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Crystal structure, spectral and thermal characterisation of gel grown cobalt (II) nicotinate tetrahydrate

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Abstract: Single crystals of cobalt(II) nicotinate tetrahydrate is grown by gel method for the first time. The 3D supramolecular crystal structure is stabilised by the intermolecular hydrogen bonding as revealed by the single crystal XRD data. FTIR confirms the various functional groups. Thermal analysis is carried out and the thermal and kinetic parameters of the complex are tabulated. Coats - Redfern plots for the thermal decomposition stages are depicted. The optical properties are studied by UV-Visible spectral analysis.
Keywords: gel growth, supramolecular structure, cobalt nicotinate.

1. Introduction

Pyridine derivatives possess a wide array of bioactivities and they are extensively used as ligands in the formation of co-ordination compounds[1, 2, 3, 4]. Nicotinic acid (NA) is chemically pyridine -3-carboxylic acid. It is widely known as Niacin or Vitamin B_3. NA has various remarkable applications in medicine. It is one of the most widely studied biologically active pyridine derivatives. Nicotinic acid possesses two potential donor sites: the pyridine ring nitrogen and the carboxyl oxygen, which makes it a multidentate ligand for the building up of metal organic frame works. The studies on the co-ordination complexes of nicotinic acid and its derivatives reveal their antiviral and antibacterial activity [5]. Plasma lipid lowering effect of NA and its derivatives makes it effective in the treatment of hyperlipidemia [6]. Cobalt is a trace element which forms an active center of cobalamins, for example vitamin B_{12} which is a natural organometallic compound and is the only vitamin with a metal atom. Co is essential for the transfer of alkyl groups from one molecule to another in biological systems. Metal complexes of biologically important ligands are often found more effective than the free ligand.

As a rule, MOFs are synthesized under solvo- or hydrothermal conditions in the presence of a base. Though solvothermal method has the advantage of growing new metal organic frameworks, it has the disadvantage of being irreversible, usually driven by fast kinetics of nucleation at high temperature, leading to poor quality crystals. The crystal structure of cobalt(II) nicotinate tetrahydrate (CoN) was reported by Anagnostopoulos et al in 1969 [7]. Later Jia et al. reported the growth of CoN by hydrothermal method in 2002[8]. No reports regarding the growth of CoN at ambient temperature is found. The main objective of the present work is to grow cobalt nicotinate, a metal organic frame work by conventional gel method and to check whether difference in the growth method affects the crystal structure. Crystallisation in gels is an effective and inexpensive technique for the formation of high quality defect free single crystals at ambient temperature [9]. Structural, spectral and thermal characterization of the grown CoN is done.

2. Experimental procedure

The crystallisation of the cobalt complex of nicotinic acid was accomplished using gel diffusion technique. Good quality single crystals were obtained by controlled nucleation and convection less growth offered by gel technique. Crystals were grown in single glass tubes of length 20 cm and diameter 2.5 cm. Silica gel of specific gravity 1.03 to 1.05 g/cc was prepared by dissolving sodium meta silicate (SMS) in double distilled water. Nicotinic acid of particular molarity (0.5 M – 1.5 M) was then dissolved in SMS solution. The gel was then acidified with 1M glacial acetic acid to get pH in the range 4 to 7. About 30 ml of above solution was taken in each test tube and kept undisturbed for setting. After the soldification of the gel, cobalt chloride of (0.5 M –1.5 M) was added as top reagent over the gel without damaging the gel system. The open end of the test tubes was covered with transparent plastic sheets to avoid contamination of the solution. The experimental set up was kept undisturbed for crystallisation at ambient temperature.

