

# **3,5-disubstituted-*N*-hydroxyalkylpyrazole Cu(II) compounds: Anion effect on dimensionality, supramolecular structure and magnetic properties**

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## Abstract

The coordination behavior of *N,O*-hybrid pyrazole ligand 2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol (**HL**) against different Cu(II) salts has been studied. Five coordination complexes (**1-5**) have been synthesized and characterized by elemental analysis, conductivity measurements and spectroscopic measurements. Moreover, the crystal structure of all five compounds has been elucidated, allowing the detailed study of their molecular and supramolecular structure. The obtained compounds are structurally diverse, as ionic monomers, neutral dimers and a polymer have been isolated. Their nuclearity seems to be very dependent on the dehydration of the pyrazole moiety, whereas co-ligands have a direct influence on their dimensionality and supramolecular structure. Upon crystallization, compound **5** adsorbs water molecules, resulting in a particularly intriguing supramolecular network. In this scaffold, the presence of three water moieties playing different supramolecular roles has been analyzed *via* computational methods and thermogravimetric analyses. Lastly, magnetic susceptibility measurements have been carried out for **3** and **5** and the results were rationalized on account of their structure.

**Keywords:** Cu(II) complexes, *N,O*-Hybrid ligand, Pyrazole ligand, Magnetic properties

## Introduction

As the design and synthesis of new functional hybrid metal-organic materials continues to evolve, it has been proven that functionality and structure are intimately entangled [1-5]. Thus, the assembly of desirable coordination architectures, or crystal engineering, has become a core discipline in materials science. This discipline focuses on the judicious selection or synthesis of suitable organic ligands, as well as the control of reaction conditions such as solvent, pH or metal salt [6-9], for the obtention of function-enhancing structural motifs and also in the study of function-structure relationship.

Among the plethora of available ligands, *N*-heterocyclic donors have proven one of the most interesting ones. Since the pioneering use of 4,4'-bipyridine as a building block for the obtention of multidimensional architectures, pyridines, pyrimidines and azoles [9-12] are gaining attention. The increasing need for smarter and more efficient materials, as well as desired functionalities such as self-selection and self-recognition [13,14], has led to the emergence of hetero donating functions, thus development of hybrid ligands bearing the *N*-heterocyclic motif and a second donor atom (*O*-, *S*-, *P*-...) is thriving [15-17]. Moreover, the presence of a second functional group in the organic scaffold lends itself to the tailoring of the supramolecular network, as it leads the way to the incorporation different hydrogen bonding synthons such as alcohols, carboxylates or amides [8,15].

One of the most studied families of ligands containing *N*-heterocyclic functionalities is that of the pyrazolyl-derived ones. In the field of crystal engineering, the pyrazolyl ring has the exciting ability to be easily modified according to the desired interest. They can be substituted in positions 1- (*N*-substitution), 3-, 4- and 5-, thus opening an immense world of possibilities for the molecular artisan [18-23]. Hence, pyrazole-derived ligands have been extensively used for constructing a wide array of architectures bearing different properties such as magnetism [24,25], photoluminescence [26,27], catalytic activity [28,29] and porosity [30]. Moreover, they also possess promising biological activities [31]

In this context, our group has a great interest in the study of pyrazole hybrid *N,O*-donors, particularly 3,5-disubstituted-*N*-hydroxyalkylpyrazole ligands. Over the

years we have synthesized several related ligands and studied its reactivity against different transition metals such as Pd(II) [32-39], Pt(II) [36-38,40], Ag(I) [38], Cu(II) [38,39,41], Zn(II) [37,39,42,43], Cd(II) [42,43] and Hg(II) [42,43].

As continuation of these studies we present a study of the reactivity of 2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol (**HL**) with different Cu(II) salts: CuCl<sub>2</sub>·2H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, and Cu(MeCO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O, yielding complexes [CuCl(μ-L)]<sub>2</sub> (**1**), [CuCl(**HL**)<sub>2</sub>]Cl (**2**), {[Cu(μ-NO<sub>3</sub>)(μ-L)]<sub>2</sub>]<sub>n</sub> (**3**), [Cu(NO<sub>3</sub>)(**HL**)<sub>2</sub>]NO<sub>3</sub> (**4**) and [Cu(MeCO<sub>2</sub>)(μ-L)]<sub>2</sub> (**5a**). This last compound is hydrated upon crystallization, yielding [Cu(MeCO<sub>2</sub>)(μ-L)]<sub>2</sub>·6H<sub>2</sub>O (**5b**). Complexes **1-5b** were characterized by elemental analysis, conductivity measurements and FTIR-ATR and UV-Vis spectroscopy. Moreover, X-ray crystals structures of **1-4** and **5b** were elucidated and phase purity of the compounds was assessed using powder X-ray diffraction. Their molecular and supramolecular structures are discussed in detail, with special emphasis in the role of the auxiliary ligand (Cl, NO<sub>3</sub>, MeCO<sub>2</sub>). Moreover, as compound **5b** contains occluded solvents, their role in the supramolecular network has been analysed with computational support and its thermal stability and desorption process studied. Lastly, the magnetic properties and magneto-structural correlations for **1** and **5a** were discussed. Although there are some reported papers studying the reactivity of **HL** with copper(II) salts [44-46], the coordination chemistry of pyrazolyl ligands seems to be really sensible to reaction conditions such as solvent or working ratios, and we are able to report four new compounds which have not been previously described (**2-5b**), one of them showing a particularly unusual architecture.

## Results and discussion

### Synthesis and general characterization

Reaction of CuCl<sub>2</sub>·2H<sub>2</sub>O with 2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol (**HL**) in a 1:1 ratio in methanol (MeOH) leads to the successive isolation of dimeric [CuCl(μ-L)]<sub>2</sub> (**1**) and ionic monomeric [CuCl(**HL**)<sub>2</sub>]Cl (**2**). A similar behavior is observed with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, yielding polymeric {[Cu(μ-NO<sub>3</sub>)(μ-L)]<sub>2</sub>]<sub>n</sub> (**3**) and ionic monomeric [Cu(NO<sub>3</sub>)(**HL**)<sub>2</sub>]NO<sub>3</sub> (**4**). Conversely, the reaction of Cu(MeCO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O with **HL** in a 1:1 ratio in MeOH only yields one product: dimeric [Cu(MeCO<sub>2</sub>)(μ-L)]<sub>2</sub> (**5a**). This

reaction requires the addition of aqueous ammonia to the mother liquors. The same reactions have also been assayed using a 1:2 ratio and ethanol (EtOH) as solvent. It is worthwhile to mention that while for reactions using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{Cu}(\text{MeCO}_2)_2 \cdot \text{H}_2\text{O}$  the same products are obtained (albeit with different yields), for reactions with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , the use of different reactants ratio and solvents leads to the isolation of the reported monomeric  $[\text{Cu}(\text{NO}_3)_2(\mathbf{HL})_2]$  [44] compound in different yields or in mixtures with **4**.

For compounds **1-4**, it has been possible to obtain crystals suitable for X-ray diffraction. Moreover, recrystallization of **5a** in MeOH yields  $[\text{Cu}(\text{MeCO}_2)(\mu\text{-L})_2] \cdot 6\text{H}_2\text{O}$  (**5b**) (Scheme 1). Although crystal structure of compound **1** has been previously reported [46], in the present work its synthetic route is different, as it is obtained as a minority product in the synthesis of **2**. Moreover, its supramolecular structure is discussed in deep. Furthermore, it illustrates how the reactions of **HL** with  $\text{Cu}(\text{MeCO}_2)_2 \cdot \text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  behave in a similar fashion, resulting in the isolation of one dimeric/polymeric product bearing a deprotonated ligand and one ionic monomeric product bearing a protonated ligand. Owing to these reasons, it has been included in the present work.

### [Insert Scheme 1]

All compounds were characterized by analytical and spectroscopic techniques. Spectroscopic details of the characterization of all compounds are found in the Materials and methods section and Supporting Information (SI). Elemental analyses (EA) of **1-5a** agree with the proposed formula. For compound **5b**, however, EA are in accordance to the formula  $[\text{Cu}(\text{MeCO}_2)(\mu\text{-L})_2] \cdot 4\text{H}_2\text{O}$  due to the loss of occluded solvent molecules. For complexes **1-3** phase purity of the bulk samples was confirmed by Powder X-ray diffraction (PXRD, Fig. S1-S3, SI). It was not possible to record the PXRD of **4** due its low yield. PXRD of **5a** and **5b** shows that the loss of their solvent molecules (two water molecules for bulk **5b** and six water molecules for bulk **5a**) does not result in the collapse of the crystal structure (Fig. S4, SI).

