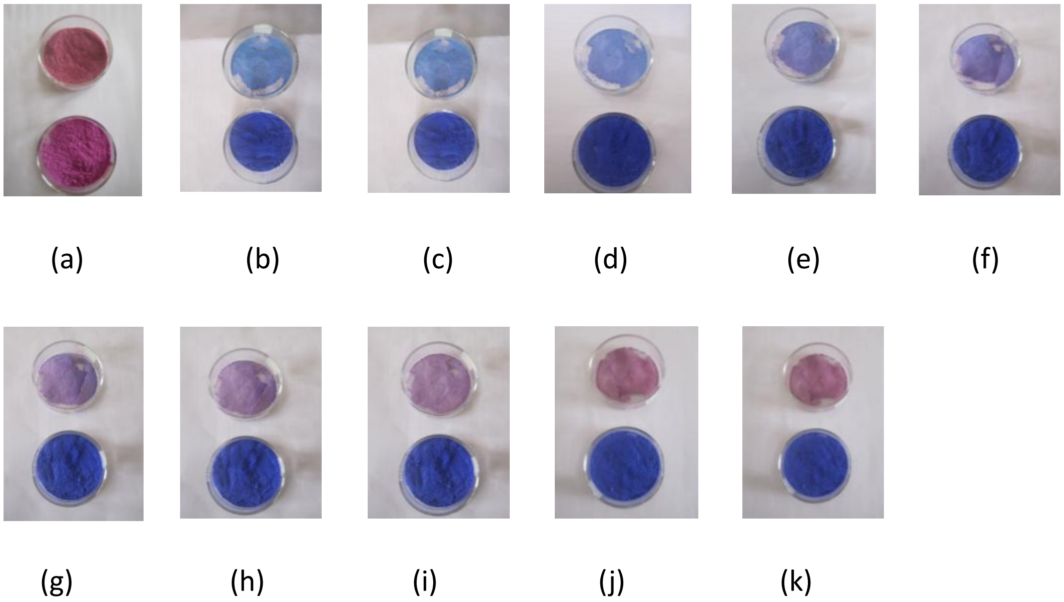


Figure 15: View of color of compound $CoCl_2.6H_2O$ (in top of each image) and compound **I** (in bottom of each image) in day light and in open air: (a) original $CoCl_2.6H_2O$ and compound **I**, (b) immediately after removing from oven (heated at 170 °C for 1 h), (c) after 5 min, (c) after 10 min, (e) after 15 min, (f) after 20 min, (g) after 25 min, (h) after 30 min, (i) after 40 min, (j) after 1h, (k) after 1 day.

The above studies indicate that compound **I** is stable in open air and moisture (water vapor) do not able to enter in the compound and the coordination environment around the cobalt ions remains intact. $CoCl_2.6H_2O$, on the other hand, is highly sensitive for water vapor and it cannot able to differentiate between liquid water and water vapor.

This studies indicate that that the dehydrated compound **I** can return to original state only in presence of liquid water. To verify this, we have studied the powder X-ray diffractions of the dehydrated and rehydrated compounds and compared with the as synthesized original compound (Figure 16).