The single crystal XRD analysis of the crystal was carried out using Bruker AXS Kappa Apex2 CCD diffractometer. FT-IR spectrum was recorded using KBr pellets on a Thermo Nicolet, Avatar 370 spectrometer with resolution of 0.9 cm^{-1}, in the range 4000-400 cm^{-1}. Absorption spectrum of the crystals was studied using Varian Cary 5000 UV-Vis-NIR spectrometer in the range 200-1200 nm. TGA/DTA experiments were carried out in SDT Q600 V8.3 Build 101 instrument with a heating rate of 10 $^{\circ}$C/min in nitrogen atmosphere. The carbon and hydrogen contents in the sample were determined using ElementorVario-EL III CHNS Analyser.

3. Results and discussion

3.1. Crystal Growth

Using the growth procedure described in section 2.1, crystals of the complex, CoN were formed at the gel interface after two weeks. The growth process took three weeks for completion. Series of experiments were done to obtain the optimum conditions to get good quality single crystals. Nicotinic acid gets precipitated below pH 5 and above which poly crystals were grown. Good quality single crystals suitable for single crystal XRD studies were grown in gel medium of pH 5 and density 1.04g/cc with 0.5M nicotinic acid as inner reactant and 1M cobalt chloride as the top solution. The characteristic shape of the crystal is shown in Fig. 1.

Fig. 1 Photo of gel grown CoN

3.2. Crystal structure

The single crystal XRD data of a well formed crystal were collected using Bruker AXS Kappa Apex2 CCD diffractometer with graphite monochromated Mo Kα (λ= 0.71073Å) radiation. Data reduction was done using SAINT/XPREP program [11]. The program SIR92 was used for solving the crystal structure and the refinement was carried out by Full-Matrix least squares on F^2 using SHELXL-97 [12, 13]. Anisotropic thermal parameters were applied to refine all the nonhydrogen atoms. The hydrogen atoms were located from the difference Fourier maps and refined isotropically. Molecular graphics were constructed using the IUCR software Mercury (Version 3). Table1 provides the crystallographic data and processing parameters. The co-ordination environment with the atom numbering scheme of CoN is given in fig 2.

Table 1 Crystal data and structure refinement for CoN

Identification code	**CoN**
Empirical formula	$C_{12}H_{16}CoN_2O_8$
Formula weight	375.20
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/m
Unit cell dimensions	a = 14.1512(6) Å α= 90°. b = 6.8828(2) Å β= 118.273(3)°. c = 8.4897(5) Å γ = 90°.
Volume	728.25(6) $Å^3$
Z	2
Density (calculated)	1.711 g/cc
Absorption coefficient	1.224 mm^{-1}
F(000)	386
Crystal size	0.300 x 0.250 x 0.200 mm^3
Theta range for data collection	2.724 to 28.194°.
Index ranges	-18<=h<=18, -8<=k<=8, -11<=l<=11
Reflections collected	5667
Independent reflections	967 [R(int) = 0.0219]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7103 and 0.6739
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	967 / 0 / 76
Goodness-of-fit on F^2	1.187
Final R indices [I>2sigma(I)]	R1 = 0.0202, wR2 = 0.0553
R indices (all data)	R1 = 0.0213, wR2 = 0.0559
Extinction coefficient	n/a
Largest diff. peak and hole	0.333 and -0.278 e.$Å^{-3}$
CCDC No.	1435761

