Synthesis and Biological Activities Of Mixed Ligands Metal Imidazole carboxylates

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Abstract:

Copper and Nickle metal complex with ligands as imidazole and benzoic acid derivatives are synthesised .For synthesis of complexes slow evaporation method is used that result in shiny crystals as a product complexes.These newly synthesised complexes of Cu and Ni are studied by FTIR spectroscopy and Uv analysis.After that biological activity of these complexes is checked and they are proven with having anti bacterial property.Therefore,these newly synthesised complexes can be used for anti bacterial purposes.

Keywords: *imidazole, complex,anti-bacterial propert*

1 Introduction

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Imidazole is a monoacidic base with acids that can make crystal-like salts. The m.p of most of important imidazole containing salts are high[1]. It is soluble in water and other polar solvents, which is a 5-membered planar ring. As evidenced by a calculated dipole of 3.61D, Imidazole is highly polar compound, so completely dissolved in water. Due to the existence of a sextet of p-electrons it is categorized as aromatic. From the protonated nitrogen atom and one from each of the remaining four atoms of the ring including of a couple of electrons.[2]**B**y the solvothermal reaction a new europium complex, constructed as $\{[Eu_4(H_3Pimda)_4\ (Himba)_2{\cdot}4H_2O]{\cdot}4H_2O\}_n$ (**1**) (H_3Pimda = 2-propyl-1H-imidazole-4,5-dicarboxy acid, and Himba = 4-(1H-imidazole-1-ly) benzoic acid), has been formulated.[3] Cao, T., Peng and coworker synthesized Eight mixed-ligand coordination compounds through the reaction of zinc and cadmium salts with pamoic acid and different N-donor ligands.[4]Two isostructural transition-metal (TM) triphosphonates, have been hydrothermally synthesized and structurally characterized by Thermogravimetric analysis, IR spectroscopy, elemental analysis, and single-crystal/powder X-ray diffraction. Studied complex show a pillar-layer structure with the TM-triphosphonates as layers and the rigid tib ligand as a pillar. The lumi-

nescence and magnetic properties have been found. Complex **1** show strong blue luminescence, while compound **2** shows weak ferromagnetic phenomenon.[5]Li, F., Zhang, X., Sun and their fellows studied that Five CPs show different structural forms and unique properties. Compound 1 exhibit $[Cd_2(Hmidc)_2]$ layer, that can be pillared by the bpp spacer into a 3D MOF with the point symbol of $\{4^{12}\cdot6^3\}$.They found that Complex 2 have a $[Zn_3(midc)_2]$ layer, pillared by bpp spacer into a 3D MOF with the point symbol of $\{8^3\}_2\{8^5\cdot10\}$. Complex 3 has the same $[Zn_3\ (midc)_2]$ layer as complex 2 which is different from 2.As the layering in complex 3 is further joined by a rigid $HCOO^-$ linker into a 3D MOF with the point symbol of $\{6.8^2\}_4\{6^2\cdot8^2\cdot10^2\}$.Additionally, complex 4 contain an infinite 1D zigzag chain and that elongates as a final 3D supramolecular framework through H-bond interactions. BY tuning the coordination modes of their ligands Complex 5 shows a wavelike chain with bpp and $Hmidc^{2-}$. So, a varied structures can be derived.[6]Six zinc naproxen complexes were synthesized and fully characterized by UV-Vis, IR, ^1H , NMR, ^{13}C and $\{^1H\}$ NMR spectroscopy. X-ray crystal structure for complex **3** was also examined. These complexes showed divergent antibacterial property against the tested bacterial species also complex 2 was only complex that had little anti-bacterial activity at the same time complex 3 showed effectiveness as anti-malarial drug[7]Sun, X.Y, et al (2015) narrated that Imidazole group has two nitrogen atoms. Those compounds that has imidazole are not only monodentate and neutral ligand even also can act as bidentate and negative ligands, it depends at what position of imidazole substituents are attached. If hydrogens are removed from imidazole, then ligands can arrange themselves with metal to form frame work which is known as zeolitic imidazole frame work (ZIFs).All that Ligands which have distinct numbers of imidazole groups can make 1D,2D as well as 3D complexes accompanied by Zn and Cd salts of these metals [8] Romero et al (2014) described that Imidazole play an important part in curative chemistry, because most of imidazole derivatives have revealed conspicuous biological activity. Most of the Imidazole derivatives have shown biological activity as antibacterial, antibiotic, analgesic, antifungal, antitumor, anti-depressive, along with inside the biological activities of different therapeutic disease.[9] Ikram et al (2010) explained that Metal complexes have biological activity in biological system like many metals ions have antimicrobial, anti-tumor activity, in addition to ability of protecting against prokaryotes. Along all of these novel metal complexes derivatives that appear to have appreciable physiological active may show an amusing clue for representing fresh antibiotics.[10] Kuai et al (2010) described that By hydrothermal reactions of Zn (II) and Cd (II) salts using bifunctional ligands 5(imidazole-1-ylmethyl) Isophthalic acid, five new polymers were synthesized. The resulting structure of coordination polymers changed by changing alkaline reagent. Cadmium complexes, namely 1-3 are [Cd(L)(DMF).(H2O)]H2O **(1),** [Cd(L)(H2O)2]2.5H2O **(2**) and

