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-hydroxybutanedioc acid and Cobalt nitrate dissolved in 15 ml distilled water was placed in a Teflon-lined stainless steel Auto clave 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-hydroxybutanedioc acid, Auto clave, 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 be Robson, Fujitha , and others[1-3]. MOFs 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-hydroxybutanedioc 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 π-π 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-hydroxybutanedioc 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 Co(NO$_3$)$_2$.6H$_2$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.

![Optical Microscopic Picture of complex](image1)

**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.

![UV spectrum of complex](image2)
UV spectrum shows the $\lambda_{\text{max}}$ absorption bands in the region of 255nm due to $\pi-\pi^*$ transitions and 350nm corresponds to $\pi-\pi^*$ transitions. This behaviour may be attributed to the metal ligand coordination behaviour and their different conjugated structures. $\lambda_{\text{max}}$ value corresponding to $\pi-\pi^*$ is shifted to higher range (red shift) due to $\pi-\pi$ stacking interaction fascinating the formation of 2D structures between the parallel layers through $\pi-\pi$ stacking interactions.

**Table 1. Observed $\lambda_{\text{max}}$ values of complex**

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ in nm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>255</td>
<td>$\pi-\pi^*$</td>
</tr>
<tr>
<td>350</td>
<td>$\pi-\pi^*$</td>
</tr>
</tbody>
</table>

**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.

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

The absorption peak at 1173 cm$^{-1}$ and 1157 cm$^{-1}$ is due to C-O stretching of carboxylic acid and 1101 cm$^{-1}$ 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 1710 cm$^{-1}$ 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, 768 cm$^{-1}$ - 736 cm$^{-1}$ and 679 cm$^{-1}$ - 652 cm$^{-1}$ 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

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

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

<table>
<thead>
<tr>
<th>MOF</th>
<th>TGA range(°C)</th>
<th>Weight loss</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(2,2'-Bipy)(C₆H₄O(COO)₂)₂. x H₂O]</td>
<td>40°C-300°C</td>
<td>20.42%</td>
<td>20.7%</td>
</tr>
<tr>
<td></td>
<td>300°C-600°C</td>
<td>42.59%</td>
<td>44.5%</td>
</tr>
</tbody>
</table>

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 CuKα radiating at a scan speed of 0.045/min.

![XRPD pattern of complex](image1)

The XRPD patterns of the MOF fig.5 showed less intense peaks at lower 2-θ values. The lower intense peaks at specific 2theta 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 dentrities with low magnifications.

![SEM image of complex](image2)
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-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 [Co(2,2’-bipy)(C_2H_4O(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.

References