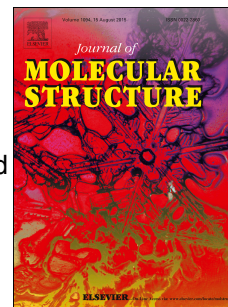


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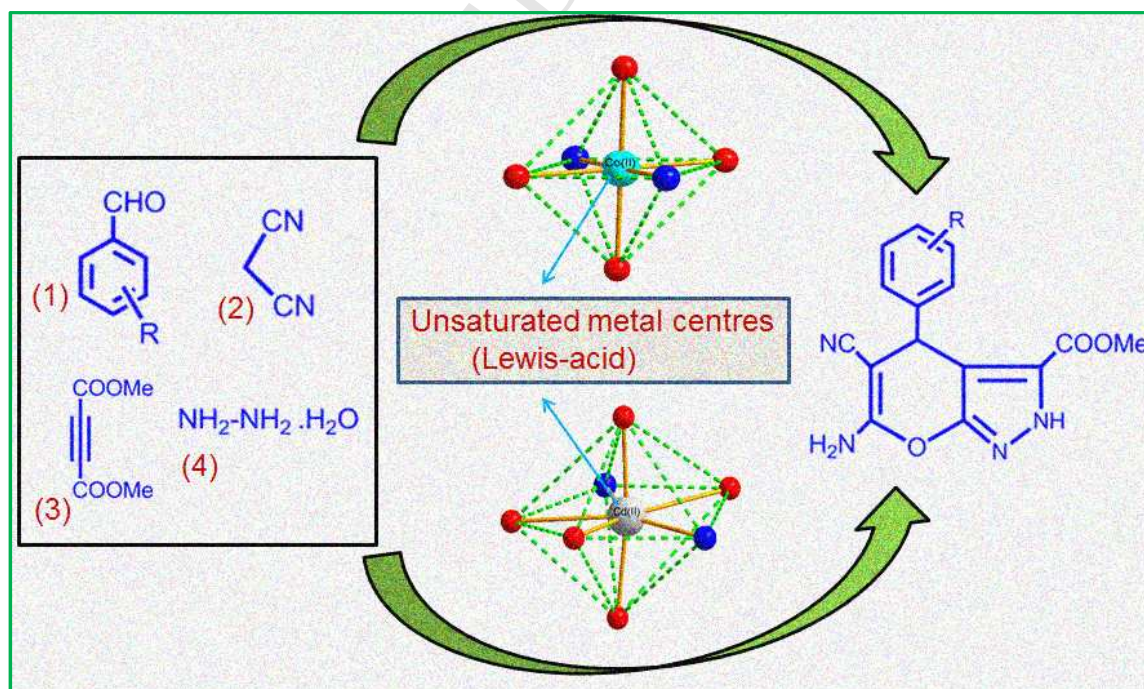
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Graphical Abstract:



Synthesis, characterisation and catalytic activity of 4, 5-imidazoledicarboxylate ligated Co(II) and Cd(II) metal-organic coordination complexes

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Abstract:

Two mono nuclear coordination complexes, namely, [Co(4,5-Imdc)₂(H₂O)₂] (**1**) and [Cd(4,5-Imdc)₂(H₂O)₃].H₂O (**2**) were constructed using Co(II) and Cd(II) metal salts with 4,5-Imidazoledicarboxylic acid (4,5-Imdc) as organic ligand. Both **1**, **2** were structurally characterized by single crystal XRD and the results reveal that **1** belongs to *P21/n* space group with unit cell parameters [*a* = 5.0514(3) Å, *b* = 22.5786(9) Å, *c* = 6.5377(3) Å, β = 111.5°] whereas, **2** belongs to *P21/c* space group with unit cell parameters [*a* = 6.9116(1) Å, *b* = 17.4579(2) Å, *c* = 13.8941(2) Å, β = 97.7°]. While Co(II) in **1** exhibited a six coordination geometry with 4,5-Imdc and water molecules, Cd(II) ion in **2** showed a seven coordination with the same ligand and solvent. In both **1** and **2**, the hydrogen bond interactions with mononuclear unit generated 3D-supramolecular structures. Both complexes exhibit solid state fluorescent emission at room temperature. The efficacy of both the complexes as heterogeneous catalysts was examined in the green synthesis of six

pyrano[2,3,c]pyrazole derivatives with ethanol as solvent via one-pot reaction between four components, a mixture of aromatic aldehyde, malononitrile, hydrazine hydrate and dimethyl acetylenedicarboxylate. Both **1** and **2** have produced pyrano[2,3,c]pyrazoles in impressive yields (92-98%) at room temperature in short interval of times (< 20 min), with no need for any chromatographic separations. With good stability, ease of preparation and recovery plus reusability up to six cycles, both **1** and **2** prove to be excellent environmental friendly catalysts for the value-added organic transformations using green principles.

Keywords: Metal-organic coordination compound; 4,5-imidazoledicarboxylic acid; Hydrothermal synthesis; Heterogeneous catalysis; Multi-component reaction; Pyranopyrazoles.

1. Introduction

Metal-organic coordination compounds form important division of advanced materials which generally possess both the organic and inorganic characteristics [1-4]. The construction of coordination compounds involves the combination of metal ions/clusters and organic linkers, which cause the unique characteristics to their structures [5-7]. The high surface area, tunable pore apertures and low density etc., of compounds provide prospective scope in the catalysis, gas storage, drug delivery, magnetism and optical fields [8-11]. The Coordination compounds are preferred as finest choice for many value-added applications due to their permanent porous nature which can be utilized for a cause and then regained without any damage to the framework [12-15]. The structural integrity of coordination compounds mainly depends upon the nature of metal ion and ligand, while pH, solvent, temperature and metal/ligand ratios have significant influence [16-19]. Appropriate selection of ligands is of main priority for a well-designed compound with unique properties [20-23]. N-heterocyclic aromatic

carboxylates, especially 4,5-imidazoledicarboxylic acid (4,5-Imdc) is a well-known polycarboxylate ligand with versatile coordination modes, with two nitrogen and four oxygen atoms that can form coordination bonds in the preparation of adaptable coordination compounds [24, 25]. In addition to the six donor atoms, 4,5-Imdc can also induce non-covalent interactions like hydrogen bonding, which tend to develop a new supramolecular topology and higher dimensionality compounds. More than thirteen coordination modes are possibly exhibited with six donor atoms of 4,5-Imdc ligand and in a supramolecular assembly, probable connections between the units can be achieved only through deprotonation of carboxylic groups of ligand [26-30].

One of the distinct advantages of metal-organic coordination compounds is in heterogeneous catalysis, as they possess active sites in both the metal centre and organic linker which can possibly contribute to their enhanced activity [31, 32]. The flexibility in their synthesis and effective control over their pore sizes, place the compounds in the frontier ahead of activated carbon and zeolites. For the last one decade, the utilization of coordination compounds has increased as alternative catalysts due to their simple separation, reusability and lesser leaching tendencies [33, 34]. As of now, variety of coordination compounds have been employed as solid catalysts or catalyst supports for a various organic transformations viz. Knoevenagel condensation [35], oxidation [36], aldol condensation [37], Friedel–Crafts reactions [38], hydrogenation [39], Biginelli reaction [40] etc. Most of the catalysed organic reactions occur due to the development of unsaturated metal sites in complex structure and their Lewis or Brønsted acidic character [41]. To build chemically and thermally stable coordination complexes, in addition to the use of modern synthetic techniques, high valence metal ions and N, O containing ligands are employed [42].

