



## Metal–organic frameworks based on pyridyl-tetrazole ligands containing ester or carboxylate pendant arms



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### ABSTRACT

The coordination of pyridyl-tetrazole derivatives containing ester substituents, at either the N-1 or N-2 position of the tetrazole ring, with copper(II) chloride results in the formation of either 1:1 or 1:2 copper to ligand complexes, depending on the ligand. However, when the ester functionality is changed to a carboxylate group, the resulting complexation reactions yield metal–organic frameworks. The resulting structures vary dramatically in pore size, depending on both reaction solvents and position of carboxylate group on the tetrazole ring. Despite the presence of sodium cations in the reaction mixtures, no sodium incorporation was ever observed in any of the complexes. This report represents the first attempts at producing copper(II) complexes of the N-1 and N-2 carboxylate derivative of this ligand.

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## 1. Introduction

Metal–organic frameworks (MOFs) have attracted remarkable attention in the past decade as a result of their amazing structural topographies [1], as well as their excellent properties and applications, including storage of gases, catalysis, drug delivery, magnetism and luminescence [2]. A large variety of MOFs have already been synthesised through the self-assembly of ligands and metal ions. However, the prediction of a final outcome in MOF synthesis remains a great challenge. The attainment of MOFs depends on many parameters such as coordination geometries of the metal centres, the coordination sites of the ligand used, metal–ligand ratio, the nature of the counter ions and solvent. Carboxylates and tetrazoles have been studied previously for their abilities to form coordination polymers [3]. However, research on coordination polymers composed of *n*-pyridyl-tetrazole derivatives (*n* = 3 or 4) is limited [4] while those composed of *n*-pyridyl-tetrazole derivatives (*n* = 2) are rare [5]. Our research with pyridyl-tetrazole ligands [6] has led to derivatives containing either pendant ester or carboxylate groups as organic linkers in MOFs (Scheme 1). The use

of carboxylate derivatives are of interest from a structural point of view, since the carboxylate group can adapt various coordination modes including monodentate and bidentate [7]. The combination of a pyridine ring and a tetrazole ring provide more coordination sites for metals to bind to and could impart rigidity in the final supramolecular structure. In this paper, we report on the reactions of these ligands with copper(II) chloride, including five crystal structures.

