COBALT(II) COORDINATION POLYMERS- ITS SYNTHESIS, CHARACTERISATION AND APPLICATIONS

A MSc. Dissertation report by:

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CERTIFICATE

This is to certify that the dissertation entitled “**Cobalt(II) Coordination polymers- its synthesis, characterization and applications**” is bonafide work carried out by Ms. Canesha Colaco under my supervision (Sunder N. Dhuri) in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

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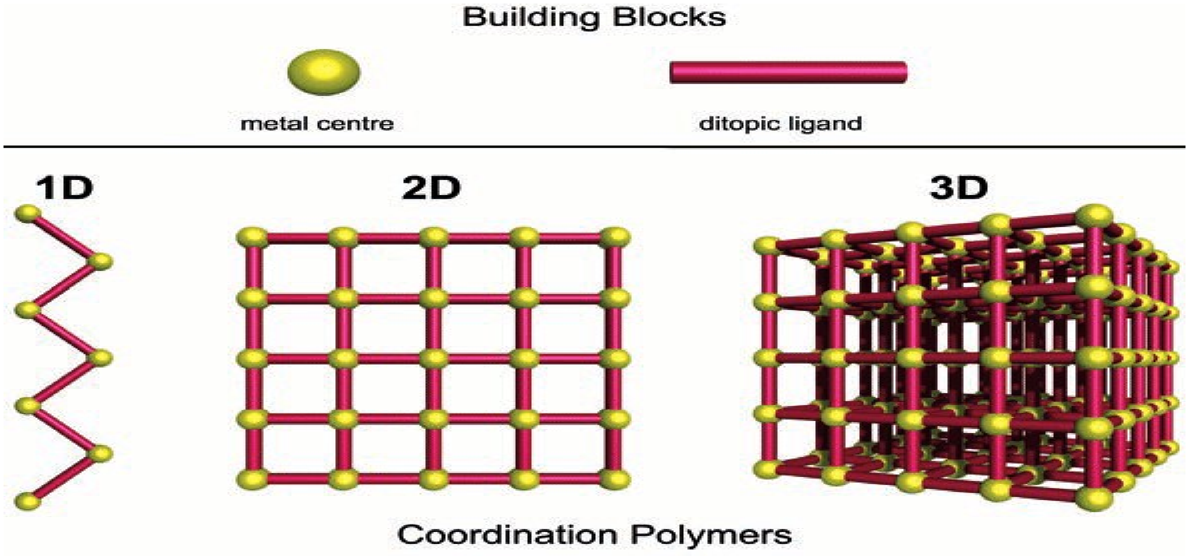
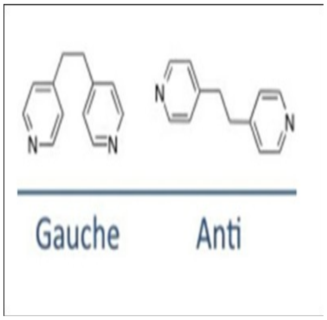
Cobalt(II) Coordination Polymers its synthesis, characterization and application.

1.1) Introduction

The development of polymer materials with coordination complexes as repeating units has increased in recent years .In the past decade, there have been rapid growth in coordination polymers and this defines one of the most exciting fields in solid state chemistry. The surprising variety of structures, compositions and properties of these polymers as well as their easy modification and synthesis has attracted many research.[1] As a consequence of the various synthetic procedures followed with modifications of the structures of these polymers, solid state chemistry has moved in several different directions depending on the particular property being investigated. Coordination polymers have very many unique properties that its applications can never be over emphasized. Their relevance in many fields like organic and inorganic chemistry, biochemistry, material science, electrochemistry and pharmacology with very many potential applications has led to extensive study of these polymers.[2] Coordination polycation centers connected by organic ligands with repeating coordination entities extending in one, two or three dimensions.

