MOFCompound Based on Azide (N_3^-) and Nicotinamide ligands withCd(II),[$Cd_3(\mu$-N_3^- $)_4$(Nicotinamide)$_2$]H_2O :Synthesis, Characterization and Photoluminescence Properties

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Introduction

The synthesis and study of mono or polynuclear coordination polymers and their characterization has been a hot topic in the field of molecular magnetism, because it acts as building blocks with applicability in molecular-based materials. In order to achieve molecular based magnets linkers such oxo, chlorido, hydroxido, alkoxo, carboxylato, or azido are often used to react with metal ions. These small bridges are very good candidate for the magnetic exchange phenomenon. The azide anion is an excellent ligand to build low dimensional coordination polymer. It is so versatile that μ-1, 1(end-on, EO), μ-1,3(end-to-end, EE), μ-1,1,3 and other modes are allowed. The most important aspects of these azido-bridged complexes are the exchange of magnetic interactions [1].

To study the magneto-structural correlation of azido-bridged complexes, various suitable co-ligands were used and magnetic properties of the complexes have systematically been investigated. Many azido-complexes including dinuclear, trinuclear, and tetranuclear species, together with 1D, 2Dand 3D coordination polymers have been reported [2]. For example, metal organic frameworks based on 4,4bipyridne or polycarboxylic ligands have been extensively studied.

The investigation reports show that introduction of nicotinic acid derivatives as coligand to the metal based azido complex may produce some interesting structures and magnetic properties due to the coordination flexibility of the various nitrogen donor atoms of the co-ligand. Nicotinamide ligand has much biological importance such as it is the component of the vitamin B-complex as well as component of the coenzyme, (NAD). It plays important role in the metabolism of living cells and some of its compounds are biologically active e.g. insulin-mimetic agents [3].Thus the structure of nicotinamide attracted the attention of many researchers. Another most important reason for using nicotinamide as ligand is that these ligands with aromatic rings such as pyridine, 2,2-bipyridine, 4,4-bipyridine, 1,10-phenanthroline and nicotinic acid

derivatives act as an antenna for the energy absorption in photoluminescent materials [4].If distance of aromatic ring in the complex is appropriate then pi-pi interaction may exist. These pi-pi interactions stabilise the MOFs structure further.

In Metal organic framework compounds, supramolecular networks are usually built through strong covalent bond and extensive lateral weak intermolecular interactions like hydrogen bonding, pi-pi stacking, C-H···pi interactions etc. Among these interactions, hydrogen bonding and pi-pi stacking interactions generally play an important role in the synthesis of coordination supramolecular architecture because of their relative strength and directional properties. As a result, many 1D,2D and 3D metal organic frameworks have been reported with weak interactions. Thus these non-covalent interactions are very important in the stabilization of self-assembly of supramolecular architectures [5].

Here we have selected metal for synthesis of metal organic frameworks i.e. Cd^{2+} because Cd^{2-} (d^{10}) metal complexes have attracted attention due to their luminescent property [6] and their coordination network structures. Many d^{10} metal coordination polymers namely $[Cd(SCN)_2(isonicotinamide)_2].H_2O$, $[Cd(SCN)_2(nicotinic\ acid)_2].H_2O$, $[Cd(SCN)(nicotinic\ acid)(H_2O)]$ and $[Cd(SCN)_2(nicotinamide)_2]_3$ are reported in literature with thiocyanate and nicotinamide as mixed ligands.

In this paper, complex $[Cd(\mu\text{-}N_3)_4(Nicotinamide)_2]H_2O(1)$ is discussed. In these complex, N_3^- and nicotinamide ligand is used. To the best of our knowledge, no framework has been reported in the literature using this combination of mixed ligands. Complex characterized through IR spectroscopy, TGA and X-ray single crystal analysis techniques. The coordination polymer $[Cd(\mu\text{-}N_3)_4(nicotinamide)_2]_n$ (1) was characterized and photoluminescence spectra was recorded at excitation wavelength of 275 nm the azide ligand has no emission band between 200 to 600 nm but nicotinamide shows luminescent behaviour and emits at 372 and 442 nm upon excitation at 275 nm. We observe two strong emissions bands centred at 425nm and 456 nm when excited to 326 nm.

Experimental

Materials and Physical Measurements

Cadmium (II) chloride (Sigma Aldrich), Sodium azide (Sigma Aldrich), Nicotinamide (Aldrich), were purchased and used without further purification. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. In order to reveal the thermal stability of compound TGA measurement has been carried out on Perkin-Elmer Diamond TGA/DTA instrument with a flow of Dry nitrogen at a heating rate of 5^0C/min from room temperature to 1000^0C (for compound-1).The fluorescent spectra were performed for compound 1 on HITACHI F-2500 fluorescence spectrometer in solid state at room temperature.

