

INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)
www.ijrcrps.com



Research Article

MOLECULAR ORGANIC FRAME WORK AND ARCHITECTURE FORMED BY 2-HYDROXYBUTANEDIOIC ACID AND 2,2'- BIPYRIDYL WITH METAL

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Abstract

Supramolecular frame works have been prepared based on the principle of crystal engineering. A mixture of 2,2'-bipyridyl, 2-hydroxybutanedioic acid and Cobalt nitrate dissolved in 15 ml distilled water was placed in a Teflon-lined stainless steel Autoclave and heated to 180°C for 4 days and cooled to room temperature. Metal complex was obtained. The functional groups were confirmed by the Fourier Transform Infrared spectroscopy. The transmittance and absorbance of electromagnetic radiation is studied through UV-Visible spectrometer. It is examined using the PXRD studies powdered pattern. The well-defined peaks at specific 2theta values show high crystallinity of the metal complex. The morphology of the metal complex studied by SEM/EDAX analysis

Keywords: Supramolecular, 2,2'-bipyridyl, 2-hydroxybutanedioic acid, Autoclave, FTIR, PXRD, SEM/EDAX.

Introduction

Crystal engineering of complexes, especially the design and synthesis of extended network materials (MOFs) has been an area of intense research over the past decade. Recently, the studies on the synthesis of MOFs from transition metals and organic ligands have received much attention in coordination chemistry because of their interesting molecular topologies. Specifically the porous nature of many of these materials makes them attractive for numerous applications. Such as tremendous applications in catalysis, non linear optics, molecular selection, electronic materials, sensors, ion exchange, separation and gas storage. MOF's can be designed through a node linker approach that was first detailed by Robson, Fujitha, and others [1-3]. MOF_s are constructed from two key components; Inorganic connectors and organic linkers. In principle, a wide range of structural, optical, electrical, sensors, magnetic, catalytic properties can be incorporated into the frameworks by rational design. The metal centres are coordinated to multidentate rigid ligands containing O

or N donor atoms. Carboxylate ligands are used to bind metal centers forming moderately robust frame work, with the example of 2-hydroxybutanedioic acid, exhibiting high symmetry and excellent multidentate ligand. The design of one or two or three dimensional crystalline network structures thus can be achieved by choosing the desired combination of nodes and connectors resulting from coordination bonding, hydrogen bonding, aromatic - stacking interactions [4-8]. By selecting suitable multi-carboxylates, 2,2'-bipyridyl and metal ions, a variety of attractive networks with various structural motifs, including honeycomb, brick wall, bilayer, ladder, herringbone, diamondoid, rectangular grid and octahedral geometries, have been deliberately designed [9-10]. The polycarboxylic acid and bipyridyl ligands are containing O- and N- donor ligands, which are capable of connecting metal centers to form polymeric structure. 2-hydroxybutanedioic acid as O- donor ligand, due to the versatile bonding modes has been widely used in combination of N-donor ligands

to hydrothermal synthesizes coordination polymers containing transition metals. Here in, we have reported new two and three dimensional coordination polymers.

Synthesis

The new mixed ligand metal organic frame work compound was synthesised from 2,2'-bipyridyl, 2-hydroxybutanedioic acid and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1:2:1 molar ratios dissolved in 15 ml (pH:5) of distilled water, placed in a Teflon Lined Stainless Steel Autoclave and heated to 180°C for 4 days and then cooled to room temperature more than 12 hrs.

Characterization

The prepared metal complex has been subjected to various characterizations. Photographs of the

compounds were taken using LX400 Optical Imaging Microscopy. The transmittance and absorbance of electromagnetic radiation is studied through UV-Visible spectroscopy. The functional groups were confirmed by the Fourier Transform Infrared spectroscopy. Thermal behaviour has been analysed by TGA. Powder XRD, SEM/EDAX studies also have been carried out to study the morphology of the metal complex.

Optical Imaging Microscopy

The photograph of the compound was taken using Optical Microscopy LX400. This is shown in fig.1. The Optical Microscopic picture shows that the network structure is in the form of honeycomb structure.

