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Research Article

SOLVOTHERMAL SYNTHESIS AND CHARACTERISATION OF COBALT METAL ORGANIC MATERIAL WITH 2, 2'- BIPHENYL DICARBOXYLIC ACID AND AUXILIARY LIGAND

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Abstract

A new metal-organic material of Cobalt with 2,2'- biphenyl dicarboxylic acid (Diphenic acid) and benzimidazole as an auxiliary ligand has been solvothermally synthesized and characterized by UV-Visible spectroscopy, Fourier transform infrared spectroscopy, Thermogravimetric analysis, X-ray powder diffraction studies, Mass spectroscopy, Scanning electron microscopic analysis and energy dispersive spectroscopic studies.

Keywords: Solvothermal synthesis, Metal-organic material, Diphenic acid, Thermogravimetric Analysis.

Introduction

Metal-Organic Materials (MOMs) have received great attention in recent years due to their fascinating architectures and topologies as well as their increasing properties and potential applications such as functional materials, magnetism, luminescence, catalysis, gas separation, drug delivery and gas storage[1-6]. The assembly process of coordination polymers are highly influenced by lots of factors such as the structural characterisation of organic ligands, coordination nature of metal ions, temperature, P^H value of the solution and counter ions [7, 8]. In the designed synthesis of coordination polymers, diphenic acid is found to be an excellent aromatic dicarboxylate ligand due to its two distinct features. (a) In deprotonated 2, 2'- biphenyl dicarboxylic acid, two phenyl rings are not coplanar owing to the steric hindrance of 2,2'-positioned carboxylate groups in the coordination process. (b) The distortion of biphenyl space about the central bond allows diphenic acid to link metal ions or metal clusters into macrocycles, helical chains, and one dimensional chains [9-11]. Herein, We reported the solvothermal synthesis of Cobalt Metal Organic Materials using Cobalt nitrate hexahydrate, 2, 2'- biphenyl dicarboxylic

acid (Diphenic acid) and benzimidazole as the starting materials.

2. Experimental

2.1. Materials and Instrumentation\

All reagents and solvents were purchased from Sigma Aldrich and Merck and used as received without further purification.

UV-visible absorption spectrum was recorded using Varian Cary 500 UV-VIS-NIR double beam spectrophotometer in the range 190-900 nm covering the entire ,near ultraviolet,visible and the higher energy part of near infrared region.

FT-IR Spectra was recorded with a Perkin –Elmer FT-IR Spectrophotometer as a dry KBr pellet in the range 400-4000 cm^{-1} . Thermal behaviour of the metal complex was studied using TGA Q 500 V_{20.10} instrument. High Resolution Scanning electron microscopic analysis and energy dispersive spectroscopy were studied using FEI Quanta FEG 200 scanning electron microscope.

Powder X-ray diffraction analysis was recorded on Bruker D8 advanced diffractometer. Mass spectroscopy of the material was studied by JEOL GC MATE 11 quadrupole double focusing mass analyser. Surface area analysis was carried out in Micromeritics AFAP 2020 Porosimeter.

dicarboxylic acid (0.242g,1mmol) was dissolved using 13 ml of Methanol solution . Then Cobalt nitrate hexahydrate (0.118g, 1mmol) was dissolved in 2ml of methanol was added to the mixture and sealed in a 25 ml Teflon-lined stainless steel vessel and heated at 130°C for 96 hours. After cooling to room temperature , the purple colour metal-organic material was obtained as shown in fig. 1(a).Optical microscope image of the material are shown in fig. 1(b).

2.2 Synthesis of the Metal-Organic Material

A mixture of Cobalt nitrate hexahydrate(0.291g,1mmol),and 2,2'-biphenyl



Fig.1(a)digital camera image of the Metal-organic material

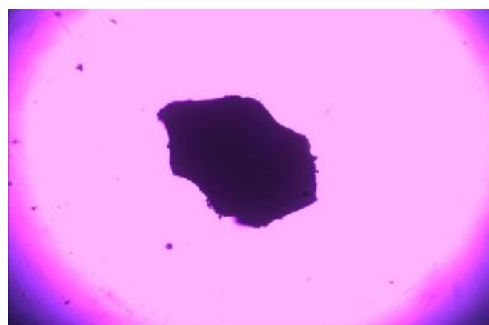


Fig.1(b) Optical microscope image of the Metal-organic material

3. Characterization Studies:

3.1. UV-Vis Spectroscopic analysis:

The UV-Visible spectral data of the synthesized material are shown in table 1.

