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Synthesis and Characterization of a Tetranuclear Cu(II) Coordination Polymer Containing Pyridine-2,6-Dicarboxylic Acid and 4-Amidinopyridine Co-Ligand

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Abstract

This research demonstrates the preparation of a new coordination polymer, {[$Cu_4(H_2pydc)_2(H_1apy)(H_2O)_2DMF$].DMF}$_n$, ($H_2pydc$ = pyridine-2,6-dicarboxylic acid, H_1apy = 4-amidinopyridine) under solvothermal condition by the self-assembly of pyridine-2,6-dicarboxylic acid, 4-amidinopyridene and copper(II) acetate. The compound was characterized by elemental analysis and infrared spectroscopic technique. The analysis indicated that the 4-amidinopyridine coordinated to the copper ions through the terminal nitrogen in a monodentate fashion while the pyridine-2,6-dicarboxylic acids coordinated through the carboxylate oxygens in monodentate mode. Both the elemental analysis and the infrared spectroscopic data agreed with the proposed stoichiometry. This result represent the first report of a tetranuclear Cu(II) coordination polymer having coordinated 4-amidinopyridine as the nitrogen donor moiety in its structure.

Keywords: Coordination polymer, 4-amidinopyridine, pyridine-2,6-dicarboxylic acid, copper (II), infrared spectroscopy

INTRODUCTION

A coordination polymer has a metal or metal ion centre surrounded by array of electron rich complexing agents known as ligands (Sánchez-Serratos *et al.*, 2016). There is continuous interest in the synthesis of these class of compounds due to their structural diversity and wide applications in important areas such as catalysis (Henschel *et al.*, 2008), material chemistry (Kitagawa *et al.*, 2004), magnetism (Maspoch *et al.*, 2007), pollution control (Tella *et al.*, 2018), hydrogen generation (Silva *et al.*, 2010) and gas sorption (Rowland *et al.*, 2018). It is possible to change either the linker or inorganic unit in their structures and there is tendency to include functional groups while adjusting the cavity size (Wang *et al.*, 2009). One of the most crucial

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properties of porous coordination polymers has been their exceptional thermal stability. Zeolites usually have shown stability ranging from 150°C to over 800°C, most porous coordination polymers decompose at temperature below 300°C. However, research has shown that thermal stability of coordination polymers can be substantially increased by production of neutral frameworks with stable chelating segments such as carboxylate units (Dzhardimalieva, and Uflyand, 2017). Porous coordination polymers exhibiting high degree of crystallinity could be easily obtained by solvothermal treatment of the reagents in high boiling solvent or solvents mixtures. The regularly repeated patterns in coordination polymers encourage reproducible surface areas, without serious loss in stability (Burgess *et al*., 2016). Application of porous coordination polymers as catalysis require the utilization of metal precursor in the structures with encapsulation of active species, and exploiting the concept of isoreticularity (Li and Zhou, 2010; Furukawa *et al*., 2013). A large number of coordination polymers with specific catalytic sites have been constructed using this approach (Mai and Liu, 2019; Bueken *et al*., 2014).

Multidentate N- or O- donor ligands have attracted a great attention for the synthesis of coordination polymers, as they ensure structural stability and versatile coordination modes (Zhu *et al*., 2018). Pyridine-2,6-dicarboxylic acid has been a ligand of choice in this regard, and a number of functional coordination polymers with fascinating properties and various topologies have been constructed from this ligand (Zhang *et al*., 2020). In addition, the N-centred ligands could easily fulfil the requirement in terms of geometry of metal ions as far as coordination is concerned. For these reasons, we have designed and synthesized a tetranuclear Cu(II) coordination polymer containing carboxylate ligand and amidinopyridine. The interaction of the O- donor ligand, H_2pydc, and an N-donor co-ligand, H_1apy, with Cu(II) centre results in a new tetranuclear Cu(II) coordination polymer presented in this paper.

METHODOLOGY

Chemicals: Pyridine-2,6-dicarboxylic acid (98%, Thermo Scientific), 4-amidinopyridine (98+%, Alfa Aesar), copper(II) acetate monohydrate (ACS reagent, ≥ 98%) and N,N-dimethylformamide (DMF) (99.8%, Sigma-Aldrich) were commercially sourced and were used without further purification.

Methods: The melting point was determined with JA3103 S. Mettler/Electrothermal apparatus. Stirring was done with 78HW-1 constant temperature magnetic stirrer. The solvothermal synthesis was performed with DHG-9202 Series Thermal-Electric Thermostatic Drying Oven. IR spectra was recorded as KBr pellets on Happ-Genzel FTIR spectrophotometer in the 4000 – 400 cm^{-1} region. Elemental analyses for C, H, N was performed with a Perkin-Elmer 240 analyzer.