Conductivity values in MeOH for complexes **1** and **5a** agree with a non-electrolyte behavior ( $20\text{-}24 \text{ } \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ). For complexes **2** and **4**, their conductivity values are consistent with the presence of a 1:1 electrolyte ( $94\text{-}111 \text{ } \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ). The conductivity

measurements of **3** were carried out in dimethylformamide (DMF) due its insolubility in MeOH, showing the presence of a non-electrolyte ( $36 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ).

The FTIR-ATR spectra of **1-5a** in the range of  $4000\text{-}500 \text{ cm}^{-1}$  confirm the coordination of the ligand to the metal centre (Fig. S5-S9, SI). Moreover, the FTIR-ATR spectrum of a crystalline sample of **5b** was also recorded (Fig. S10, SI). The most characteristic band of the IR spectra are those attributable to  $[\nu(\text{C}=\text{C}/\text{C}=\text{N})_{\text{ar}}]$  ( $1585\text{-}1547 \text{ cm}^{-1}$ ),  $[\delta(\text{C}=\text{C}/\text{C}=\text{N})_{\text{ar}}]$  ( $1403\text{-}1387 \text{ cm}^{-1}$ ) and  $[\delta(\text{C-H})_{\text{ip}}]$  ( $1086\text{-}1019 \text{ cm}^{-1}$ ) [47]. Moreover, the presence of protonated or deprotonated pyrazole can be seen in compounds **1-5a**, as in **2** and **4** bands attributable to  $[\nu(\text{OH})]$  can be seen ( $3191$  and  $3125 \text{ cm}^{-1}$ ) [47], whereas for **1**, **3** and **5a** no signals can be seen in this region. Furthermore, for compounds **3** and **4** bands attributable to  $[\nu(\text{NO}_3)]$  can be seen at  $1454\text{-}1422 \text{ cm}^{-1}$  and  $1280\text{-}1269 \text{ cm}^{-1}$  [47]. The region between  $1800\text{-}1700 \text{ cm}^{-1}$ , which hosts bands attributable to  $\nu_1+\nu_4$  vibrations of nitrate groups [48], has been studied for **3** and **4**. For **3**, the presence of four identifiable bands in the region of  $1760\text{-}1710 \text{ cm}^{-1}$  suggests a complicate behaviour of the nitrate moiety. In fact, this pattern indicates to the presence of monodentate and bidentate coordination modes [48], which is in agreement with the chelate and bridging behavior of the nitrate moiety on **3**. For **4**, three bands are detected. The intense band at  $1750 \text{ cm}^{-1}$  is typical of ionic nitrates, whereas the two bands at  $1770 \text{ cm}^{-1}$  and  $1712 \text{ cm}^{-1}$  suggest a bidentate coordination behaviour [48]. This may indicate the existence of two different nitrate moieties in **4**. FTIR-ATR spectra of **5a** displays characteristic  $[\nu_{\text{as}}(\text{COO})]$  ( $1547 \text{ cm}^{-1}$ ) and  $[\nu_{\text{s}}(\text{COO})]$  ( $1423 \text{ cm}^{-1}$ ) bands. The difference between these bands ( $\Delta = [\nu_{\text{as}}(\text{COO})] - [\nu_{\text{s}}(\text{COO})]$ ),  $124 \text{ cm}^{-1}$ ) suggests a bidentate chelate coordination mode [47,49]. Compound **5b** presents a similar spectrum to **5a**, except for a broad band centred at  $3368 \text{ cm}^{-1}$ , attributable to  $[\nu(\text{OH})]$ , confirming the presence of occluded water molecules [47]. Upon further investigation, this broad band appears to be formed by the overlapping of three smaller bands at  $3473 \text{ cm}^{-1}$ ,  $3368 \text{ cm}^{-1}$  and  $3269 \text{ cm}^{-1}$ , which suggests the presence of three types of occluded water molecules. The IR spectral data, therefore, agrees with the elucidated crystal structures, which are described below.

### Crystal and extended structure of compound $[\text{CuCl}(\mu\text{-L})]_2$ (**1**)

Compound **1** (Fig.1) crystallizes in the triclinic  $P\bar{1}$  space group, showing a dimeric structure with a Cu:L:Cl 1:1:1 ratio. In this oxygen bridged centrosymmetric

dimers, Cu(II) ions adopt a [CuO<sub>2</sub>NCl] *core*, where one oxygen and one nitrogen are provided by a deprotonated **L** ligand, while one oxygen of a different deprotonated **L** ligand and a chlorine atom complete the coordination environment. The parameter  $\tau_4$  describes the geometry of a four-coordinate system, 0.00 corresponding to a square-planar geometry and 1.00 to a tetrahedral geometry [50]. Thus, Cu(II) atoms in **1** have a seesaw geometry ( $\tau_4 = 0.27$ ), which could be promoted by the chelating behavior of **L**. This distortion is reflected in the *trans* O-Cu-N/Cl bond angles (162.39(3)°/159.67(4)°), which deviate from linearity. Therefore, **L** acts as a bidentate chelated and bridged ligand, forming a six-member metallacycle ring with a boat conformation, the bite angle O1-Cu1-N1 value being 91.09(4)°. Other selected bond lengths and angles for **1** are provided on Table 1. These values are in agreement with related pyrazole compounds [44-46,51].

[Insert Figure 1]

[Insert Table 1]

The dimeric units of **1** are held together *via* a set of H-bond interactions, forming a 2D supramolecular layer along the *ab* plane (Fig. 2). In this layer, each dimer is linked to four other dimers thanks to two centrosymmetric head-to-head H-bond interactions, chlorine atoms playing an interesting role in them. The first involves the chlorine atoms and the methyl groups in the pyrazolyl group (C5-H5A...Cl1, Table 1) and is responsible for the expansion along the crystallographic *b* direction. The second one involves the alkylic chain and coordinated oxygens (C6-H6B...O1, Table 1) both belonging to the pyrazolyl groups (Fig. 2). This interaction is responsible for the expansion in the crystallographic *c* direction. In this arrangement, the closest intermolecular Cu...Cu distance is 4.2990(3) Å in the crystallographic *a* direction and 8.5545(5) Å in the *b* direction.

[Insert Figure 2]

### Crystal and extended structure of compound [CuCl(HL)<sub>2</sub>]Cl (**2**)

Compound **2** crystallizes in the orthorhombic Pccn space group (Fig. 3). It has an ionic structure, comprising a monomeric cation and a chlorine as an anion in a Cu:HL:Cl 1:2:2 ratio. In this monomer, Cu(II) ions adopt a heavily distorted ( $\tau_5=0.40$ ) [52] square pyramidal [CuO<sub>2</sub>N<sub>2</sub>Cl] *core* geometry. The basal plane is formed by one

chlorine atom, one oxygen and one nitrogen from the first **HL** ligand and one nitrogen from the second **HL** ligand. The apical position is occupied by the oxygen of the second **HL** ligand, lying at a longer distance due to Jahn-Teller effect [53]. In this compound, **HL** acts as a bidentate chelate ligand forming a six-member metallacycle ring with a boat conformation, the bite angle O1-Cu1-N1 value being 85.61(4)° and O2-Cu1-N3 being 88.57(5)°. Selected bond lengths and angles are gathered in Table 2. Bond lengths and angles are in agreement with related pyrazole compounds [54-58].

[Insert Figure 3]

[Insert Table 2]

Once again, chlorine atoms play a key role in their supramolecular structure. Each monomer is linked to three other dimers *via* three distinct supramolecular interactions, forming a 2D supramolecular layer along the *bc* plane (Fig. 4). The first one involves the pyrazolyl hydrogen and the free chlorine atom (C3-H3...Cl2, Table 2). The second one involves the same chlorine atom and the protonated alcohol moieties (O1-H1...Cl2, O2-H2...Cl2, Table 2). The combination of both results in the formation of a *zig-zag* 1D-chain along the crystallographic *c* direction. The third one, involving a head-to-head H-bond between coordinated chlorine atoms and the methyl groups (C6-H6B...Cl1, Table 2) of the pyrazolyl ring, binds together these chains along the crystallographic *b* direction (Fig. 4). In this arrangement, closest Cu...Cu distances are 7.4796(6) Å and 10.1644(5) Å in the crystallographic *c* and *a* direction respectively.