S.NO	Name of the compound	Wavelength in nm	Transitions
1.	Co(NO) ₃ .6H ₂ O	229 519	- n - *
2.	Diphenic acid	248 272 365	- - n - *
3.	Benzimidazole	241 247 358	- - n - *
4.	Synthesised material	212 269 276	- n - n - *

The UV-Visible spectra of the material are as shown in fig.2

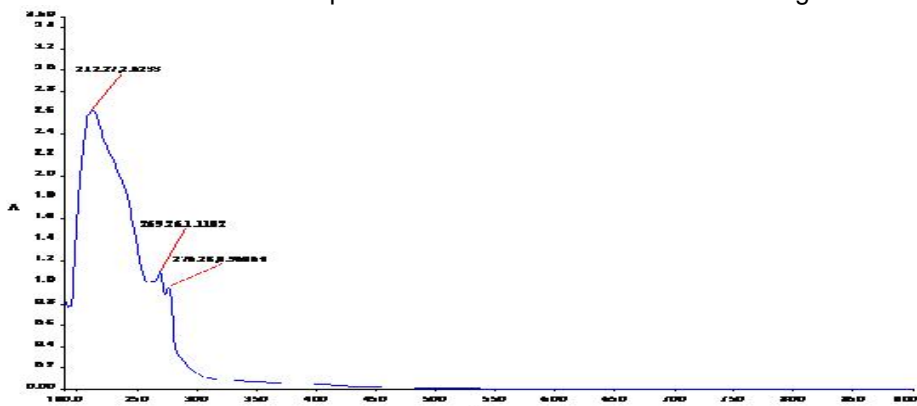


Fig.2. UV-Vis spectra of the material

The UV-Visible Spectra of synthesized material exhibits three bands at 212, 269 and 276 nm. The absorption at 212 nm are assigned to $\pi \rightarrow \pi^*$ transition and the two absorption bands at 269 and 276 nm are assigned to $n \rightarrow \pi^*$ transitions. When compared to pure ligands and metal nitrate, the complex has absorption,

which is shifted to shorter wavelength (hypsochromic shift or blue shift). The hypsochromic shift indicates that metal is coordinated to diphenate ion, benzimidazole and metal-organic material formation is confirmed.

3.2. FT- IR Spectroscopic analysis:

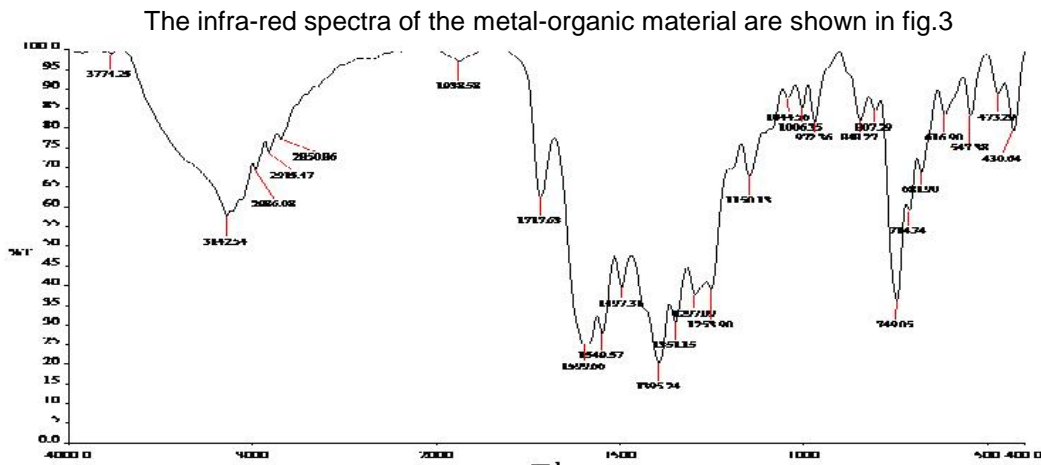


Fig.3. FT-IR spectra of metal-organic material

UV-Visible spectral data of the metal-organic material are given below in table 2.

