

Synthesis and crystal structure of dinuclear based coordination polymer derived from *N*-6-[(4-pyridylmethylamino)carbonyl]-2-pyridinecarboxylic acid methyl ester

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Abstract. This study describes the facile synthesis and crystal structure of one dimensional coordination polymer which has been successfully obtained from reaction between semi rigid monoamide ligand namely *N*-6-[(4-pyridylmethylamino)carbonyl]-2-pyridinecarboxylic acid methyl ester (L2) with copper perchlorate. The synthesized coordination polymer, with formula given by elemental analysis and X-ray crystallography as $\{[\text{Cu}_3(\text{L2}-\text{CH}_3)_3(\text{L2})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})](\text{ClO}_4)_3\}_n$ was crystallized in monoclinic crystal system and space group C2/c. The asymmetric unit of this complex consists of three copper atoms, three anionic carboxylate forms of ligand L2, two neutral forms of ligand L2 and four partially-occupied non-coordinated perchlorate anions. This asymmetric unit acts as the repeating fragment to form one-dimensional networks which was stabilized by intramolecular hydrogen bonds.

1. Introduction

The derivatives of aminopyridine and aminomethylpyridine have been widely used as organic linker in the synthesis of coordination polymers [1-2]. Rigid linkers such as bipyridine or aminopyridine normally provide limited access to complex supramolecular architectures, while in reverse, flexible ligands such as aminomethylpyridine can be readily used to construct interesting and complex supramolecular structures [3-6]. The flexibility conferred by the ligands would allow for the formation of larger metallo- supramolecular assemblies. We in particular have deep interest in the use of aminomethylpyridine and aminopyridine derivatives as organic linker due to their propensity to form various motifs of coordination polymers and discrete metallomacrocycles. It was evidenced from our previous studies that the ligand derived from 3-aminomethylpyridine prefer to self-assemble with copper(II) and formed dinuclear ($[\text{M}_2\text{L}_2]$) metallo-macrocyclic complexes.

Meanwhile, the rigid ligand derived from 3-aminopyridine provides formation of planar macrocycles [6-7]. Upon reaction with transition metals, the ester of this ligand was hydrolyzed and formed a tridentate 2,6-pyridine dicarboxylate (ONO) donor moieties and the pyridine N donor remains as monodentate binding site (Figure 1). Hence, to continue our interest in the study of aminomethylpyridine derivatives as organic linker, we have synthesized *N*-6-[(4-pyridylmethylamino)carbonyl]-2-pyridinecarboxylic acid methyl ester (L2) from combination of 2,6-pyridinedicarboxamide with 4-



aminomethylpyridine. The obtaining ligand was reacted with copper salts to identify its tendency to form either dinuclear ($[M_2L_2]$) metallo-macrocyclic complexes or coordination polymers. We have confidence that new motifs of coordination will be obtained by L2, thus this study is pursued to investigate the coordination chemistry of L2 with copper salts. Thus, in this account, the synthesis, characterization and crystal structure of the complex are discussed.

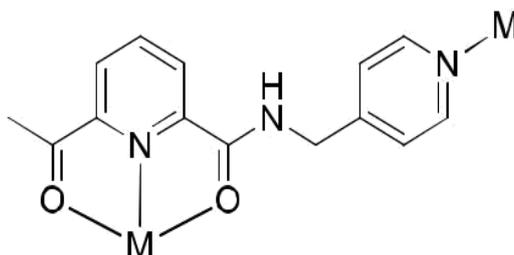


Figure 1. The structure of L2 with ONO tridentate donor monodentate N donor (where M= metal ion)

2. Materials and Methods

Elemental analysis was performed by the Campbell Microanalytical Laboratory at the Universiti Malaysia Terengganu. Infrared spectra were collected on a Perkin Elmer Spectrum BX Infrared spectrometer as KBr disk in the spectral range of $4000 - 400 \text{ cm}^{-1}$. All chemicals were obtained from commercial sources and used as received. The surface morphology of the composite was observed using Scanning Electron Microscope (SEM; JEOL JSM-6360LA). Crystals were mounted under paratone-N oil on a plastic loop. X-ray diffraction datasets were collected with Mo-K α radiation (0.71073 \AA) using Bruker-AXS Single Crystal Diffraction System fitted with an Apex II CCD detector at $110(2) \text{ K}$.