[Insert Figure 4]

### Crystal and extended structure of compound $\{[\text{Cu}(\mu\text{-NO}_3)(\mu\text{-L})_2]_n\}$ (**3**)

Compound **3** (Figure 5a) crystallizes in the monoclinic  $P2_1/c$  space group. It has a polymeric structure, formed by oxygen bridged centrosymmetric dimeric units in a 1:1:1 Cu:L:NO<sub>3</sub> ratio. In those dimers, Cu(II) ions adopt a distorted octahedral  $[\text{CuO}_4\text{N}_2]$  core ( $\text{ata} = 46.92^\circ$ ) [59,60]. The basal plane comprises two bridging oxygen atoms of deprotonated **L** ligands, one nitrogen atom of a **L** ligand and one oxygen atom of the nitrate moieties. The apical positions are occupied by the bridging oxygen atoms of the nitrate ligand, which lie at a longer distance due to Jahn-Teller distortion [53]. The spatial constraints of this chelated nitrogen ligand induce a distortion of the

octahedral geometry in the apical position, as the apical atom deviates from linearity (O1#1-Cu1-O3, 113.09(9)° instead of ca. 90°)

Thus, in this compound both **L** and nitrate act as bidentate chelate and bridging ligands. Moreover, **L** forms a six-member metallacycle ring with a boat conformation, the O1-Cu1-N1 bite angle being 91.31(1)°. The nitrate, on the other hand, chelates in an anisobidentate fashion, as seen by Cu(1)-O(2) and Cu(1)-O(3) distances (2.004(2) Å and 2.594(2) Å,  $d_1-d_2 < 0.6$  Å) and Cu(1)-O(2)-N(3) and Cu(1)-O(3)-N(3) angles (107.18(2)° and 79.94(2)°,  $\theta_1-\theta_2 < 28^\circ$ ) [61]. The nitrate moiety is also responsible for bridging those dimeric units, forming an edge-sharing bioctahedral 1D polymeric chain in the crystallographic *b* direction, distance between repeating units being 4.777(3) Å (Fig. 5b). It is worth to remark the disposition of pyrazolyl rings, as they are completely parallel to both its contiguous and alternate pyrazolyl rings. Relevant distances and angles are summarized in Table 3.

**[Insert Figure 5]**

**[Insert Table 3]**

The supramolecular structure of **3** consists of 2D planes parallel to the crystallographic *bc* directions (Fig. 6). The nitrate ligand is key in maintaining this supramolecular scaffold, as it forms a double-hydrogen bond linking consecutive chains. Not only does its non-coordinated oxygen atom participates in strong H-bonds with hydrogens from the alkylic chain (C7-H7A...O4, Table 3), but also the chelate and bridging oxygen is involved in interactions with hydrogens from the methyl groups (C5-H5A...O2, Table 3). These two interactions result in a dense network of hydrogen bonds between neighbouring chains (Fig. 6). In this arrangement, closest interchain Cu...Cu distances are 8.070(1) Å in the *c* direction.

**[Insert Figure 6]**

#### **Crystal and extended structure of compound [Cu(NO<sub>3</sub>)(HL)<sub>2</sub>]NO<sub>3</sub> (**4**)**

Compound **4** (Fig. 7) crystallizes in the monoclinic P2<sub>1</sub>/c space group. It has an ionic structure, comprising a monomeric cation and a nitrate as an anion in a Cu:HL:NO<sub>3</sub> in a 1:2:2 ratio, much in the same manner of **2**. However, as opposed to **2**, which has a square pyramidal geometry, in **4**, Cu(II) ions adopt a distorted octahedral [CuO<sub>4</sub>N<sub>2</sub>] core ( $\alpha = 47.28^\circ$ ) [59,60], due to the chelating behavior of a nitrate moiety.

The basal plane is formed by one oxygen and one nitrogen atom from the first **HL** ligand, one nitrogen from the second **HL** ligand and one oxygen from the nitrate moiety. The apical positions are occupied by the oxygen of the second **HL** ligand and the second oxygen of the chelate nitrate. The chelate coordinating mode of the nitrate promotes the distortion of the octahedral geometry, resulting in angles ranging from 52.75(5)° to 149.18(5)°. However, these chelate behavior could be considered weak, as the Cu(1)-O(3) / Cu(1)-O(5) distances (2.0102(13) Å / 2.700(2) Å,  $d_1-d_2 = 0.69$  Å) and Cu(1)-O(3)-N(5) / Cu(1)-O(5)-N(5) angles (109.90(10)° / 78.54(10)°,  $\theta_1-\theta_2 = 31.36^\circ$ ) are on the verge of the anisobidentate ( $d_1-d_2 < 0.6$  Å,  $\theta_1-\theta_2 < 28^\circ$ ) and unidentate ( $d_1-d_2 > 0.6$  Å,  $\theta_1-\theta_2 > 28^\circ$ ) coordination modes [61]. Regarding **HL**, it acts as a bidentate chelate ligand with a boat conformation, having a O-Cu-N bite angle ranging between 88.06(6)°-90.83(6)°. Selected bond lengths and angles are gathered in Table 4. These values are in agreement with the Co(II) analogue [Co(NO<sub>3</sub>)(**HL**)<sub>2</sub>]NO<sub>3</sub> [45] and other similar nitrate Cu(II) compounds [44,58,62].

[Insert Figure 7]

[Insert Table 4]

The supramolecular structure of **4** is dominated by the formation of H-bond interactions between the alcohol moiety of **HL** and the anionic NO<sub>3</sub> ligands. This double O1-H1O...O7 and O2-H2O...O6 H-bond (Table 4) results in the formation of supramolecular chains along the *c* axis (Fig. 8). In this arrangement, closest Cu...Cu distances are 8.1751(6) Å.

[Insert Figure 8]

### Crystal and extended structure of compound [Cu(MeCO<sub>2</sub>)( $\mu$ -**L**)]<sub>2</sub>·6H<sub>2</sub>O (**5b**)

Compound **5b** (Fig. 9) crystallizes in the monoclinic P2<sub>1</sub>/c space group, showing a dimeric structure with a Cu:**L**:Acetate 1:1:1 ratio and six non-coordinated water molecules per dimer. In this oxygen bridged centrosymmetric dimers, the Cu(II) ions adopt a square pyramidal ( $\tau_5=0.03$ ) [52] [CuO<sub>4</sub>N] *core*. The basal plane consists of two asymmetric bridging alkoxy groups provided by two **L** ligands, one nitrogen atom of a **L** ligand and oxygen atom of the chelated acetate group. The apical position is occupied by the other oxygen of the acetate group. In this compound, **L** acts as a bidentate bridging and chelate ligand forming a six-member metallacycle ring with a boat conformation, while the acetate acts as a chelate ligand. The bite angles values are

92.90(4)° (O1-Cu1-N1) for **L** and 57.71(3)° (O1-Cu1-N1) for the acetate moiety. Selected bond lengths and angles are provided on Table 5. They are in agreement with similar compounds found in the literature [63].

**[Insert Figure 9]**

**[Insert Table 5]**

The supramolecular structure of **5b** is dominated by the presence of six non-coordinated water molecules per dimer (Fig. 10). Not only do they form strong hydrogen bonds between themselves, but also with coordinated oxygen atoms of the acetate moiety (O3W-H3WB...O2, O1W-H1WB...O3, Table 6) and with a proton of the alkylic chain (C6-H6B...O1W, Table 6). As a result, compound **5b** has a clathrate-like structure of alternating layers of H<sub>2</sub>O molecules and dimers. Thus, **5b** has a solvent accessible surface of 293.14 Å<sup>3</sup>, which represents 21.1 % of its unit cell volume (measured with a probe radius 1.2 Å, Fig. 10).