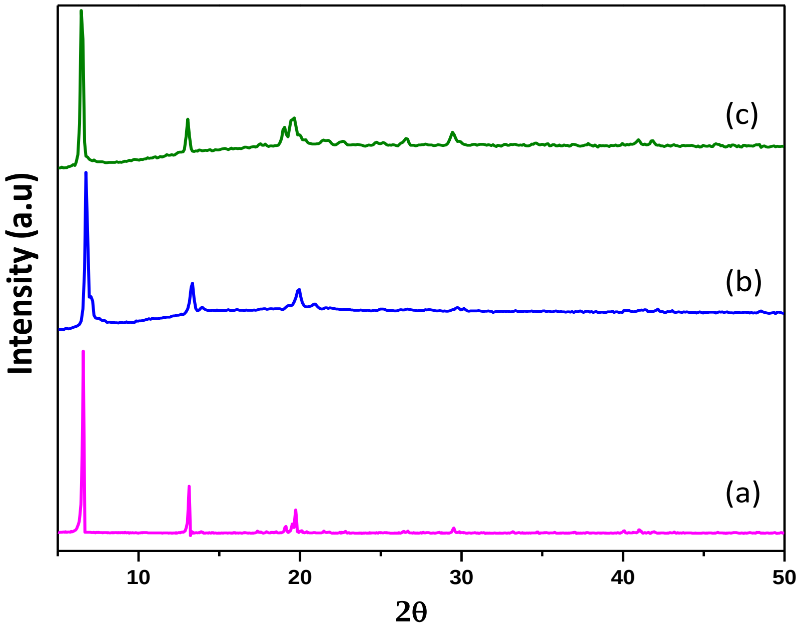


Figure 16: Powder X-ray diffraction patterns: (a) compound **I**, (b) dehydrated compound **I**, (c) rehydrated compound **I**.

The rehydrated compounds have been prepared by mixing the blue colored dehydrated and the minimum amount of water (few drops of water) and the mixture was dried at room temperature by keeping in open air for 1 day. The powder X-ray diffraction patterns (figure 16) indicate the original compound and the rehydrated compound is almost identical. The pattern of the XRD of the dehydrated compounds is similar but not identical with the original and the rehydrated compound. As can be seen, some of the small intense peaks are missing in dehydrated compound. But the presence of the high intense and their position indicate that there are not much change in the structure after the dehydration.

To understand the minor change of the structure based on the inter layer distances, we have plotted the X-ray diffraction pattern from 5.5 to 8° (2θ) and shown in Figure 17. As can the highest intense peak observed at 6.6° in original compound has been shifted to 6.8° in the dehydrated compound. These changes indicate that after removal of the coordinated water, the inter-layer distance is reduced, but the extent of this reduction is very small.

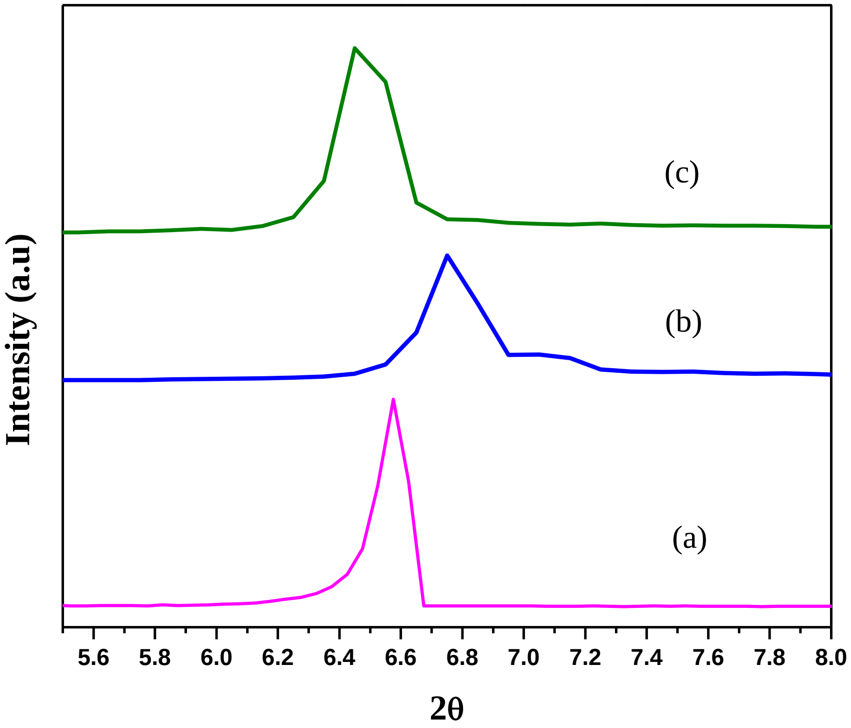


Figure 17: Powder X-ray diffraction patterns in 5.5 - 8° (2θ) range: (a) compound **I**, (b) dehydrated compound **I**, (c) rehydrated compound **I**.

The visible spectra of the powdered samples (original, dehydrated, rehydrated and resolvated using water and ethanol) have also been studied in diffuse reflectance mode and the plots are shown in Figure 18. The original compound, rehydrated and the resolvated (using water and ethanol) show almost identical spectra. The highest intense peak is observed at 534 nm and a shoulder and low intense broad peaks are observed at 475 and 715 nm, respectively. On the other hand, the visible spectra of the dehydrated (blue compound) are completely different. In this case two high intense peaks are observed at 582 and 620 nm. Additionally, two shoulders have also been observed at 480 and 543 nm. The powder and the visible spectra prove that the reversibility of the dehydration and rehydration behavior.