S.No	Frequencies (cm ⁻¹)	Band Assignment
1.	3774	O – H (Solvent band)
2.	3142 - 2986	N – H stretching
3.	1938 - 2915	C – H aromatic stretching
4.	1717	C= O stretching
5.	1599, 1549	COO _{asym} stretching
6.	1497	C- H bending
7.	1395, 1351	COO _{sym} stretching
8.	1297, 1253	C- N stretching
9.	1150 - 1006	C – H in- plane bending
10.	972 - 547	C – H out-of-plane bending
11.	473	M –N band
12.	430	M –O band

The FT-IR Spectrum of the synthesised material shows absorption band at 3774 cm⁻¹ corresponds to O- H stretching of methanol which is used as a solvent in synthesis. The absorption band at 3142 and 2986 cm indicates N-H stretching vibration present in the complex. The N-H stretching frequency is slightly shifted to lower energy compared with normal N-H stretching frequency (3300 cm⁻¹) indicates that large hydrogen bonded association in the complex. The bands at 1938 to 2915 cm⁻¹ are due to aromatic stretching vibrations. The presence of sharp band at 1717 cm⁻¹ proves the existance of protonated

uncoordinated carboxylic groups in the synthesised complex [12, 13]. The asymmetric vibrations of coordinated carboxylic group appeared at 1599 and 1549 cm⁻¹ and the symmetric vibrations at 1395 and 1351 cm⁻¹. The difference between asymmetric vibrations and symmetric vibrations are 204 cm⁻¹ (>200) and 198 cm⁻¹ (< 200), showing the presence of monodentate and bidentate ligands via the carboxylate groups [14]. The band at 1497 cm⁻¹ may be attributed to C-H bending vibrations of the aromatic ring and the heterocyclic ring [15]. The C-N stretching vibrations

are observed to produce bands at 1297 and 1253 cm^{-1} . The bands between 1150 -1006 cm^{-1} are due to C-H in-plane bending vibrations. The aromatic C-H out-of-plane vibrations observed between 972- 547 cm^{-1} . The absorption band at 473 cm^{-1} are due to metal-nitrogen coordination. The metal-oxygen coordination band appeared at 430 cm^{-1} .

3.3. Thermal analysis:

The thermal analysis curve of synthesised product is shown in fig.4.