[Cd2(L)2(H2O)2]2.H2O **(3)** that exhibited 1D,2D and 3D respectively. The alkaline reagent was dimethyl amine from DMF KOH and carbonated salts respectively. In the same way, structure [Zn (L)] (4) ZN (L) H2O (5) are Zn complexes that exhibited 2D and 3D structure pattern. Alkaline reagent for complex 4 is tetra butyl ammonium hydroxide and carbonate salt for complex 5.Coresponding result explain that all the alkaline reagent used were non-innocent for structure elucidation, similarly for crystal growth they have very minute effect in homogeneous and heterogeneous nucleation. At the end all five complexes exhibited water sorption and emerged as potential hybrid due to their attractive fluorescence property organ-ic-inorganic light sensitive substances .[11] Du,J.Q et al (2019) explained that Establishing a stiff ligand **L** and aromatic carboxylic acids ligands applying solvothermal conditions three fresh coordination polymers were synthesized which are named as [Co(L)(1,2,4,5-BTC)1/2(H2O)]n (1), {[Ni(L)(1,2-BDC)(H2O)3]·H2O}n (2) and {[Zn3(L)2(1,3,5-BTC)2(H2O)2]·3H2O}n (3) while ligands using imidazole and carboxylates were used. Single-ray diffraction IR spectroscopy, elemental analysis, thermal gravimetric analysis and powder X-ray diffraction techniques were used for structure determination for complex of 1-3.IN the same way help from UV visible spectroscopy was also taken for fining large band gaps. All these analysis represent that structure 1 has 2 dimensional layer structure 2D with six joining topologies net. Second complex represent one dimensional pattern which is zigzag and third complex rep-resent three dimensional network. Finally, light emitting property and lifetime of third complex was found at room temperature [12] Liu,k,Dang et al (2018) demonstrated that four coordination polymers are syn-thesized after that they were characterized these polymers were of different 3d metals like Zn and Cd using different ligands ,these structures showed captivating 2D and 3D patterens.variation in structural diversity tells the primary and auxiliary ligand have major effect for final structure determination. By measuring their light emitting property it is revealed that structure 1-4 are photoluminecent, this work helped for further coordination polymers synthesis by using mixed ligands .[13]

2. Materials and Methods

2.1. Materials and methods

Cu.No3 and Nicl2 and imidazole were purchased from Sigma-Aldrich Chemical Company , Further *p*-chlorobenzoic acid, *0-nitrobenzoic* acid,ethanoll, DMSO, and NaOH were purchased from chemical company Merck and were used as received.

2.2. Instrumentation

UV–visible spectra were verified in DMSO using a Mega-2100 Double Beam UV–visible spectrophotometer.FT-IR absorption spectra were recorded as KBr pellets with an Avatar 360 E.S.P. Nicolet FT/IR spectrometer from 4000–400 $cm^{-1.}$

2.3. Syntheses of complexes 1–2

Alike practice was performed comprising the reaction of CuNo3 salt with imidazole For the synthesis of **1–2**, after that addition of carboxylate is done.

Synthesis of Complex 1.[Ni(imidazole)(o-nitro BA)2(H20)6]

In 30 cm^3 methanol solvent, prepared a solution of $NiNo3{\cdot}6H_2O$ (0.290 g, 1 mmol). Furthermore , in 10 cm^3 methanol also prepared imidazole solution (0.136 g, 2 mmols) that was placed in solution of $NiNo3{\cdot}6H_2O$ (0.290 g, 1 mmol) dropwise slowly with nonstop stirring. Then resultant green solution was stirred for 40 minutes without giving heat . Separately prepared a solution of o-nitro benzoic acid in methanol (0.225 g, 2 mmols)) having 25 drops of 1 M $NaOH_{(aq)}$ was dropwise added with non-stop stirring. As a result, solution formed was heated at 55 °C with stirring for 60 miutes. Finally,The solution formed at the end was filtered and saved at room temperature, and after seven days, appropriate crystals for further analysis were obtained. The sea green crystals were washed in cold methanol and dried in air.