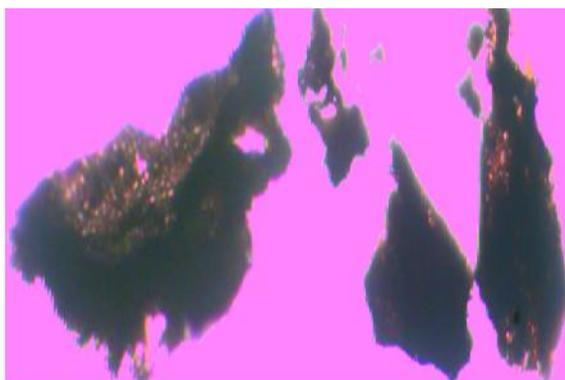


Fig.1 Optical Microscopic Picture of complex

The above structures clearly indicate that the structure corresponds to the compound consisting of crystallographically unique Co^+ cation, bipyridyl anion, dicarboxylic acid, a coordinated water molecule and a lattice water molecule. Generally the d⁷ block transition metal ions configuration have the stronger tendency to coordinate to N- donors. Intriguingly each structural unit $\text{Co}(\text{bipy})(\text{malic acid})_2 \cdot \text{H}_2\text{O}$ is combined with adjacent unit generating the 2D extended sheet architecture and displays the beautifully alternative grid motif. Hence because of this only the Fig.1 shows two dimensional picture. This is further supported by

FTIR, Thermal studies, XRPD and SEM/EDAX analysis.

UV-Visible spectroscopic studies

The UV-Visible absorption spectrum of the metal complex was recorded using Varian Cary 500 UV-Vis-NIR double beam spectrophotometer in the range 200nm-800nm and shown in Fig.2 covering the entire ultraviolet visible and the higher energy part of near infra red region to find the transmission range to know the suitability of optical applications.

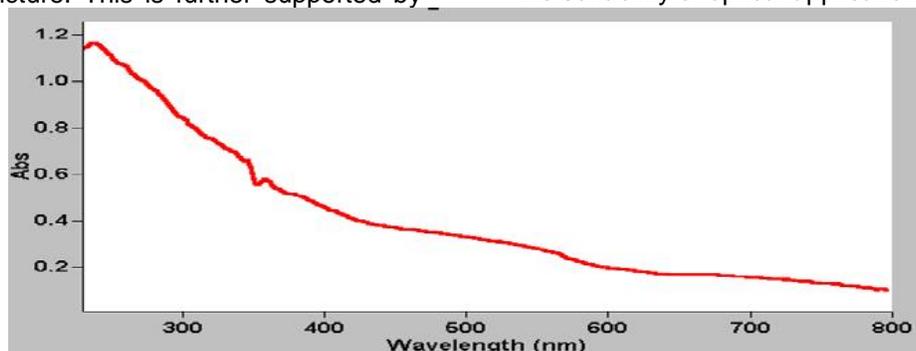


Fig.2 UV spectrum of complex

UV spectrum shows the λ_{max} absorption bands in the region of 255nm due to $\pi \rightarrow \pi^*$ transitions and 350nm corresponds to $n \rightarrow \pi^*$ transitions. This behaviour may be attributed to the metal ligand coordination behaviour and their different conjugated structures.

λ_{max} value corresponding to $\pi \rightarrow \pi^*$ is shifted to higher range (red shift) due to π - π stacking interaction fascinating the formation of 2D structures between the parallel layers through π - π stacking interactions.

Table.1. Observed λ_{max} values of complex

λ_{max} in nm	Assignment
255	$\pi \rightarrow \pi^*$
350	$n \rightarrow \pi^*$

FTIR Spectral Analysis

The FTIR spectra of metal complex recorded in KBr pellet technique and organic matrix are presented in

fig.3. The main IR bands with their tentative assignments are summarized in table.2.