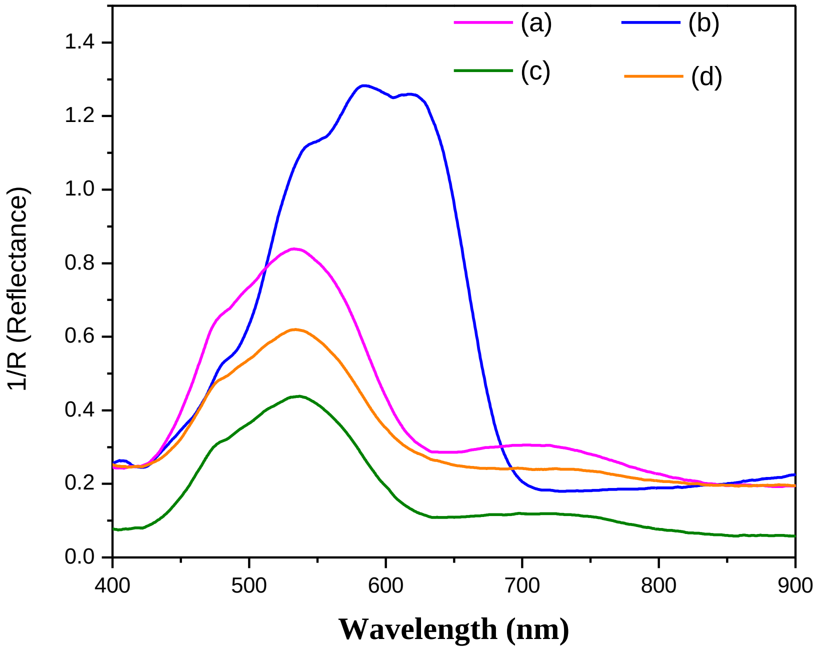
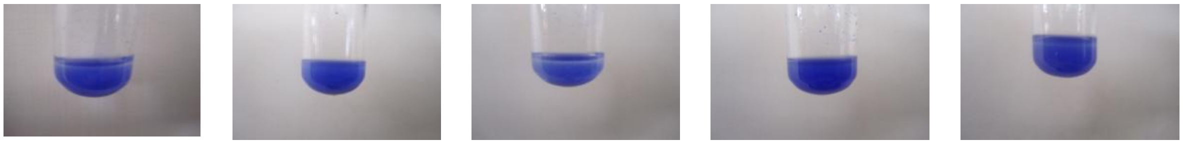


Figure 18: Visible spectra of the powder samples: (a) compound **I**, (b) dehydrated compound **I**, (c) rehydrated compound **I**, (d) re-solvated compound **I**.

We have also tested the visible color of dehydrated blue compound in different solvents – methanol, acetone, ethyl acetate, DMF, DMSO, nitro benzene, 1,2-dichloro benzene, ethanol, water and ethanol mixture (1:1), pure water (Figure 19). As can be seen the dehydrated compound form blue suspension in all the cases except for water and ethanol and water mixture. This study suggests that the compound can also detect water in presence of other solvent as well.

We have also carried out time dependent studies to estimate the amount required to regain the pink color from the blue color by varying the concentration of water (volume %) in ethanol by keeping amount the dehydrated compound same. The results are plotted in Figure 20. As can be seen the time is inversely proportional to the amount of the water in ethanol.



Methanol **Acetone** **Ethyl acetate** **DMF** **DMSO**

Nitro benzene **1,2 Dichlorobenzene** **Ethanol** **50:50 mixture of Water and Ethanol** **Water**

Figure 19: Visible color of the dehydrated blue compound in different solvents.