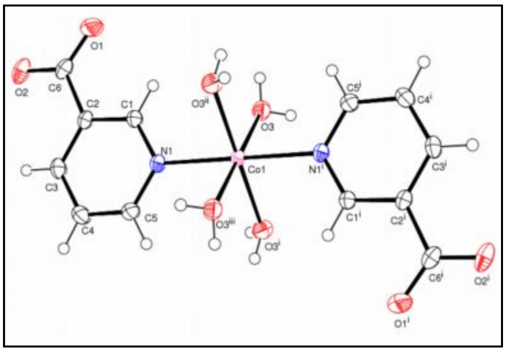

Fig. 2 Co-ordination environment in CoN

The asymmetric unit of CoN consists of a nicotinic acid ligand, a cobalt ion and one co-ordinated water molecule. Considering the co-ordination environment in the CoN crystal, each cobalt ion is co-ordinated to two different nicotinic acid ligand through the pirydil nitrogen and to four water molecules. The four water molecules define an equatorial plane. The two nitrogen atoms of the nicotinate ligands occupy the axial position of the co-ordination sphere. The nicotinate ligand co-ordinate with Co ions monodendately. The nicotinate ligands are in trans position. Here the Co-O distance has a value of 2.108A°, more or less comparable with those in the reported structure where Co-O1 and Co-O2 bond lengths are 2.104A° and 2.125A° respectively. Same in the case with the bond Co-N with a value of 2.152 A° and the bond angle N1-Co-N1 with a value of 180° [8]. The six co-ordinated cobalt ion is having an octahedral geometry. The carboxylic oxygen atoms are not co-ordinated with the metal atom, while it is engaged in hydrogen bonding with the four oxygen atoms of the co-ordinated water molecules. All atoms except the co-ordinated oxygen atoms are coplanar and the oxygen atoms are out of plane. In this case two O-H---O hydrogen bonding interactions are witnessed. The hydrogen bond O3-H3A---O1#5 with a distance of 2.6962A° forms a two dimensional hydrogen bonded plane and the hydrogen bond O3-H3B---O2#4 with a distance of 2.711A° forms the interlayer hydrogen bond chains. The distance between the centroids of two parallel pyridyl ring is 3.747 A°, indicating the existence of spatial π-π interaction [14]. In the reported structure, the distance between two rings is 3.4253 A°. Hydrogen bonding and intermolecular weak interactions are main tools for the design of supramolecular polymeric networks [15]. Here in CoN, a 3D supramolecular structure is formed by hydrogen bonding along with the spatial π-π stacking, which inturn stabilise the crystal structure. The packing in CoN is given in fig. 3

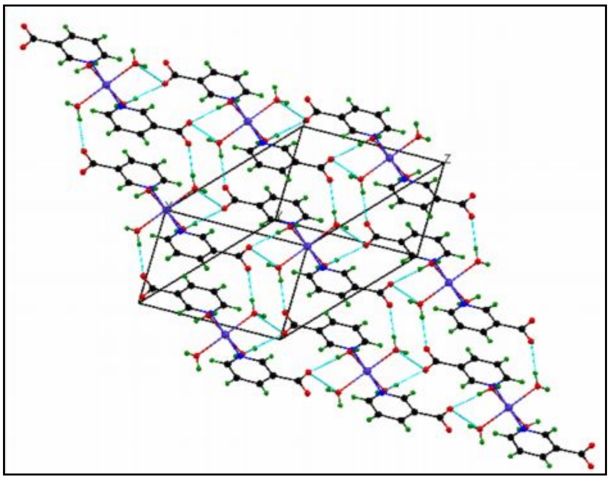

Fig. 3 Packing in CoN

3.3. FT-IR analysis

The FTIR spectrum of CoN is shown in fig. 4. The co-ordination of the metal with the organic linker is witnessed as the change in the molecular vibrational frequency. The broad band at 3270cm^{-1} due to ν(O-H) shows the presence of intermolecularly hydrogen bonded water molecules [2]. For a deprotonated carboxylic acid, the symmetric stretching frequency shifts to a lower frequency around 1600 cm^{-1} [16]. The bands at 1612cm^{-1} and 1368cm^{-1} are attributed to the asymmetric and symmetric stretch of the carboxylate groups in CoN. This supports the deprotonation of all the –COOH groups in the complex as revealed by the SXRD data. In CoN, metal atoms are co-ordinated through two pyridine nitrogen and four water molecules. The stretching vibration of the pyridine ring observed at 1588cm^{-1}in the ligand spectrum is shifted to 1565cm^{-1} in the CoN spectrum. This negative shift with respect to the ligand indicates the co-ordination of metal. The band at 529cm^{-1} may be due to the Co-N stretching. The band at 448cm^{-1} corresponds to δ(C-N-C) [17].