Crystallographic Details of complex-1

The crystal structure was solved by direct methods using the program SHELXS of the SHELX-97 program package [7]. Single crystal X-ray data were collected at 293(2) K on a Bruker SMART APEX diffractometer using graphite monochromatic MoKα radiation (λ = 0.71073Å).The diffraction radiation source of 'fine focused sealed tube'. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography [8]. The data integration and reduction were processed with SAINT software.An empirical absorption correction was applied to the collected reflections with SADABS using XPREP. The structure was refined on F2 by full-matrix least-squares technique using non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically fixed and treated as riding atoms using SHELXL default parameters. Crystal data and structure refinement parameters are listed in Table 1. The final R =0.0121, wR=0.0568'calc [w= $1/[\sigma 2(F_o^2)+(0.0290P)^2+7.0000P]$ where $P=(Fo^2+2Fc^2)/3$) S = 1.062, $(\Delta\rho)_{max}$ = 273 e/Å^3 , $(\Delta\rho)_{min}$ = - 0.652 e/Å^3 and $(\Delta/\sigma)_{max}$=0.090.

Geometrical Special Detail

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement Special Details

Refinement of F^2 against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2> 2sigma (F^2) is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on all data will be even larger.

Synthesis of complex-1

An aqueous solution (10 ml) of Cadmium chloride (0.183g, 1mmol) and Sodium azide (0.196g, 2mmol) was slowly added drop wise to hot aqueous solution (10ml) of Nicotinamide (0.244g, 2mmol) with stirring. Transparent colour solution was obtained. After filtration the final clear solution left undisturbed at room temperature for slow evaporation. After one week, needle shaped transparent crystals were collected and

dried in vacuum over silica gel. The crystal for X-ray study was selected manually and immersed in silicon oil.

Results and Discussion

Metal estimation for Cd (II) was done by standard procedures. The metal ion and C, H, N and S were found in relevant percentage and are listed in Table 1

Table 1: Elemental Analysis of both compounds

S.N.	Compound	Physical state	Colour	Elemental Analysis	
				Calculated (%)	Found (%)
1	'C12 H14 Cd N122 N8 O3'	Crystalline	Colourless(transparent)	C 28.9, H 2.7, N 22.2, Cd 33.2.	C 28.5, H 2.5, N 22.6, Cd 32.9.

IR Spectral Analysis for (1)

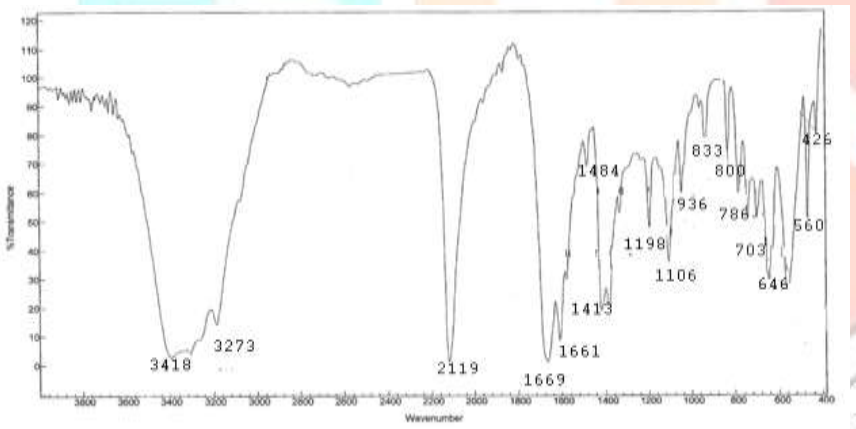

Figure 1: IR Spectrum of $[Cd(\mu\text{-}N_3)_4(Nicotinamide)_2]H_2O(1)$

In the spectrum, the absorption peak in range of 3394-3307 cm^{-1} corresponds to the symmetric- asymmetric stretching vibrations of water molecules.The broadness in the peak may be due to water molecules involve in hydrogen bonding. The sharp peak at 3156 cm^{-1} is assigned to stretching vibrations of amide groups.The carbonyl (C=O) group of amide as usual absorbs at 1669 cm^{-1} in spectrum . The free pyridine ring vibration which normally occurs at 1592 cm^{-1} shifts at lower frequency indicating pyridine ring coordination.The peak in the range of 1611-1419 cm^{-1} and 1200-700 cm^{-1} may be responsible for C-C and C-N stretching and bending vibrations respectively. The sharp peak at 2110 cm^{-1} in spectrum correspnd to N-N stretching vibration of azide molecule which is same as the value reported in literature [9].

X-ray Single Crystal Structure for (1)

X-ray analysis reveals that the compound crystallizes in triclinic space group C2/c. Each Cadmium ion is located at an inversion centre and takes octahedral coordination geometry. Each cadmium ion is surrounded by four nitrogen atoms of azide ligands at equatorial position and two nitrogen atoms of nicotinamide molecules axially completing therefore octahedral environment. Generally nicotinamide molecule exhibits bidentate coordination mode with pyridine nitrogen atom and oxygen atom of carbonyl group, but in this polymer nicotinamide act as unidentate ligand coordinated by pyridine ring nitrogen and oxygen atom of amide group is involved in hydrogen bonding. The polymer is air stable and insoluble in common organic solvents.