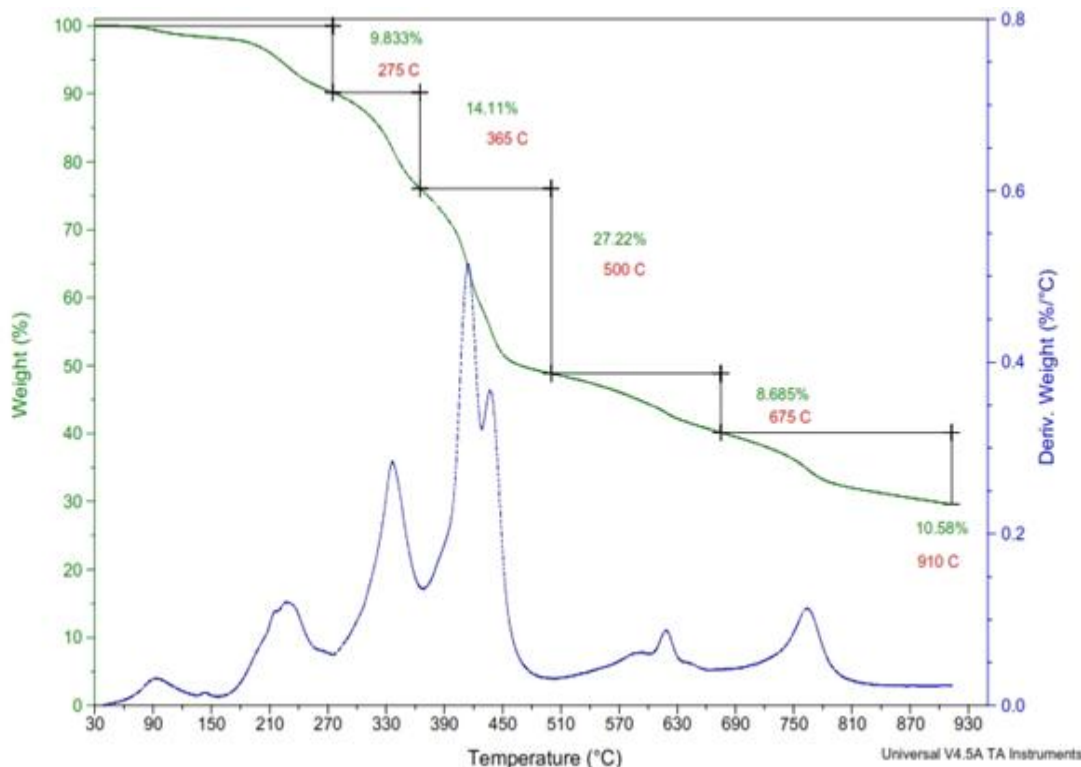


Fig.4. Thermal analysis curve of the material

The thermal stability of the material was studied by thermogravimetric analysis in nitrogen atmosphere. The thermogravimetric curve of the complex exhibits five weight losses. The first weight loss (9.83%) at 275°C represents the loss of solvent molecules. The second step of weight loss (14.11%) at 365°C corresponds to loss of coordinated benzimidazole ligands. In third weight loss (27.22%) at 500°C involves the loss of diphenic acid molecule. The remaining diphenate and imidazole group (8.68%) lose at 675°C in fourth step. The fifth weight loss (10.58%) at 910°C due to cobalt oxides. The DTA analysis of the complex shows the sharp endothermic peak at about 420°C, which is assigned to melting point of the complex [15].

3.4. Powder X-ray diffraction (PXRD) analysis:

The Powder diffraction pattern of pure compounds and synthesized complex are shown in figure.5. Powder X-ray diffraction pattern of the complex was carried out in order to obtain an idea about the lattice dynamics and purity of the compound. When compared to the PXRD pattern of pure ligands, the powder X-ray diffraction pattern of the complex confirms the formation of new material. The PXRD pattern represents a definite compound of a definite structure which is not contaminated with starting materials. Such facts suggest that the complex was amorphous in nature. PXRD pattern shows high intensity Bragg diffraction peaks. The 2θ values are 7.37°, 9.02°, 10.95°, 15.78°, 19.78°, 23.78°, 38.39°, 50.73°, 82.31°.