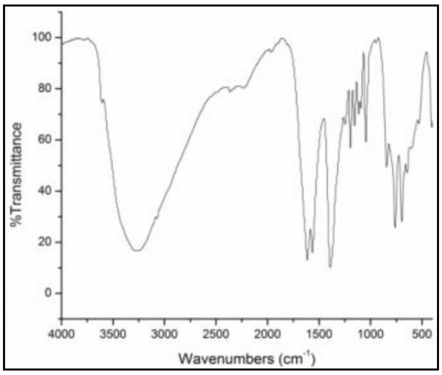

Fig. 4 FTIR spectrum of CoN

3.4 Elemental analysis

The stoichiometry of the grown CoN crystals was determined both theoretically and experimentally. Both the values are in agreement with each other and the molecular formula is derived as $(C_6H_4NO_2)Co.4H_2O$

Experimental: C- 38.43%, H- 4.33%, N- 7.58%;
Calculated: C- 38.40%, H- 4.29, N- 7.46%.

3.5 Thermal analysis

The thermal decomposition behavior of the complex has been studied from the TGA/ DTA data in nitrogen atmosphere from ambient temperature to 800ºC. The TGA/DTA curve is shown in fig. 5.

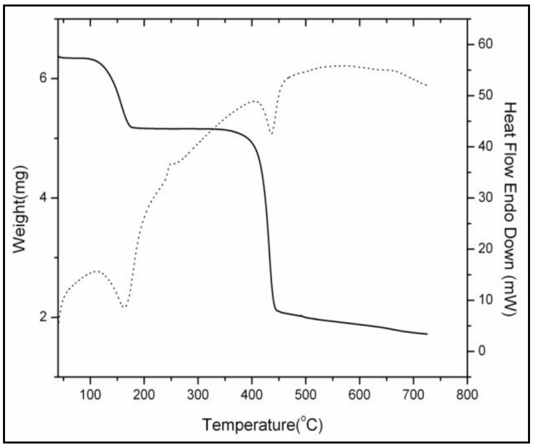

Fig. 5 TGA/DTA curves of CoN

The complex CoN shows two decomposition stages as shown by the endothermic peaks. The crystal is stable upto 160ºC indicating the absence of lattice water. The first decomposition is due to the loss of 4 co-ordinated water molecules with a mass loss of 19% (Cal. 19.2%). The endothermic peak at 163ºC corresponds to this dehydration. Thereafter the complex is found to be stable upto 400ºC. The major decomposition occurs due to the degradation of ligand with a mass loss of 49% (cal. 49.09%) leading to the formation of $CoCO_3$. This is witnessed by an endothermic peak at 434.1 ºC.

The kinetic parameters like activation energy (E), order of reaction (N), frequency factor (A) of decomposition were determined using the Coats and Redfern method [18]. The thermodynamic parameters such as standard enthalpy and standard Gibbs's free energy were also calculated and tabulated in table5 [19]. The positive value of ΔH indicates the endothermic nature of the decomposition process. The nonspontaneous nature of dissociation process is identified from the positive ΔG values. The Coats - Redfern plots for the first and second stages of thermal decomposition are given in fig. 6.

Table 5. Kinetic and thermodynamic parameters of various stages of decomposition

Kinetic parameters				**Thermodynamic parameters**		
stage	**n**	**E kJ/mol**	**logA S^{-1}**	**ΔS J/Kmol**	**ΔH kJ/mol**	**ΔG kJ/mol**
I	1.8	226.89	25.94	248.92	219.64	111.11
II	1.6	496.10	35.27	423.61	484.34	184.85

