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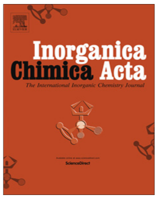

Zinc complexes of pyridyl-tetrazole derivatives – Highly fluorescent materials

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ABSTRACT

The ligands **L1Et** and **L2Et** were synthesised and hydrolysed *in situ* to form carboxylates, utilising methods previously established, for the purpose of investigating the ability of carboxylate functionalised pyridyl tetrazoles to form coordination polymers. These ligands were then reacted with $ZnCl_2$ and displayed interesting coordination chemistry as the position of the alkylation site appeared to have some effect on the coordination sphere of the metal centre. Solid state fluorescence spectroscopy was carried out on Zn(II) compounds and their corresponding free acid ligands at room temperature. The crystal structure of **L1Et** was also solved and showed the co-planarity of the two rings.

1. Introduction

Interest in metal–organic frameworks (MOFs) has increased dramatically over the last decade due in no small part to their potential applications in gas storage, drug delivery, luminescence and magnetism [1]. The self-assembly of various ligands and metal ions has resulted in a large number and variety of MOFs being synthesised and characterised [2]. When compared to the proliferation of symmetrical bidentate ligands such as 2,2′-bipyridine or 1,10-phenanthroline, the use of unsymmetrical 2-pyridyl-tetrazole derivatives in this regard is limited, thus far, to a small number of papers [3]. Our research with pyridyl-tetrazole ligands [4] has led to derivatives containing pendant carboxylate groups as organic linkers in MOFs (Fig. 1). Herein, we report on the *in situ* reactions of these ligands with zinc(II) chloride, including NMR spectroscopy and fluorescence studies.

2. Results and discussion

2.1. Synthesis of ligands *L1* and *L2*

The reaction of 2-(2*H*-tetrazol-5-yl)pyridine (**L**) 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 (**L1Et**) and ethyl 2-(5-(pyridine-2-yl)-(2*H*-tetrazol-2-yl)acetate (**L2Et**) in a 1:1 ratio, as has been previously reported [3a]. The reactions of these two compounds with NaOH were carried out in a mixture of methanol and water to give **L1** and **L2** (as in Scheme 1) which were used *in situ* without purification or characterisation, as previously reported [3a].

Single crystals were obtained for **L1Et** and were analysed by X-ray crystallography. The structure is shown in Fig. 2 and reveals that the pyridine and tetrazole rings are almost co-planar with respect to each other at 6.15(14)° (A) and 2.60(14)° (B), with the ester pendant arm not having a pronounced effect on deviations from co-planarity; Table 1 gives the relevant crystallographic data. The methylene group connecting the ester moiety to the tetrazole ring allows the group to orientate itself out of the heterocyclic planes, being at an angle of 78.60(12)° (molecule A) and 74.37(12)° (molecule B) to the tetrazole ring, calculated when using the five ester atoms (O1, O2, C1, C2, C3). There are no intermolecular hydrogen bonds of note in the crystal structure apart from weak C–H…N/O interactions.

2.2. Synthesis and characterisation of zinc complexes of *L1* and *L2*

The reaction of **L1Et** with NaOH in methanol followed by the addition of a methanolic solution of $ZnCl_2$ yielded a clear solution which was allowed to stand for several days. A crystalline creamy

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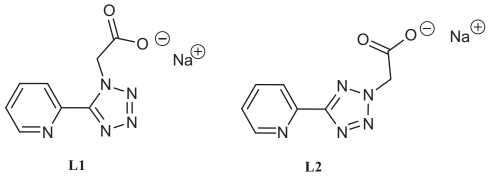
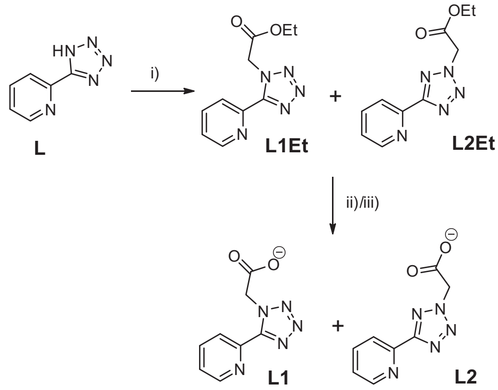


Fig. 1. Ligands used in complexation reactions with zinc(II) ions [3a].



Scheme 1. Synthesis of **L1** and **L2**. Reagents and conditions: (i) K_2CO_3, $BrCH_2CO_2Et$, MeCN, Δ, 24 h; (ii) NaOH, MeOH or (iii) NaOH, MeOH:H_2O.

Table 1
Crystallographic data for **L1Et**.