**[Insert Figure 10]**

The detailed analysis of the supramolecular structure reveals that H<sub>2</sub>O molecule II (H2WA-O2W-H2WB) is the lynchpin of the whole architecture, as it binds together H<sub>2</sub>O molecule I (H1WA-O1W-H1WB) and H<sub>2</sub>O molecule III (H3WA-O3W-H3WB). In turn, each H<sub>2</sub>O I links two dimers due to the presence of the O1W-H1WB...O3 (Table 6) and the C6-H6B...O1W (Table 6) interactions, involving coordinated oxygens of the acetate ligand and the alkylic chain. Meanwhile, H<sub>2</sub>O III only interacts with only one dimer through the O3W-H3WB...O2 (Table 6) interaction, involving coordinate oxygens of the acetate ligand. Thus, it is the interaction of each H<sub>2</sub>O molecule II with two H<sub>2</sub>O I (O1W-H1WA...O2W, O2W-H2WB...O1W, Table 6) and two H<sub>2</sub>O III (O3W-H3WA...O2W, O2W-H2WA...O3W, Table 6) which holds together the three-dimensional network. In this arrangement, the closest Cu...Cu distances are 6.6263(4) Å (Fig.11a).

**[Insert Table 6]**

Further detailed analysis of compound **5b** using Hirshfeld surface analysis performed with Crystal Explorer 2.1 [64], allows a deeper insight in its supramolecular architecture. The Hirshfeld surface analysis has been calculated at an isovalue of

$0.5e \cdot \text{au}^{-3}$ , and being **5b** a multi-component crystal, has been performed for each unique molecule in the unit cell (a dimer and three water molecules). Hirshfeld surface analysis explores interactions in the crystal structure based on electron densities. Color codes are used to predict the strength of the interactions by mapping the *dnorm* functions onto the Hirshfeld surface. The de 3D *dnorm* functions can be resolved into 2D fingertip plots which show the contributions of the molecular interactions. Individual plots of occluded H<sub>2</sub>O molecules allow to ascertain their differences, as each one displays a distinct plot showing their unique roles in supramolecular structure (Fig. 11b). In all of them two sharp peaks appear, related to the reciprocal O-H...O hydrogen bonds. For the dimer, its main supramolecular interactions are highlighted in the *dnorm* representation and the 2D fingertip plot. (Fig. 12). Its analysis once again confirms its interaction with only water molecules I and III, as red spots highlight these interactions. Additional mapping surfaces can be seen in the SI. (Fig. S11 and S12, SI).

[Insert Figure 11]

[Insert Figure 12]

### Structural discussion for compounds 1-5b

The reactivity of **HL** against the selected Cu(II) salts yielded monomeric ionic (**2**, **4**), neutral dimeric (**1** and **5b**) and polymeric (**3**) compounds. Regarding the pyrazole ligand, in monomeric ionic **2** and **4**, acts as a bidentate chelate ligand and the alcohol group remains protonated, whereas in neutral dimeric and polymeric **1**, **3** and **5b**, it acts as a bidentate bridged ligand and is deprotonated. A search in the CCDC [65] database reveals a total of twenty-five different reported crystal structures of coordination compounds bearing the **HL** ligand. Their analysis shows that in all monomeric reported crystal structures (40% of the total) the alcohol is protonated. Moreover, the ligand shows two different coordination modes in monomeric compounds: monodentate or bidentate chelate, the last one being somewhat more favored (40% and 60% of the reported monomers respectively). Regarding dimeric compounds (44% of the total), two different coordination behaviors are observed: bidentate chelate (36.4%) or bidentate bridge (72.1%), bearing in mind that compound  $[\text{Cu}(\mu\text{-L})(\text{HL})]_2 \cdot (\text{ClO}_4)_2$  [45] shows both coordination modes. In all dimeric compounds bearing the bidentate bridge coordination mode the pyrazole is deprotonated.

This data suggests that by promoting the deprotonation or preventing it, the nuclearity of the resulting compounds bearing **HL** or similar *N*-hydroxyalkylpyrazole ligands can be modulated. Moreover, this could explain why in the reaction of **HL** against  $\text{Cu}(\text{MeCO}_2)_2 \cdot \text{H}_2\text{O}$  only the dimeric product is obtained, as the addition of a base in the form of aqueous ammonia promotes the deprotonation of the ligand, preventing the formation of the monomeric product.

In compounds **1-5b** the pyrazole ligand always forms a six-membered ring metallacycle with a boat conformation, playing a similar role in the supramolecular structure. Therefore, the auxiliary ligands are the ones playing a differentiating role in the dimensionality and the formation of its supramolecular network as demonstrated in its structural analysis. This is especially noticeable in compound **3**, where the nitrate moieties act as a chelate and bridged ligand, allowing the formation of a polymeric chain, whereas the monotopic chlorine and chelated acetate co-ligands prevent a higher dimensionality in compounds **1**, **2** and **5b**. In all the compounds the co-ligands have key roles in sustaining the network, notably in **5b**, where the hydrogen bonds and water moieties are the strongest interactions.

### Thermogravimetric Analysis of **5a** and **5b**

Simultaneous TG/DTA determinations were carried out to evaluate the thermal stability of compounds **5a** and **5b** (Fig. S13 and S14, SI). The measurements were performed using 73.7 mg of **5a** and 72.9 mg of **5b** without crushing. For compound **5a** no water loss is observed, which agrees with EA and IR data. In fact, the only thermal event observed for **5a** is its decomposition, starting at 167°C and ending at 450°C, corresponding to the loss two pyrazole and two acetate moieties (weight loss exp. 71.1 %, calc. 75.8 %). For compound **5b**, on the other hand, the loss of water follows a two-step process. In the first step, one water molecule is lost between 38°C and 121°C (weight loss exp. 4.3%, calc. 3.0%). The next step takes place between 121°C and 189°C, resulting in the loss of three water molecules (weight loss exp. 8.9%, calc. 9.1%). From this temperature, the compound continues its decomposition ending at 450°C, corresponding to two pyrazole and two acetate moieties (weight loss exp. 54.7 %, calc. 66.6 %). Note that two water molecules of **5b** are readily lost in contact with the atmosphere.

### Magnetic susceptibility measurements of **3** and **5a**

Solid-state, variable temperature (5-300 K) magnetic susceptibility data was collected for **3** and **5a** using a 100 Oe field (Fig. 13 and Fig. 14). The  $\chi_M T$  value for **3** and **5a** at 300 K is 0.187 and 0.161 cm<sup>3</sup>mol<sup>-1</sup> respectively, substantially lower than the expected for two uncoupled  $S = 1/2$  spins assuming  $g = 2.00$  (0.75 cm<sup>3</sup>mol<sup>-1</sup>). Upon decreasing temperature, this value decreases almost linearly to a value of 0.0343 and 0.0230 cm<sup>3</sup>mol<sup>-1</sup> for **3** and **5a**, respectively, at 5 K, suggesting a strong antiferromagnetic interaction. The experimental data were fitted using the Bleany-Bowers equation [66] for dinuclear copper(II) complexes with the Hamiltonian in the form  $H = -JS_1S_2$ . The best fit parameters in the temperature range from 5 to 250 K were found for:  $g = 2.01$ ,  $\rho = 5.31\%$  and  $-2J = -535$  cm<sup>-1</sup> (**3**) and  $g = 2.14$ ,  $\rho = 3.95\%$  and  $-2J = -571$  cm<sup>-1</sup> (**5a**). This result agrees with Haase's magneto-structural correlations [67]. However, it is important to note that for strong antiferromagnetic compounds, where the diamagnetic correction is of the same order of magnitude as the uncorrected molar susceptibility, uncertainty of the corrected values is large, thus uncertainty of the estimated  $-2J$  values is 5%-10% [68-70]. Despite this, trends can still be assessed.