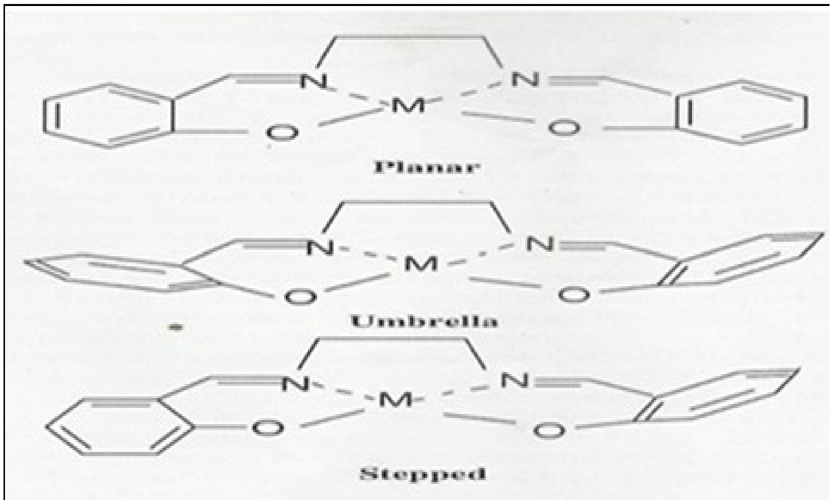


Coordination polymers and metal–organic frameworks (MOFs) form an interdisciplinary area of research with MOFs endorsing high porosity, thermal stability, robustness, tunable metrics, and organic functionality, resulting in intriguing structural diversities.[3] The sewing of molecular building units by strong bonds into predetermined extended structures alongside weak non covalent interactions (hydrogen bonding,π–π stacking, and van der Waals forces) generates supra molecular assemblies.[4] These play promising roles in applications such as catalysis[5–7] ,chemical adsorption,[8,9] gas adsorption, and magnetism.[10] The work of Alfred Werner and his contemporaries laid the groundwork for the study of coordination polymers. Various authors have defined the concept based on their perceptive but all are the same or nearly related. Nearly 30 years ago, John C. Bailar, Jr. drew an analogy between organic polymers and a class of inorganic coordination complexes that he called “coordination polymers. His seminal review described and classified the synthesis and structures of inorganic chain compounds. Since that time, one-dimensional coordination polymers of metal complexes have been intensely studied. The fundamental chemistry and physics behind their fascinating structures have stipulated interest in their possible uses as unusual materials for new technologies.[11] Roswell & Yaghi noted that coordination polymers (CPs) are solid species produced by metal clusters ligated to polydentate organic complexones. By this definition, enormous variety of species containing organic molecules and metals defined by characteristic properties such as porosity, non-porosity, crystallinity and amorphosity with emphasis on metal organic frameworks. as special group of coordination polymers.[2] The terms coordination polymers and metal organic frameworks have been currently used interchangeably. Cheetham et al. noted that coordination polymers, or metal organic frameworks (MOFs) defines extended network arrays of metal clusters joined to poly functionally defined organic species. Metal organic frameworks (MOFS) according to O' Keeffe used to be interchangeably used as coordination polymers but it specifically apply to materials with frameworks built by linking polyatomic clusters (secondary building units or SBUs) formed holistically by strong covalent bonds unlike coordination polymers which have some interplay of weaker bonds and lower stability. Long & Yaghi observed that inorganic joints are linked with organic units regarded as struts through strong interaction to yield non-porous or porous metal organic framework wrapped in architecturally extended network. Thus, the term ''coordination polymers'' refers to molecular crystal assembly or systems in which metal atoms multitypically coordinates to organic components. The metal organic framework currently discussed as reticular chemistry include components linked by strong bonds as indicated in metal carboxylates and is differentiated from coordination polymers.[2] Common ligands in coordination polymers include; polypyridines, phenanthrolines, hydroxyquinolines and poly carboxylates. Common binding sites are oxygen and nitrogen atom through other atoms like sulphur and phosphorous. As a consequence, the hard soft acid base theory (HSAB) trends are likely followed by ligands and metal cations. Ligands can either be flexible or rigid. A rigid ligand has no freedom to rotate around bonds or orient again within a structure. Flexible ligands produce more variety in the structure because they can bend, rotate around bonds and orient themselves again.[2] There are examples of coordination polymers with two configuration of the same ligand within one structure and two separate structures with different ligand orientation. Metal phosphonate coordination polymers [CoII[(RPO_3)(H_2O)], R = CH_3, C_2H_5, C_4H_9, or C_6H_5) are among the best characterized coordination polymers reported to date. Inspired by the works of Nocera and co-workers who discovered that a film of cobalt phosphate obtained by anodic deposition in a phosphate buffer containing cobalt(II) ion is a highly active catalyst for water oxidation reaction.[12]



Fig;1-Example of flexible ligand showing Gauche and Anti conformations.

Fig;2-Planar, umbrella and stepped molecular conformations of Salen complexes.

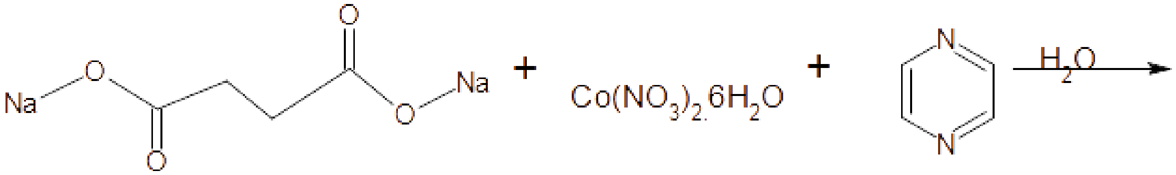


The employment of mixed ligands favors frameworks with diverse structural motifs, in comparison to using only one type of ligands. Flexible dicarboxylates in combination with linear rodlike ligands mediate the construction of coordination polymers (CPs) ranging from 1D to 3D networks. Hence the ligands chosen, i.e., succinic acid and pyrazine, serve as suitable candidates. Succinic acid is flexible containing two carboxylate groups in 1,4-positions adopting monodentate, bridging, and bridging chelate coordination modes to the metal as seen in our work, while pyrazine is a rigid-planar bidentate diimine ligating through the μ2 bridging mode.[13] However, it is still a challenge to now to control the final products because many factors, such as the coordination geometry of the central metal ions, connection modes of organic ligands as well as the synthetic conditions, have a great influence on the structure of the resulting complexes. According to previous studies, organic ligands play an important role in directing the final structure and properties. Compared to rigid carboxylate containing ligands, flexible multi-carboxylate ligands are of special interest because their varied coordination modes, abundant structural motifs, and flexible molecular backbones can lead to a variety of coordination polymers with appealing structures and related functions.[14] By properly selecting experimental parameters such as a choice of solvents, starting metal salts, additional ligands, temperature, hydrothermal conditions, pH value of the reaction mixture etc., it is possible to optimize the design of the desired coordination polymers, and thus control the outcome of the crystallization experiments.[15] Among the vast variety of metal-complex and coordination polymer catalysts, coordination compounds that incorporate cobalt nodes and carboxylate blocks as spacers or linkers have deserved a special attention in catalysis.[16] In fact, cobalt coordination compounds can catalyze a wide range of organic reactions, which span from C−H activation and cross-coupling to CO2 reduction and water oxidation.[17] One of the obvious challenges is the rational and controllable preparation of metal-organic frameworks, the formation of which is greatly affected by the organic ligands, the nature of the metal ions, the counter ions, and other factors. Among the reported studies, organic ligands with carboxylate groups are especially interesting because they can adopt a variety of coordination modes and result in diverse multidimensional architecture.[18] However most of the reported work has been devoted to the use of 1,3-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, and so on, while the use of the large steric hindrance of the H_2tbip ligand remains largely unexplored. There has been only one reported polymer based on the H_2tbip ligand hitherto. The presence of the electron-donating (-C $(CH_3)_3$) non coordinating groups in di carboxylate ligands changes their electronic and steric properties, which can generate complexes different from those of the common di carboxylate ligands.

1.2)Synthesis of Cobalt(II) coordination polymers.

1) $[Co(H_2O)(pyz)(suc)]$

Is a 3D structure synthesized in solvothermal condition the same starting materials $Co(NO_3)_2\cdot 6H_2O$, Na_2suc, and pyz under the influence of temperature (conventional slow evaporation and hydro(solvo)thermal methods at105 °C for 2 days) and solvent (water, DMSO, and DMF) were vital for obtaining the product.[13]