2.1 Synthesis of *N*-6-[(4-Pyridylmethylamino)carbonyl]-2-pyridinecarboxylic acid methyl ester (L2)
Ligand L2 was prepared following the method described in the literature [8]. A suspension of dimethyl pyridine-2,6-dicarboxylate (3.92 g, 20.0 mmol) and 4-aminomethylpyridine (2.00 mL, 20.0 mmol) was refluxed in toluene (80 mL) for 36 h. The toluene was removed using rotaevaporator under reduced pressure. The residue was redissolved in dichloromethane (100 mL), washed with dilute hydrochloric acid (0.2 M, $2 \times 100 \text{ mL}$) and the dichloromethane layer was discarded. The aqueous extract was neutralized with sodium bicarbonate until pH 7-8. The neutral solution was extracted with dichloromethane ($3 \times 100 \text{ mL}$), dried over sodium sulfate and the solvent removed using rotaevaporator under reduced pressure. The resulting residue was purified by column chromatography on silica gel eluting with 1:9 methanol–dichloromethane. The product was obtained as oil from column. The oil was solidified on standing in two days to give L2 as yellow precipitate (2.31 g, 85 %).

2.2 Synthesis of $\{[Cu_3(L2-CH_3)_3(L2)_2(H_2O)_2(CH_3OH)](ClO_4)_3\}_n$

$Cu(ClO_4)_2 \cdot 6H_2O$ (0.034 g, 0.12 mmol) was dissolved in methanol (5 mL) to give a pale blue solution. This solution was heated for a few minutes before being added dropwise to a solution of L2 (0.063 g, 0.23 mmol) which was also dissolved in hot methanol (15 mL). The addition of copper perchlorate solution has given to a light blue solution. The mixture was heated for 45 minutes and left to evaporate at room temperature. After a week, the blue solution afforded turquoise blue crystals as product (0.095 g, 45%).

3. Results and Discussion

Reaction of L2 with copper salts led to formation of oily product except for copper perchlorate. Due to its polarity in methanol, this complex crystallized as blue crystals in 45% yield of products. Elemental

analysis suggested that this compound has general formula of $\text{Cu}_3(\text{L}2)_3$, incorporated with methanol or water to meet the experimental value (Table 1).

Table 1. Elemental analysis data for copper complex

Compound	C(%)		H(%)		N(%)	
	Calcd	Found	Calcd	Found	Calcd	Found
Complex	42.43	42.27	3.55	3.09	10.56	10.51

FTIR spectrum show several important stretching bands for $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C-N})$, $\nu(\text{Cl-O})$ and $\nu(\text{Cu-O})$ at 3409, 1708, 1523, 1082 and 513 cm^{-1} , respectively (Figure 2). The stretching band of $\nu(\text{N-H})$ has shifted to higher frequency compared to its ligand due to the additional electron withdrawing group near to the NH moiety. The strong absorption bands around 1690-1708 cm^{-1} are attributed to the stretching of $\nu(\text{C=O})$. The increasing in C=O frequencies are affected by the increasing of electron densities from aminopyridine pendant arms and central pyridine. This phenomenon has also resulted to intramolecular hydrogen bonding at amide moieties which at end given rise to a new peak at 3202 cm^{-1} . A strong stretching vibration for $\nu(\text{C=N})$ was indicated at 1523 cm^{-1} . The medium intensity band around at 513 and 618 cm^{-1} were assigned for Cu-O and Cu-N , respectively [9-10]. The data obtained from FTIR shows promising formation of a copper complex as expected. Involvement of solvents such water molecule and methanol were indicated 3558 and 3000 cm^{-1} , standing for OH stretching, respectively.