Multi-component reaction (MCR) is an attractive synthetic option for various organic reactions relative to the traditional multi-step procedure, where all reactants (more than two)

are placed in a single container for producing the desired products with no need for separation and purification of intermediates [43, 44]. The use of MCR approach has rapidly expanded in the synthetic chemistry in developing novel multi-substituted heterocyclic molecules. Heterocyclic compounds, especially pyranopyrazoles have been extensively explored for their pharmacological and physiological active characteristics. Pyranopyrazole derivatives are widely utilised in the manufacturing of active compounds containing the anticancer, antimalarial, antiulcer and anti-depressant activities [45]. Hence, the methods for synthesis of pyranopyrazoles in an environmentally benign manner are of importance. Various researchers have reported synthesis of pyranopyrazoles derivatives by using different methods and catalysts with different magnitude of limitations and successes [46, 47]. Literature shows that Moosavi et al. [48] have prepared pyrano[2,3-*c*]pyrazole derivatives through one-pot, four-component condensation of mixture of aromatic aldehyde, malononitrile, hydrazine hydrate and ethyl acetoacetate under no solvent condition at 80 °C by using heterogeneous ionic liquid catalyst as disulfonic acid imidazolium chloroaluminate {[Dsim]AlCl₄}. Zolfigol et al. [49] have synthesised varied pyrano[2,3-*c*]pyrazoles using isonicotinic acid as catalyst under solvent free conditions at 85 °C by employing aromatic aldehydes, malononitrile, hydrazine hydrate and ethyl acetoacetate. Tamaddon and Alizadeh [50] have reported the preparation of pyrano[2,3-*c*]pyrazoles and the reaction comprised of aryl aldehyde, malononitrile, hydrazine hydrate and ethyl acetoacetate in water at 50-60 °C and biodegradable surfactant Cocamidopropyl betaine (CAPB) as catalyst giving 88-96 % yields. In most cases, those reactions demanded refluxing or higher temperature conditions plus and needed longer reaction times. In earlier studies, we have reported the synthesis of varied heterogeneous catalysts and their catalytic performance in the preparation of different heterocyclic moieties of interest with excellent yields [51-53].

In this communication we report the preparation of two coordination complexes, namely $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ (**1**) and $[\text{Cd}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**2**) by hydrothermal technique and elucidation of their structures. The efficacy of the two complexes as heterogeneous catalysts was examined for selective synthesis of pyrano[2,3,c]pyrazole derivatives involving four components and one-pot reaction.

2. Experimental

2.1 Materials and methods

Reagent grade chemicals and solvents were used as supplied with no further purification. Cadmium nitrate tetrahydrate, $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (Acros Organics); Cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (Merck, Germany); 4,5-Imidazole dicarboxylic acid (Sigma-Aldrich); N,N'-dimethylformamide, Ethanol, Methanol (Merck, Germany); All aromatic aldehydes, hydrazine hydrate, malononitrile, and dimethyl acetylene dicarboxylate were purchased from Sigma Aldrich. De-ionised water was used throughout the experiment. Perkin Elmer "Spectrum Two" FT-IR spectrophotometer was used to obtain the infrared spectra. "Mettler Toledo TGA/DSC-1" apparatus was used for thermogravimetric analysis under N_2 in the temperature range 25 and 800 °C, with a heating rate of 10 °C min⁻¹. The C, H, and N microanalyses were performed with the Thermo Scientific FLASH-2000 elemental analyzer. Luminescence spectrum of the solid sample was recorded at room temperature using a Perkin Elmer LS-55 Fluorescence Spectrometer. ¹H-NMR, ¹⁵N and ¹³C spectra of organic products were obtained using Bruker advance 400 spectrometer at ambient temperature conditions.

2.2 Preparation of $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ (**1**)

$\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.0582 g, 0.2 mmol), 4,5-Imidazoledicarboxylic acid (0.0312 g, 0.2 mmol) and NaOH (0.008 g, 0.2 mmol) in H_2O (10.0 mL) was placed in a Teflon-lined stainless steel

(23 mL) container and the sealed container was heated for 48 h at 140 °C. Then, at a cooling rate of 6 °C/h the mixture was cooled to room temperature. The reddish color crystals suitable for diffraction studies were recovered by filtration followed by subsequent washings with water. Elemental analysis found: C 29.60%, H 2.46% and N 13.71%. Calculated for $C_{10}H_{10}CoN_4O_{10}$: C 29.65%, H 2.48% and N 13.83%

2.3 Preparation of $[Cd(4,5-Imdc)_2(H_2O)_3].H_2O$ (**2**)

A similar procedure described for Co(II) was also used for the Cd(II) containing complex, using $Cd(NO_3)_2 \cdot 4H_2O$ (0.0616 g, 0.2 mmol), 4,5-Imidazoledicarboxylic acid (0.0312 g, 0.2 mmol) and NaOH (0.008 g, 0.2 mmol). In complex **2** preparation, a mixture of water (8.0 mL) and methanol (2.0 mL) was used in place of pure water. White color crystals of pure compound were collected by filtration followed by washings with water. Elemental analysis found: C 24.20%, H 2.83% and N 11.43%. Calculated for $C_{10}H_{14}CdN_4O_{12}$: C 24.28%, H 2.85% and N 11.32%

2.4 X-ray crystal structure determination

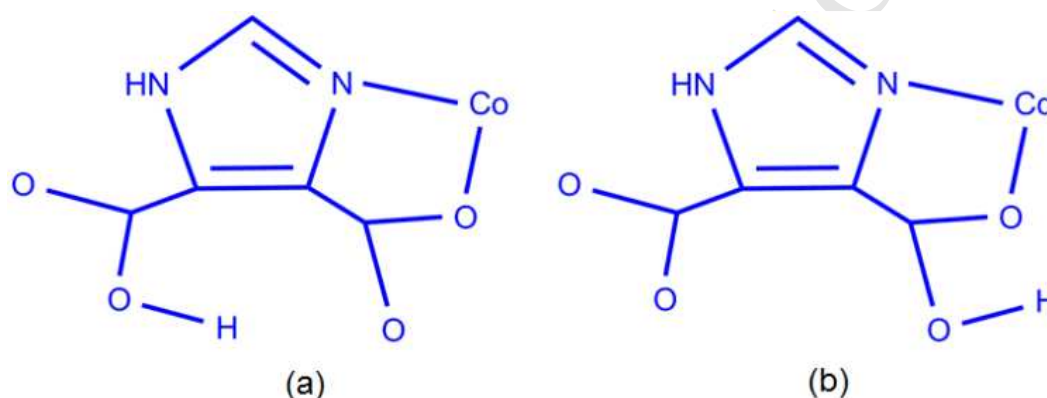
A CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer was employed to generate the single-crystal X-ray diffraction data for both the complexes. Graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(2) K was used for collection of data. The crystal data was analysed using the CrysAlisPro CCD software and standard phi-omega scan techniques for scaling and reducing were done by CrysAlisPro RED software. While SHELXS-97 [54] by direct methods was used for solving the structures, SHELXL-97 software with full matrix least-squares [55] was employed for further refining the structures. All the hydrogen atom locations were identified based on differences in

electron density map and were forced to ride on the respective non-hydrogens. Anisotropically, all non-hydrogen atoms were refined.

3. Results and Discussion

3.1 Crystal structure of $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ (**1**)

Single crystal X-ray indicates that the asymmetric unit contains one crystallographically unique Co(II) ion, one unit of ligand, and two coordinated water molecules. The organic linker 4,5-Imdc in this complex exhibits single kind of coordination mode.



Scheme 1. Bonding modes of 4,5-Imdc in (a) **1** and (b) **2**

As shown in the scheme 1a, the nitrogen and oxygen atoms chelate the central metal atom, whereas the second carboxylate group is involved in hydrogen bonding. Table 1 summarised the details of crystal data and refinement details.

Table 1: Crystal data, Data collection and Refinement details of **1** and **2**

Complex	1	2
Empirical formula	C ₁₀ H ₁₀ Co N ₄ O ₁₀	C ₁₀ H ₁₄ Cd N ₄ O ₁₂
Formula weight	405.15 g/mol	494.65 g/mol
Wavelength (Å)	0.71073	0.71073
Space group	P21/n	P21/c
T(K)	150	150
a (Å)	5.0514(3)	6.9116(1)
b(Å)	22.5786(9)	17.4579(2)
c(Å)	6.5377(3)	13.8941(2)
$\alpha(^{\circ})$	90.0	90.000(0)

$\beta(^{\circ})$	111.50(1)	97.76(0)
$\gamma(^{\circ})$	90.0	90.000(0)
$V(\text{\AA}^3)$	693.75(17)	1661.14(45)
Z	2	4
$\rho_{\text{cal}}(\text{g}/\text{cm}^3)$	1.93938	1.97776
$F(000)$	410	984
$\mu(\text{MoK}\alpha)(\text{mm}^{-1})$	10.389	1.390
θ range, deg	3.92- 70.54	2.96-25.0
Index range	$-4 \leq h \leq 6,$ $-27 \leq k \leq 16,$ $-7 \leq l \leq 5$	$-8 \leq h \leq 7,$ $-20 \leq k \leq 20,$ $-16 \leq l \leq 16$
Data/restraints/parameter	1286/0/121	2930/9/284
R_1 [on F_o^2 , $I > 2\sigma(I)$]	0.0518	0.020
wR_2 [on F_o^2 , $I > 2\sigma(I)$]	0.1282	0.052
Crystal size (mm^3)	0.21*0.18*0.16	0.23*0.18*0.14
GOOF	1.095	1.061

As illustrated in Fig. 1, the central Co1 is coordinated by six atoms i.e., two nitrogen atoms (N1, N1ⁱ) from two different 4,5-Imdc ligands, two oxygen atoms (O2, O2ⁱ) from carboxylate groups and two oxygen atoms (O1, O1ⁱ) from two coordinated water molecules and consequently adopts an octahedral geometry (Fig. 2a). For the central metal atom (Co²⁺), the positioning of donor atoms from 4,5-imdc and water molecules perpendicular to each other, further confirms its octahedral geometry.