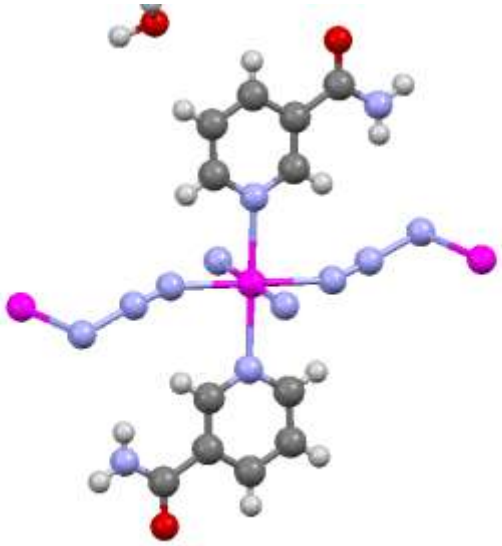

Figure 4.3: Ball and Stick model of single molecule of [Cd(μ-N^-_3)$_4$(Nicotinamide)$_2$] polymer(1)

The azide ion molecule is almost linear, with (N10-N11-N12) angle is equal to 178.1(2)° but coordinates in bent fashion exhibiting Cd-N(10)-N(11) angle of 156.0(2) and Cd-N12-N(11) angle of 97.84(2). The bond distance between Cd-N(10) (azide) and Cd-N(1)(nicotinamide) is 2.32(2) Å and 2.34(2) Å respectively. Each molecule is associated with one uncoordinated water molecule. This lattice uncoordinated water molecule is involves in hydrogen bonding with oxygen atom of amide group from nicotinamide molecules and give additional strength to the structure. The bond angles between N(12)CdN(11) and N12CdN(11) are 90.13(7)° and92.16(5)° respectively (shown in Figure 4.3). Crystal structure data are listed in Table 2.

Table 2: Crystal data for (1)

(CCDC 855589)	
Chemical formula	C12 H14 Cd N10 O3
Formula weight	497.61
Colour	transparent

Lattice Type	triclinic
Space group	C 2/c
A	24.0807(10)
B	9.8161(3)
C	7.5317(2)
A	90.00
B	93.50
Γ	90.00
V	1777
Z	4
Diffraction d	1.872
Λ	0.7107
Radiation type	MoK/a
T	293(2)K
d (max)	0.277
d(min)	-0.652
R(obs/all)	0.0199/0.0208
wR(obs/all)	0.0564 /0.0568
μ	1.562
F000	992
Goodness of fit F^2	1.059
Theta(max)	25.01
Theta(min)	3.28

Figure 4: 1D chain of [Cd(μ-N_3)$_4$(Nicotinamide)$_2$] along the b axis for (1)

Further 1D chain formed by coordination of nitrogen atoms of azide molecule to adjacent cadmium atom. As shown in Figure 4 the N_3^- ligand connect to the Cd (II) atom in end-to-end bridging fashion, giving 1D chain with (Cd···· Cd separation within each chain is 6.1Å) and angle CdN(12)N(11)= 97.84(2), N(11)N(10)Cd=156.0(2). Interestingly, these 1D chains are well arranged in structure without intermolecular forces such Hydrogen bonding, van-der Waals etc. The azide ligand is acting in the μ(1,3) fashion to bridge each cadmium centre with its nearest cadmium centre [Cd-N_3^-Cd] and having bond distance [(Cd-N10= 2.32(2), (Cd-N12=2.74(7)]. The Cd-N10 and Cd-N12 distance is in the range of the values reported in the literature[10]. The structure of the title complex may be compared with that of $[Cd(picolinato)(NCS)]_n$ in which thiocyanate shows μ(N,S) bridging mode and cadmium metal centre shows six coordination number [11].

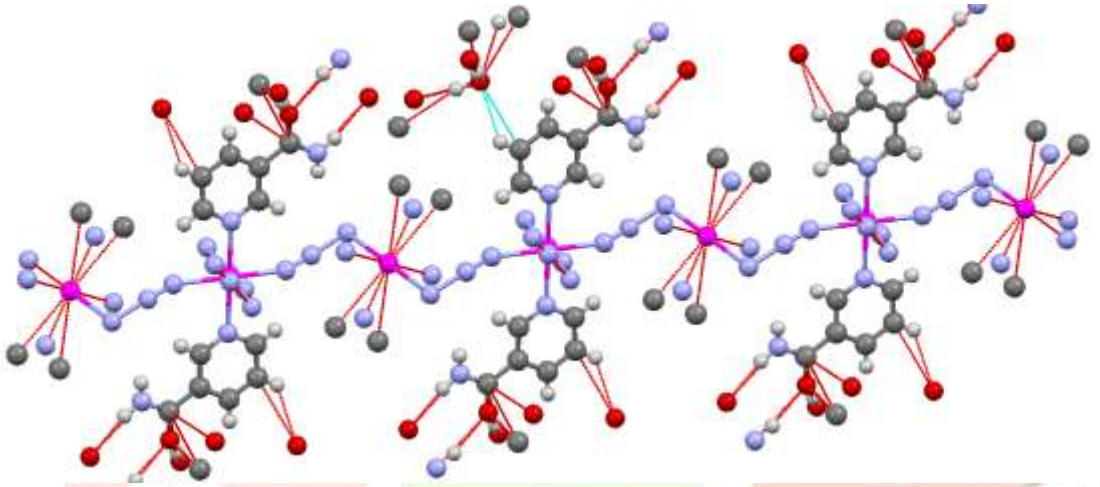

Figure 5: 1D chain of $[Cd(\mu\text{-}N_3)_4(Nicotinamide)_2]H_2O(\ )$ along the b axis (short contacts are shown in dotted red line)