[Insert Figure 13]

[Insert Figure 14]

Previous studies show that the magnetic interaction value in alkoxo-bridged Cu(II) dimers strongly depend of its topological features. The general consensus is that six of them are key: (i) Cu...Cu distance, (ii) Cu-O-Cu angle ( $\theta$ ), (iii) Cu-O distance, (iv) torsional angle (angle of the carbon bonded to the bridging oxygen atom,  $\tau$ ), (v) planarity of the bonds around the bridging oxygen and (vi) hinge distortion (roof shape) [67, 71-74]. However, it has been established that parameters (i), (ii), and (iii) show some intrinsic relationship [72-74], thus Cu-O-Cu angle is considered to be the main parameter for predicting  $-2J$  values. The magnetic susceptibility values for compound **1**, which shows notable structural similarities to compounds **3** and **5a**, have been previously reported ( $g = 2.16$ ,  $-2J = -587$  cm<sup>-1</sup>) [46]. For **1** and **5a** the value of  $\tau$  is the same (11.2°), have similar Cu-O-Cu angles, show no hinge distortion and the bonds around the bridging oxygen are coplanar (sum of the angles around the bridging oxygen is 359.08° in **1** and 358.03° in **5a** compared to the expected 360° for totally coplanar bonds). This is reflected in their  $-2J$  values, -587 cm<sup>-1</sup> for **1** and -571 cm<sup>-1</sup> for **5a**, with **1**

having both the smallest  $-2J$  value and the highest  $\theta$ , as expected by the cited models (Table 7).

Compound **3**, on the other hand, shows a bigger  $\tau$  value ( $26.5^\circ$ ) and a slightly smaller Cu-O-Cu angle ( $101.3^\circ$ ). Once again, no hinge distortion is appreciated and the bonds around the bridging oxygen are coplanar (sum of the angles around the bridging oxygen is  $350.8^\circ$ ). In the case of alkoxo-bridged dimers, smaller Cu-O-Cu values and bigger  $\tau$  values lead to ferromagnetic interactions [75], which agrees with the reported results.

[Insert Table 7]

### UV-Vis Spectroscopy

UV-Vis electronic spectra have been recorded for compounds **1**, **2** and **5a** in MeOH and for **3** in DMF as solvent (Fig. S15-S18, SI). Unfortunately, UV-Vis spectra of **4** could not be recorded due to its low yield. For compounds **1**, **3** and **5a**, all spectra show one band in the visible region between 670 and 696 nm, with  $\epsilon$  values between 46 and  $113 \text{ M}^{-1}\text{cm}^{-1}$ . These broad absorption bands can be attributed to  ${}^2\text{E}_g$  to  ${}^2\text{T}_{2g}$  (or  ${}^2\text{B}_{1g}$  to  ${}^2\text{A}_{1g}$  for square planar **1**) transitions and are in range of typical Cu(II) square planar (**1**), octahedral (**3**) or square pyramidal (**5a**) compounds [76-79]. Compound **2**, on the other hand, shows one band at 840 nm, which is red shifted with respect to the previous ones, and  $\epsilon = 46$ . The presence of this single  $d-d$  band at  $\lambda > 800$  nm is typical for compounds with trigonal bipyramidal stereochemistry. Thus, this large red shift in **2** can be attributed to a heavily distorted square pyramidal geometry [55], which is consistent with its observed geometry in solid state ( $\tau = 0.40$ ) [52]. All  $\epsilon$  values are consistent with Laporte-forbidden transitions.

### Conclusions

We have successfully isolated five *N*-hydroxyethylpyrazole based compounds by reaction against different Cu(II) salts. The elucidation of the crystal structure for **1-5b** allowed to ascertain a great structural diversity, as monomers (**2**, **4**), dimers (**1** and **5b**) and polymers (**3**) were obtained. Structural analysis of the title compounds and comparison with previous reported structures revealed that their nuclearity is heavily dependent on the pyrazole moiety dehydronation, whereas auxiliary ligands play a key

role in its dimensionality and supramolecular structure. A potential candidate for water absorption-desorption applications was obtained (**5b**), as loss of this occluded solvents does not result in the collapse of the crystal structure. To gain more insight in its behavior, the thermal stability of **5b** was studied, showing a stepwise water desorption process. Lastly, the magneto structural correlations in **1**, **3** and **5a** were studied, showing a strong antiferromagnetic behavior, which can be rationalized based on their Cu-O-Cu angle values.

This study provides insight to the principles for a smart design of *N*-hydroxyalkylpyrazole derived materials, as pH control and careful selection of auxiliary ligands would allow the fine-tuning of the desired molecular structures. As such, by controlling pH we can modulate the obtention of monomeric or dimeric pyrazole-containing sub-units. On the other hand, by selecting the appropriate auxiliary ligands those secondary units can either grow into polymeric materials or be prevented from forming higher dimensionality complexes, resulting in molecular materials. Moreover, supramolecular architecture can also be modulated by selecting auxiliary ligands possessing desired H-bond synthons.

## Materials and Methods

### Materials and general details

Copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), copper(II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), copper(II) acetate monohydrate ( $\text{Cu}(\text{MeCO}_2)_2 \cdot \text{H}_2\text{O}$ ), acetylacetone, 2-hydroxyethylhydrazine, aqueous ammonia 30%, methanol (MeOH), ethanol (EtOH), diethyl ether ( $\text{Et}_2\text{O}$ ), acetone, acetonitrile ( $\text{CH}_3\text{CN}$ ), chloroform ( $\text{CHCl}_3$ ) and hexane were purchased from Sigma Aldrich and used without further purification. Reactions and manipulation were carried out in air at room temperature (r.t.). The 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethanol (**HL**) ligand was synthesised as described in the literature [80]. Elemental analyses (C, H, N) were carried out on a Thermo Scientific Flash 2000 CHNS Analyses. Powder X-ray diffraction (PXRD) patterns were measured with a Siemens D5000 apparatus (with 40 kW and 45 mA using  $\text{CuK}\alpha$  radiation with  $\lambda = 1.5406 \text{ \AA}$ ). Patterns were recorded from  $2\theta = 5^\circ$  to  $40^\circ$  with a step scan of  $0.02^\circ$  counting for 1s at each step. Conductivity measurements were performed at r.t. in MeOH (**1**, **2**, **4**, **5a**, **5b**) or DMF (**3**) solutions ( $\approx 1 \cdot 10^{-3} \text{ M}$ ), using an EC-Meter BASIC

30 (Crison Instruments) conductometer. FTIR-ATR spectra were recorded on a Tensor 27 (Bruker) spectrometer, equipped with an attenuated total reflectance (ATR) accessory model MKII Golden Gate with diamond window in the range 4000-600  $\text{cm}^{-1}$ . The electronic spectra in MeOH (**1**, **2**, **5a**) or DMF (**3**) solution ( $4.88 \cdot 10^{-5}$ - $1.17 \cdot 10^{-3}$  M) were run on a JASCO V-780 UV-Visible/NIR Spectrophotometer with a quartz cell having a path length of 1 cm in the range of 500-1100 nm. Simultaneous TG/DTA determinations were carried out in a Netzsch STA 409 instrument, with an aluminium oxide ( $\text{Al}_2\text{O}_3$ ) crucible and heating at  $5 \text{ K} \cdot \text{min}^{-1}$  from 298 to 723 K, under a nitrogen atmosphere with a flow rate of  $80 \text{ mL} \cdot \text{min}^{-1}$ . Aluminium oxide powder (PerkinElmer 0419-0197) was used as a standard. Magnetic measurements from 5 K to 300 K were carried out with a Quantum Design MPMS-5S SQUID spectrometer using a 100 Oe field. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms [81] and effects of the capsule container.

### Synthesis of compounds $[\text{CuCl}(\mu\text{-L})_2]$ (**1**) and $[\text{CuCl}(\text{HL})_2]\text{Cl}$ (**2**)

To a solution of **HL** (365 mg, 2.60 mmol) in MeOH (10 mL), a solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (446 mg, 2.62 mmol) in MeOH (10 mL) was added dropwise. The resulting dark green solution was stirred for 48 h at r.t. After that period, a dark blue precipitate appeared (**1**), which was filtered off and dried under vacuum. The remaining mother liquors were concentrated until a dark green oil appeared, which after treatment with  $\text{Et}_2\text{O}$ , resulted in dark green solid (**2**). This solid was filtered off, washed with  $\text{Et}_2\text{O}$  and dried under vacuum. Suitable crystals for X-ray diffraction of compound **1** were obtained by recrystallization in an acetone:hexane 1:1 mixture for three weeks. Suitable crystals for X-ray diffraction of **2** were obtained by slow diffusion of hexane to a  $\text{CHCl}_3$  solution.