Structural and refinement data	**L1Et**
Chemical formula	$C_{10}H_{11}N_5O_2$
M_r	233.24
Crystal system, space group	triclinic, $P\bar{1}$ (no. 2)
T (K)	294(2)
a (Å)	9.3222(18)
b (Å)	9.591(2)
c (Å)	14.147(3)
α (°)	70.50(2)
β (°)	78.456(18)
γ (°)	84.105(18)
V (Å^3)	1167.3(4)
Z	4
μ (mm^{-1})	0.10
Crystal size (mm)	0.26 × 0.26 × 0.08
T_{min}	0.975
T_{max}	09.992
No. of measured, independent and observed reflections	8885, 5053, 2449
R_{int}	0.054
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.178, 1.03
No. of reflections, parameters, restraints	5053, 310, 0
H-atom treatment	H atoms treated by constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.19

white solid formed which was filtered and washed with MeOH. The IR spectrum of the solid showed the absence of the characteristic band for the protonated carboxylate group (1724 cm^{-1}) indicating the complete deprotonation of **L1**. A $\nu_{asym}(COO^-)$ band could clearly be seen at 1650 cm^{-1}, and the corresponding $\nu_{sym}(COO^-)$ band was observed at 1365 cm^{-1}. This gave a $\Delta(\nu_{asym}(COO^-) - \nu_{sym}(COO^-))$ value of 285 cm^{-1}, suggesting a monodentate coordination of the carboxylate group to the Zn(II) atom [5]. Shifts for the heterocyclic ν(C═N) and ν(N═N) were also noted to have shifted from 1478, 1438 and 1354 cm^{-1} to 1610, 1474 and 1462 cm^{-1} respectively. This indicated that Zn(II) coordination to the pyridine and tetrazole nitrogen atoms was also occurring. There was no indication of coordinating solvent molecules or hydrogen bonding in the IR spectrum, as the only peaks in the region of 3000 cm^{-1} were aliphatic C–H stretching vibrations. Elemental analysis suggested that the composition of the complex had a 1:2 metal to ligand ratio. Therefore it was proposed that the Zn(II) atom was in an octahedral geometry, with four coordination sites taken up by chelation to two **L1** ligands *via* four nitrogen atoms and the remaining two coordination sites taken up by two carboxylate oxygen atoms from two different **L1** ligands bonding to the Zn(II) ion in a monodentate manner. This would lead to a 1-D polymeric chain as observed previously in the corresponding copper(II) complex of this ligand, which we have previously reported [3a]. The proposed structure of the Zn(II) complex (Zn(**L1**)$_2$) and the crystal structure of the copper(II) complex are presented in Fig. 3.

The ^{1}H NMR analysis of Zn(**L1**)$_2$ was carried out in d_6-DMSO and resulted in a simple spectrum. The spectrum showed differences in shifts from those found in the ^{1}H NMR spectrum of the free protonated ligand **L1**, indicating that the complex was not breaking apart into free ligand in the DMSO solution. Five peaks in total were observed, which would be expected if the complex had the structure as depicted in Fig. 3. Four multiplets arising from the pyridyl protons were seen at 7.57, 8.04, 8.25 and 8.68 ppm and a

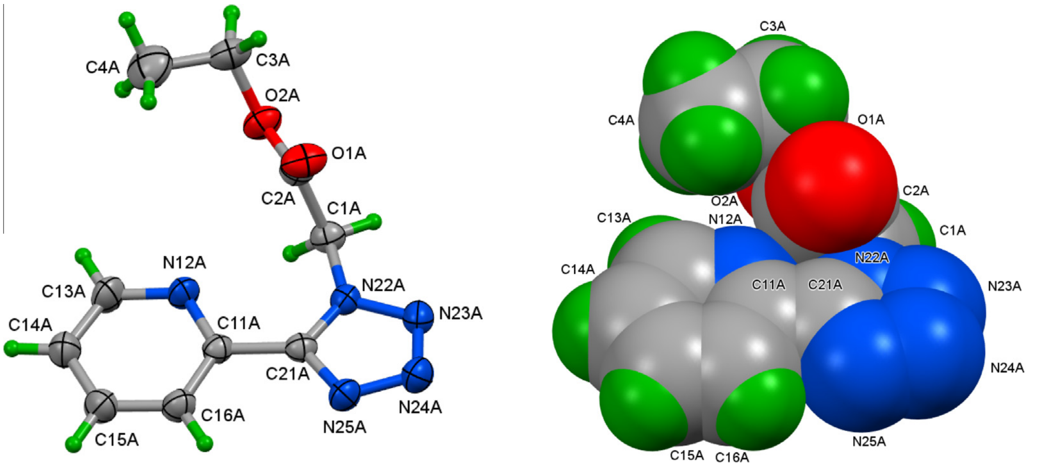


Fig. 2. An ORTEP (left) and CPK-style diagram (right) of molecule A in the crystal structure of **L1Et**, demonstrating the non-planar nature of the ester arm with respect to the pyridyl tetrazole rings. Molecule B (not shown) is labelled in an analogous fashion with displacement ellipsoids at the 30% level in both molecules.