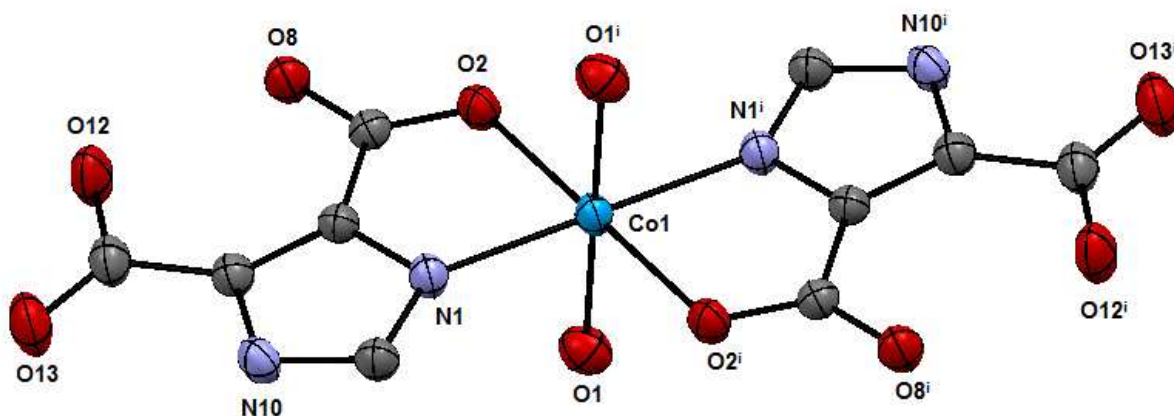


Fig. 1. Coordination environment of Co(II) metal ion of complex **1** in ortep view with 50% probability (hydrogen atoms omitted for clarity)

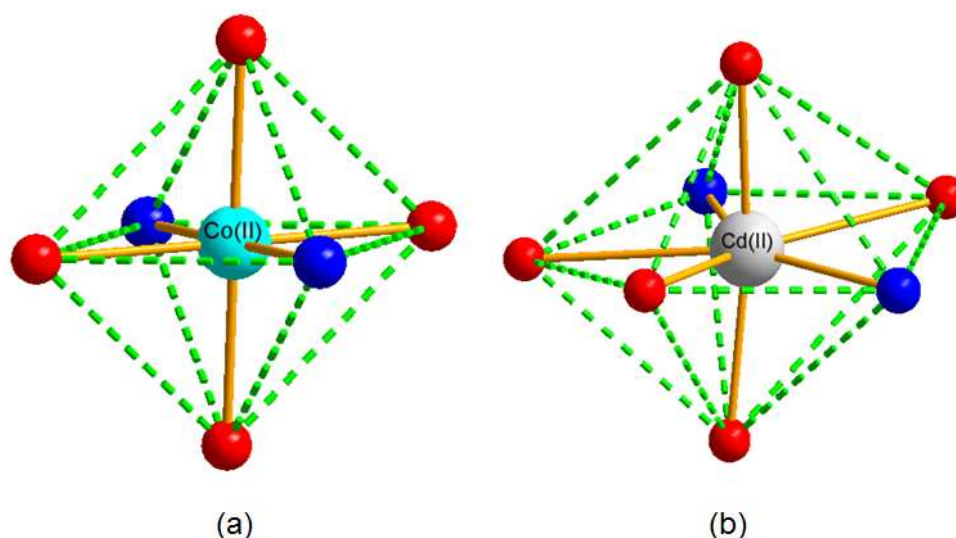


Fig. 2. Geometries (a) complex **1** and (b) complex **2**

All atoms are arranged in the same plane with respect to metal centre, which is confirmed by bond angles $\text{N1-Co1-N1}^i = 180.00(5)^\circ$, $\text{O1}^i\text{-Co1-O1} = 180.00(5)^\circ$, $\text{O2}^i\text{-Co1-O2} = 180.00(5)^\circ$. The ligand, 4,5-Imdc and coordinated water molecules are almost perpendicular to each other is indicated by the fact that the angle O1-Co1-O2 , N1-Co1-O1^i are $89.56(8)^\circ$ and $93.35(9)^\circ$, respectively. In this complex the bond distance of imidazole nitrogen to Co(II) is $2.119(2) \text{ \AA}$ (Co-O), while the ortho carboxylate oxygen of the ligand to Co is 2.096 \AA (Co-N). The hydrogen bonding interactions between the ligand and water molecules possess bond distances of 2.729 , 2.886 , 3.121 and 2.525 \AA ($\text{O1-H4A} \cdots \text{O2}$, $\text{N2-H10} \cdots \text{O4}$, $\text{N2-H10} \cdots \text{O5}$, $\text{O4-H12} \cdots \text{O3}$ respectively) (Table 2) connect the adjacent molecules together and form a three dimensional supramolecular architecture.

Table 2: H-bonds list (\AA , $^\circ$) for **1**

D-H---A	D-H	H---A	D---A	D-H---A
O1-H4A---O2	0.86	1.94	2.729	152
N2-H10---O4	0.92	1.99	2.886	166
N2-H10---O5	0.92	2.57	3.121	119
O4-H12---O3	0.82	1.71	2.525	176

Symmetry codes: $1-x, -y, 1-z$; $1/2+x, 1/2-y, -1/2+z$

While Fig. 3, depicts the hydrogen bonding pattern, Fig. 4 shows the polyhedral view of supramolecular network of the complex. The respective bond lengths and bond angles are summarised in Table S1.