Preparation of the polymer: A mixture of copper acetate (0.200 g, 1 mmol), H_2pydc (0.0836 g, 0.5 mmol), H_1apy (0.079 g, 0.5 mmol) was dissolved in 18 ml DMF-H_2O (volume ratio of 1:2) mixed solvent. After stirring for 30 minutes, the mixture was sealed in a 25 ml Parr Teflon-lined stainless autoclave under autogenous pressure and heated at room temperature at 145°C for 3 days. After slow cooling at 10°C/h to room temperature, the blue precipitate obtained was collected by filtration and dried in air to give blue powder. Yield: 0.104 g, 28.67%; m.p.: Decomp > 400°C; IR (cm^{-1}): vO-H: 3100; vN-H: 3370; ν_{asym}(COO): 1625; ν_{sym}(COO): 1360; vC=N: 1568; ν(M-O): 640; ν(M-O): 538. Cacld. (Found): C 37.22 (36.84), H 3.10 (3.24), N 10.48 (9.32).

RESULTS AND DISCUSSION

The complex was obtained as blue crystalline solids, the physical properties and elemental analysis are presented in the experimental section. The complex was relatively stable in air and insoluble in chloroform, dichloromethane, N,N-dimethylformamide, methanol, ethanol, hexane, pentane, tetrahydrofuran, ether and dimethylsulphoxide. The complex consist of four copper ions coordinated through the oxygen atom of the carboxylates of pyridine-2,6-dicarboxylic acid in bidentate fashion and two 4-amidinopyridine molecules in monodentate mode. The elemental analysis indicates that the molecules contain two water and one DMF molecules in its structure.

The FTIR spectra of the ligands and the polymer are presented in Fig. 1. Some significant characteristic differences were observed in the IR spectra of the ligands and the polymer. The band at 1701 cm^{-1} attributable to the $v(C=N)$ stretching in free H_1apy ligand is shifted to a lower frequency at 1658 cm^{-1} in the polymer, indicating the coordination of nitrogen atoms of 4-amidinopyridine to the Cu(II) ions (Karaagac and Kurkçuoglu, 2016).