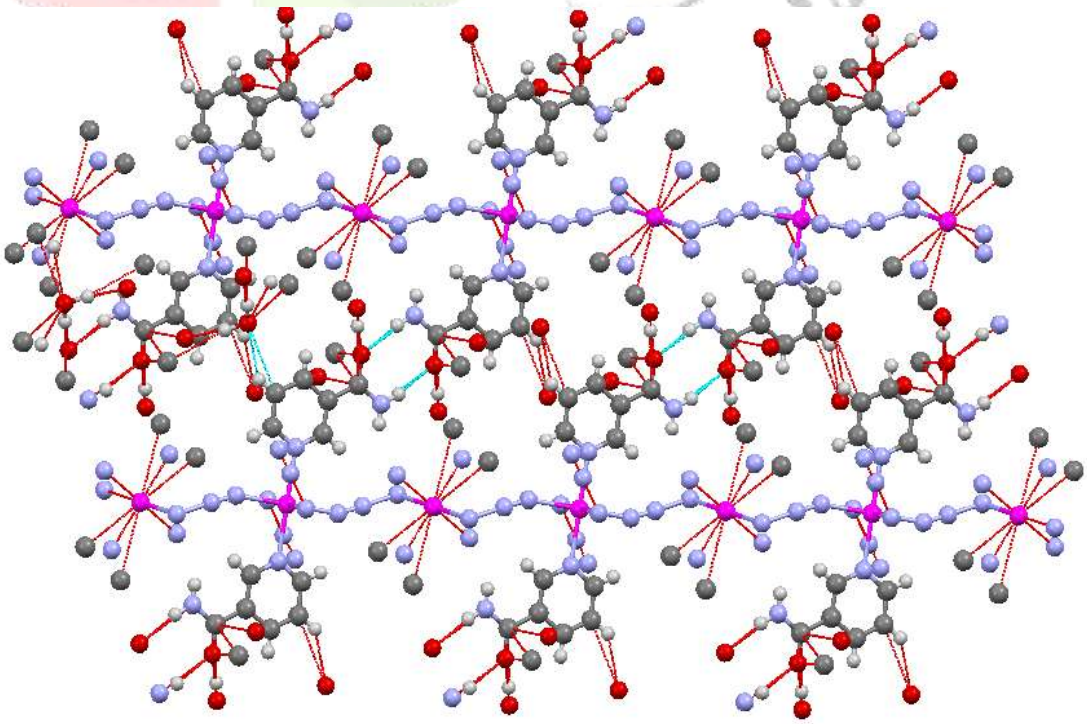

Figure 6: Hydrogen bonding between O(12)-H(12)--O(8) and N(9A)-H(9A)-O(8)

which stabilise the 2D structure along the b axis

The lattice water molecules show bifurcated hydrogen bonding with oxygen atom of carbonyl group of one nicotinamide molecules and oxygen atom of carbonyl group of another adjacent nicotinamide molecules. The oxygen atom O(12)W of water molecules donates it's both hydrogen atom and is involved in intermolecular hydrogen bonding with these layers O(12)-H(12)·····O(8) and O(12)-H(12)·····O(8). The oxygen atom of carbonyl group from nicotinamide molecule also exhibits bifurcated hydrogen bonding with hydrogen atom of water molecules and hydrogen atom of amide group of nicotinamide molecules. The interlayer interactionsO(8)····H(9A)–N(9) and O(8)····H(12)-O(12) formed between oxygen atom of nicotinamide molecule and hydrogen atom of water molecule. The bond distance between O (8)·····H(9A) and O(8)·····H(12) is 2.054Å and 1.733Å respectively. These interlayers stabilize the 2D structure. Dipole-Dipole interactions and van-der Waals interactions are also responsible for the packing of the molecules in the unit cell.

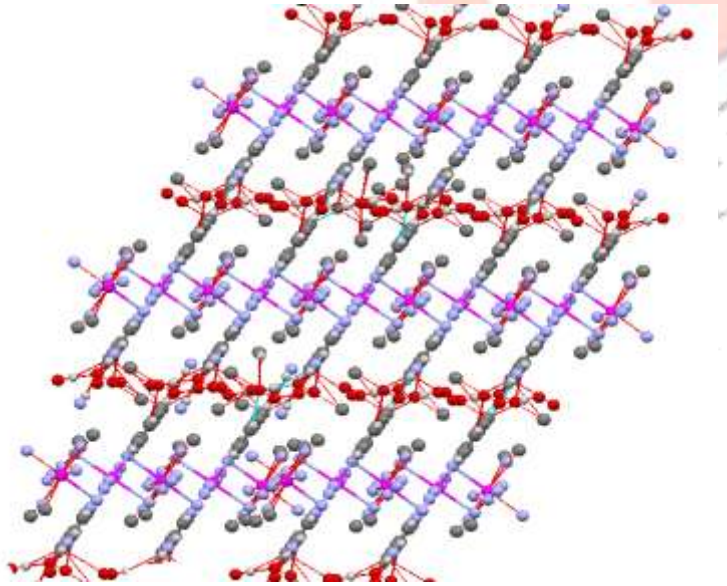

Figure 7: 2D grid like chain structure of $[Cd(\mu\text{-}N^-_3)_4(Nicotinamide)_2]H_2O(1)$ along the b axis

The ligand N_3^- adopts μ(1,3) coordination mode, it connected to adjacent Cd atom. So, it makes a bridge between two Cd atoms with Cd-Cd distance of 6.18Å (Fig.4.8).