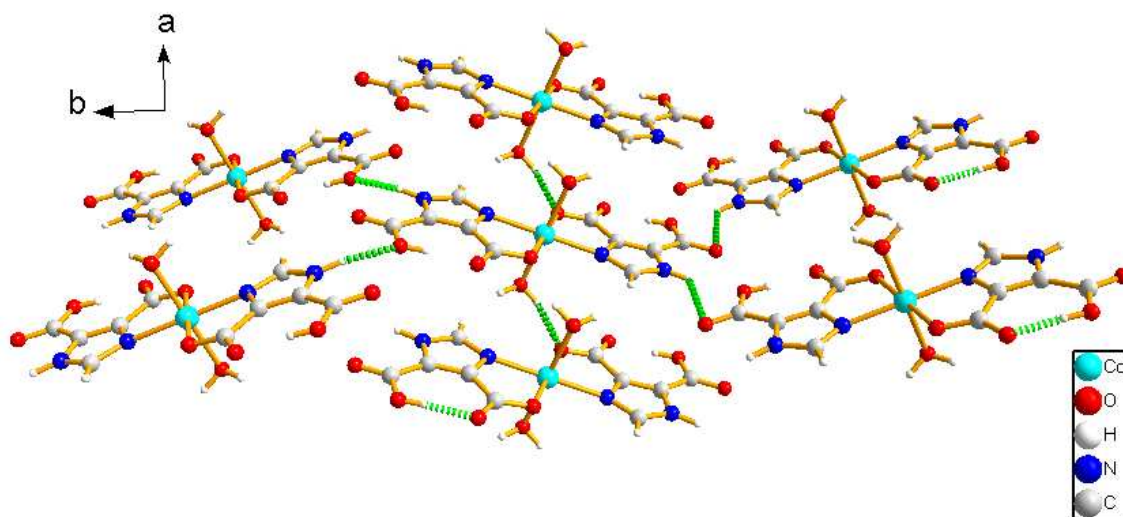


Fig. 3. Hydrogen bonding pattern in **1**

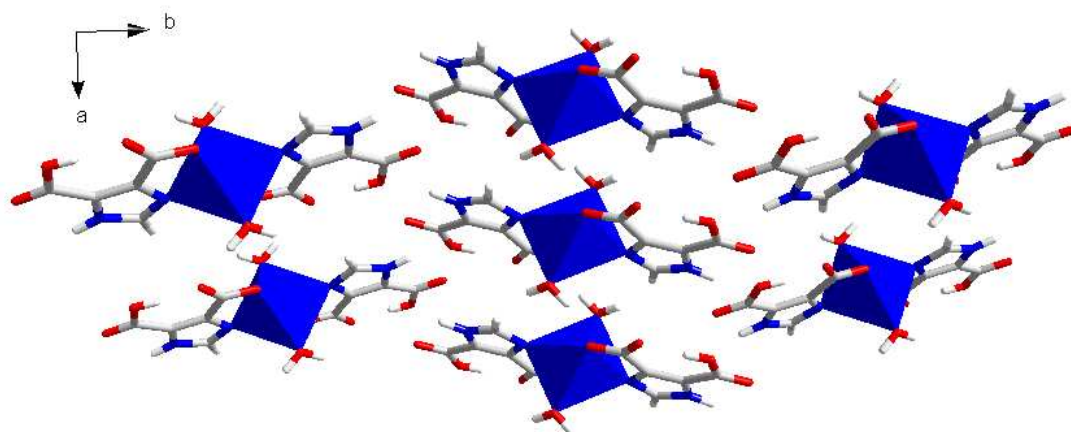


Fig. 4. (a) Prospective polyhedral view of **1**

The FT-IR spectrum of **1** is illustrated in Fig. 5. The absorption bands at 1500 cm^{-1} and 1442 cm^{-1} indicate the $\text{C}=\text{C}$ stretching vibrations of aromatic 4,5-Imdc. The bands at 1583 cm^{-1} and 1385 cm^{-1} are due to asymmetric and symmetric vibrational frequencies of COO^- group,

respectively. A weak absorption at 3317 cm^{-1} indicates the N-H stretching vibrations of imidazole ring. The appearance of a band at 3022 cm^{-1} represents the O-H stretching vibrations of free carboxylic group. The absorption band around 1725 cm^{-1} shows the vibrations of un-protonated carboxylic groups in the structure. A strong stretching vibrational frequency at 1134 cm^{-1} is attributed to the C-O group of carboxylate. The appearance of band at 1240 cm^{-1} represents the C-O stretching frequency of deprotonated carboxylic group. Moreover, the absorption bands at 453 and 632 cm^{-1} represent the Co-O and Co-N stretching vibrations [56].

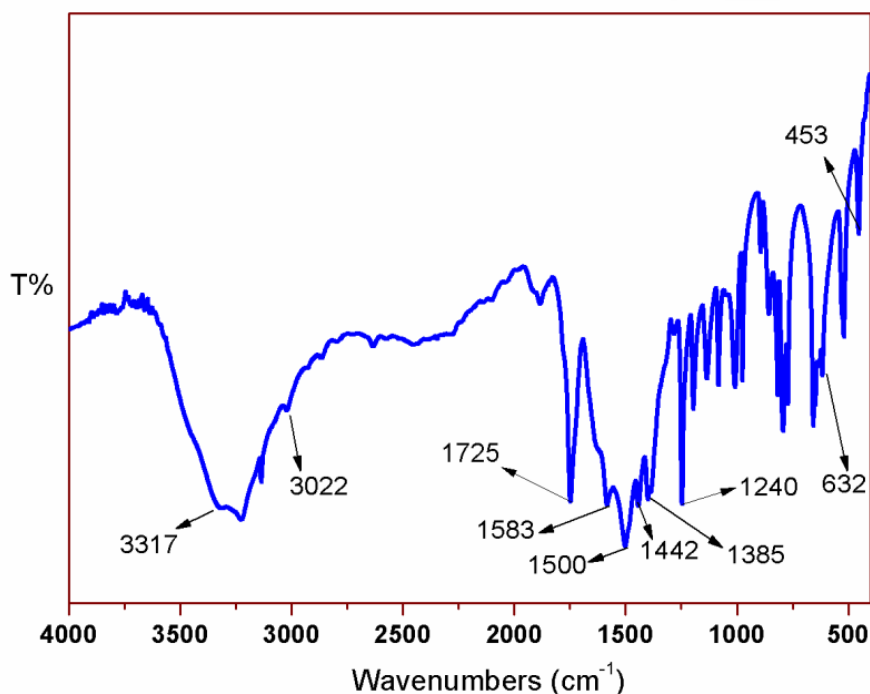


Fig. 5. FT-IR spectrum of **1**

3.2 Crystal structure of $[\text{Cd}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**2**)

The asymmetric unit of complex contains one crystallographically unique Cd(II) ion, two 4,5-Imdc ligands, three coordinated water molecules and one uncoordinated water molecule. The crystal data and refinement details are summarised in Table 1. In this complex, the central metal atom binds with nitrogen and oxygen atoms of ligand to form a five membered ring as

shown in the scheme 1b. As depicted in the Fig. 6, the central metal Cd1 ion is hepta coordinated by two nitrogen atoms (N1, N3) and two oxygen atoms (O4, O8) from two different 4,5-Imdc ligands and three oxygen atoms (O1,O2,O3) from coordinated water molecules. It exhibits a distorted pentagonal bipyramidal geometry (Fig. 2b), which is confirmed by the O1-Cd1-O3 and other bond angles recorded. The bond distances of Cd-N are 2.265 Å whereas Cd-O bond distance is between 2.277 to 2.375 Å. The coordinated nitrogen atoms occupied the axial positions with bond angles of N1-Cd1-O1:92.59(6)° and N3-Cd1-O1:90.02(6)°, while coordinated water molecules sit in the equatorial positions. The hydrogen bond interactions occur between imidazole (N, O atoms) and water molecules. The bond distance of O—H----O is around 2.450 to 3.084 Å and N—H----O is around 2.815 to 3.005 Å (Table 3). These hydrogen bonds between the mononuclear units make the molecule extend into a three dimensional supramolecular architecture. Fig. 7 shows the hydrogen bonding pattern in the complex and Fig. 8 illustrates the extended polyhedral view. The details of bond lengths and bond angles are summarised in Table S1.

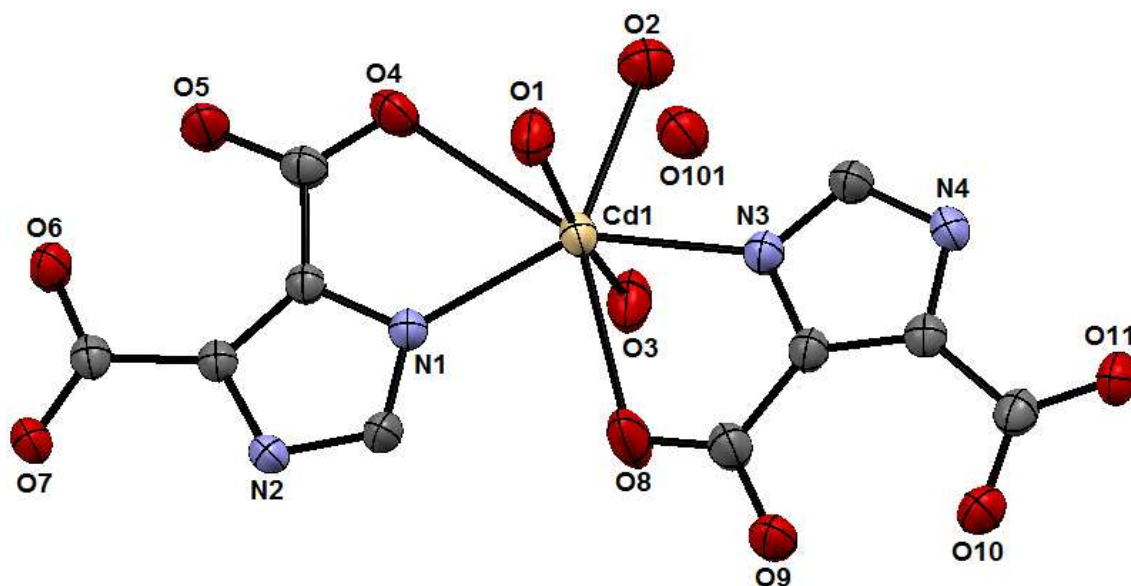


Fig. 6. Coordination environment of Cd(II) metal ion of complex **2** in ortep view with 50% probability (hydrogen atoms omitted for clarity)