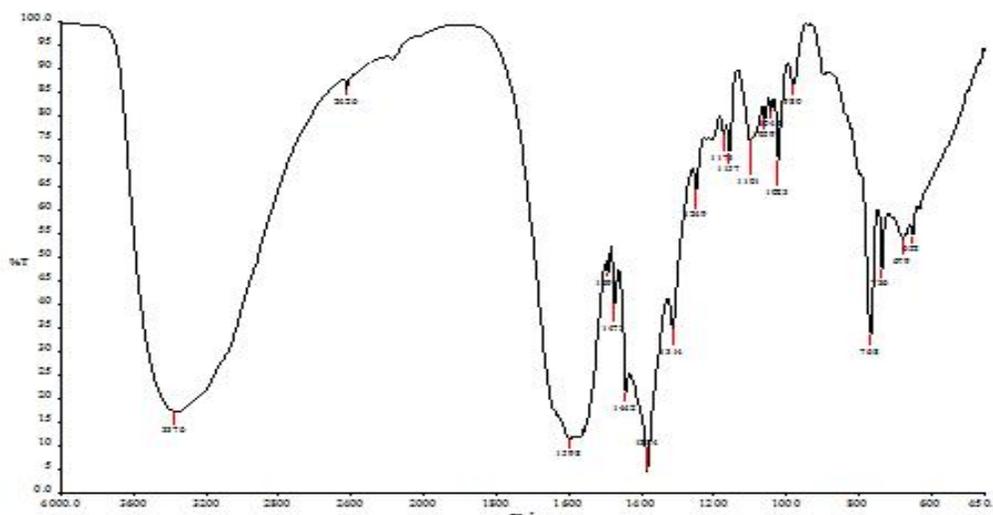


Fig.3 FTIR spectrum of complex

The O-H stretching over band of 3376cm^{-1} correspond to O-H group of water molecule and the 2-hydroxybutanedioic acid ligand. In general asymmetric and symmetric stretching vibrations bands of carboxylic acid are expected to the frequency at $1500\text{-}1630\text{cm}^{-1}$ and $1350\text{-}1460\text{cm}^{-1}$ respectively. Hence the characteristic absorption bands mainly attributed to the asymmetric stretching (1598cm^{-1}) and symmetric stretching (1384cm^{-1}) vibrations of deprotonated carboxylic groups of 2-hydroxybutanedioic acid. The $\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$ is 214cm^{-1} (larger than 200cm^{-1}) indicates that the carboxyl groups are monodentately coordinated with Co (II) centers via two monodentate carboxylate groups. It establishes the MOF is formed as possible in octahedral. The peak at 2426cm^{-1} may be due to $-\text{NH}^+$ -stretching of amine establishes the presence of free bipyridyl ring. The region between 1491cm^{-1} and 1473cm^{-1} stretching can be attributed to the C=N stretching inplane ring deformation bands of the bipyridine moiety.

The absorption peak at 1173cm^{-1} and 1157cm^{-1} is due to C-O stretching of carboxylic acid and 1101cm^{-1} is may be due to C-O & O-H stretching plane bending vibration of the secondary alcohol establishes the presence of 2-hydroxybutanedioic acid. Due to the co-existence of carboxylic groups and bipyridine groups, it is difficult to differentiate the contribution of carboxylic species from that of bipyridine groups. The absence of strong absorption peak at 1710cm^{-1} indicates the absence of the $-\text{COOH}$ group and carboxyl groups are coordinated or bridged.

The spectra of the metal complex display the in plane ring deformation bands of the bipyridyl moiety, 768cm^{-1} - 736cm^{-1} and 679cm^{-1} 652cm^{-1} and which are higher than the free bipyridyl ring suggesting the coordination of the bipyridyl Nitrogen to the Cobalt (II) ion. Hence, FTIR studies reveal that molecular organic frame work is formed by 2-hydroxybutanedioic acid, 2,2'-bipyridyl and Cobalt Nitrate.

Table 2 IR Absorption Frequencies of complex

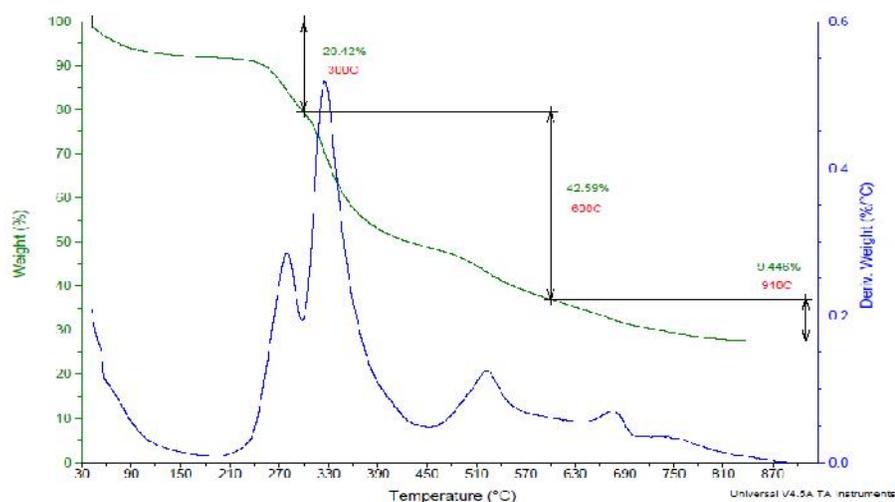
S.No	Wave. No in cm^{-1}	Assignment	Remarks
1	3376	(O-H) Stretching	H-bonded OH of coordinated water molecule
2	2426	(-NH ⁺)stretching	presence of free bipyridyl ligand
3	1598 & 1384	COO ⁻ asymmetric stretching & COO ⁻ symmetric stretching	Coordinated monodentate Carboxylate anion
4	1491 & 1473	(C=N) stretching	deformation bands of the bipyridine moiety
5	1173 & 1157	(C-O) stretching	Coordinated Carboxylic acid
6	1101	(C-O) stretching & (O-H) in plane bending vibration	Secondary alcohol
7	768-736 & 679-652	(N-H) plane bending	Coordinated bipyridyl Nitrogen to Co (II) ion