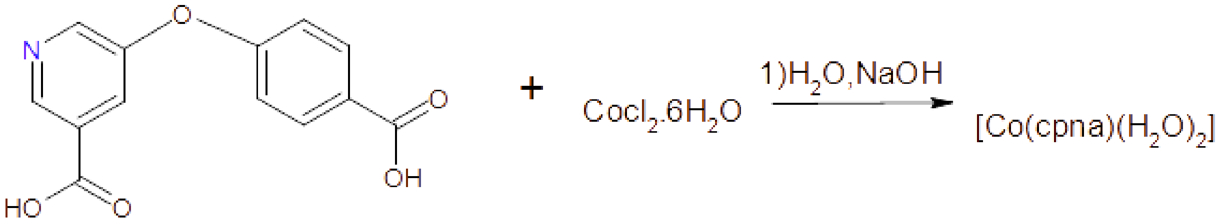


$[Co(H_2O)(pyz)(suc)$

2) $[Co(\mu_4\text{-cpna})(H_2O)_2]_n$

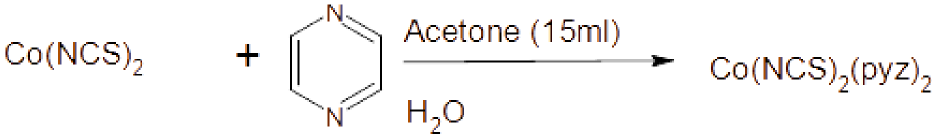
$CoCl_2\cdot 6H_2O$ (0.3 mmol, 71.0 mg), H_2cpna (0.3 mmol, 77.7 mg), NaOH (0.6 mmol, 24.0 mg), and H_2O (10 mL) were combined in a stainless steel (Teflon-lined) reactor of the 25 mL capacity. After vigorous stirring for 15 min at ambient temperature, a reactor was closed and kept at 160 °C for 3 days in the oven. Then, the reactor was gradually cooled down (10 °C/h) to ambient temperature and opened. Yellow crystals (needles) were removed from the reaction mixture manually or by filtration, washed with H_2O, and then air dried to furnish the product.[17] Yield: 65%, based on H_2cpna. Cobalt (II) product is a three-dimensional MOF that is composed of a Co(II) center, a μ_4-cpna^{2-} block, and two H_2O molecules of crystallization (per asymmetric unit).

H_2cpna stands for (5-(4-carboxyphenoxy)nicotinic acid)



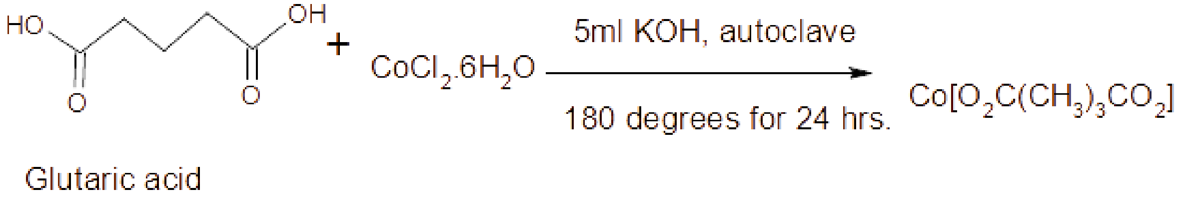
3)$Co(NCS)_2(pyz)_2$

An acetone solution (15 mL) of pyrazine was slowly diffused into an aqueous solution (10mL) of $Co(NCS)_2$. Orange block crystals of **1**were formed in 1 week. In other solvents (e.g., ethanol, methanol,THF, and acetonitrile), crystalline material was also obtained, but the acetone/water combination gave the best-quality crystals. The typical yield was 80% based on $Co(NCS)_2$. The compound is not soluble in water or common organic solvents.[19]



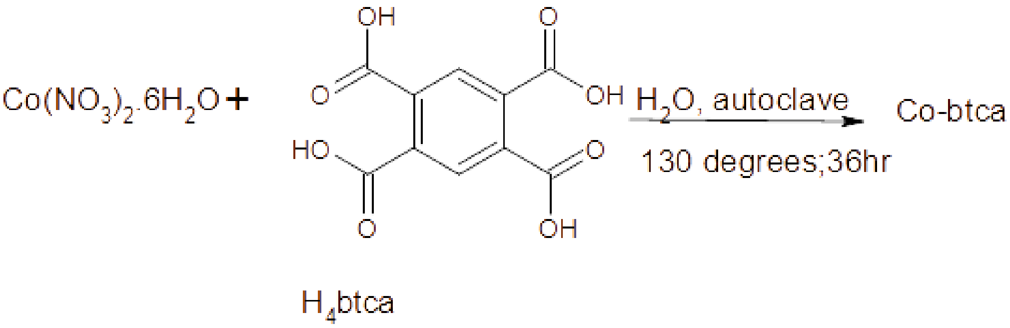
4)$Co[O_2C(CH_3)_3CO_2]$

The compound exhibits two-dimensional arrangements of cobalt(II) cations interconnected by dicarboxylate anions. Conformational freedom of α,ω-dicarboxylate ligands in transition-metal containing coordination polymers was observed in the crystal structure of the compound. Two distinct conformations (anti and gauche) in compound are presented in the alkyl chains of the glutarate ligands. This is the first example of inorganic-organic hybrid layered structures consisting of gauche- and anti-form dicarboxylate layers stacked alternatively between the inorganic layers along the same direction. $Co[O_2C(CH_2)_3CO_2]$ was prepared by the following procedure: glutaric acid (5 mmol) was dissolved in 5 mL of 1.5 M KOH solution. To this solution (pH-4) was added $CoCl_2.6H_2O$ (5 mmol) to attain a pH of 3.5 after homogenization. The solution was heated under hydrothermal conditions in a 23 mL Teflon vessel at 180 °C for 24 h. Then the heated autoclave was quenched with cold water. Plate like dark purple crystals of $Co[O_2C(CH_2)_3CO_2]$ were obtained with a small amount of glutaric acid by filtration. The product was dried in air after the residual glutaric acid was washed with ethyl alcohol and the yield was 70% based on the utilized cobalt.[10]



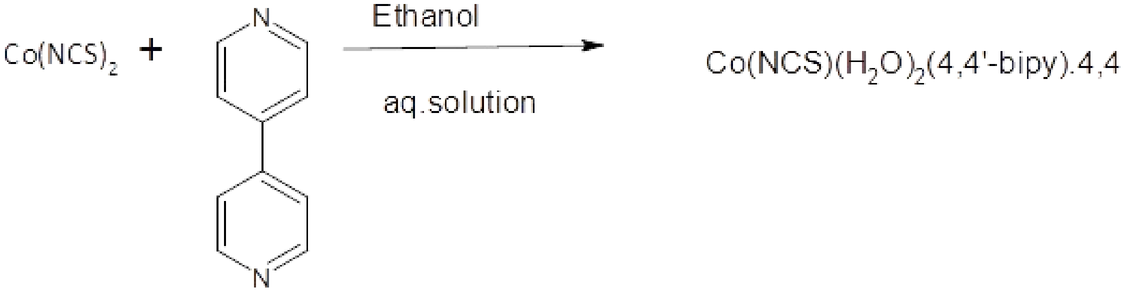
5)Co-btca

$Co(NO_3)_2\cdot 6H_2O$ (1.164 g, 4 mmol) and 1,2,4,5-benzenetetracarboxylic acid (H_4btca) (0.254 g, 1 mmol) were dissolved in distilled water (20 mL), and stirred for about 30 min. The resulting solution was transferred into a Teflon-lined autoclave and heated at 130ºC for 36 h, finally cooled down to room temperature. The reddish-orange product was filtered off, washed with ethanol and distilled water, and dried at 80 ◦C for 12 h. The prepared Co-btca was used for characterization without any further activation.[20]