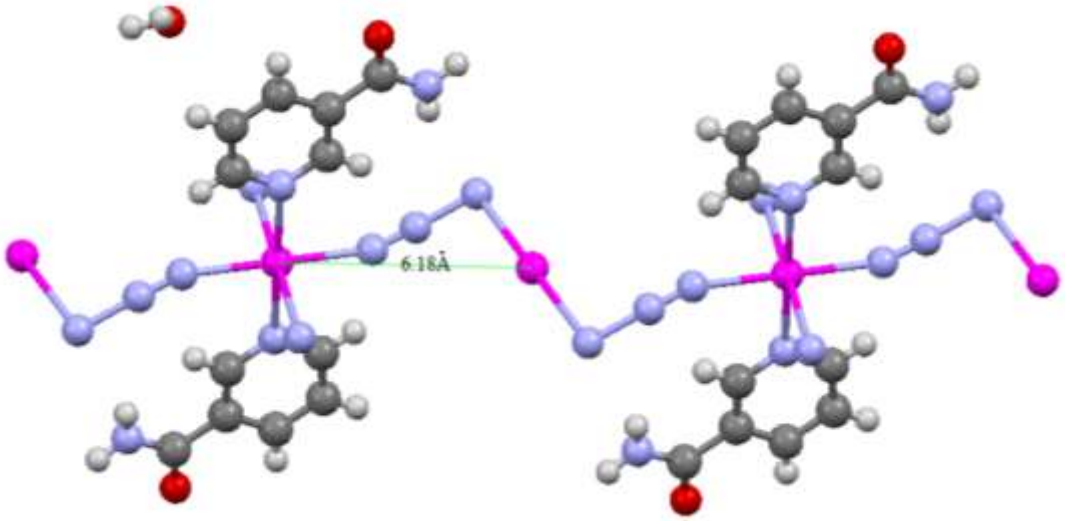

Figure 8: shows distance between Cd-Cd atoms of neighbouring molecule of $[Cd(\mu\text{-}N^-_3)_4(Nicotinamide)_2]H_2O(1)$ along the b axis

The azide ligand shows ambidentate ability. This ligand may adopt end to end (μ-1, 3) or end on coordination mode. In this compound central Cd ion (having octahedral environment) coordinates with four neighbouring Cd ion through bridging (end-to-end 1, 3μ) azide ligand (as shown in Figure 9).

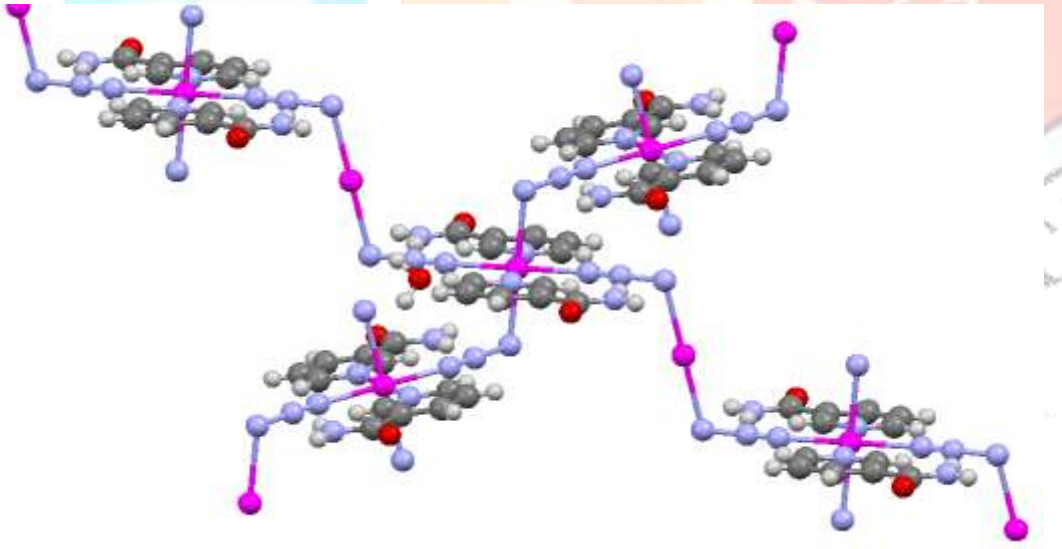

Figure 9: showing ($\mu_{1,3}$) bridging through azide along the a axis (central Cd ion bonded with four different Cd ion through bridging N_3^- anion ligand) in $[Cd(\mu\text{-}N^-_3)_4(Nicotinamide)_2]H_2O(1)$polymer