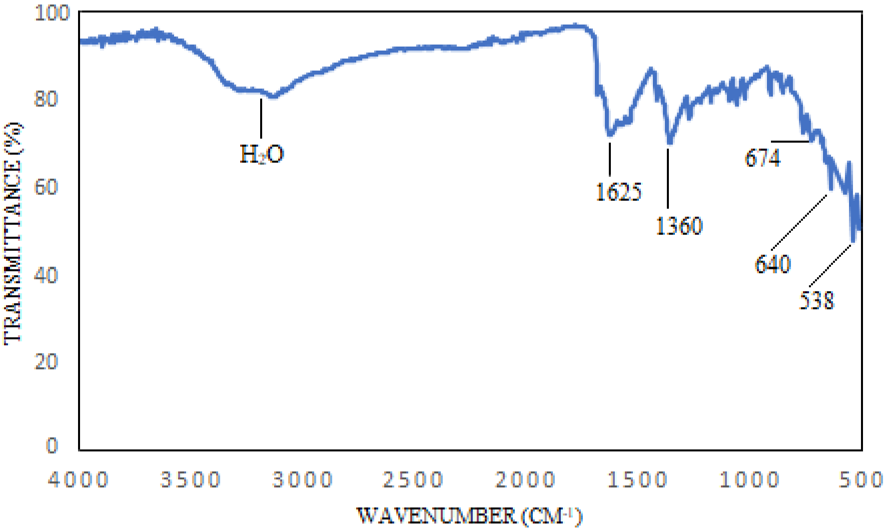

Fig. 1 FTIR spectrum of the title polymer

A broad band was present in the region close to 3100 cm^{-1} in the coordination polymer, since the oxygen atom of the OH group of the H_2pydc ligand already formed a coordination bond with the Cu(II) ions, the broadening of this band could only be attributed to the presence of coordinated water molecules. This is confirmed by the presence of IR bands at 815-855 and 752-770 cm^{-1} attributable to coordinated water molecules, an indication of the binding of the water molecules to the metal ions (Abd El-Wahed *et al.*, 2014). The asymmetric and symmetric stretching frequencies of the carboxylate groups in the polymer were observed at 1625 and 1360 cm^{-1} respectively in the polymer. The difference between the asymmetric stretching bands, $\nu_{asym}(COO)$ and the symmetric bands, $\nu_{sym}(COO)$, i.e., $\Delta\nu[\nu_{asym}(COO) - \nu_{sym}(COO)]$ is 265 cm^{-1}. This value ($\Delta v > 200$ cm^{-1}) indicates that the coordination mode of the carboxylate group is monodentate (Debnath *et al.*, 2020). No band was observed between 1680 and 1720 cm^{-1} in the polymer suggesting a full deprotonation of H_2pydc ligands (Zhao *et al.*, 2020). The band at the region around 674 cm^{-1} in the polymer is due to the ring wagging vibration of the pyridine groups (Zang *et al.*, 2015). The sharp band present in the region around 538 cm^{-1} can be assigned to $v(M-N)$, an indication that the nitrogen of the 4-amidinopyridine is involved in coordination (Patel *et al.*, 2012). The presence of a band of medium intensity at 640 cm^{-1} attributed to $\nu(M-O)$ supports M-O coordination (El-Tabl *et al.*, 2021). The elemental analysis data combined with the FTIR spectral features confirmed the proposed structure of coordination polymer displayed in Fig. 2.

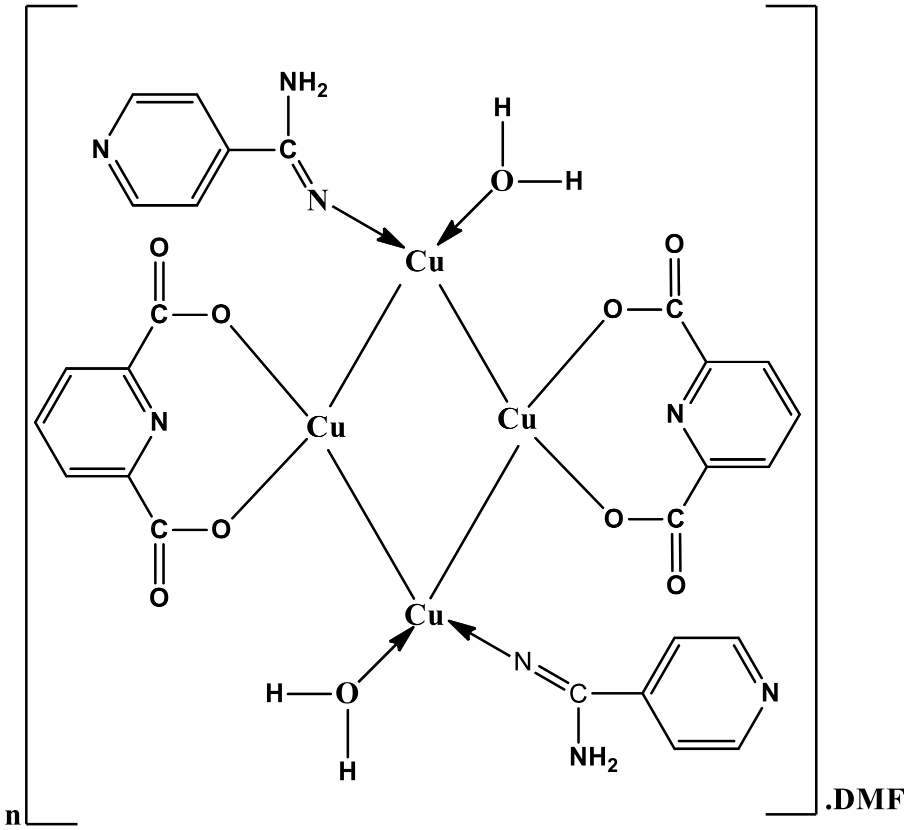

Fig. 2 The proposed structure for the polymer

CONCLUSION

The coordination polymer 1 was prepared based by the reaction of pyridine-2,6-dicarboxylic acid ligand and 4-amidinopyridine as co-ligand with the Cu(II) salt under solvothermal condition. The IR spectroscopy suggested the metal ions in the polymer coordinated with the 4-amidinopyridine through the terminal N- group while the coordination of the pyridine-2,6-dicarboxylic acids were through the carboxylate groups. The data from the elemental analysis agreed with the proposed stoichiometry. The water molecules in the polymer help to complete the coordination sphere of the metal atoms. Activation of this polymer upon heating could cause the removal of the water molecules; in addition, the possible redox properties of the Cu(II) metal in the polymer could present the metal as a good Lewis acid candidate for catalysis.

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