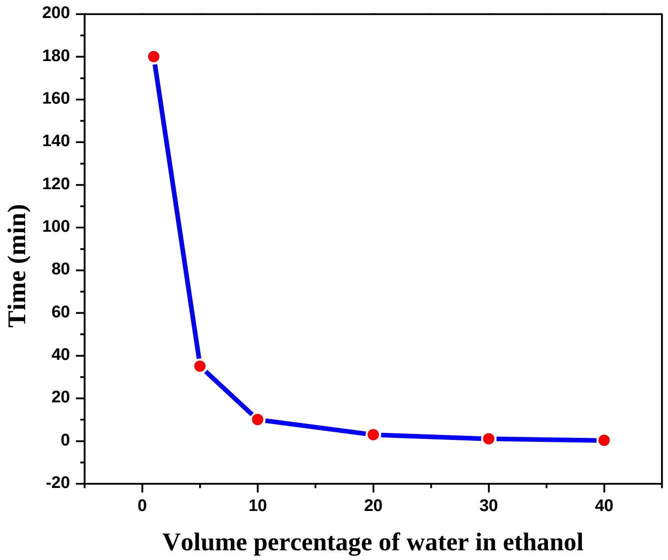


Figure 20: Plot of the volume % water in ethanol vs the amount of time required to regain the pink color from the dehydrated blue compound **I**.

Materials and Methods

Material required

The reagents needed for the synthesis are $CoCl_2.6H_2O$ [CDH (India), 98%], 4,4′-oxybis(benzoic acid) [Alfa Aesar(India),99%],and NaOH [CDH (India), 98%]. The water used was double distilled through a Millipore membrane.

Large scale synthesis of [Co $(H_2O)_2$(OBA)](compound I)

Compound **I** was prepared by simple solvent evaporation reaction. In this preparation, 3.808 g (16mM) $CoCl_2.6H_2O$ was dissolved in 80 ml of water in 250 ml beaker and 4.176 g (16mM) of 4,4’-oxy-bis(benzoic)acid and 1.28 g (32mM) of NaOH was dissolved in 80 ml of water through heating at 100^oC in separate beaker. Then the dissolved sodium salt of the acid was poured in to the cobalt salt solution and the resulting solution was kept in water bath at 80^oC for 2 days. The final product, containing pink colored micro crystals, was washed with deionized water under a vacuum, and dried at ambient conditions. The yield of reaction was around 85%.

Dehydration & Rehydration Studies of [Co$(H_2O)_2$(OBA)] and $CoCl_2.6H_2O$

0.5 g of compound **I** and 0.5 g of $CoCl_26.H_2O$ was taken in two separate equal sized petri dishes. The images of the powdered compounds were also captured from a good quality camera. Both the compounds heated at 170^0C for one hour in an oven and compound **I** changed to dark blue color from pink and the $CoCl_26.H_2O$ changed to light blue color from pale pink. After removing the petri dishes from the oven, the images of both the compounds were captured. Both the petri dishes were kept in open air and the images of the compounds were taken in regular time intervals (after 5, 10, 15, 20, 25, 30 ,40, 60 min and 1 day). The compound **I** remain blue color after 1 day, whereas the $CoCl_26.H_2O$ changed slowly to the original pale pink color. Dehydrated compound **I** was rehydrated by mixing with minimum amount of water (few drops) and dried at ambient conditions. The original compound **I**, the dehydrated and the rehydrated compound were characterized by solid state diffuse reflectance visible spectroscopy and powder X-ray diffraction.

Effect of different type of solvents on the dehydrated compound

80 mg of dehydrated compound **I** and 1ml of various solvents was taken separately in 10 equal sized test tubes. The solvents are methanol, acetone, ethyl acetate, DMF, DMSO, nitro benzene, 1, 2 Dichlorobenzene, ethanol, 50:50 mixture of water and ethanol, and water. All the test tubes were shaken, colors were noted and images of each test tube were also captured.

Time dependent studies

30 mg of dehydrated compounds were taken in each of 6 test tubes. A mixture of water and ethanol in 1:99, 5:95, 10: 90, 20:80, 30:70, and 40:60 ratio were added to test tubes (numbered as 1, 2, 3, 4, 5, and 6, respectively). All the test tubes were shaken and time was noted when color changed.

Conclusion

1. We have synthesized a cobalt based metal – organic network on gram scale.
2. The product was microcrystalline and pink in color and it became blue when heated at 170 ^{0}C for one hour.
3. We have shown that it is sensitive to liquid water but not to water vapor.
4. We have also compared its sensitivity with $CoCl_2.6H_2O$.
5. The compound (original and dehydrated) is not soluble in water and is lighter than $CoCl_2.6H_2O$.
6. The dehydrated compound can be used as liquid water sensor in presence of water vapor.

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