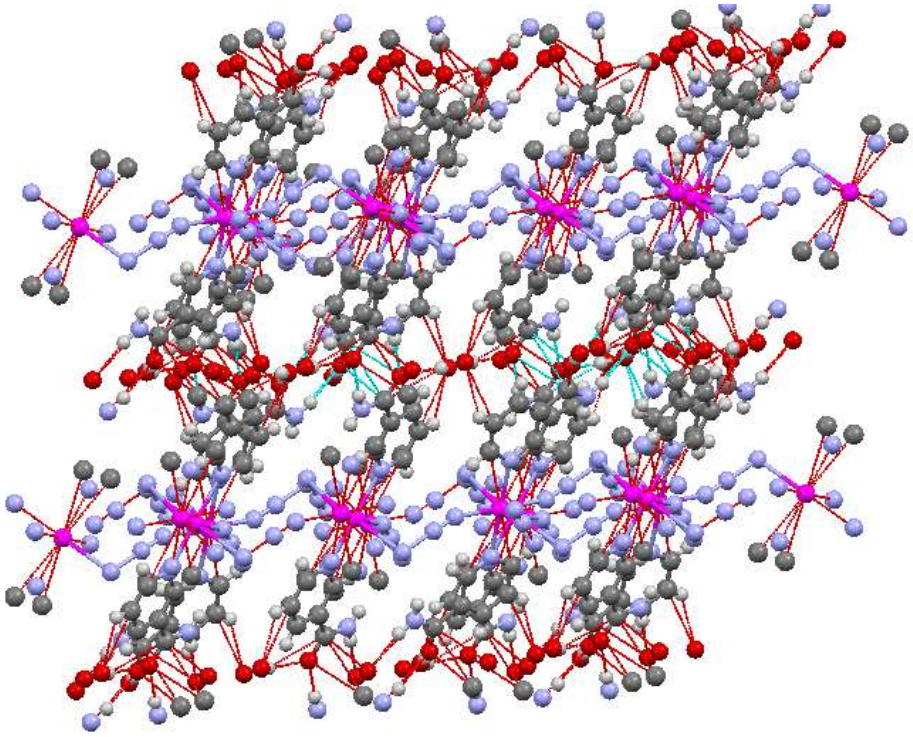

Figure 10: Perspective view of 3D structure of [Cd (μ-N_3^-)$_4$(Nicotinamide)$_2$]H_2O(1) polymer along the b axis

The cadmium atom equatorially coordinated with four bridging N_3- ligand. The two N_3- ligands bridged two cadmium ions along the x-axis and another two more N_3- ligand coordinated along y and z axis, producing thereby 3D network. The 3D array is further stabilised through pi-pi stacking and supramolecular forces such as intermolecular hydrogen bodings via N (9)-H(9A)····O(8) and Van-der Waal forces etc.

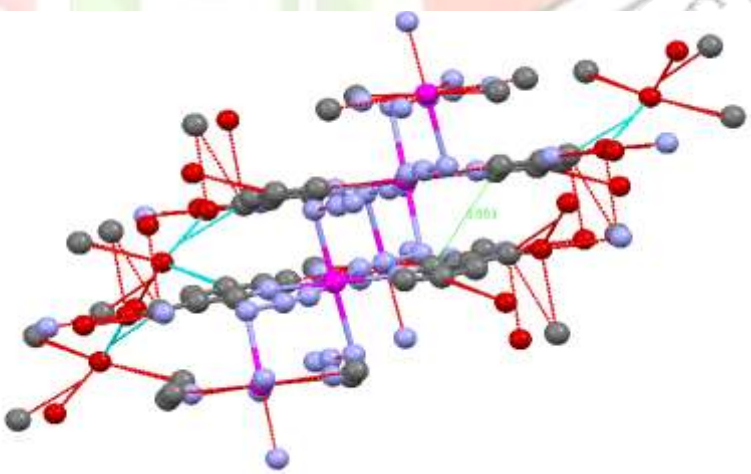

Figure 11: shows distance between two pyridine ring along the b axis

The cadmium metal centre is coordinated with two nicotinamide molecules axially with bond angle N1CdN1=180.00(5).Thus in 3D structure two pyridine rings of neighbouring molecules are parallel to each other. However, no pi-pi stacking is observed as distance between the two benzene rings is more than 4.0Å. The selected bond length and bond angles are listed in Table 3 and 4 respectively.

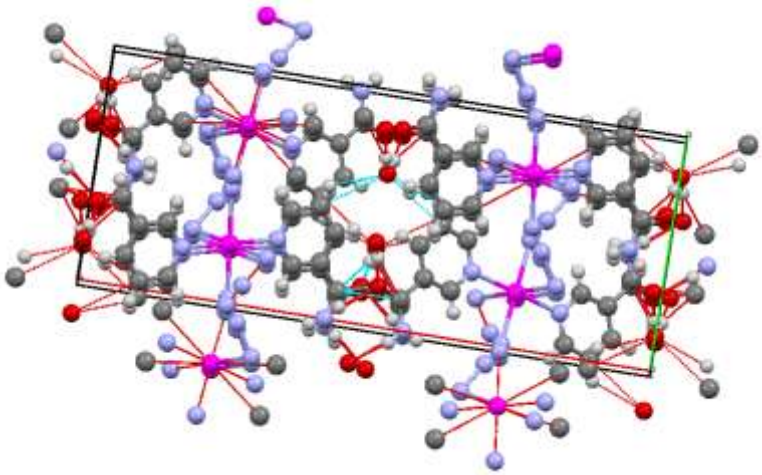

Figure 12: Packing Diagram of [Cd (μ-N^-_3)$_4$(Nicotinamide)$_2$]H_2O polymer along the b axis

The crystal packing reveals that interesting supramolecular interactions are generated from multiple hydrogen bonding between lattice hydrogen (H12) atom of water molecules and oxygen atom (O8) of carbonyl group from nicotinamide molecules.