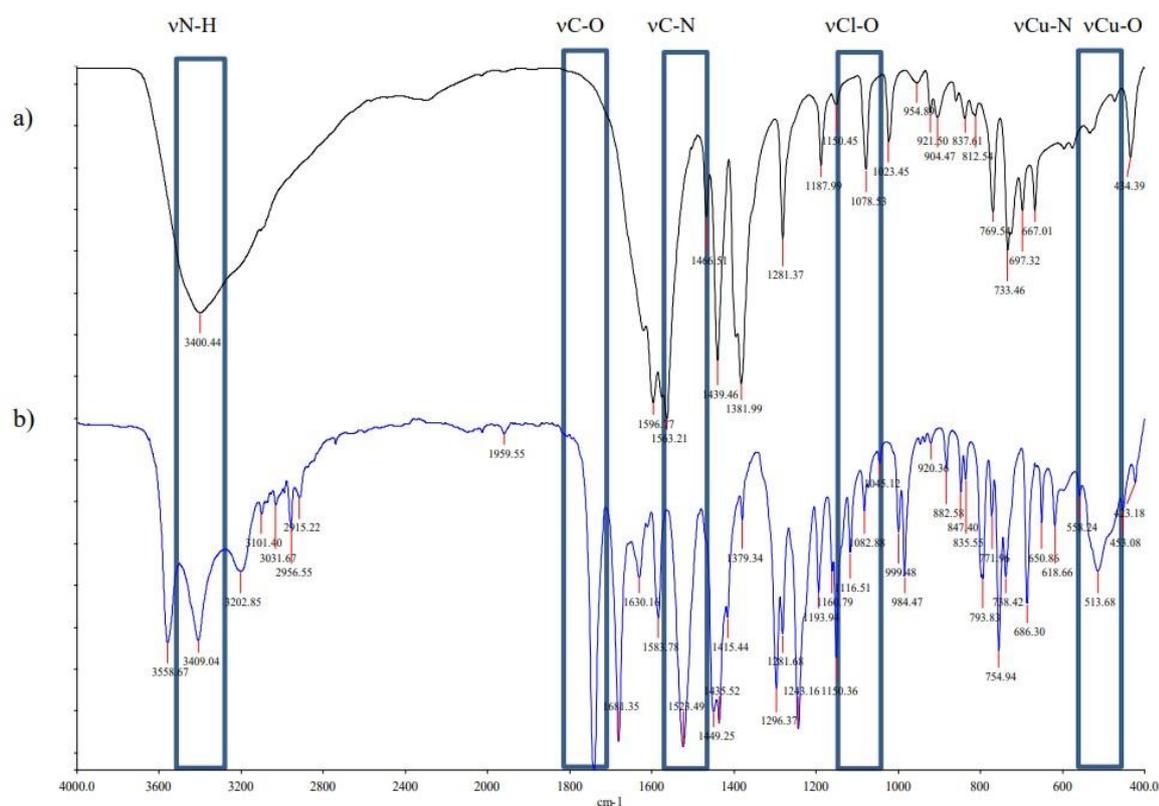


Figure 2. FTIR spectrum of the ligand(a) compared with copper complex (b)

4. X-ray crystallography

Due to the limited solubility of this complex, the only method that is suitable to determine the crystal structure of the blue crystals is single crystal X-ray crystallography techniques. These blue crystals were grown from the reaction solutions of ligand L2 with copper perchlorate in methanol and obtained as irregular shape crystals. The crystals crystallized in monoclinic space group $C2/c$. The asymmetric unit contains a repeating unit of the coordination polymer, with three copper atoms, three anionic carboxylate forms of the ligand L2, two neutral forms of ligand L2 and four partially-occupied non-coordinated perchlorate anions (Figure 3). An extended view of this structure reveals that it is a 1-D coordination polymer in which M_2L_2 units are linked by the carboxylate donors (Figure 4). The copper ion exhibits six coordination number and displayed distorted octahedral geometry as observed in Figure 4. The bond lengths about the copper environment are in the range of 2.361-2.423 Å. The present of weak hydrogen bonds between the amide moieties ($N-H \cdots N = 2.205 \text{ \AA}$) and perchlorate molecules ($N-H \cdots Cl = 2.172 \text{ \AA}$) were defined to stabilize the crystal structure (Figure 5). It was witnessed from the x-ray crystallography that the copper ion was coordinated by ONO tridentate donor and the repeating unit was linked by N monodentate from the pyridine pendant arm. This also has supported the formation of *in situ* ligand when reacted with metal salts as reported by us [6-7]. The detailed on the crystal data is shown in Table 2.