Thermo gravimetric analysis

The TGA curves of complex are shown in fig.4. The thermogram exhibits three main distinct decomposition steps.

Table.3. Stepwise thermal degradation data of complex

MOF	TGA range($^{\circ}\text{C}$)	Weight loss		Assignment
		Found	Calculated	
[Co(2,2'-Bipy)(C ₂ H ₄ O(COO) ₂) ₂ . x H ₂ O].	40 $^{\circ}\text{C}$ -300 $^{\circ}\text{C}$	20.42%	20.7%	loss of 5.5 lattice water molecules
	300 $^{\circ}\text{C}$ -600 $^{\circ}\text{C}$	42.59%	44.5%	Decomposition of MOF

**Fig.4.** TGA data of complex

The first step of decomposition with the temperature range 40°C-300°C correspond to the loss of 5.5 lattice water molecule of mass loss 20.42% (Cal.20.7).The rapid weight loss can be attributed to guest solvent molecules that are not bound or not tightly bound with the framework. The second step weight loss of mass 42.59% (Cal.44.5%) occurs at around 300°C-600°C and a third step weight loss of mass 9.44% (Cal.9.4) at around 600°C which can be attributed to decomposition of the framework

X-Ray powder diffraction analysis

The synthesised complex has been subjected to powder X-ray diffraction. The powder form of the complex was taken for the analysis using Bruker D8 advance X-ray diffractometer with CuK radiating at a scan speed of 0.045/min .

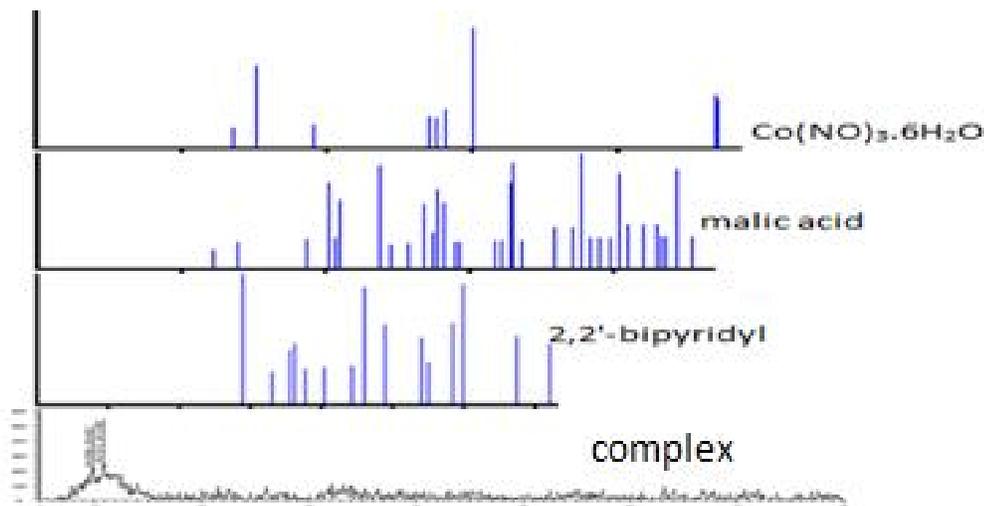


Fig.5. XRPD pattern of complex

The XRPD patterns of the MOF fig.5 showed less intense peaks at lower 2θ values. The lower intense peaks at specific 2θ values show low crystallinity of the metal complex. The progress of the reaction and the formation of the complex are well established by the new pattern of XRPD.

Scanning Electron Microscopy

The morphology and surface phenomenon of the material was carried out using HITACHI model 5-3000H scanning electron microscopic analysis. Fig.7.14 shows the SEM images of typical cross link Hyper branched Co dendrities with low magnifications.