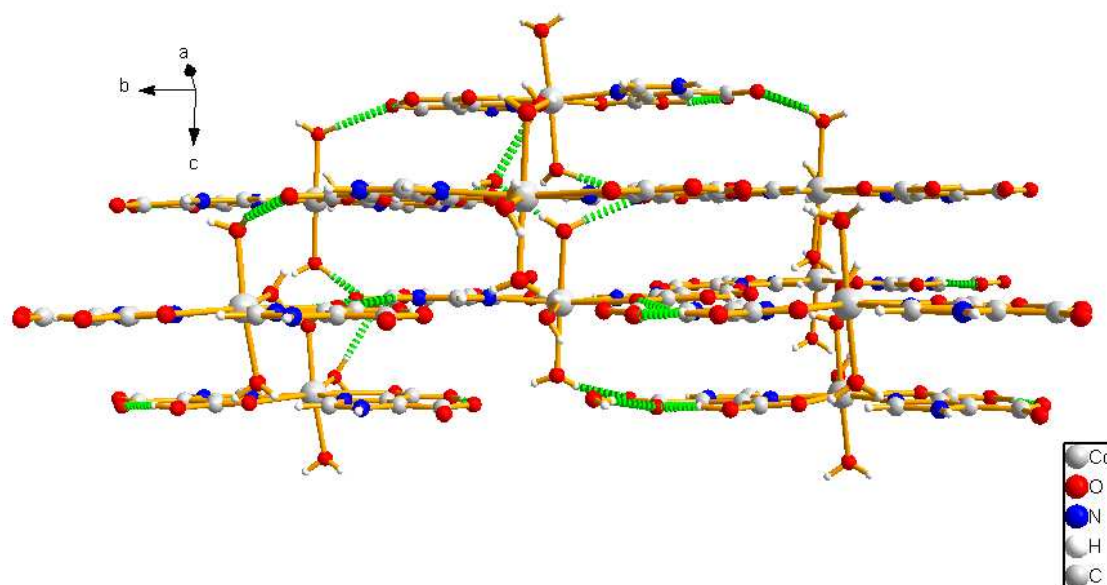


Fig. 7. Hydrogen bonding between mononuclear units in complex **2**

Table 3: H-bonds list (Å, °) for **2**

D-H---A	D-H	H---A	D---A	D-H---A
N2-H2---O7	0.88	1.96	2.815(2)	163
N2-H4---O4	0.88	2.15	3.005(2)	164
O101-H101---O10	0.82(3)	2.02(3)	2.835(2)	177(17)
O101-H102---O9	0.80(3)	2.14(3)	2.939(3)	175(3)
O2-H103---O11	0.79(3)	2.53(3)	3.084(3)	128(3)
O2-H104---O101	0.80(3)	2.02(3)	2.810(3)	178(3)
O1-H105---O101	0.81(2)	1.90(2)	2.707(3)	174(3)
O1-H106---O7	0.78(2)	2.00(2)	2.760(2)	163(2)
O3-H107---O11	0.79(3)	1.96(3)	2.730(2)	164(4)
O3-H108---O6	0.79(3)	2.07(3)	2.853(2)	169(4)
O5-H111---O6	1.14(3)	1.31(3)	2.450(2)	172(3)
O9-H222---O10	1.03(2)	1.44(2)	2.459(2)	175(2)
C1-H1---O1	0.95	2.54	3.218(3)	128
C1-H1---O8	0.95	2.29	2.909(3)	122
C6-H6---O5	0.95	2.34	2.935(3)	120

Symmetry codes: 1-x, 1-y, -z; x, 1/2-y, -1/2+z; 2-x, 1/2+y, 1/2-z; 1-x, 1/2+y, 1/2-z; -x, 1-y, -z; 2-x, -1/2+y, 1/2-z; -1+x, y, z; 1+x, 1/2-y, 1/2+z

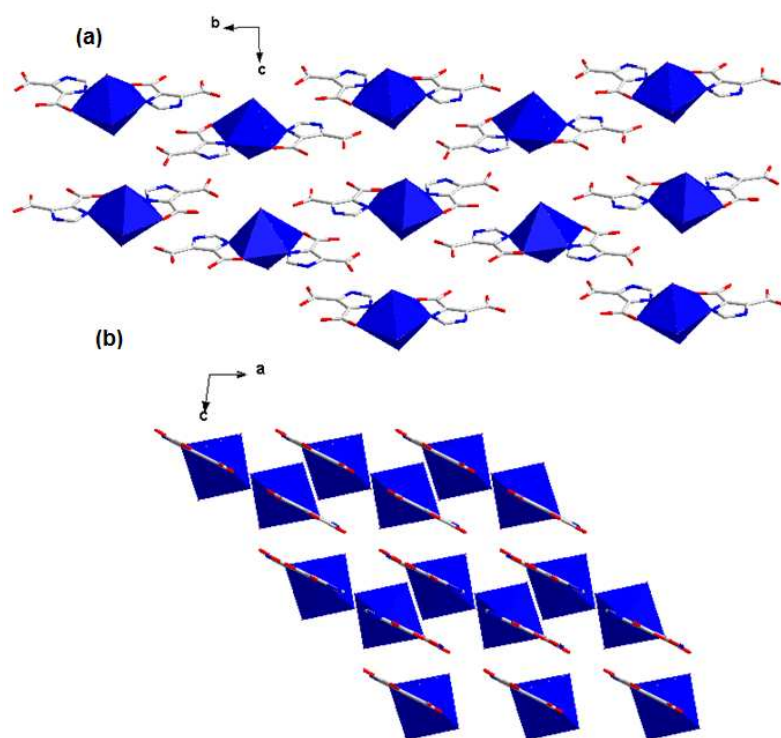


Fig. 8. Polyhedral view of complex **2** and arrangement of mononuclear species along (a) a- axis (b) b-axis

Fig. 9 reveals the FT-IR spectrum of complex **2**. The broad absorption band at 3111 cm^{-1} is indicative of the presence of coordinated and lattice water molecules in the crystal structure.

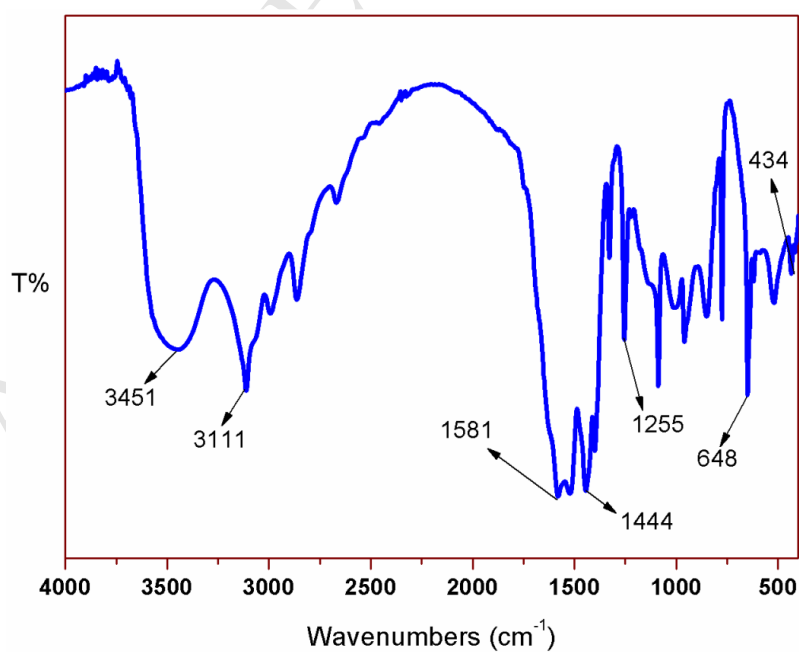


Fig. 9. FT-IR spectrum of **2**

The absorption band at 3451 cm^{-1} represents the N-H stretching frequency of imidazole ring. The characteristic bands at 1444 and 1581 cm^{-1} represent C=C stretching vibrations and aromatic character of ligand in the crystal structure. The appearance of band at 1255 cm^{-1} indicates the C-O stretching frequency of deprotonated carboxylic group. Moreover, the band at 648 and 434 cm^{-1} represent the formation of bond between cadmium to nitrogen and oxygen, respectively. The FT-IR spectra of both the complexes indicate the successful coordination of 4,5-Imdc with corresponding metal ions. The varied stretching vibrations of C=C and N-H in 4,5-Imdc and vibrational frequencies of M-O and M-N in complexes **1** and **2** are attributed to involvement of 4,5-Imdc in bonding with different coordination number of metal ions.