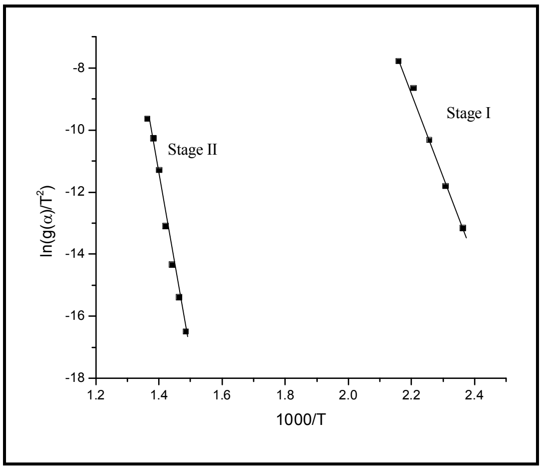

Fig. 6 Coats - Redfern plots for the first and second stages of thermal decomposition

3.6 UV- Visible spectral studies

The UV-Vis spectral analysis of the crystalline sample CoN is carried out in the range 200-800 and the spectrum is given in fig.7. The absorption band at 251 nm is attributed to the nicotinic acid ligand. In CoN, the band at 481 nm may be due to the d-d transition in cobalt. The material is found to have indirect forbidden transitions as the band gap of CoN is estimated by plotting $(\alpha h\nu)^{(1/2)}$ versus (hν) as in fig. 8. The band gap of the material is obtained by extrapolating the linear portion of the curve to zero absorption and the value is estimated as 3.64eV.

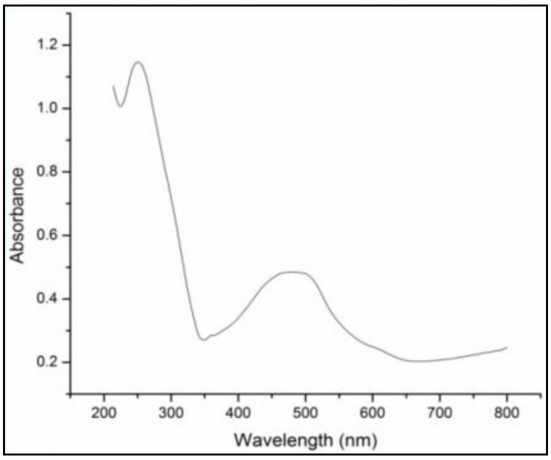

Fig. 7 Absorbance spectrum of CoN

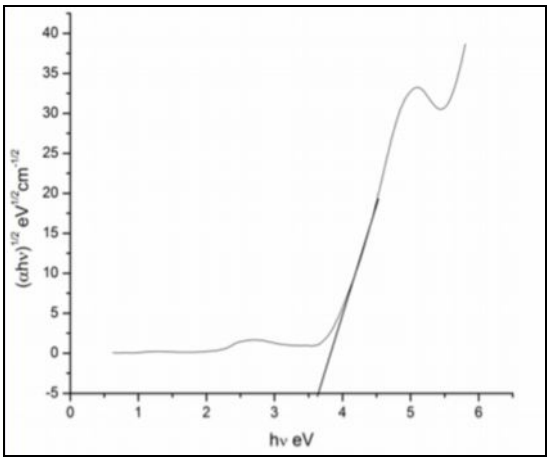

Fig. 8 Plot of alphaenergy versus energy

Conclusions

Single crystals of cobalt nicotinate are grown successfully by conventional gel method for the first time. Good quality single crystals belonging to monoclinic system, C2/m space group are grown from the gel medium of pH 5 and density 1.04g/cc with 0.5M nicotinic acid and 1M cobalt chloride. The change in the method of crystallisation does not affect the crystal structure. The 3D supramolecular crystal structure is stabilised by the intermolecular hydrogen bonding as revealed by the single crystal XRD data. The FTIR spectral analysis confirms the presence of various functional groups in the grown crystals. The elemental analysis is consistent with the chemical formula $(C_6H_4NO_2)$ $Co.4H_2O$.The thermal stability of the complex is provided by the TGA/ DTA. The porosity of the complex offers the potential for gas adsorption and storage.

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