Table 3: Selected bond angles (˚) for (1)

Atom1	Atom2	Atom3	Angle
N1	Cd	N10	90.13(7)
N1	Cd	N1	180.00(7)
N1	Cd	N10	89.87(7)
N1	Cd	N12	92.16(5)
N1	Cd	N12	87.84(5)
N10	Cd	N1	89.87(7)
N10	Cd	N10	180.00(7)
N10	Cd	N12	92.38(5)
N10	Cd	N12	87.62(5)
N1	Cd	N10	90.13(7)
N1	Cd	N12	87.84(5)
N1	Cd	N12	92.16(5)
N10	Cd	N12	87.62(5)
N10	Cd	N12	92.38(5)
N12	Cd	N12	180.00(2)
N11	N12	Cd	97.84(9)
Cd	N1	C2	123.0(2)
Cd	N1	C6	118.9(2)
C2	N1	C6	118.1(2)
N1	C2	H2	118.5(2)
N1	C2	C3	122.9(2)
H2	C2	C3	118.5(3)
C2	C3	C4	117.9(2)
C2	C3	C7	123.4(2)
C4	C3	C7	118.7(2)
C3	C4	H4	120.2(3)
C3	C4	C5	119.6(2)
H4	C4	C5	120.2(3)
C4	C5	H5	120.4(3)
C4	C5	C6	119.1(3)
H5	C5	C6	120.5(3)
N1	C6	C5	122.5(2)

Atom1	Atom2	Atom3	Angle
N1	C6	H6	118.7(3)
C5	C6	H6	118.8(3)
C3	C7	O8	119.2(2)
C3	C7	N9	119.2(2)
O8	C7	N9	121.6(2)
C7	N9	H9A	117(2)
C7	N9	H9B	123(2)
H9A	N9	H9B	120(3)
Cd	N10	N11	156.0(2)
N12	N11	N10	178.1(2)
N11	N12	Cd	97.84(9)
Cd	N1	C2	123.0(2)
Cd	N1	C6	118.9(2)
C2	N1	C6	118.1(2)
N1	C2	H2	118.5(2)
N1	C2	C3	122.9(2)
H2	C2	C3	118.5(3)
C2	C3	C4	117.9(2)
C2	C3	C7	123.4(2)
C4	C3	C7	118.7(2)
C3	C4	H4	120.2(3)

Table 4: Selected bond length (Å) for (1)

Atom1	Atom2	Length
Cd	N1	2.340(2)
Cd	N10	2.322(2)
Cd	N1	2.340(2)
Cd	N10	2.322(2)
Cd	N12	2.7454(7)
Cd	N12	2.7454(7)
N12	N11	1.657(3)
N12	Cd	2.7454(7)
N1	C2	1.345(3)
N1	C6	1.339(4)
C2	H2	0.930(3)
C2	C3	1.383(4)
C3	C4	1.391(4)
C3	C7	1.502(4)
C4	H4	0.929(3)
C4	C5	1.371(4)
C5	H5	0.929(3)
C5	C6	1.379(4)
C6	H6	0.930(3)
C7	O8	1.235(3)
C7	N9	1.329(4)
N9	H9A	0.88(4)
N9	H9B	0.82(3)
N10	N11	1.158(3)
N12	N11	1.657(3)
N12	Cd	2.7454(7)
N1	C2	1.345(3)

N1	C6	1.339(4)
C2	H2	0.930(3)
C2	C3	1.383(4)
C3	C4	1.391(4)
C3	C7	1.502(4)
C4	H4	0.929(3)
C4	C5	1.371(4)
C5	H5	0.929(3)
C5	C6	1.379(4)
C6	H6	0.930(3)
C7	O8	1.235(3)
C7	N9	1.329(4)
N9	H9A	0.88(4)
N9	H9B	0.82(3)
N10	N11	1.158(3)
O12	H12	1.03(3)
O12	H12	1.03(3)

Thermal Analysis for $[Cd(\mu\text{-}N_3)_4(Nicotinamide)_2]H_2O(1)$

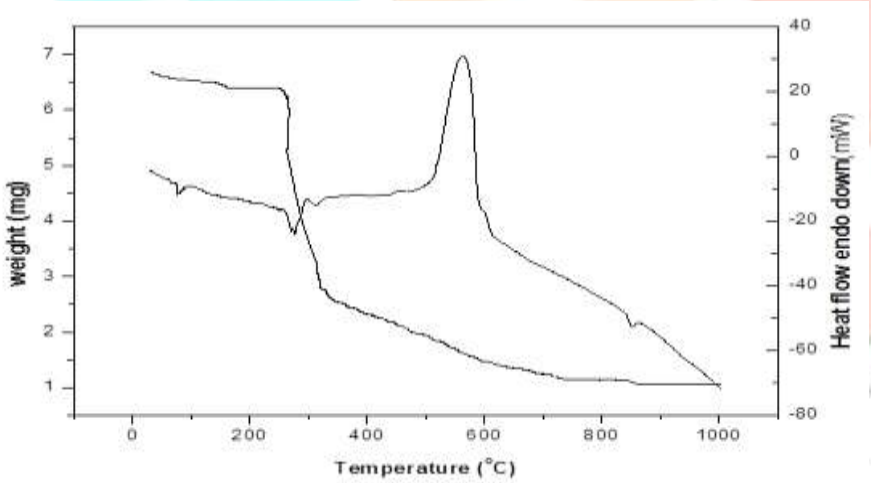

Figure 13: Thermo-gram of $[Cd(\mu\text{-}N_3)_4(Nicotinamide)_2]H_2O$ polymer (1)

