Molecular organic framework formed by the ligand of diphenylamine and succinic acid with nickel nitrate

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Abstract

The crystal of Diphenylamine, succinic acid with metal of different concentration can be grown. The crystals of Diphenylamine, succinic acid with Nickel Nitrate of different concentration can be easily prepared and it is done by simple solution technique by adopting hydrothermal method to produce quality crystals. The crystals were subjected to various characterization studies like UV, FTIR and optical Microscopic Analysis.

Keywords: FTIR, Hydrothermal method, UV, optical Microscopic Analysis.

INTRODUCTION:

The rational design and synthesis of novel co-ordination polymers have achieved considerable progress in the field of supramolecular chemistry owing to their potential applications. Crystal engineering of solid state supramolecular entities such as coordination polymers has provided a nice bit of successful example for the rational assembly of ligands with adjustable connectivity and selection of metal ions with specific co-ordination tendency\textsuperscript{(1-3)}. There are several factors that can influence the networks structure of compound such as the co-ordination environment of metal nodes and the structural characterization of ligand solvent, template and counter ions\textsuperscript{(4-7)}. Metal –organic frameworks are crystalline compounds consisting of metal ions (or) clusters coordinated to often rigid organic molecules to form one’, two, (or) three’ dimensional structures that can be porous. In some cases, the porous are stable to elimination of the guest molecules and can be used for the storage of gases such as hydrogen and
carbon. The choice of metal and linker has significant effects on the structure and properties of the MOF (8-10).

**Materials and methods**

1. Hydrothermal synthesis

   Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapour pressure, also termed ‘hydrothermal method’. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water.

2. Characterisation techniques

   About 0.846g of Di-phenyl amine dissolved in ethanol and 1.453g of Nickel Nitrate and 0.590g of succinic acid were dissolved in small amount of conductivity water. These two solutions were mixed stirred well and the solution is heated in a magnetic stirrer for few minutes, till the clear solution was obtained. The hot solution is transferred into a Teflon lined stainless steel autoclave, heated to 180°C for 5 days and then cooled to room temperature for 12 hrs. The crystals were harvested after five days.

3. Results and Discussion

   The obtained crystals are subjected to characterization studies like, UV, FTIR and photographed using optical Imaging microscope LX 400

   (i) Optical Imaging microscopy

   The photograph of the metal complex is taken by using optical microscopy LX 400. This is shown in the fig:1
FTIR SPECTRAL ANALYSIS

The Fourier transform Infrared Spectrum (FTIR) of metal complex was recorded using Perkin -Elmer FTIR spectrometer ranging between 4000-400 cm$^{-1}$

FTIR STUDIES OF NICKEL NITRATE, DIPHENYL AMINE AND SUCCINIC ACID

Fig.2
The observed frequencies electronic transition & functional group are assigned and is shown in the Table.1

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Metal complex 1:1:1 molar ratio</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3447&amp;3341</td>
<td>υ(O-H) Stretching</td>
<td>H- bonded OH of coordinated water molecule</td>
</tr>
<tr>
<td>2</td>
<td>3041</td>
<td>υ(C-H)Stretching</td>
<td>Aromatic CH group gets hydrogen bonded with the oxygen atom of the water molecule present in the lattice.</td>
</tr>
<tr>
<td>3</td>
<td>2825&amp;2736</td>
<td>υ(NH⁺)Stretching</td>
<td>Presence of free Diphenylamine ligand</td>
</tr>
<tr>
<td>4</td>
<td>1581&amp;2736</td>
<td>COO asymmetric stretching &amp; COO Symmetric stretching</td>
<td>Coordinated monodendate Carboxylate anion</td>
</tr>
<tr>
<td>5</td>
<td>1150</td>
<td>υ(C-O)Stretching</td>
<td>Coordinated Carboxylic acid</td>
</tr>
<tr>
<td>6</td>
<td>991,875&amp;741</td>
<td>υ(N-H)plane bending</td>
<td>Coordinated Nitrogen to Ni(II)ion</td>
</tr>
<tr>
<td>7</td>
<td>685</td>
<td>Presence of metal ion</td>
<td>Presence of Nickel ion</td>
</tr>
</tbody>
</table>

The absorption peaks at 3447 cm⁻¹ correspond to O-H stretching frequency of coordinated water molecule. The free ligand shows frequency at 3383 cm⁻¹ whereas the frequency gets shifted to lower frequency namely 3041 cm⁻¹ which suggests that the hydrogen atom of the aromatic CH group gets hydrogen bonded with the oxygen atom of the water molecule present in the lattice. In general asymmetric and symmetric stretching vibration bands of carboxylic acid or expected to the at 1500-1630 cm⁻¹ 1350-1460 cm⁻¹ respectively. Hence the characterized absorption bands mainly attributed to the asymmetric stretching (1581 cm⁻¹) and symmetric stretching (1308 cm⁻¹) vibrations of coordinated carboxylate groups of succinic acid. The Δυ=Δυ asy (coo`)Δυ sys(coo`) is 273 cm⁻¹ (larger than 200 cm⁻¹) indicates that the
carboxyl groups are monodentately coordinated with Ni(11) centers via two monodentate carboxylate groups. Due to the co-existence of carboxylic groups and diphenylamine groups, it is difficult to differentiate the contribution of carboxylic species from that of diphenylamine groups. The absence of strong absorption peak at 1710 cm⁻¹ indicates the absence of the –COOH group and carboxyl groups are coordinated or bridged.

The absorption peaks at 941 cm⁻¹, 875 cm⁻¹ and 741 cm⁻¹ are ascribed to coordination of amine nitrogen to the Nickel(11) ion. Hence, FTIR studies reveal that molecular organic framework is formed by succinic acid, diphenylamine and Nickel nitrate.

(ii) UV–Spectral Analysis

The UV-visible spectral studies for metal complex were carried out in VARIAN CARY 500UV-VIS –NIR double beam spectrophotometer(13).

For optical application the transmission range and transference cut off are important for the crystals. The crystals were characterized by UV double beam spectrophotometer. The absorption spectrum of the crystals Nickel Nitrate, Diphenylamine and succinic acid measured in wavelength region of 210-280 nm and this was shown in fig.3
The observed $\lambda_{\text{max}}$ values of metal complex is shown in the table 2:

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ in nm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>210</td>
<td>$\pi-\pi^*$</td>
</tr>
<tr>
<td>280</td>
<td>$n-\pi^*$</td>
</tr>
</tbody>
</table>

UV spectrum show the $\lambda_{\text{max}}$ absorption bands in the region of 210nm due to $\pi-\pi^*$ transition and 280nm corresponds to $n-\pi^*$ transitions. This behavior may be attributed to the metal ligand coordination behaviors and the different conjugated structures. A wide band of absorption with smaller value appears in the entire region and it shows that the material can be used the optical window application.
4. Conclusion

The crystal that comprise of the Diphenylamine, succinic acid and Nickel Nitrate of various concentration. The above crystal is prepared by hydrothermal synthesis. The harvested product are subjected to characterization studies like UV, FTIR and optical microscopic studies were carried out. The above crystals forms a molecular organic framework, in UV spectra it shows 100% transmission property and cutoff wavelength indicates that it can be applied for laser application in the nano technology. FTIR spectra it explains functional group present in the product. In various concentration of Nickel Nitrate at high concentration it become has a tertiary ammonium salt in nature.

REFERENCE