3.3 Thermogravimetric analysis of **1** and **2**

An examination of the TG analysis curve for **1** suggests that foremost weight loss is initiated at $230\text{ }^{\circ}\text{C}$ and continued till $300\text{ }^{\circ}\text{C}$, which indicates the removal of coordinated water molecules from the structure and weight loss was 9.5% (Cald. 8.9%). The subsequent decomposition is noticed beyond $450\text{ }^{\circ}\text{C}$ with weight loss of 82% (Cald. 84.5%), which corresponds to the decomposition of two 4,5-Imdc molecules (Fig. 10 a). For complex **2**, TG analysis reveals that complex is stable up to $120\text{ }^{\circ}\text{C}$. As shown in the Fig. 10 b, the first decomposition step around $120\text{ }^{\circ}\text{C}$ indicates the removal of lattice water molecule in the crystal structure with weight loss of 3.50% (Cald. 3.63%), the subsequent decomposition between 150 to 250°C indicates the loss of three coordinated water molecules with weight loss of 12.50% (Cald. 11.32%). Loss of two molecule of 4,5-Imidazoledicarboxylate with weight loss of 73.50% (Cald. 73.35%) on heating the complex at $400\text{ }^{\circ}\text{C}$. Finally the structural integrity is lost, when temperature reaches more than $500\text{ }^{\circ}\text{C}$. Lesser stability of complex **2** over complex **1** confirmed by TGA, was ascribed to the coordination of Cd^{2+} in

complex **2**, which was partially accomplished with more water molecules than in complex **1**, which renders the decomposition of complex **2** earlier than complex **1**.

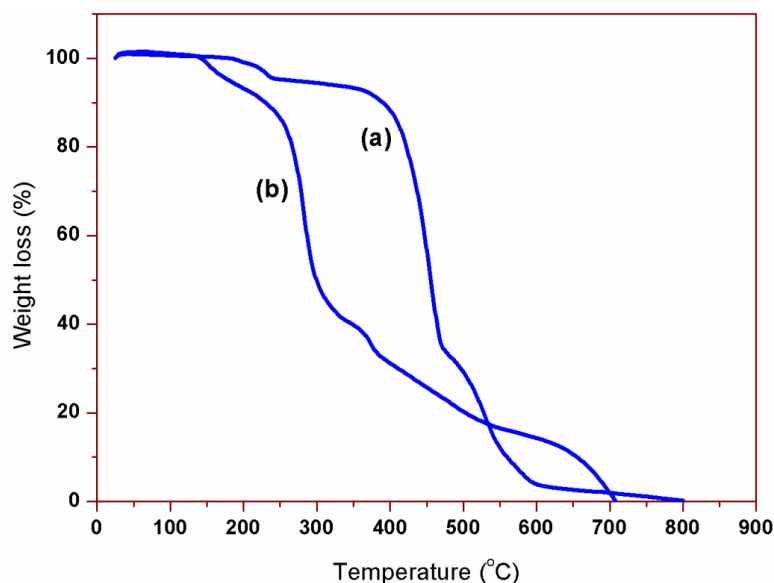


Fig. 10. TGA curve of (a) [Co(4,5-Imdc)₂(H₂O)₂] (b) [Cd(4,5-Imdc)₂(H₂O)₃].H₂O

3.4 Fluorescent properties of **1** and **2**

Complexes constructed with the ligands containing N-donor atoms are promising photoactive materials in chemical sensors, electroluminescent display and photochemistry [57, 58]. The solid state fluorescence property of this complex in addition to free ligand was examined at room temperature. Upon excitation at 365 nm, pure ligand, 4,5-Imdc exhibits maximum emission at 575 nm, which can probably be assigned to the π to π^* transitions [59]. The maximum fluorescence emission (yellowish green) for the complex takes place at 521 nm upon excitation at 365 nm. It was observed that the emission peak undergoes blue shift (54 nm) on compared to the free ligand. Ren et al. [60] reported that metal complexes constructed with N-donor ligand exhibit fluorescence due to ligand to metal charge transfer (LMCT). Varying degree of blue-shift observed in **1** was probably due to different coordination environments of N-containing ligand and the enhancement in the energy gaps between the

HOMO and LUMO of the ligand, when coordinating to the metal ions [61, 62]. Fig. 11 (a & c) depicts the emission spectrum of **1** and free ligand.

It is well known that metal organic coordination complexes have the ability to influence the emission wavelength and intensity of the organic materials through coordination. The fact that the d^{10} metal centres and conjugates organic ligands exhibit florescent properties has also been well documented [63]. As depicted in the Fig. 11 (b & c), both complex **2** and the free ligand display similar emission spectrum at the same excitation wavelength of 365 nm. The maximum yellowish emission of complex and the ligand 4,5-Imdc were observed at 573 and 575 nm, respectively. Furthermore, in addition to a slight blue shift observed in the emission band of **2**, a marginal increase in intensity of emission was also observed. The emissions band of **2** may be attributed to the ligand-to-ligand charge transfer [64].

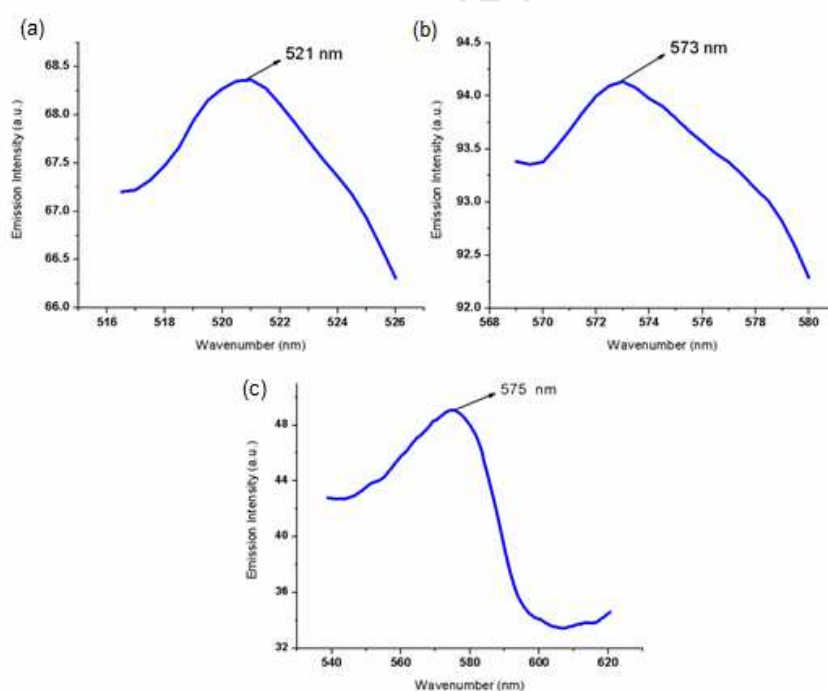


Fig 11. Fluorescent spectra of (a) [Co(4,5-Imdc)₂(H₂O)₂] (b) [Cd(4,5-Imdc)₂(H₂O)₃].H₂O (c) free ligand (4,5-Imdc).

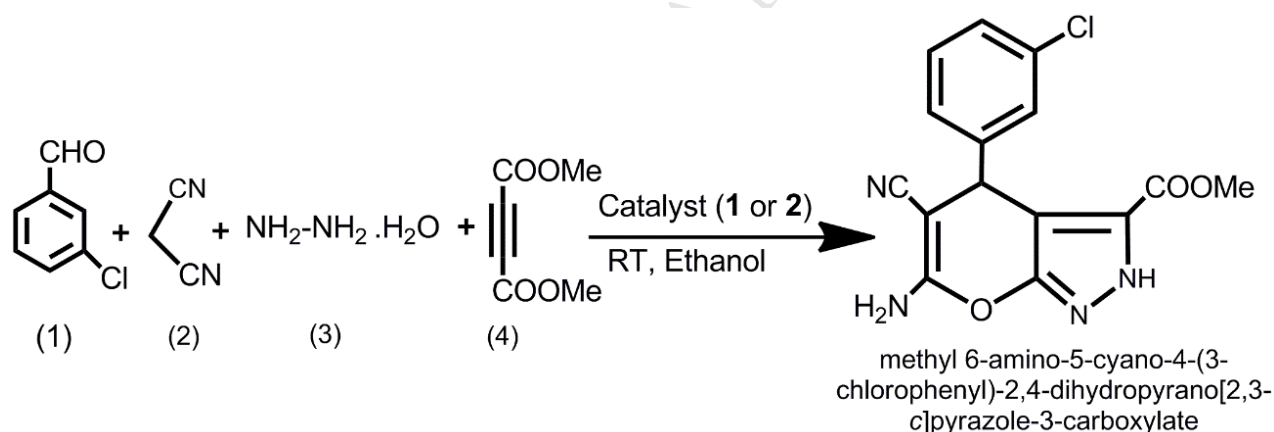
The nature of bonding of 4,5-Imdc with metal ions (Co^{2+} , Cd^{2+}) in complex **1** and **2** with different coordination numbers would influence their emission spectra. Both the complexes exist in different coordination environments. Co^{2+} with octahedral geometry in complex **1**, emitted light due to availability of vacant orbital for the charge transfer from ligand to metal, while in the case of complex **2**, the higher coordination of Cd^{2+} provide no flexible orbital for charge transfer from ligand. Hence, the emission in complex **2** is attributed to ligand to ligand charge transfer.