The coordination polymer is stable up to 70°C followed by a rapid and very small weight loss due to release of uncoordinated water molecule. The weight loss due to release of uncoordinated water molecule is 2.1% (found) (calculated-2.0%). The TGA curve also shows two major step weight losses. The first major step weight loss is in the temperature range of 220^0C -330^0C, which corresponds to the loss of four molecule of azide. The calculated weight loss is 42.87% (found- 42.66%) which is supported by endothermic peak. The second major weight loss is recorded in temperature range of 250°C-650°C, where both nicotinamide molecules were released and corresponds to sharp exothermic peak. Finally sample oxidised to cadmium oxide. (Figure 13)

Photoluminescence property of $[Cd(\mu\text{-}N^-_3)_4(Nicotinamide)_2]H_2O(1)$

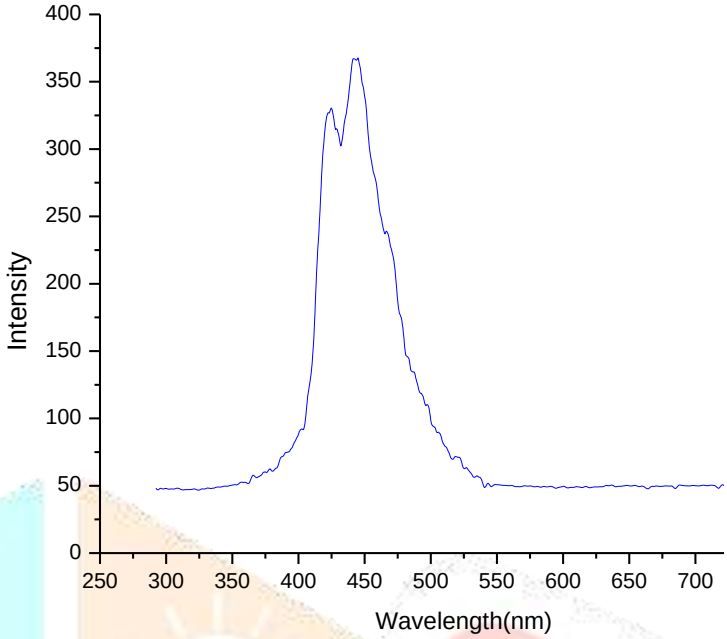

Figure 14: Luminescence spectra for $[Cd(\mu\text{-}N^-_3)_4(Nicotinamide)_2]H_2O(1)$

Inorganic and organic luminescent materials have been explored and realized for their various functionalities and applications in different devices. Their unique functionalities can be attributed to the narrow emission and high colour purity generation. The interest in organic luminescent materials has been motivated due to their applications in organic light emitting diodes (OLEDs) in which a thin film of a luminescent organic material is incorporated between the two conductors. Assembly of both inorganic and organic components into metal organic frameworks (MOFs), or coordination networks are certainly very promising as a multifunctional luminescent materials. Both inorganic and the organic moieties can provide the platforms to generate luminescence, while metal ligand charge transfer generated luminescence within MOFs can add another aspect to luminescent properties.

As on today, hundreds of luminescent MOFs have been reported by different research groups and these are of many types. In our compound the azide ligand has no emission band between 200 to 600 nm but nicotinamide shows luminescent behaviour and emits at 372 and 442 nm upon excitation at 275 nm [12]. We observed two strong emission bands centred at 425nm and 456 nm when excited to 326 nm. These emission bands seem to arise mainly from intraligand pi-pi transitions. The large red shifts in the band and large increase in the intensity of the band may be due to interaction of ligand orbital and metal orbital, giving thereby a ligand to metal charge transfer transition(LMCT).Similar emissions have also been observed in other Cd(II) polymers of thiocyanate ligand [13].

Conclusion

This paperis mainly based on azido complexes with nicotinamide as coligand. The compound is synthesized of Cd^{2+} $[Cd(\mu\text{-}N^{-}_{3})_4(Nicotinamide)_2]H_2O$ (1). Compound is characterized with X-ray Single Crystal Analysis, IR spectroscopy thermal analysis and variable temperature magnetic susceptibility. In compound (1) each cadmium centre shows distorted octahedral geometry. Each cadmium ion is surrounded by four nitrogen atoms of azide ligands at equatorial position and two nitrogen atoms of nicotinamide molecules axially. The N_3^- ligand connects to the Cd (II) atom in end-to-end bridging fashion. Each molecule is associated with one uncoordinated water molecule. This lattice uncoordinated water molecule is involved in hydrogen bonding with oxygen atom of amide group from nicotinamide molecules and gives additional strength to the structure.The photoluminescence spectra of coordination polymer $[Cd(\mu\text{-}N_3)_4(nicotinamide)_2]_n$ (1) was recorded at excitation wavelength of 326 nm, two emission bands centred at 425 nm and 456 nm were obtained. These emission bands seem to arise mainly from ligand to metal charge transfer transition (LMCT).

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