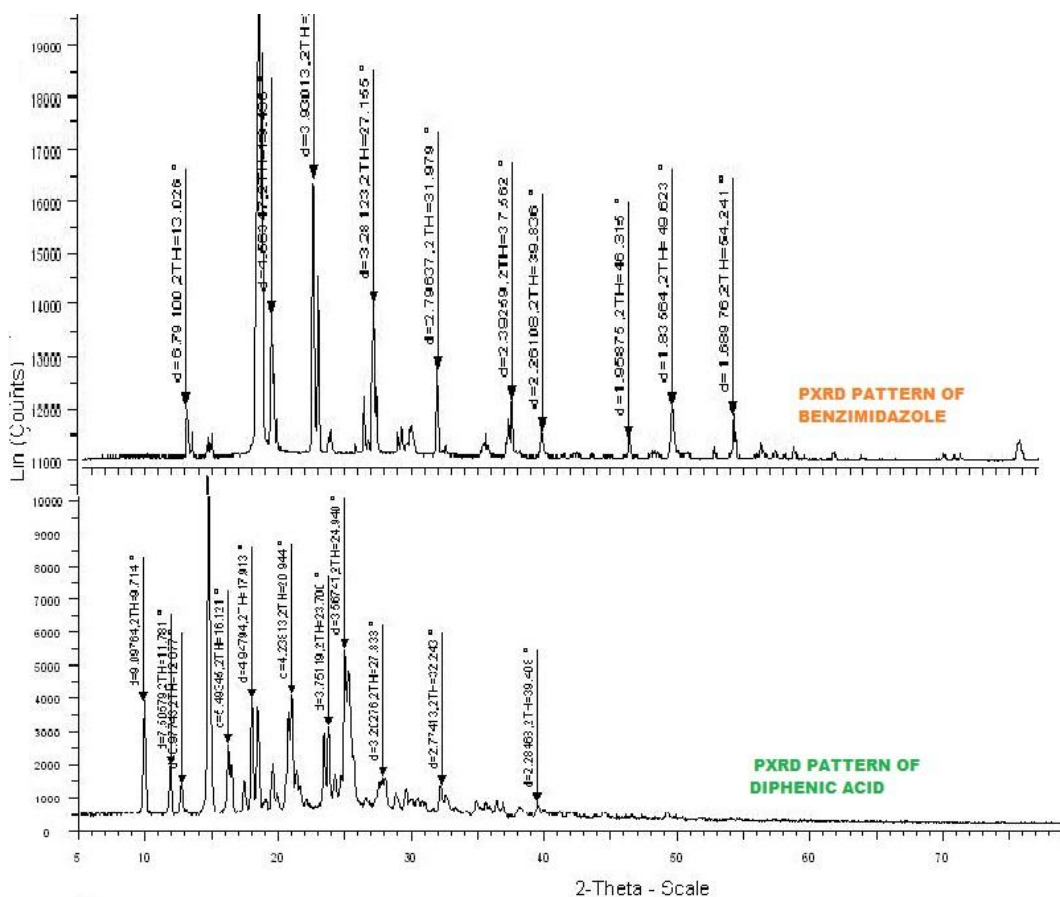


Fig.5(a) PXRD pattern of pure ligands

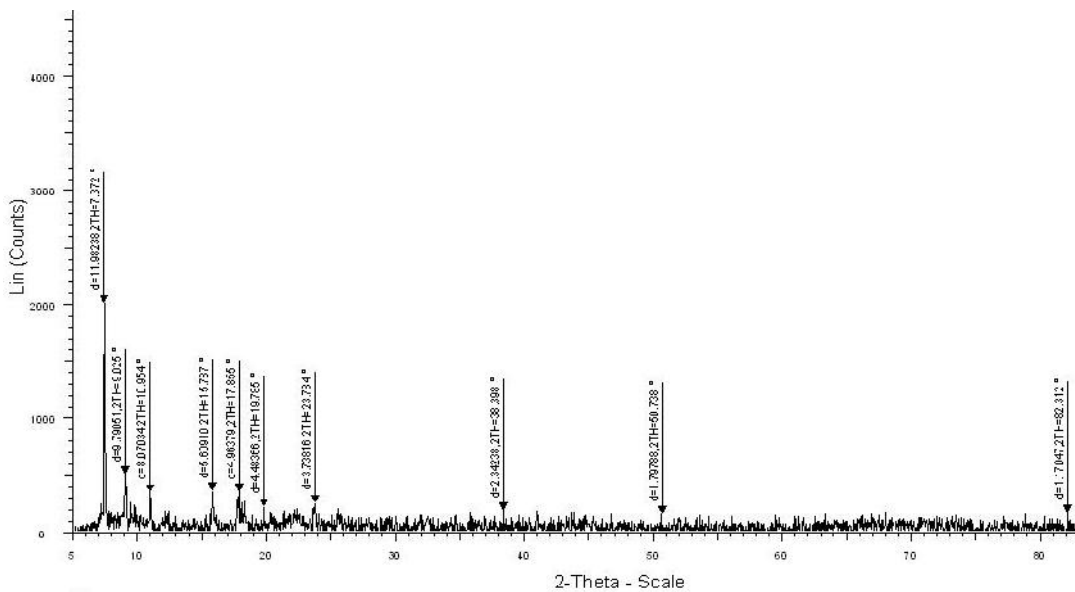


Fig.5(b) PXRD pattern of synthesized material

3.5. High Resolution Scanning Electron Microscope (HR-SEM) analysis:

High resolution scanning electron microscopic images of the synthesized material are shown in figure.6.