6)Co(NCS)(H_2O)(4,4’-bipy).4,4’-bipy

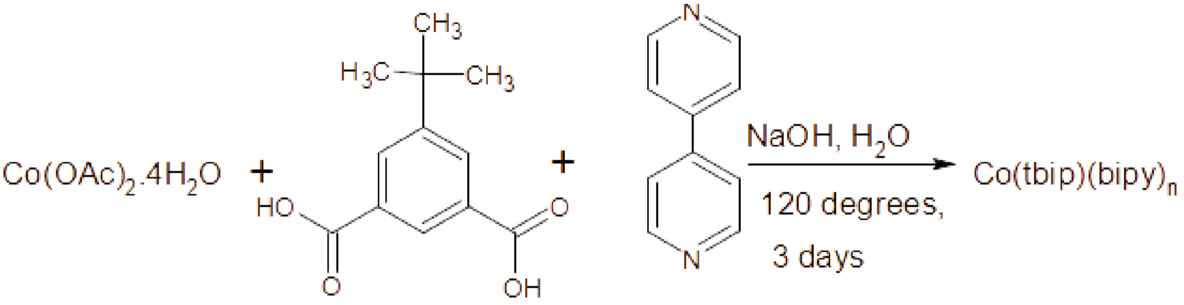
A 0.315 g sample of 4,4’-bipy dissolved in 15 mL of ethanol was layered on top of an aqueous solution (10 mL) of $Co(NCS)_2$. In about 1 week, light orange plate crystals of **2** were formed. After diffusion was completed, the product was filtered off and dried under vacuum, giving 0.374 g of product. The yield was 79% based on $Co(NCS)_2$. Compound does not dissolve common organic solvents or water.[19]



7)Co(tbip)$(bipy)_n$

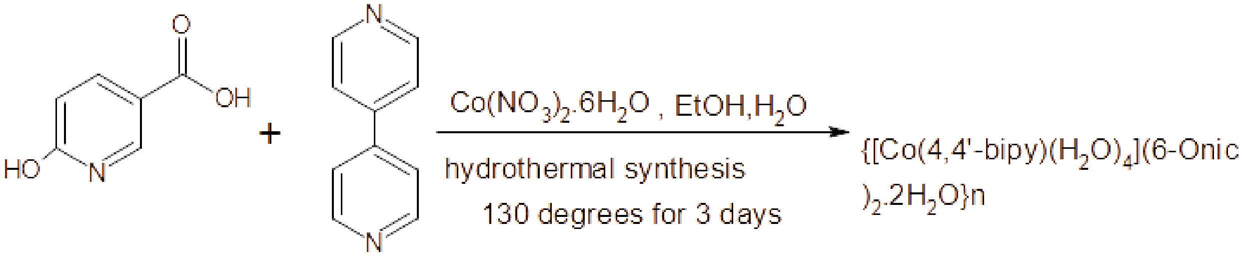
A mixture of 5-*tert*-butyl isophthalic acid (0.1 mmol, 23.1 mg), bipy (0.1 mmol, 15.9 mg), $Co(OAc)_2\cdot 4H_2O$ (0.05 mmol, 12.0 mg), NaOH (0.2 mmol, 8.0mg), and H_2O (15 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for 3 days, and then cooled to room temperature over 24 h. Pink crystals were formed.[18]

(H_2tbip) 5-*tert*-butyl isophthalic acid.



8)$\{[Co(4,4'\text{-}bpy)(H_2O)_4](6\text{-}Onic)_2\cdot 2H_2O\}_n$

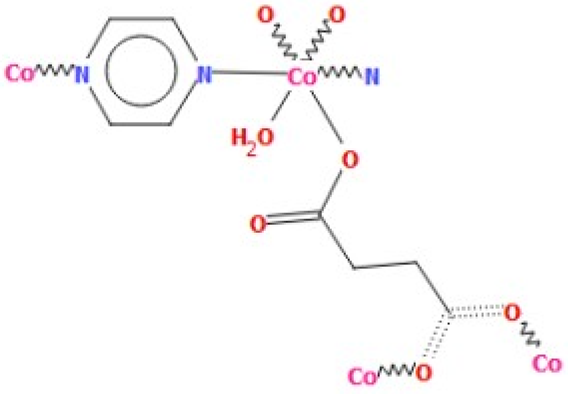
6-Hydroxynicotinic acid (0.050 g, 0.358 mmol) was dissolved in 4 mL of distilled water, 4,4'-bipyridine (0.028 g, 0.179 mmol) was dissolved in 2 mL of ethanol and cobalt(II) nitrate hexahydrate (0.052 g, 0.179 mmol) was dissolved in 2 mL of distilled water. The solutions of the ligands were mixed together under stirring. The resulting solutions was then slowly added to the cobalt(II) nitrate solutions under stirring. The pH of the final solutions was adjusted to 7 by adding a sodium hydroxide solution dropwise. The reaction mixtures were heated in the Teflon lined autoclave for 3 days at 130ºC and then left to cool slowly at room temperature over 1 day. Pink precipitate of was obtained, collected by filtration, washed with water and dried in a desiccator over $CaCl_2$. Yield oobtained was 0.0376 g (35%).The clear solutions, remained after filtration, were left to evaporate slowly at room temperature until pink crystals suitable for X-ray diffraction measurements, were obtained. It took approximately two days for the crystals.[15]



1.3)Characterization of Cobalt coordination polymers.