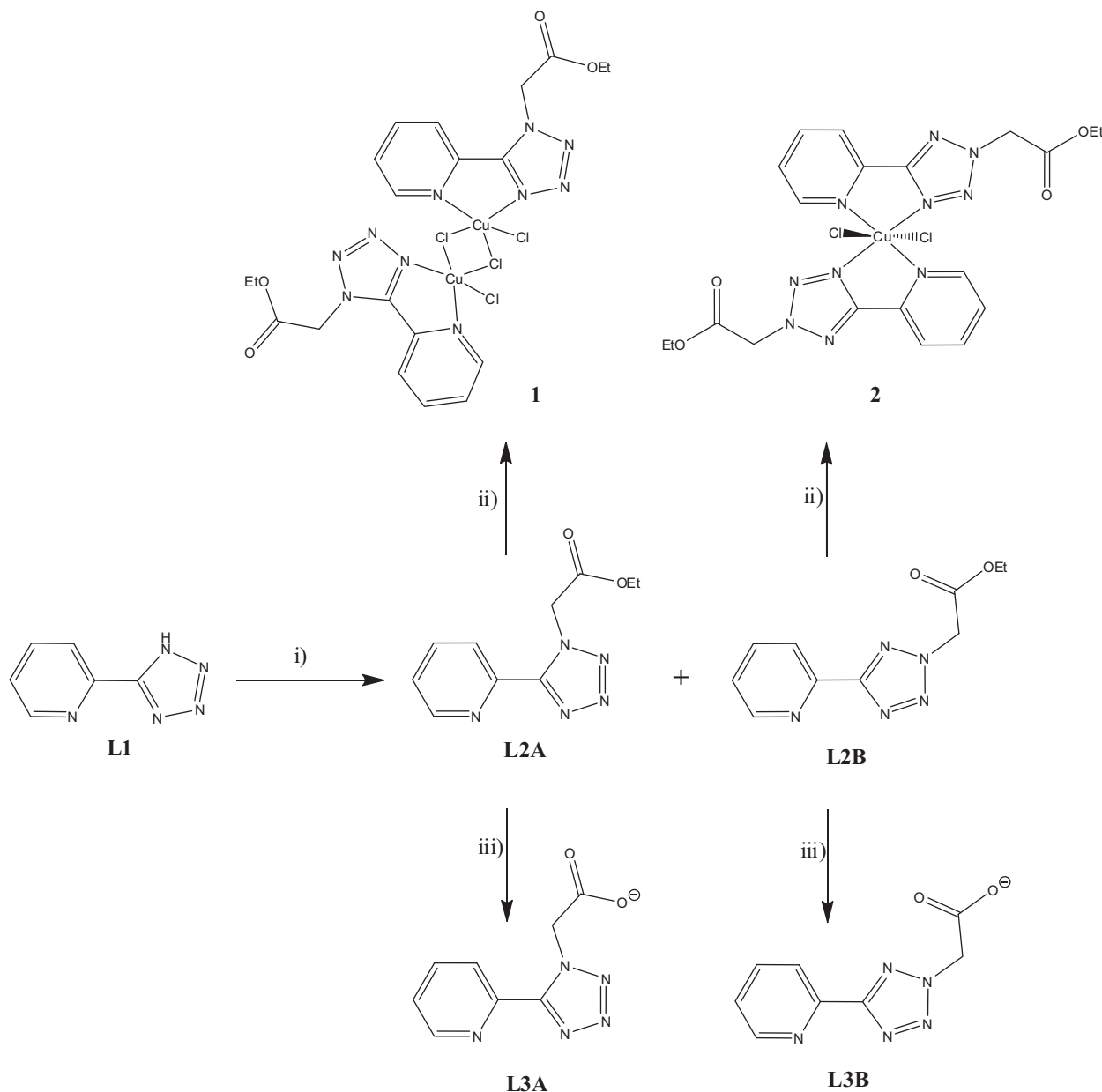
## 2. Results and discussion

### 2.1. Synthesis of ester ligands **L2A** and **L2B**

The reaction of 2-(2*H*-tetrazol-5-yl)pyridine (**L1**) with ethyl bromoacetate using potassium carbonate as base resulted in the formation of ethyl 2-(5-(pyridine-2-yl)-1*H*-tetrazol-1-yl)acetate (**L2A**) and ethyl 2-(5-(pyridine-2-yl)-2*H*-tetrazol-2-yl)acetate (**L2B**) in a 1:1 ratio, as shown in Scheme 1. The alkylation process at either the 1-*N* or 2-*N* positions is similar to what we have previously reported in the literature [7b,7c]. Column chromatography was used to separate the two products. In both cases, the loss of the CH<sub>2</sub>Br signal and the appearance of a triplet at 5.74 ppm for the 1-*N* compound **L2A** and 5.50 ppm for the 2-*N* compound **L2B**

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**Scheme 1.** Reaction conditions: (i) ethyl bromoacetate,  $\text{K}_2\text{CO}_3$ , MeCN,  $\Delta$ , 24 h; (ii)  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , MeOH, , 2 h; (iii) NaOH, MeOH/ $\text{H}_2\text{O}$ ,  $\Delta$ , 1 h.

in the  $^1\text{H}$  NMR spectra of the products was taken as evidence for the formation of the correct products. Furthermore, **L2A** gave a signal at  $\sim 152$  ppm, while **L2B** gave a signal at  $\sim 164$  ppm in their  $^{13}\text{C}$  NMR spectra, indicative of the formation of 1,5- and 2,5-disubstituted tetrazole rings [7a,8].

## 2.2. Synthesis and characterisation of copper complexes of **L2A** and **L2B**

The reaction of **L2A** or **L2B** with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in a 1:1 metal:ligand ratio in methanol resulted in highly coloured solutions, which were allowed to stand for several days. Green crystals of  $[\text{Cu}(\text{L2A})\text{Cl}_2]_2$  (**1**) and blue crystals of  $\text{Cu}(\text{L2B})_2\text{Cl}_2$  (**2**) crystallised from the respective solutions on standing (Scheme 1). The IR spectra of both **1** and **2** were obtained and compared with their respective starting ligands. It was observed that the carbonyl vibration remained unchanged on going from the ligand to the metal complex, which would suggest that the copper ion is not bonded to the ester group but is instead

bonded through the nitrogen atoms of the pyridine and tetrazole rings, as had been observed in other pyridine-tetrazole systems previously reported [7b,7c]. Elemental analyses of **1** and **2** suggested a 1:1 and a 1:2 metal to ligand ratio in each case. The copper complexes have a magnetic moment of 1.7 B.M. and 2.2 B.M. per copper atom, indicative of the presence of copper(II) in the complexes. Previously reported magnetic moments for complexes containing pyridyl-tetrazole ligands have been both high in value and high-spin in nature [7b,9]. The single crystal structures of both were established by X-ray crystallography. Crystallographic data for all structures are presented in Table 1 (SI).

## 2.3. Crystal structures of **1** and **2**

Compound **1** crystallises in the triclinic space group  $P\bar{1}$  and established the 1:2 nature of the molecule (Fig. 1a and b). The molecular structure consists of a dichloro-bridged dimeric  $\{\text{Cu}(\text{II})(\mu\text{-Cl})\text{Cl}\}_2$  unit, with the coordination sphere about each

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