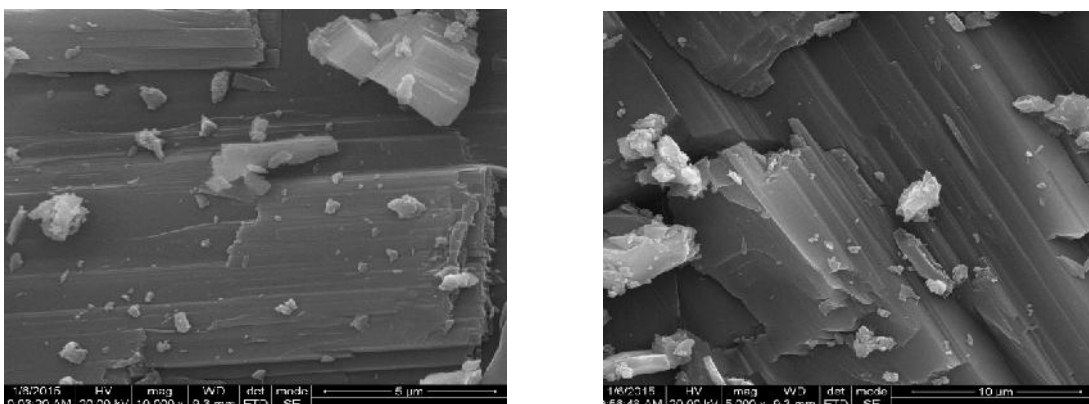


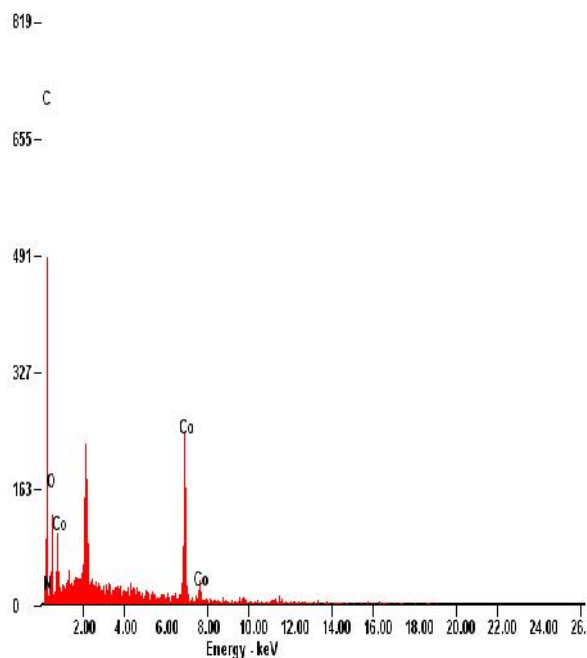
Fig.6. HR-SEM images of the material

HR-SEM images of the material represent the surface morphology of the complex. SEM images shows stepwise plate like structure and also grains present in the complex. Many single layers of the complex superimposed on one another forming the sheet-like structure. Hence, the adsorption capacity may be

more and the adsorbant can be absorbed in- between the sheets and grains.

3.6. Energy Dispersive Spectroscopy (EDS):

The Energy dispersive spectroscopy of the complex is shown in figure.7.



ELEMENT	Wt %	At %
CK	62.08	79.28
NK	05.02	05.50
OK	09.53	09.14
CoK	23.37	06.08
Matrix	Correction	ZAF

Fig.7. EDS spectra and Elemental composition of the complex

The Mass spectra of the synthesized complex are shown in figure.8.