**1.** Yield: 45.8 mg (7.4%). Elem. Anal. Calc. for  $\text{C}_{14}\text{H}_{22}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_2$  (476.33 g/mol): C 35.30; H 4.65; N 11.76. Found: C 35.22; H 4.58; N 11.57 %. Conductivity ( $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$   $1.4 \cdot 10^{-3}$  M in MeOH): 20. FTIR-ATR (wavenumber,  $\text{cm}^{-1}$ ): 3012(w) [ $\nu(\text{C-H})_{\text{ar}}$ ], 2925-2873(w) [ $\nu(\text{C-H})_{\text{al}}$ ], 1548(m) [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ]<sub>ar</sub>, 1469(m), 1421(m), 1389(m) [ $\delta(\text{C}=\text{C})$ ,  $\delta(\text{C}=\text{N})$ ]<sub>ar</sub>, 1326(w), 1301(m), 1227(w), 1158 (m), 1140(w), 1082(m), 1058(s) [ $\delta(\text{C-H})_{\text{ip}}$ ], 995(w), 895(s) [ $\delta(\text{C-H})_{\text{oop}}$ ], 774(s) [ $\delta(\text{C-H})_{\text{oop}}$ ], 626(s) [ $\delta(\text{C-H})_{\text{oop}}$ ]. UV-Vis: (MeOH,  $1.09 \cdot 10^{-3}$  M)  $\lambda_{\text{max}}$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ) = 696 nm (59).

**2.** Yield: 414 mg (76.8%). Elem. Anal. Calc. for  $C_{14}H_{24}Cl_2CuN_4O_2$  (414.81 g/mol): C 40.54; H 5.83; N 13.51. Found: C 40.48; H 5.80; N 13.30 %. Conductivity ( $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$   $9.9\cdot 10^{-3}$  M in MeOH): 94. FTIR-ATR (wavenumber,  $\text{cm}^{-1}$ ): 3125(m) [ $\nu(\text{OH})$ ], 3112(w) [ $\nu(\text{C-H})_{\text{ar}}$ ], 2921-2632(w) [ $\nu(\text{C-H})_{\text{al}}$ ], 1551(m) [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ] $_{\text{ar}}$ , 1468(m), 1421(m), 1396(m) [ $\delta(\text{C}=\text{C})$ ,  $\delta(\text{C}=\text{N})$ ] $_{\text{ar}}$ , 1329(w), 1306(m), 1261(w), 1225(w), 1158 (w), 1141(w), 1079(m), 1063(s), 1044(s) [ $\delta(\text{C-H})_{\text{ip}}$ ], 876(s) [ $\delta(\text{C-H})_{\text{oop}}$ ], 834(m), 805(s) [ $\delta(\text{C-H})_{\text{oop}}$ ], 691(s) [ $\delta(\text{C-H})_{\text{oop}}$ ]. UV-Vis: (MeOH,  $1.04\cdot 10^{-3}$  M)  $\lambda_{\text{max}}$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ) = 840 nm (46).

### Synthesis of compounds $\{[\text{Cu}(\mu\text{-NO}_3)(\mu\text{-L})_2]_n$ (**3**) and $[\text{Cu}(\text{NO}_3)(\text{HL})_2]\text{NO}_3$ (**4**)

To a solution of **HL** (0.280 g, 2.01 mmol) in MeOH (10 mL), a solution of  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  (0.481 g, 2.02 mmol) in MeOH (10 mL) was added dropwise, resulting in a green solution which was stirred for 12 h. under reflux conditions. Upon cooling, a light blue powder (**3**) appeared, which was filtered off, washed twice with cold  $\text{Et}_2\text{O}$  and dried under vacuum. The filtrate was concentrated under vacuum until a green oil was obtained. After the addition of 5 mL of  $\text{Et}_2\text{O}$ , a green powder precipitated (**4**). Suitable crystals for X-ray diffraction of **3** were obtained by recrystallization in  $\text{CH}_3\text{CN}$  for three weeks. Suitable crystals for X-ray diffraction of **4** were obtained by recrystallization in MeOH for one month.

**3.** Yield: 0.380 g (71.4 %). Elem. Anal. Calc. for  $C_{14}H_{22}Cu_2N_6O_8$  (529.46 g/mol): C 31.76; H 4.19; N 24.17. Found: C 31.88; H 4.17; N 23.98 %. Conductivity ( $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$   $1.1\cdot 10^{-3}$  M in DMF): 36. FTIR-ATR (wavenumber,  $\text{cm}^{-1}$ ): 2972-2866(w) [ $\nu(\text{C-H})_{\text{al}}$ ], 1750(w)-1732(w) [ $\nu_1+\nu_3(\text{NO}_3)$ ], 1549(s) [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ] $_{\text{ar}}$ , 1495(w), 1454(s) [ $\nu(\text{NO}_3)$ ], 1403(m) [ $\delta(\text{C}=\text{C}/\text{C}=\text{N})$ ] $_{\text{ar}}$ , 1373(w), 1351(w), 1304(w), 1269(s) [ $\nu(\text{NO}_3)$ ], 1229(w), 1156(w), 1140(m), 1081(w), 1066(s) [ $\delta(\text{C-H})_{\text{ip}}$ ], 1022(m), 997(m), 971(w), 894(m) [ $\delta(\text{C-H})_{\text{oop}}$ ], 790(w), 777(m) [ $\delta(\text{C-H})_{\text{oop}}$ ], 749(w), 632(m), 602(m), 599(m). UV-Vis: (DMF,  $1.17\cdot 10^{-3}$  M)  $\lambda_{\text{max}}$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ) = 681 nm (112).

**4.** Yield: 0.020 g (4.2 %). Elem. Anal. Calc. for  $C_{14}H_{24}CuN_6O_8$  (467.9 g/mol): C 35.94; H 5.17; N 17.96. Found: C 35.71; H 4.98; N 17.69 %. Conductivity ( $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$   $1.2\cdot 10^{-3}$  M in MeOH): 111. FTIR-ATR (wavenumber,  $\text{cm}^{-1}$ ): 3191(br) [ $\nu(\text{OH})$ ], 3149(w) [ $\nu(\text{C-H})_{\text{ar}}$ ], 2858-2651(w) [ $\nu(\text{C-H})_{\text{al}}$ ], 1770(w)-1718(w) [ $\nu_1+\nu_3(\text{NO}_3)$ ], 1555(s) [ $\nu(\text{C}=\text{C}/\text{C}=\text{N})$ ] $_{\text{ar}}$ , 1500(w), 1442(s), 1422(s) [ $\nu(\text{N-O}_3)$ ], 1403(s) [ $\delta(\text{C}=\text{C}/\text{C}=\text{N})$ ] $_{\text{ar}}$ , 1350(m), 1280(s) [ $\nu(\text{N-O}_3)$ ], 1155(w), 1142(w), 1086(w), 1056(w), 1042(w), 1019(m)

$[\delta(\text{C-H})_{\text{ip}}]$ , 993(w), 963(w), 881(m)  $[\delta(\text{C-H})_{\text{oop}}]$ , 810(m)  $[\delta(\text{C-H})_{\text{oop}}]$ , 781(m)  $[\delta(\text{C-H})_{\text{oop}}]$ , 646(w).

### Synthesis of $[\text{Cu}(\text{MeCO}_2)(\mu\text{-L})]_2$ (**5a**) and $[\text{Cu}(\text{MeCO}_2)(\mu\text{-L})]_2 \cdot 6\text{H}_2\text{O}$ (**5b**)

To a solution of **HL** (337.8 mg, 2.410 mmol) in MeOH (20 mL), a solution of  $\text{Cu}(\text{MeCO}_2)_2 \cdot \text{H}_2\text{O}$  (481.0 mg, 2.40 mmol) in MeOH (25 mL) was added dropwise. In addition, 0.1 ml of aqueous ammonia 30% were added to the previous solution. The resulting blue solution was stirred for 48h at r.t. After that period, the solution was concentrated up to 5 mL, and 20 mL of  $\text{Et}_2\text{O}$  were added. After 20 minutes, a blue precipitate appeared. The resulting solution was kept overnight on the fridge. Then, the blue precipitate was filtered off, washed with 5 mL of cold  $\text{Et}_2\text{O}$  and dried under vacuum (**5a**). Recrystallization of this solid in MeOH for 36h yielded suitable crystals for X-ray diffraction of molecular formula  $[\text{Cu}(\text{MeCO}_2)(\mu\text{-L})]_2 \cdot 6\text{H}_2\text{O}$  (**5b**). Although the molecular formula of **5b** has been established after resolution of its crystal structure by single crystal X-ray diffraction, this compound loses solvent molecules after being removed from solution. For this reason, we found that the manipulation required to prepare the sample for EA unavoidably leads to the loss of two water solvent molecules. Thus, EA results were adjusted considering a  $[\text{Cu}(\text{MeCO}_2)(\mu\text{-L})]_2 \cdot 4\text{H}_2\text{O}$  molecular relation.