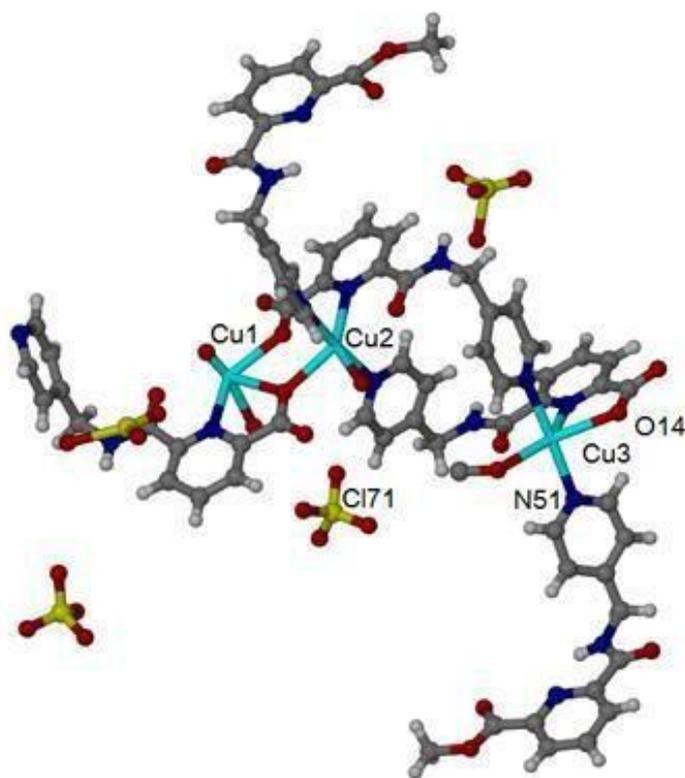


Figure 3. The asymmetric unit of $\{[Cu_3(L2-H_3)_3(L2)_2(H_2O)_2(CH_3OH)](ClO_4)_3\}_n$

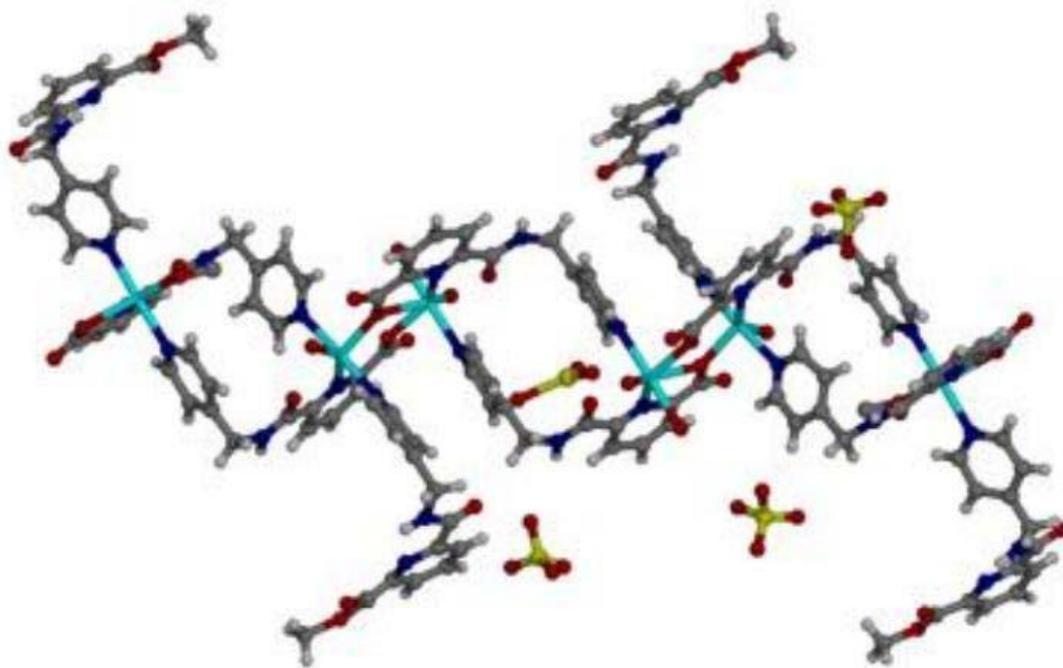


Figure 4. Extended structure of one dimensional coordination polymer with copper ions displayed distorted octahedral environment (turquoise colour)