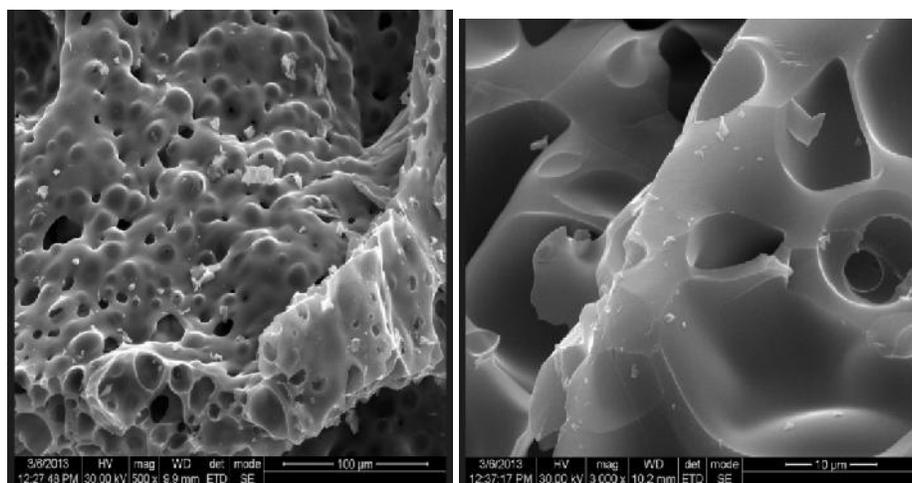


Fig.6 SEM image of complex

The high magnification images taken from the centre and the outer parts of the structure imply that the branches are composed of honeycomb structure (Fig.6). As Cobalt ion is having the tendency to form octahedral coordination only, even in the smaller ratio 1:2:1, it forms 2D structures through π -stacking interactions and form honeycomb structures with larger pore size. This is well depicted by SEM pictures. The above SEM images of the complex exhibits the

formation of MOFs prepared by hydrothermal synthesis.

EDAX

Further evidence for the formation of metal complex $[\text{Co}(2,2'\text{-bipy})(\text{C}_2\text{H}_4\text{O}(\text{COO})_2)_2]$ proved by EDAX spectrum is shown in fig.7. The EDAX analysis shows characteristic peaks and the composition of the complex powder.

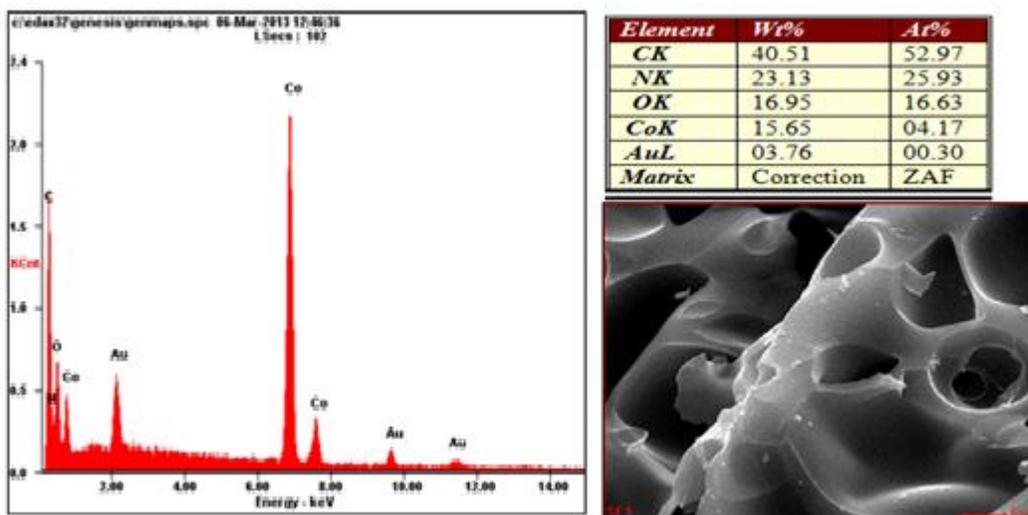


Fig.7. EDAX spectrum of complex

Conclusion

MOF has been synthesised with the contemporary use of two different kinds of ligands of rigid 2,2'-bipyridyl and the V-shaped flexible multi-carboxylic ligand 2-hydroxybutanedioic acid with Cobalt metal. The successful synthesis of the new complex was demonstrated the great potential of using mixed rigid and flexible ligands to assemble metal organic framework structures.

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