3.5 Catalytic activities of **1** and **2**

The catalytic performance of **1** and **2** was tested for the synthesis of methyl 6-amino-5-cyano-4-(3-chlorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate in an one-pot reaction using four-component namely, 3-chloro benzaldehyde, malononitrile, hydrazine hydrate and dimethyl acetylenedicarboxylate as precursors. An equimolar mixture of each 1.0 mmol of the four substrates was made in ethanol at room temperature under stirring. An amount of 20 mg of catalyst (**1** or **2**) was added to the reaction mixture to accelerate the reaction (Scheme 2). After the TLC examination for the completion of the reaction, the solid catalyst was filtered off from the reaction mixture and thereby the final product was recovered through extraction with ethyl acetate. In order to estimate the need of catalyst, the reaction was carried out in the absence of catalyst under otherwise similar reaction conditions. The uncatalysed reaction took 2.5 h to get the desired product with a yield of 65%. The introduction of either **1** or **2** to the reaction mixture as catalyst, positively influenced the reaction time as well as yields. With complex **1**, the reaction finished in 10 min with excellent yield (98%), whereas with **2**, the reaction took 15 min and yield was 92%. The significant improvement in the product yield and reaction time suggest that the complex **1** possibly possess more accessible coordination sites in metal centre over **2**, which is the

prerequisite for the metal centre to act as active catalytic site. The introduction of unsaturated coordination environment in metal centres upon de-solvation makes the catalyst to gain more Lewis-acidic character, which accelerate the subsequent transformation of substrate molecules [65-67]. Relatively soft Lewis-acidic nature of Cd^{2+} metal nodes typically make the weak coordinating bond, which ultimately reduce the complex resistance towards the attack of reactive substrates [68, 69].

The structure and purity of the organic product was confirmed and finalised by the spectroscopic analysis using ^1H , ^{15}N , and ^{13}C - NMR spectra (Fig.S1-S3). The ^1H -NMR signals observed at δ 3.77, 7.07 and 12.46 ppm respectively corresponding to the methoxy ($-\text{OCH}_3$), amino ($-\text{NH}_2$) and secondary amine ($-\text{NH}$) protons and the ^{15}N spectrum further confirmed the presence of amino group in the structure of the final organic compound.



Scheme 2. Typical reaction

Spectral data of methyl 6-amino-5-cyano-4-(3-chlorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate;-. ^1H NMR (400 MHz, DMSO-d_6) 3.77 (s, 3H, OCH_3), 4.79 (s, 1H, CH), 7.07 (s, 2H, NH_2), 7.09 – 7.27 (m, 4H, ArH), 12.46 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 15.09, 36.58, 50.67, 51.72, 57.09, 79.10, 103.31, 120.06, 126.18, 126.70, 127.27, 128.89, 130.18, 132.04, 132.69, 147.24, 155.20, 158.24, 160.24; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.07 (s, 2H, NH_2).

After selecting complex **1** as an efficient catalyst, the amount of catalyst required for optimum conditions were investigated. The reaction was conducted with varied amounts of **1**

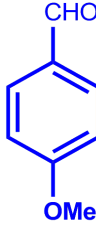
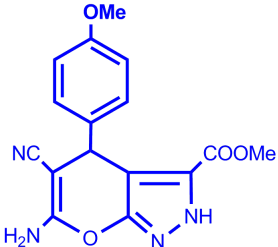
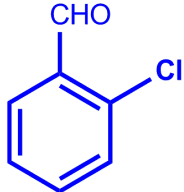
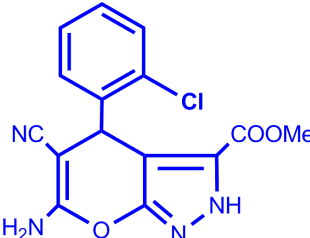
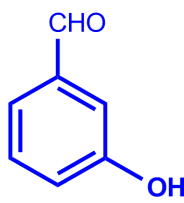
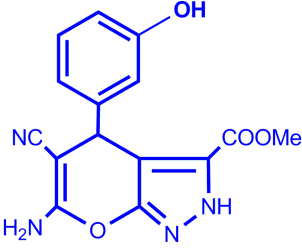
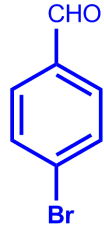
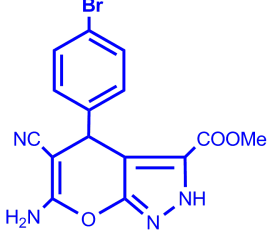
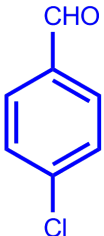
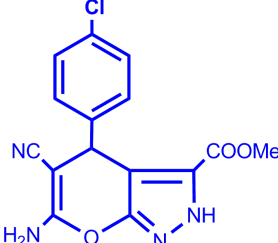
from 10 to 50 mg and the results summarised in Table S2, establish that 20 mg of **1** was sufficient to afford the good yields of product in short interval of time. No additional advantage was observed with respect to reaction time or yield, when catalyst amount was increased from 20 to 40 mg, use 50 mg marginally, but negatively impacted on the yield and reaction time. Hence, the 20 mg of **1** was taken as a preferred amount to initialize the reaction.

Further to establish, ideal choice of solvent for effective synthesis, reactions were conducted in presence of **1** at RT, with different polar and non-polar solvents. When non-polar solvents toluene and n-hexane were employed, the reaction does not occur, but with acetonitrile and DMF, the moderate yields were observed. The reaction gave impressive yields with the polar solvents viz. methanol, ethanol and water. Relatively, ethanol proved to be outstanding in terms of yield and reaction time, hence confirmed as optimum solvent for the protocol (Table S3).

To assess the efficiency of **1** as multipurpose catalyst, the successive reactions were repeated with five differently substituted aromatic aldehydes. In all the reactions, the product yields (92- 98%) and reaction times (10 to 20 min) were good to excellent (Table 4).