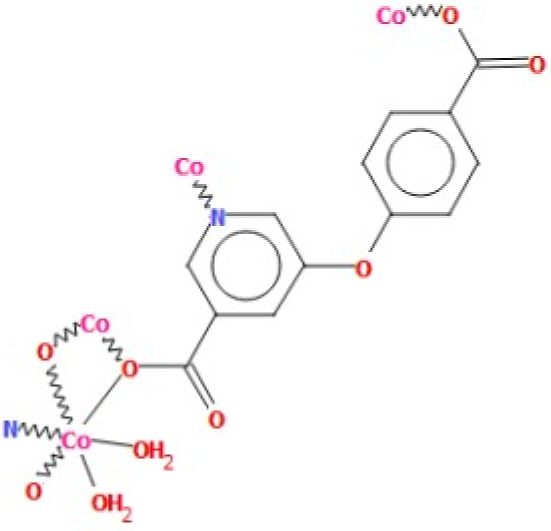
1) $[Co(H_2O)(pyz)(suc)]$

X-ray analysis revealed its crystallization in the monoclinic P21/c space group .The asymmetric unit consists of one Co(II), one pyz, one suc^{2-}, and one water molecule. Three oxygen atoms from each succinate ligand, one water molecule, and two nitrogen atoms from the bridging pyrazine complete the octahedral coordination of Co(II).[13] The typical Co−O bond length varies from 2.061 to 2.101Å, with Co−N distances ranging 2.169−2.188 Å, and that for Co−O is 2.083 Å , which clearly indicates distortion from the ideal octahedral geometry. The X-ray diffraction pattern of the bulk samples of compounds were measured and compared with the calculated X-ray powder patterns. It showed trace impurities which are evident from profile fitting of the powder patterns using the Le Bail method with the help of FullProf software. The morphological examination of the powdered sample showed well-defined octahedral-shaped particles. [13]



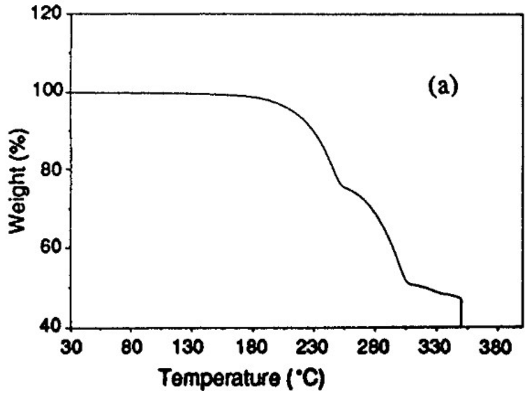
2)[Co(μ-cpna)$(H_2O)_2$]$_n$

Single crystal X-ray data was collected on a Bruker Smart CCD diffractometer λ = 0.71073Å, graphite-monochromated Mo Kα radiation .Crystal system monoclinic.[17] Space group $P2_1/n$; a,(Å 6.1155(2) ;b,(Å) 8.1678(3); c,(Å)26.0705(10) ;α,(deg)90 ;β, (deg) 92.335(4); γ,(deg)90;V, Å^3 1301.14(8) ;T,(K) 293(2); Z 4;D_c, g cm^{-3} 1.798; μ, mm^{-1} 1.357; F(000) 716; reflns measured 4587;unique reflns (R_{int}) 2306 (0.0355); GOF on F^2 0.998; R1 [$I > 2\sigma(I)$] 0.0373;wR2 [$I > 2\sigma(I)$] 0.0689.In TGA a loss of two water ligands was observed at a rather high temperature interval(151-297ºC), the dehydrated sample then decomposes starting at 351ºC.



3)$Co(NCS)_2(pyz)_2$

TGA showed a weight loss corresponding to one pyrazine(observed 23.82%, calculated 23.88%) in the temperature range 170-260ºC, immediately followed by another weight loss corresponding to one pyrazine molecule (observed 23.80%, calculated 23.88%) from 260 to 310ºC. The weight loss continued above 310ºC and the final residue was black and amorphous.[19]



4)$Co(tbip)(bipy)_n$

The asymmetric unit contains one Co^{2+} cation, one bipy ligand, and one tbip anion. Each Co atom is octahedrally coordinated by two nitrogen atoms of two bipy ligands and four oxygen atoms from three tbip ligands. In order to check the phase purity of the compounds, the P-XRD patterns of the compound was checked at room temperature. The peak positions of the simulated and experimental P-XRD patterns are in agreement with each other, demonstrating the good phase purity of the compounds. The differences in intensity may be due to the preferred orientation of the crystalline powder samples.[18]

5)$Co[O_2C(CH_3)_3CO_2]$

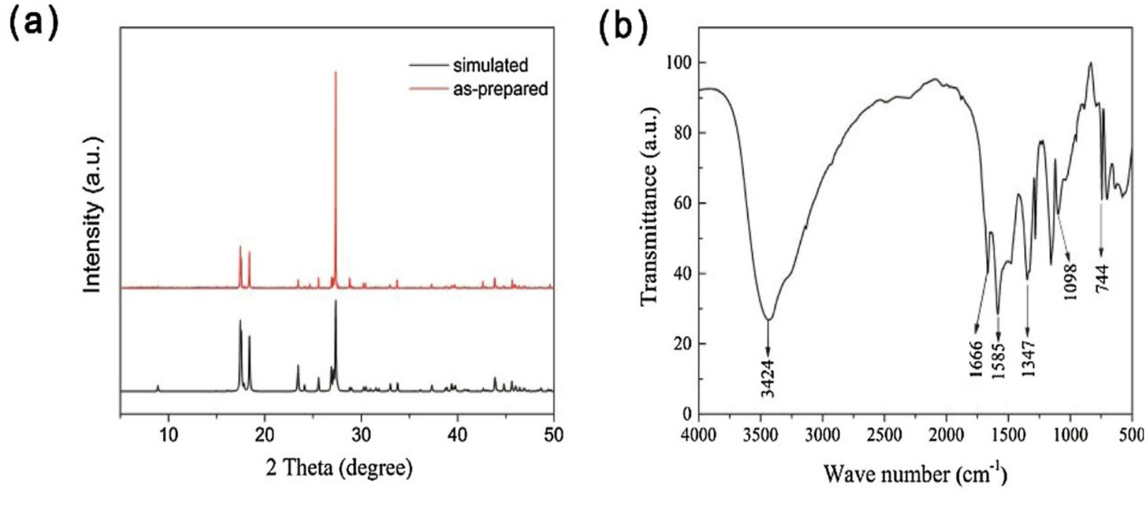
IR spectra were obtained in the 4000-400 cm^{-1} range using a Nicolet 1700 FT-IR spectrometer. The sample was ground with dry KBr and pressed into a transparent disk. Thermogravimetric analyses were conducted under a nitrogen atmosphere. Only one distinct mass loss region is seen in TGA of the title compound. The 43% mass loss (300-450 °C) corresponds to the decomposition of the organic chains through the pyrolysis reaction. The weight loss curve was not observed around 200 °C, indicating that the compound has no hydrate water in the lattice, corresponding to the absence of bands at above 3000 cm^{-1} in the IR spectroscopic data. The dark purple Co-glutarate crystallizes in the monoclinic system in the space group *P*2/*c*, with *a)*14.002(3) Å, *b*) 4.8064(10) Å, *c*) 9.274(3) Å, *â*)90.5(2)°, and *Z*) 4. The Co^{2+} centers are tetrahedrally coordinated to four oxygen atoms from the dicarboxylate ligands. The anhydrous-pillared three-dimensional structure consists of infinite $Co-CO_2-Co$ inorganic layers, which are stacked by the coordinated glutarate alkyl chain along the *a*-axis. There are two different conformations for glutarate ligands, i.e., the gauche- and the anti-forms. These ligands reside between the inorganic layers alternatively to separate each layer by 7.01 Å (gauche) and 6.99 Å (anti). Magnetic measurement reveals that the predominant magnetic interactions are antiferromagnetic below 14 K.[10]