**5a.** Yield: 281 mg (44.7%). Elem. anal. Calc. for  $\text{C}_{18}\text{H}_{28}\text{Cu}_2\text{N}_4\text{O}_6$  (523.53 g/mol): C 41.30; H 5.39; N 10.70. Found: C 41.18; H 5.31; N 10.52 %. Conductivity ( $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  9.6 · 10<sup>-3</sup> M in EtOH): 24. FTIR-ATR (wavenumber, cm<sup>-1</sup>): 2964(w)-2825  $[\nu(\text{C-H})_{\text{al}}]$ , 1570(s)  $[\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})]_{\text{ar}}$ , 1547(s)  $[\nu(\text{COO})_{\text{as}}]$ , 1472(m), 1423(s)  $[\nu(\text{COO})_{\text{s}}]$ , 1388(s)  $[\delta(\text{C}=\text{C}), \delta(\text{C}=\text{N})]_{\text{ar}}$ , 1349(m), 1328(s), 1304(s), 1241(w), 1228(m), 1155(w), 1138(m), 1086(s)  $[\delta(\text{C-H})_{\text{ip}}]$ , 1071(s), 982(w), 972(w), 923(w), 893(s), 795(s)  $[\delta(\text{C-H})_{\text{oop}}]$ , 676(s)  $[\delta(\text{C-H})_{\text{oop}}]$ , 627(s), 616(m), 579(s). UV-Vis: (MeOH, 9.93 · 10<sup>-4</sup> M)  $\lambda_{\text{max}}$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ) = 670 nm (113).

**5b.** Elem. anal. Calc. for  $\text{C}_{18}\text{H}_{36}\text{Cu}_2\text{N}_4\text{O}_8$  (595.59 g/mol): C 36.29; H 6.09; N 9.40. Found: C 36.14; H 6.16; N 9.13%. Conductivity ( $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  9.6 · 10<sup>-3</sup> M in MeOH): 28. FTIR-ATR (wavenumber, cm<sup>-1</sup>): 3467(w)  $[\nu(\text{OH})]$ , 3367(w)  $[\nu(\text{OH})]$ , 3263(w)  $[\nu(\text{OH})]$ , 2967(w)-2825(w)  $[\nu(\text{C-H})_{\text{al}}]$ , 1585(s)  $[\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})]_{\text{ar}}$ , 1546(s)  $[\nu(\text{COO})_{\text{as}}]$ , 1470(w), 1421(s)  $[\nu(\text{COO})_{\text{s}}]$ , 1387(s)  $[\delta(\text{C}=\text{C}), \delta(\text{C}=\text{N})]_{\text{ar}}$ , 1328(m), 1303(m), 1228(m),

1154(w), 1138(w), 1086(s) [ $\delta(\text{C-H})_{\text{ip}}$ ], 1069(m), 967(w), 924(w), 894(s), 795(s) [ $\delta(\text{C-H})_{\text{oop}}$ ], 676(s) [ $\delta(\text{C-H})_{\text{oop}}$ ], 625(s), 579(s).

## X-ray Crystallography

For compounds **1-4** and **5b** blue prism-like specimens were used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus ( $\lambda = 0.71073 \text{ \AA}$ ). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. For **1**, the integration of the data using a triclinic unit cell yielded a total of 23008 reflections to a maximum  $\theta$  angle of  $30.59^\circ$  ( $0.70 \text{ \AA}$  resolution), of which 2733 were independent (average redundancy 8.419, completeness = 99.5%,  $R_{\text{int}} = 2.23\%$ ,  $R_{\text{sig}} = 1.10\%$ ) and 2622 (95.94%) were greater than  $2\sigma(F^2)$ . The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6649 and 0.7461. For **2**, the integration of the data using an orthorhombic unit cell yielded a total of 163709 reflections to a maximum  $\theta$  angle of  $30.60^\circ$  ( $0.70 \text{ \AA}$  resolution), of which 5675 were independent (average redundancy 28.843, completeness = 99.7%,  $R_{\text{int}} = 5.26\%$ ,  $R_{\text{sig}} = 1.53\%$ ) and 4946 (87.14%) were greater than  $2\sigma(F^2)$ . The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6897 and 0.7461. For **3**, the integration of the data using a monoclinic unit cell yielded a total of 12549 reflections to a maximum  $\theta$  angle of  $30.61^\circ$  ( $0.70 \text{ \AA}$  resolution), of which 2916 were independent (average redundancy 4.303, completeness = 97.8%,  $R_{\text{int}} = 5.61\%$ ,  $R_{\text{sig}} = 5.32\%$ ) and 2288 (78.46%) were greater than  $2\sigma(F^2)$ . The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6202 and 0.7461. For **4**, The integration of the data using a monoclinic unit cell yielded a total of 4667 reflections to a maximum  $\theta$  angle of  $27.57^\circ$  ( $0.77 \text{ \AA}$  resolution), of which 4667 were independent (average redundancy 1.000, completeness = 99.4%,  $R_{\text{int}} = 18.26\%$ ,  $R_{\text{sig}} = 9.74\%$ ) and 2953 (63.27%) were greater than  $2\sigma(F^2)$ . The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6571 and 0.7456. For **5b**, the integration of the data using a monoclinic unit cell yielded a total of 45761 reflections to a maximum  $\theta$  angle of  $30.58^\circ$  ( $0.70 \text{ \AA}$  resolution), of which 4228 were independent (average redundancy 10.823, completeness = 99.2%,  $R_{\text{int}} = 2.70\%$ ,  $R_{\text{sig}} = 1.38\%$ ) and 3831 (90.61%) were greater than  $2\sigma(F^2)$ . The

calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6182 and 0.7461.

The structures were solved and refined using the Bruker SHELXTL Software Package [82]. For **1**, the final anisotropic full-matrix least-squares refinement on  $F^2$  with 111 variables converged at  $R1 = 1.62\%$ , for the observed data and  $wR2 = 4.39\%$  for all data. For **2**, the final anisotropic full-matrix least-squares refinement on  $F^2$  with 212 variables converged at  $R1 = 2.80\%$ , for the observed data and  $wR2 = 6.63\%$  for all data. For **3**, The final anisotropic full-matrix least-squares refinement on  $F^2$  with 138 variables converged at  $R1 = 4.90\%$ , for the observed data and  $wR2 = 9.31\%$  for all data. For **4**, the final anisotropic full-matrix least-squares refinement on  $F^2$  with 257 variables converged at  $R1 = 3.29\%$ , for the observed data and  $wR2 = 5.49\%$  for all data. For **5b**, the final anisotropic full-matrix least-squares refinement on  $F^2$  with 184 variables converged at  $R1 = 2.32\%$ , for the observed data and  $wR2 = 6.16\%$  for all data. The final cell constants for **1**, **2**, **4** and **5b**, are based upon the refinement of the XYZ-centroids of reflections above  $20 \sigma(I)$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS).

Crystal data and relevant details of structure refinement are reported in Tables 8 and 9. Molecular graphics were generated with Mercury 4.1.3 [83,84] with POV-Ray package [85]. Color codes for molecular graphics: grey (C), white (H), green (Cl), red (O), blue (N), orange (Cu).

[Insert Table 8]

[Insert Table 9]

## Appendix A. Supplementary Data

CCDC contain the supplementary crystallographic data for 2001254 (**3**), 2001255 (**5b**), 2001256 (**4**), 2001257 (**1**) and 2001258 (**2**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB2 1 Ez, UK; fax: (+44)1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

Complete Powder X-ray diffractograms, FTIR-ATR spectra, additional figures and UV-Vis spectra are available as Supporting Information. Supplementary data for this article can be found online at <https://doi.org/10.XXX/XXXXX>.