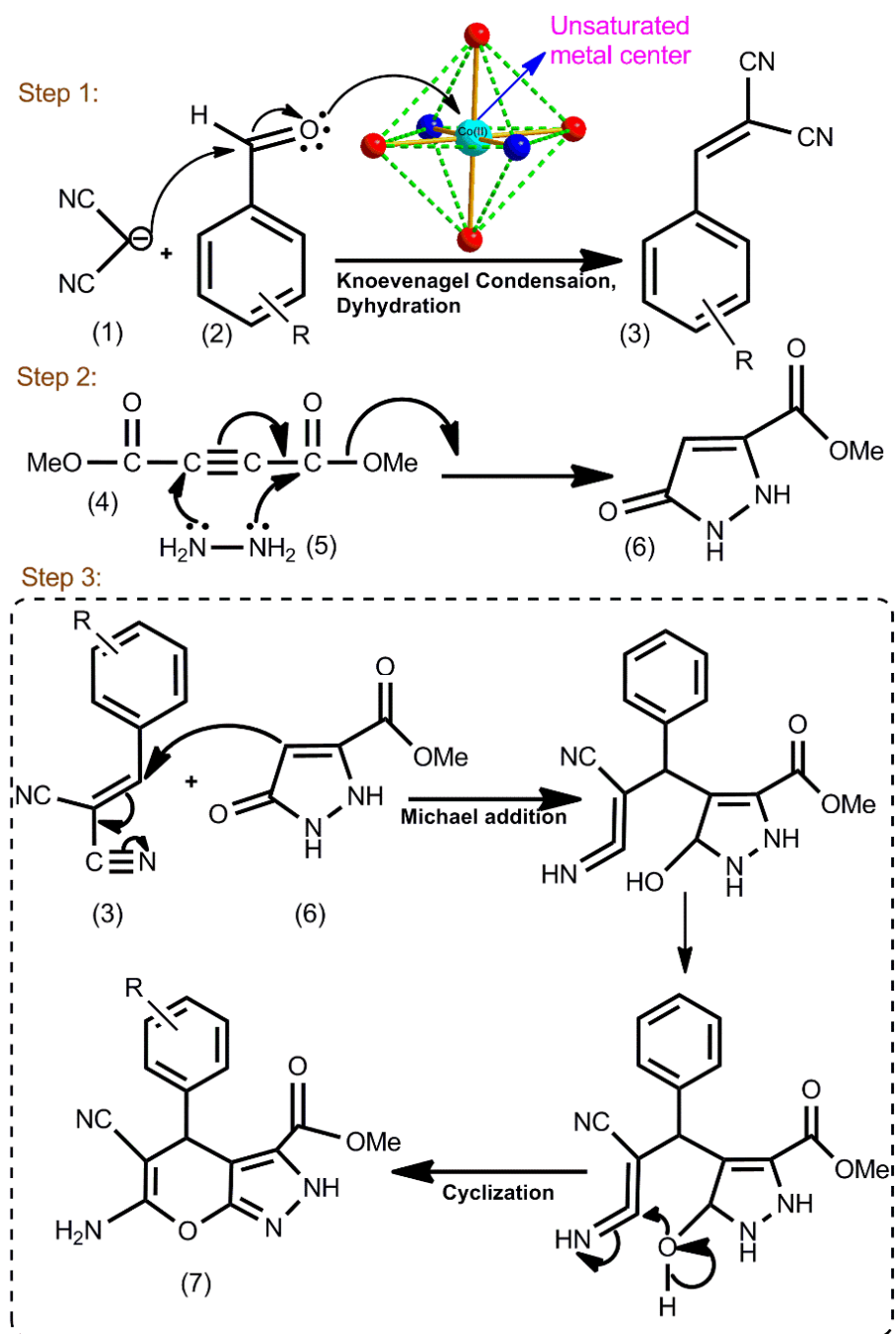
Based on the experimental results and products, a plausible reaction mechanism is proposed in Scheme 3. On the catalyst surface, the unsaturated metal centres of Co(II) or Cd(II) initiate the crucial Knoevenagel condensation between malononitrile (**1**) and aldehyde (**2**), resulting in formation of benzyldine malononitrile intermediate (**3**), while hydrazine hydrate (**4**) and dimethyl acetylenedicarboxylate (**5**) combine to produce a pyrazolone intermediate (**6**). In the subsequent step, both the intermediates (**3**) and (**6**) undergo Michael addition, followed with cyclization on the catalytic surface selectively yielding the final product of pyrano[2,3,c]pyrazole moiety.

Table 4: List of synthesis of pyrano[2,3-c]pyrazole moiety with different substituted aromatic aldehydes with $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ as catalyst^{*,a}

Entry	aldehyde	Product	Yield (%)	Time(min)
1			94	10
2			96	10
3			92	15
4			95	20
5			92	15

*Reaction conditions: substituted benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), hydrazine hydrate (1.0 mmol), dimethyl acetylenedicarboxylate (1.0 mmol), $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ and ethanol (5.0 mL) at RT

^a isolated yields



Scheme 3: Plausible mechanism

These inspiring results endorse the usefulness of the protocol using the complexes first time as reusable heterogeneous catalysts in synthesis of pyrano[2,3,c]pyrazole derivatives. Moreover of the total six pyrano[2,3,c]pyrazoles synthesised in the current study, the moiety synthesised in the title reaction reports a new molecule.

3.6 Reusability of the catalyst

The ease of catalyst preparation, simple recovery, and reusability are paramount of its utilization for the development of catalysed organic processes. One of the attractions of coordination complexes as heterogeneous catalysts is their easy post reaction separation. The recovery and reusability of complex **1** was examined with the title reaction. The separated catalyst material was washed with acetone few times and dried in a vacuum oven at 80 °C for 2 h. The efficiency of successive reactions up to six cycles were investigated using recovered catalyst by assessing the product yield and reaction time. No significant changes in yield or reaction time was observed up to six cycles except for the marginal loss of catalyst material in each cycle of recovery (< 2%), but after sixth cycle about 12% depletion in the catalytic performance was noticed. The observed results suggest catalyst remained stable during the repetitive use and no leaching of metal occurred.

4. Conclusions

In summary, two varied structural architectures of complexes, $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ (**1**) and $[\text{Cd}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**2**) were synthesized by hydrothermal process. The Co(II) and Cd(II) metallic nodes respectively adopted octahedral and pentagonal bipyramidal geometries with N and O coordination points of 4,5-imidazolecarboxylic acid. The chelating five-membered rings were observed in both the structures of complexes with Co(II) and Cd(II) metal nodes. The mononuclear units were further interconnected with hydrogen bonds existing between nitrogen and carboxylate oxygen atoms building impressive 3D supramolecular networks. The unsaturated metal centres generated by activation of water molecules acted as Lewis acid sites, which effectively catalysed the value added production of pyrano[2,3-c]pyrazole moieties. Both **1** and **2** complexes showed activity under benign reaction conditions (ethanol, RT). Among **1** and **2**, the catalyst **1** proved to be superior in

giving impressive yields of product (92-98%) selectively in short interval time (< 20 min) the yields. The flexibility in the synthesis, thermal stability, simple separation with reusability, mild reaction conditions prompt these complexes to catalyse the MCRs yielding valued organic molecules selectively.

Acknowledgements

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Supplementary Information

The CCDC numbers 998828, 998827 contain the information regarding the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or [from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21 EZ, UK; Fax: +44(0)1223-336,003; E-mail: deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors. The bond length, bond angle of two complexes and spectral data of all organic products are presented.

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Figure Captions

Scheme 1. Bonding modes of 4,5-Imdc in (a) **1** and (b) **2**

Scheme 2. Typical reaction

Scheme 3: Plausible mechanism

Table 1: Crystal data, Data collection and Refinement details of **1** and **2**

Table 2: H-bonds list (Å, °) for **1**

Symmetry codes: 1-x, -y, 1-z; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-1/2+z$

Table 3: H-bonds list (Å, °) for **2**

Symmetry codes: 1-x, 1-y, -z; $x, 1/2-y, -1/2+z$; $2-x, 1/2+y, 1/2-z$; $1-x, 1/2+y, 1/2-z$; $-x, 1-y, -z$; $2-x, -1/2+y, 1/2-z$; $-1+x, y, z$; $1+x, 1/2-y, 1/2+z$

Table 4: List of synthesis of pyrano[2,3-c]pyrazole moiety with different substituted aromatic aldehydes with $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ as catalyst*.^a

*Reaction conditions: substituted benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), hydrazine hydrate (1.0 mmol), dimethyl acetylenedicarboxylate (1.0 mmol), $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ and ethanol (5.0 mL) at RT

^a isolated yields

Fig. 1. Coordination environment of Co(II) metal ion of complex **1** in ortep view with 50% probability (hydrogen atoms omitted for clarity)

Fig. 2. Geometries (a) complex **1** and (b) complex **2**

Fig. 3. Hydrogen bonding pattern in **1**

Fig. 4. Prospective polyhedral view of **1**

Fig. 5. FT-IR spectrum of **1**

Fig. 6. Coordination environment of Cd(II) metal ion of complex **2** in ortep view with 50% probability (hydrogen atoms omitted for clarity)

Fig. 7. Hydrogen bonding between mononuclear units in **2**

Fig. 8. Polyhedral view of **2** and arrangement of mononuclear species along (a) a- axis (b) b-axis

Fig. 9. FT-IR spectrum of **2**

Fig. 10. TGA curve of (a) $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ (b) $[\text{Cd}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$

Fig. 11. Fluorescent spectra of (a) $[\text{Co}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_2]$ (b) $[\text{Cd}(4,5\text{-Imdc})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (c) free ligand (4,5-Imdc).

Synthesis, characterisation and catalytic activity of 4, 5-imidazoledicarboxylate ligated Co(II) and Cd(II) metal-organic coordination complexes

Highlights

- Hydrothermal synthesis of Co(II) and Cd(II) based complexes with 4,5-Imdc
- Diverse coordination geometries attained by Co(II) and Cd(II) in their complexes
- 3D supramolecular networks developed through H-bond interactions in both complexes
- Unsaturated metal centres generated upon heating acted as Lewis acidic sites
- Exhibit superb catalytic activity in the synthesis of pyrano[2,3,c]pyrazoles