Synthesis of complex 2. $[Cu(imidazole)(p\text{-}chloroBA)_2(H_2O)_3]$

In 30 cm^3 methanol solvent, prepared a solution of $CuNo3{\cdot}3H_2O$ (0.241 g, 1 mmol).Furthermore , in 10 cm^3 methanol also prepared imidazole solution (0.136 g, 2 mmols) that was placed in solution of $CuNo3{\cdot}3H_2O$ dropwise slowly with nonstop stirring. . Then resultant blue solution was only stirred for 40 minutes without giving heat. Then a mixture of p-chloro benzoic acid in methanol (0.312 g, 2 mmols)) having 25 drops of 1 M $NaOH_{(aq)}$ was dropwise added with non-stop stirring. As a result, solution formed was heated at 55 °C with stirring for 60 miutes. Finally,The solution formed at the end was filtered and saved at room temperature, and after seven days, appropriate crystals for further analysis were obtained. The purple blue crystals were washed in cold methanol and dried in air.

3. Results and discussion

3.1. IR spectroscopy

The FTIR spectra of 1–2 display complex patterns of many peaks. For instance, in the FTIR spectrum of 1, the absorption at 3448 cm^{-1} is due to the ν(O–H) stretch of coordinated water. The absorption at 3151 cm^{-1} is ascribed to ν(=C–H) stretch of alkene, while its trans alkene bend is observed at 979 cm^{-1}. Complex 2 shows asymmetric ν_{as}(N–H) and symmetric ν_s(N–H) stretches of amino (-NH_2) group of p-aminobenzoate at 3441 and 3351 cm^{-1}, respectively. The overtone of N–H bending vibration of NH_2 occurs as a shoulder at 3298 cm^{-1}. Complex 3 has a characteristic ν(C–Cl) stretch at 775 cm^{-1}. The absorptions at 3246, 3298, and 3297 cm^{-1} in 1–3 correspond to ν(=N–H) imidazolic stretches, respectively. The peaks at 3068, 3062, and 3054 cm^{-1} are attributed to ν(=C–H) aromatic stretches of 1–3, respectively.

Upon coordination to Cu(II), new absorption bands appear at 1638 and 1391 cm^{-1} for **1**, 1608 and 1394 cm^{-1} for **2**, which correspond to the asymmetric
[ν_{asym}(OCO)] and symmetric [ν_{sym}(OCO)] stretching vibrations of the coordinated carboxylates. The large difference in ν_{as}(OCO) and ν_s(OCO) frequencies ($\Delta\nu$ = 247 cm^{-1}, 214 cm^{-1} and
203 cm^{-1} for **1-2** is indicative of monodentate-O coordination of the carboxylate groups . The other absorption bands at 1581–1447 cm^{-1} correspond to ν(C=N) and aromatic ν_s(C=C) and stretching vibrations. The low-energy absorptions from 611–402 cm^{-1} can be associated to ν(Cu–O) and ν(Cu–N) stretches. A comparison of the selected IR frequencies of free ligands, including imidazole.

3.2. UV–visible spectroscopy

UV–Visible spectra of all the complexes were recorded in DMSO solution from 200–1000 nm. Complexes **1–2** exhibited three absorptions. The intense absorptions at higher energy, 268 nm and 210 nm for **1**, 254 nm and 216 nm for **2**, and 252 nm and 213 nm for **3**, are assigned to the intraligand π→π* and n→π* transitions,

Biological Activity Discussion:

Results of biological activity indicates that both complex have anti-bacterial property.

Inhibition zone hole measurements:

Bacterial culture	Complex1 PP2	Complex2 PP3
E.coli	18	23
B.subtilis	16	0

4. Conclusions

Two mixed-ligand, one with Cu(II) metal and second complex with Ni metal salt have been created by reactions of $CuNo3{\cdot}6H_2O$ and imidazole by suitable carboxylate in 1:2:2 M ratios in aqueous solution. The FT-IR and UV–visible spectroscopic data are similar to previous literature. In both complex, imidazole linked to Cu(II) and Ni(II) with the nitrogen atom in imidazole .Biological activity results indicate that both complex have anti-bacterial property against two bacteria i.e.E.coli and B.sublitis.

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