6)$\{[Co(4,4'\text{-}bpy)(H_2O)_4](6\text{-}Onic)_2 \cdot 2H_2O\}_n$

The TGA/DTA curve shows that the compound are thermally stable up to 100 ◦C, followed by a release of four coordinated and two lattice water molecules in a single step with an endothermic peak at 137.2ºC(observed mass losses 18.4% , calculated 18.0%). Both coordinated and lattice water molecules are released at the same temperature most probably due to the existence of thermally stable hydrogen- bonded frameworks(as revealed by their crystal structures), in which these water molecules participate extensively.The thermal decomposition continues through two consecutive, not well-resolved steps; first one representing an endothermic process (peak at 342.7ºC) and the second representing an exothermic process (peaks at 403.5ºC). These endothermic (observed mass losses 41.9%) and exothermic (observed mass losses 27.5%) steps correspond to the complete decomposition of 6-oxonicotinate and 4,4'-bipyridine ligands. The observed residues (12.2%) at 800ºC correspond to CoO. The last decomposition step is exothermic, which is in accordance with the formation of thermodynamically stable metal oxides (CoO) upon total decomposition. In the hydrogen-bonded framework, the one-dimensional polymeric chain of $\{[Co(4,4'\text{-bpy})(H_2O)_4]^{2+}\}$n, the 6-oxonicotinate anions and the lattice water molecules were assembled via strong intermolecular O–H···O and N–H···O hydrogen bonds and π–π interactions, leading to the formation of the representative hydrogen-bond ring motifs.[15] The crystallographic data shows: Mr 599.41;Crystal system, space groupmonolinic,C2/c(No.15);a(Å)=19.0114(13);b(Å)=11..4133(7); c(Å)=12.0374(7);β(º)=99.333(2);V(Å^3)=2577.3(3);Z=4.

7)Co-btca

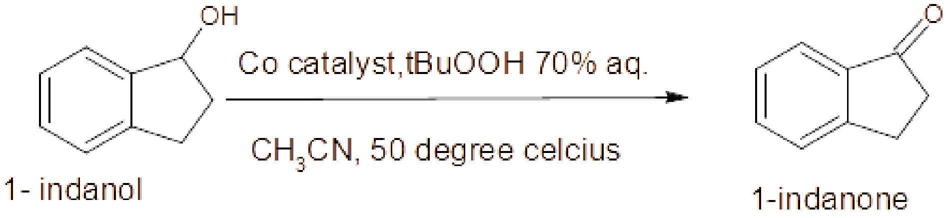
X-ray powder diffraction results of the prepared Co-btca and simulated. It can be seen that the observed diffraction peaks of the sample are in agreement with the simulated pattern, and no any impurities can be detected in the P-XRD pattern, indicating the formation of pure products. The sharp and intensive diffraction peaks confirm the well-crystallization of the products. FT-IR spectrum of the prepared Co- btca. The bands at ~3424 and ~1666 cm^{-1} could be attributed to the vibration of water. The bands at ~1585 and ~1347 cm^{-1} are ascribed to the asymmetric and symmetric stretching vibrations for the carboxylate groups. The bands at ~1098 and ~744 cm^{-1} represent the in plane and out C- H bending modes of the aromatic ring . Consequently, the successful synthesis of single phase crystalline Co-btca can be deduced. TGA analysis shows initial weight loss (~17%) of the Co-btca occurred at 150ºC which is attributed to water loss. This indicates that Co-btca is totally stable up to 150ºC. The second weight loss (~73%) occuring in the temperature range of 160–520ºC can be attributed to the decomposition of Co-btca.[20]



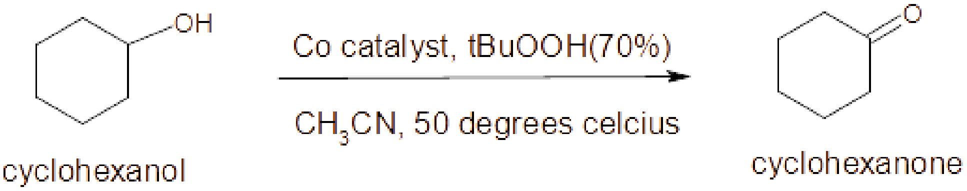
1.4)Applications

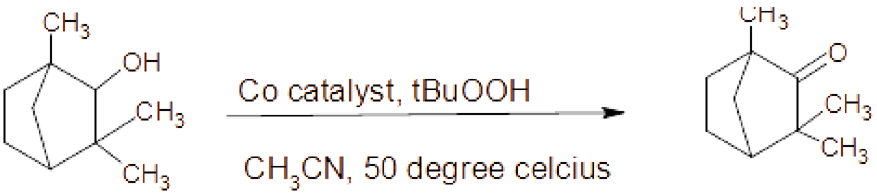
1)Catalytic study

a)Catalytic performance of $[Co(\mu_4\text{-cpna})(H_2O)_2]_n$ was evaluated for oxidation of alcohols with peroxides under mild conditions. The polymer was hydrothermally generated and are stable in water. They are insoluble in the catalytic reaction medium composed of an alcohol substrate, aqueous tBuOOH oxidant, and acetonitrile solvent thus acting as heterogenous catalysts. Oxidation of 1-indanol with tert-butylhydroperoxide catalyzed by Cobalt coordination polymer in acetonitrile afforded 1-indanone as a main reaction product.[17] Yield obtained was 26-39%.