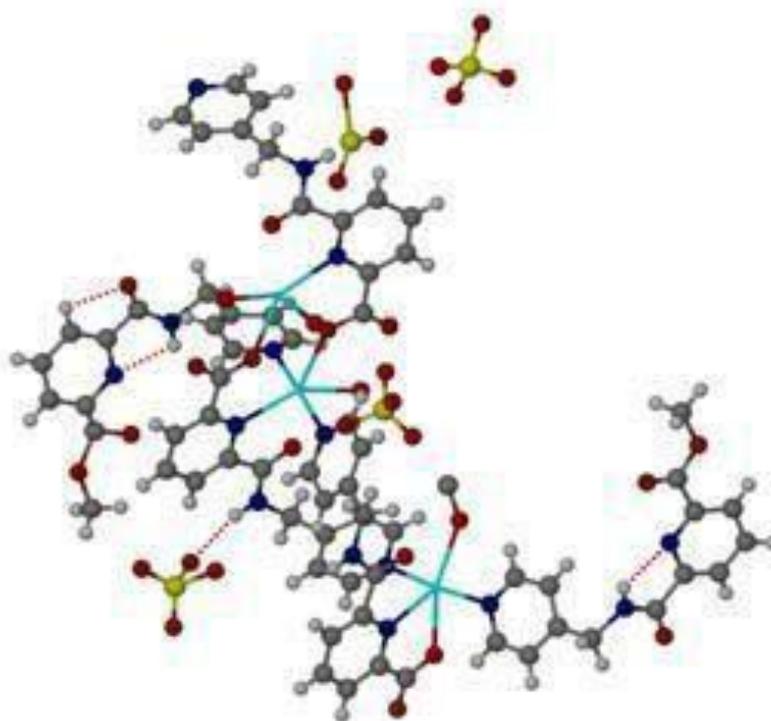


Figure 5. Hydrogen bonding interactions as pointed by dashed line

Table 2. Crystal data of the one-dimensional coordination polymer

Crystal data	Data
Empirical formula	C _{68.50} H ₆₈ Cl ₃ Cu ₃ N ₁₅ O _{33.50}
Formula weight	1934.35
Crystal system	Monoclinic
Space group	C2/c
a (Å)	49.155(10)
b (Å)	10.849(2)
c (Å)	33.877(7)
(°)	90
(°)	112.48(3)
(°)	90
Volume (Å ³)	16693(6)
Z	8
Density (calculated) (Mg/m ³)	1.539
Absorption coefficient (mm ⁻¹)	0.948
F(000)	7920
Crystal size (mm ³)	0.40x0.25x0.06
Theta range for data (°)	0.90 – 24.20
Reflections collected	12557
Observed reflections [I>2s(I)]	10953
Data/restraints/parameters	12557/6/922
Goodness-of-fit on F ²	2.146
R1 [I>2s(I)]	0.1438
wR2 (all data)	0.4275
Largest diff. peak and hole (e.Å ⁻³)	2.020 and -2.042

Figure 6 (a) depicts the micrographs of surface morphology for the ligand L2. The result shows that this ligand has irregular shaped flakes with different sizes. The size of each flake is measured as approximately 20-100µm. In contrast, the SEM results for the coordination polymer, has better surface morphology compared to the ligand. This material distributed homogeneously throughout the surface with irregular morphology and reasonable uniform sizes within 1-5µm (Figure 6(b)). This analysis has proved that the metal complex was formed in smaller sizes and homogeneous compared to the ligand.

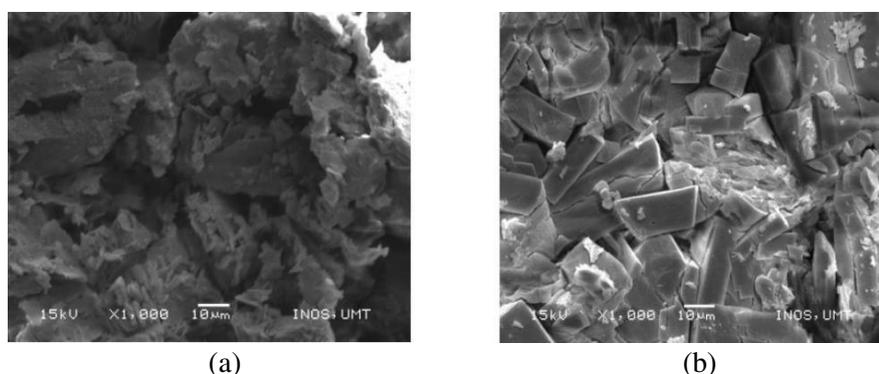


Figure 6. Surface morphology of (a) ligand
 b) $\{[\text{Cu}_3(\text{L2}-\text{CH}_3)_3(\text{L2})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})](\text{ClO}_4)_3\}_n$

5. Conclusion

In conclusion, a one-dimensional coordination polymer has been successfully synthesized using L2. Ligand *N*-6-[4-pyridylmethylamino)carbonyl]-2-pyridinecarboxylic acid methyl ester (L2) formed in situ ONO tridentate ligand when reacted with copper perchlorate and arranged in dinuclear based, one dimensional coordination polymer. Incorporation of copper ion has affected the particle size of the product.

6. References

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