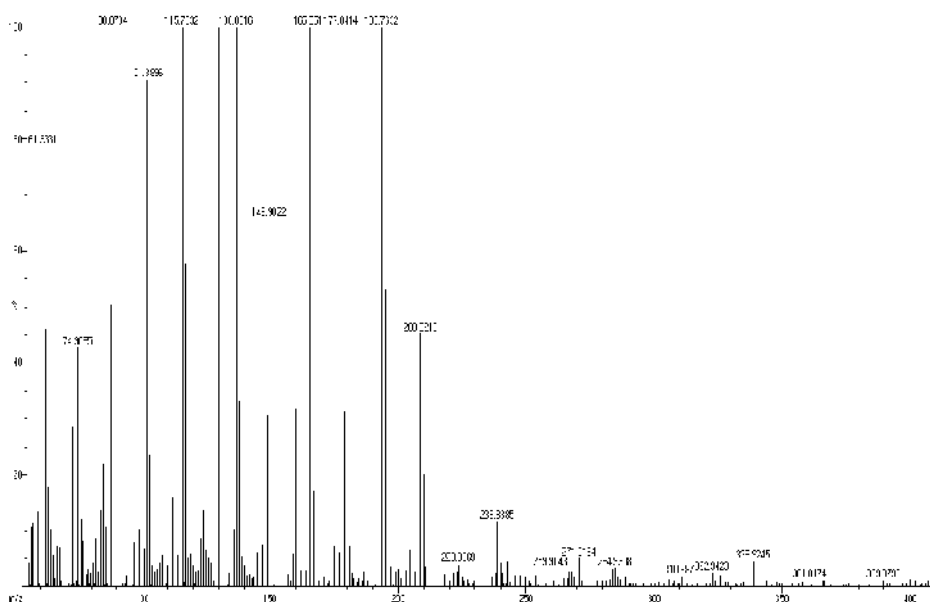


Fig.8. Mass Spectra of the complex

The mass spectrum is the plot of mass-to-charge ratio of positively charged ions against their relative abundance. The mass spectrum of the complex shows six base peaks which confirm the formation of metal-organic material. The ion with the same mass as the molecular weight of the original compound is called the molecular ion. Molecular ion has usually the highest m/z value in the spectrum. In the complex, molecular ion peak appears at 389.97. The low intensity of molecular ion peak indicates that the synthesized complex is highly branched and the rate of decomposition of parent ion is too high for its detection.

3.8. Surface Area Analysis:

Brunauer, Emmett and Teller (BET) equation explains multilayer adsorption and evaluate the surface area of metal-organic material. The BET surface area of the material was 1.46 m²/g. Surface area of metal-organic material can be evaluated using sorption isotherms.

The BET surface area data of the complex are as shown below.

BET Surface Area Report

BET Surface Area: 1.46

Slope: 2.921619 ± 0.019658 g/cm³ STP

y: 0.059276 ± 0.001569 g/cm³ STP

C: 50.288572

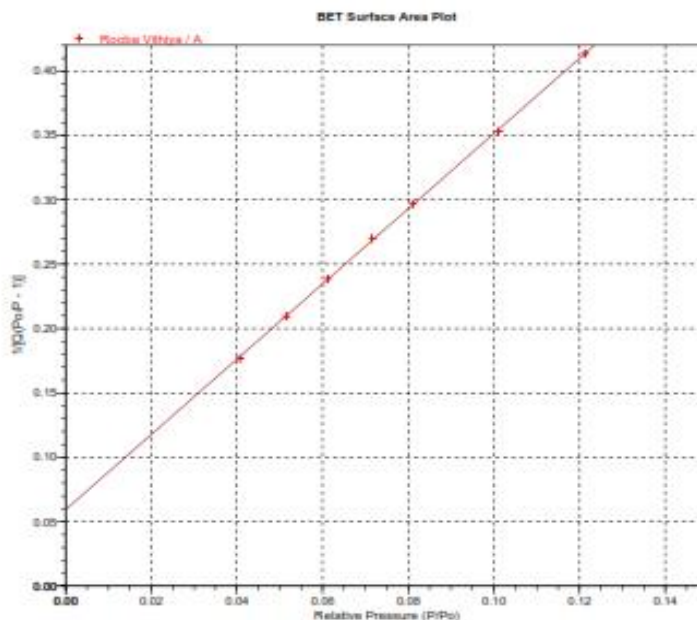
Qm: 0.335cm³/g STP

Correlation Coefficient: 0.99

Molecular Cross- Sectional Area: 0.1620 nm²

0.040664717	0.2401	0.176555
0.051425306	0.2588	0.209492
0.061118384	0.2727	0.238682
0.071529578	0.2856	0.269787
0.080970808	0.2970	0.296691
0.101095589	0.3187	0.352867
0.121195804	0.3335	0.413473

BET surface area plot of the complex are as shown below.



A plot of $1/[Q(p_0/p-1)]$ versus p/p_0 results in a straight line with a slope, $S=2.92 \text{ g/cm}^3 \text{ STP}$ and an intercept $Y = 0.06 \text{ g/cm}^3 \text{ STP}$. Then $Q_m = 0.34 \text{ g/cm}^3$ and as a result the surface area can be evaluated as $1.46 \text{ m}^2/\text{g}$. The BET Constant (C) was 50.29 and correlation coefficient was 0.99. The molecular cross – sectional area of the complex was 0.16 nm^2 .

Conclusion\

Cobalt metal-organic material of 2,2'-biphenyl dicarboxylic acid and benzimidazole have been synthesized under solvothermal conditions. On addition of benzimidazole as a neutral ligand to the reaction mixture, the dimensionality of the resulting coordination polymer increases, resulting a multi-layered structures. The complex shows good thermal stability which confirms by thermal analysis. Mass spectra of the complex show the approximate molecular weight of the complex. The formation of multi-layered structure was confirmed by HE-SEM analysis. Surface area of the complex can be calculated by surface area analysis.

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