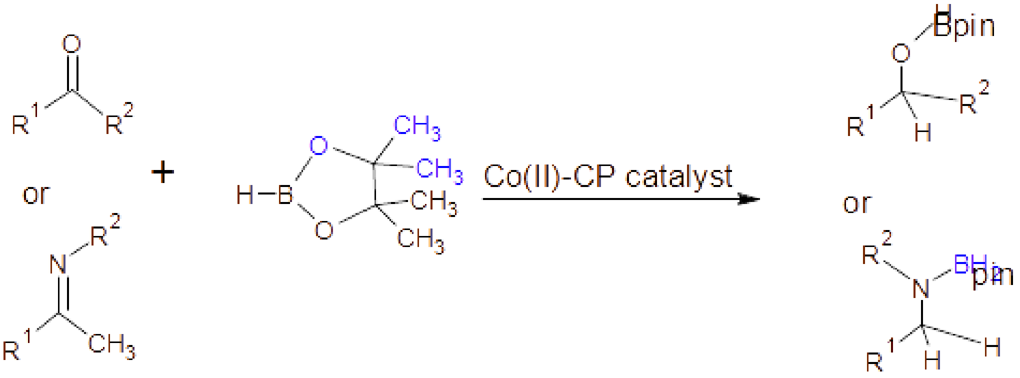


Cyclohexanol can also be used as a substrate, leading to a maximum cyclohexanone yield of 7-10%. Notably, all the catalytic systems exhibit almost 100% selectivity in the case of cyclohexanol and fenchyl alcohol oxidation as no byproducts were detected.[17]

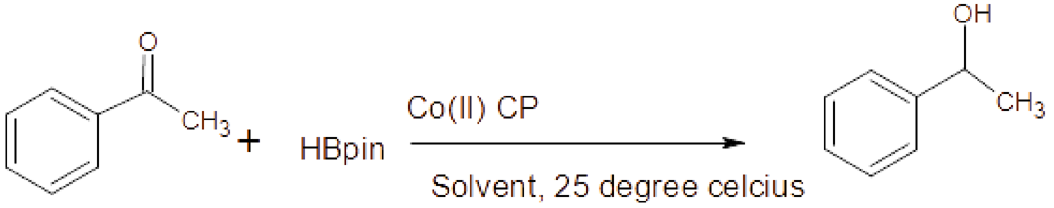




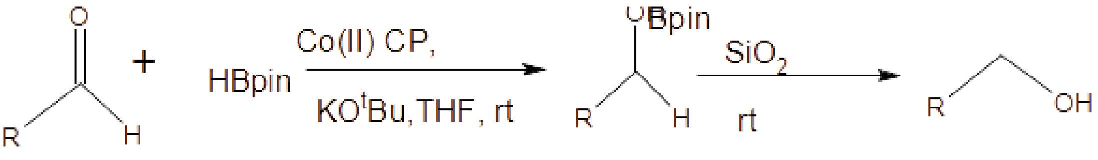
b)Catalytic hydroboration of carbonyl compounds and imines provides an important and convenient approach to functionalized alcohols and amines, respectively, comparing to the conventional stoichiometric reduction using hydride reagents (such as $LiAlH_4$, or $NaBH_4$), which usually suffer from poor functional group tolerance and product selectivity (aldehydes vs. ketones or over-reduction), modest reaction rates (with hindered ketones and imines) and often harsh conditions. Recent efforts have been made to develop efficient catalysts for the hydroboration of carbonyl compounds and imines with relatively less-active reductants, such as HBpin.Highly effective hydroboration precatalyst is developed based on a cobalt(II)-terpyridine coordination polymer(CP).The hydroboration of ketones, aldehydes and imines with pinacolborane (HBpin) has been achieved using the recyclable CP catalyst in the presence of an air-stable activator. A wide range of substrates containing polar C=O or C=N bonds have been hydroborated selectively in excellent yields under ambient conditions.[21]



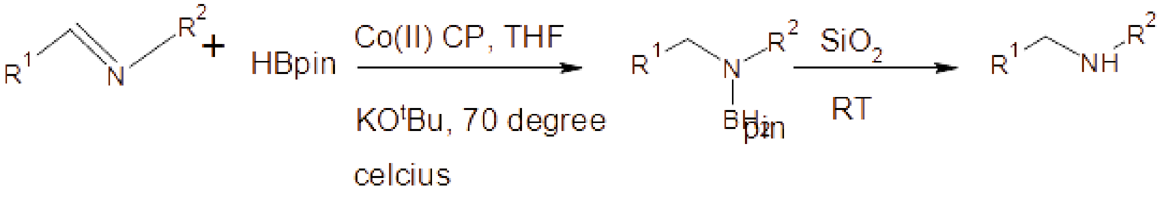
Hydroboration of Acetophenone with Pinacolborane



Hyroboration of aldehydes



Hydroboration of Imines



c)Water oxidation

With the depletion of fossil fuels and the greenhouse effects resulting from carbon dioxide emission into the atmosphere, interest has been rapidly growing in the development of new green fuels and production technologies . Hydrogen, which reacts with oxygen to form water and releases energy, is the cleanest fuel. Hydrogen can be obtained through water splitting using electrochemical or photoelectrochemical methods, which also produce oxygen at the anode. However, despite the elegance of this solution, the efficiency of water splitting process is very low due to the inherent complexity of the reactions.To make the process practically viable, catalysts are required to facilitate the reaction. Four cobalt phosphonate coordination polymers

$Co[(CH_3PO_3)(H_2O)]$ (**1**), $Co[(C_2H_5PO_3)(H_2O)]$ (**2**), $Co[(C_4H_9PO_3)(H_2O)]$ (**3**) and $Co[(C_6H_5PO_3)(H_2O)]$ (**4**) were assessed for their ability to catalyse water oxidation in both phosphate buffer and water-saturated ionic liquid [BMIM][PF_6], with **3** being synthesized and characterized for the first time. The results show that these polymers are able to catalyse water oxidation but are not stable in aqueous solution. However, they are relatively stable and show significant catalytic activity towards water oxidation in water-saturated [BMIM][PF_6] without the need to have a buffer present. The catalytic activity shows a structural dependence and decreases in the sequence of **1** > **2** > **3** > **4**, presumably due to the different intrinsic catalytic activities of these catalysts towards water oxidation reaction or/and their different rates of decomposition to form the well known CoO_x water oxidation catalysts. Water-saturated [BMIM][PF_6] provides a good medium for catalytic water oxidation by this type of coordination polymers.[12]

2) Gas storage and trapping

Flexible porous coordination polymers have attracted attention as gas storage vessel recently because of their high porosity and surface area. Fuel gases like hydrogen (H_2) and methane (CH_4) due to their economic, environmental balanced benefits have been realized as vehicle fuels and have attracted much interest as replacements of petroleum and diesel power source.[22] Recently, coordination polymers with pillared layers structures are applied in adsorption to tune the pore size to that of the adsorbed gas and are effective for stabilizing the explosive gases like acetylene. Since they are structurally transformable, pore shape and size can be adjusted towards the most stable state with guest to improve host -guest interaction.[2]The adsorption of gases at ambient temperature is important for applications, such as storage and transport. A useful strategy for the creation of suitable adsorbents is to prepare stable frameworks without guest molecules. The first report on the gas-adsorption properties of these compounds at ambient temperature appeared in 1997. The framework reported is best described as tongue-and-groove (bilayer) structure, $\{[Co\ (4,4'\text{-bpy})_3(NO_3)_4]\cdot 4H_2O$ formed from $Co(NO_3)_2$ and 4,4'-bpy units . The effective micropore cross section for the dried sample is about 3 K 6 L2 based on van der Waals radii. This host reversibly adsorbs CH_4, N_2, and O_2 in the pressure range of 0–36 atm without collapse of the crystal framework. Coordination polymer with pillared layer structure is a suitable system for the design of porous structures and properties. All these samples show typical isotherms which confirms the presence of micropores and the absence of mesopores. To achieve higher adsorption capacity, it is necessary to ensure that micropores with sizes well suited to methane molecules are densely and uniformly distributed in the solid. Porous coordination polymers are therefore good candidates as adsorbents for CH_4 storage.[1]CH_4 gas adsorption for porous coordination polymers was first reported for $\{[Co_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot 4H_2O\}n$, which adsorbs an equivalent of about 52cm^3 of CH_4 at a temperature of 298 K and a pressure of 30 atm.

3)Lithium ion batteries

Lithium-ion batteries with significantly higher specific capacity, longer storage cycle and lighter weight have been considered as the most promising energy storage system for a wide variety of applications. They have already been widely applied to mobile phones, laptops, digital cameras. The key point of lithium ion batteries properties is electrode materials. Graphite is presently used as the commercial anode material for lithium-ion batteries however, it is limited by the theoretical capacity.The Co-btca electrodes behave a good electrochemical performance even at high rates despite of slight variation as the cycles go on. Such wonderful cycle performance of the Co-btca electrode is attributed to the porous structure not only offered high surface areas, but also provides convenient and accessible route for electrolyte diffusion and intercalation of Li-ions, which may improve the electrochemical properties of the electrode. Compared MOFs or CPs anodes, the Co-btca displays enhanced reversibly capacity and excellent cycling stability. The Co-btca electrode exhibits an outstanding rate performance as an anode for lithium-ion batteries. The void space of Co-btca can effectively buffer the strong volumetric expansion during charge-discharge cycling, hence adapt to charge-discharge processes at different rate. Single crystal X-ray diffraction results indicated that the prepared Co-btca displayed unique layer structure, which was beneficial to transport Li ions and electrons. Also, owing to the porous structure and appropriate specific surface area, Co-btca electrode delivered a reversible capacity of 801.3 mA h/g after 50 cycles at a current density of 200 mA/g. The reversible capacity of 773.9 mA h/g was maintained after 200 cycles at a current density of 500 mA/g, exhibiting enhanced cycle stability. It also showed improved rate performance, making it a promising anode material and a new choice for lithium-ion batteries.[20]

4) Luminescent material

Luminescent polymers are used as fluorescent sensors and probes because of the presence of organic chromophoric ligands which absorbs light and then pass the excitation energy to the metal ion. Potentially, coordination polymers are the most versatile luminescent species because of their emission properties together with guest exchange and are efficient materials for light emitting diodes.[3,11] With industrialization, there has been exploitation of organic dyes, nitro aromatic compounds (NACs), causing a serious threat to the environment and health. This has triggered the development of fluorescent sensor materials for the selective and judicious detection of organic dyes and removal of harmful substances. One promising approach toward NAC detection is the use of fluorescent electron-rich MOFs undergoing quenching on interaction with electron-deficient nitro aromatic molecules. Fluorescence sensing is a promising strategy to tackle the detection of nitro explosives owing to its low cost, electronic tunability, portability, and easy operation.[13]

5)Electrochemical sensors

The electrochemical properties of coordination polymers have been neglected in the past ,but are attracting more interest as of recently .Cyclic voltammetry is the most frequently used electrochemical technique in the characterization of coordination polymers, providing information on redox activity of the respective metal ions and ligands, or is simply used to elucidate the electrochemical sensor properties of coordination polymers, e.g., as an electrode surface modifier because of their potential to undergo reversible single-electron processes which enable them to sense many analytes, e.g., anions ,cations or organic compounds. The electrochemical sensing ability of coordination polymers is generally affected by the type of the corresponding metal ions and functional organic ligands. For instance, cobalt(II) coordination polymers are considered to be promising candidates for electrochemical sensing because of their low cost, high accessibility and great electrocatalytic performance. On the other hand, organic ligands in coordination polymers contribute significantly to their electrochemical sensing potential, also enhancing their electron conduction rate.[15]

6)Medicine

The application of coordination polymers in medicine is currently on the rise with special emphasis on nanoparticle drug delivery. Photolytically sensitive caged compounds have been examined as containers for releasing a drug or reagent. The nanoparticle metal organic framework is important in x-ray computed tomography (CT) a type of biomedical imaging that is capable of providing three-dimensional images with excellent spatial resolution. CT is mainly and recently used to image a wide range of structures within and throughout the whole body not limited to organs, blood vessels, and bones. The technique is a relevant tool for diagnosing and monitoring abnormal health conditions and ailments throughout the body with conditions such as tumors, calcifications, embolisms, aneurysms, and inflammation efficiently and effectively treated.Cyanide coordination polymer has the ability to incorporate mono-cations and this makes it an important separating agent for certain heavy metal poison.[2]

1.5)Conclusion

The chemistry of cobalt(II) with pyrazine (rigid) and succinic acid (flexible) in water/DMSO/DMF under ambient/ solvothermal conditions was explored generating CPs with diverse architectures(1D to 3D). The construction of coordination polymers was influenced by different binding modes adopted by the carboxylate ligand and the $\mu_2$bridging mode of pyrazine. Thermal and aqueous stability and catalytic and magnetic properties of compounds were studied as well. Catalytic studies shows that they are active heterogenous catalysts in the oxidation of alcohols with tBuOOH, in gas storage and trapping, lithium ion batteries,as electrochemical sensors. Hence, the present study also widened an application of such flexible pyridine-carboxylate blocks toward designing new metal−organic architectures. Further research with a focus on assembling related cobalt (II) CPs and MOFs and on the exploration of their functional properties is in progress.

1.6)Aknowledgement

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