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**Table 1.** Selected bond lengths (Å) and bond angles (°) and intermolecular interactions for **1**.

<b>1</b>				
<i>Bond lengths (Å)</i>				
Cu(1)-O(1)	1.9289(8)	Cu(1)-Cl(1)	2.2098(3)	
Cu(1)-O(1)#1	1.9142(8)	Cu(1)···Cu(1)#1	3.0328(3)	
Cu(1)-N(1)	1.9674(9)			
<i>Bond angles (°)</i>				
O(1)#1-Cu(1)-O(1)	75.79(4)	O(1)#1-Cu(1)-Cl(1)	96.96(2)	
O(1)#1-Cu(1)-N(1)	159.68(4)	O(1)-Cu(1)-Cl(1)	162.39(3)	
O(1)-Cu(1)-N(1)	91.09(3)	N(1)-Cu(1)-Cl(1)	99.76(3)	
<i>Intermolecular interactions</i>				
	H···A (Å)	D···A (Å)	D-H (Å)	>D-H···A (°)
C5-H5A···Cl1	2.680	3.627	0.980	162.69
C6-H6B···O1	2.550	3.448	0.990	150.82

#1: -x+1, -y+2, -z+1

**Table 2.** Selected bond lengths (Å), bond angles (°) and intermolecular interactions for **2**.

<b>2</b>				
<i>Bond lengths (Å)</i>				
Cu(1)-N(3)	1.9636(12)	Cu(1)-Cl(1)	2.2584(4)	
Cu(1)-N(1)	1.9675(12)	Cu(1)-O(1)	2.2962(10)	
Cu(1)-O(2)	2.0760(10)			
<i>Bond angles (°)</i>				
N(3)-Cu(1)-N(1)	173.20(5)	N(3)-Cu(1)-O(1)	89.27(4)	
N(3)-Cu(1)-O(2)	88.57(4)	N(1)-Cu(1)-O(1)	85.60(4)	
N(1)-Cu(1)-O(2)	86.88(4)	O(2)-Cu(1)-O(1)	89.08(4)	
N(3)-Cu(1)-Cl(1)	93.32(3)	Cl(1)-Cu(1)-O(1)	121.74(3)	
O(2)-Cu(1)-Cl(1)	149.12(3)	N(1)-Cu(1)-Cl(1)	93.18(4)	
<i>Intermolecular interactions</i>				
	H···A (Å)	D···A (Å)	D-H (Å)	>D-H···A (°)
O1-H1···Cl2	2.204	3.016	0.839	162.70
O2-H2···Cl2	2.122	2.958	0.840	173.32
C3-H3···Cl2	2.827	3.669	0.930	151.20
C6-H6B···Cl1	2.873	3.745	0.970	150.06

**Table 3.** Selected bond lengths (Å), bond angles (°) and intermolecular interactions for **3**.

<b>3</b>				
<i>Bond lengths (Å)</i>				
Cu(1)-O(1)	1.929(2)	Cu(1)-O(2)	2.004(2)	
Cu(1)-O(1)#1	1.929(2)	Cu(1)-O(3)#2	2.369(3)	
Cu(1)-N(1)#1	1.970(2)	Cu(1)-O(3)	2.594(2)	
Cu(1)···Cu(1)	2.9847(9)			
<i>Bond angles (°)</i>				
O(1)-Cu(1)-O(1)#1	78.67(9)	N(1)#1-Cu(1)-O(2)	95.47(10)	
O(1)-Cu(1)-N(1)#1	169.06(9)	O(1)-Cu(1)-O(3)#2	89.54(9)	
O(1)#1-Cu(1)-N(1)#1	91.31(9)	O(1)#1-Cu(1)-O(3)#2	98.39(9)	
O(1)-Cu(1)-O(2)	93.35(9)	N(1)#1-Cu(1)-O(3)#2	96.31(10)	
O(1)#1-Cu(1)-O(2)	165.39(10)	O(2)-Cu(1)-O(3)#2	93.72(9)	
<i>Intermolecular interactions</i>				
	<b>H···A</b>	<b>D···A</b>	<b>D-H (Å)</b>	<b>&gt;D-H···A</b>
	(Å)	(Å)		(°)
C5-H5A···O2	2.436	3.387	0.980	163.34
C7-H7A···O4	2.536	3.329	0.990	136.93

#1: -x+1, -y+1, -z+1

#2: x, y-1, z

**Table 4.** Selected bond lengths (Å), bond angles (°) and intermolecular interactions for **4**.

<b>4</b>				
<i>Bond lengths (Å)</i>				
Cu(1)-N(3)	1.9801(17)	Cu(1)-O(1)	1.9944(13)	
Cu(1)-N(1)	1.9712(15)	Cu(1)-O(3)	2.0102(13)	
Cu(1)-O(2)	2.1685(15)	Cu(1)-O(5)	2.700(2)	
<i>Bond angles (°)</i>				
N(1)-Cu(1)-N(3)	173.12(7)	O(1)-Cu(1)-O(3)	166.58(7)	
N(1)-Cu(1)-O(1)	88.06(6)	N(1)-Cu(1)-O(2)	93.91(6)	
N(3)-Cu(1)-O(1)	86.57(6)	N(3)-Cu(1)-O(2)	90.83(6)	
N(1)-Cu(1)-O(3)	91.59(6)	O(1)-Cu(1)-O(2)	94.94(6)	
N(3)-Cu(1)-O(3)	92.64(6)	O(1)-Cu(1)-O(3)	98.46(6)	
N(3)-Cu(1)-O(5)	100.27(6)	N(1)-Cu(1)-O(5)	78.05(6)	
O(2)-Cu(1)-O(5)	149.18(5)	O(1)-Cu(1)-O(5)	114.21(5)	
O(5)-Cu(1)-O(3)	52.75(5)			
<i>Intermolecular interactions</i>				
	H···A (Å)	D···A (Å)	D-H (Å)	>D-H···A (°)
O1-H1O···O7	1.796	2.622	0.840	167.81
O2-H2O···O6	1.919	2.743	0.840	166.74

**Table 5.** Selected bond lengths (Å) and bond angles (°) for **5b**.

<b>5b</b>			
<i>Bond lengths (Å)</i>			
Cu(1)-O(1)#1	1.9163(8)	Cu(1)-O(2)	1.9663(8)
Cu(1)-O(1)	1.9276(8)	Cu(1)-N(1)	1.9636(10)
Cu(1)-O(3)	2.494(1)	Cu(1)···Cu(1)#1	3.0176(3)
<i>Bond angles (°)</i>			
O(1)#1-Cu(1)-O(1)	76.55(4)	N(1)-Cu(1)-O(2)	98.53(4)
O(1)#1-Cu(1)-N(1)	164.88(4)	O(1)#1-Cu(1)-Cu(1)#1	38.41(3)
O(1)-Cu(1)-N(1)	92.90(4)	O(1)-Cu(1)-Cu(1)#1	38.14(3)
O(1)#1-Cu(1)-O(2)	93.34(4)	N(1)-Cu(1)-Cu(1)#1	130.19(3)
O(1)-Cu(1)-O(2)	166.86(4)	O(2)-Cu(1)- Cu(1)#1	131.23(3)
O(1)-Cu(1)-O(3)	114.38(4)	O(3)-Cu(1)- O(1)#1	96.19(4)
O(3)-Cu(1)-O(2)	57.71(3)	O(3)-Cu(1)- N(1)	98.06(4)

#1: -x+1, -y+1, -z+1

**Table 6.** Selected intermolecular interactions for **5b**.

<b>5b</b>				
	<b>H···A (Å)</b>	<b>D···A (Å)</b>	<b>D-H (Å)</b>	<b>&gt;D-H···A (°)</b>
O1W-H1WA···O2W <sup>i</sup>	2.136(2)	2.931(2)	0.799(2)	172.82(2)
O1W-H1WB···O3	1.906(2)	2.702(2)	0.800(2)	173.67(2)
O2W-H2WA···O3W <sup>i</sup>	2.015(2)	2.808(2)	0.797(2)	173.27(2)
O2W-H2WB···O1W <sup>ii</sup>	1.974(2)	2.753(2)	0.799(2)	164.14(2)
O3W-H3WA···O2W	2.052(2)	2.843(2)	0.794(2)	173.85(2)
O3W-H3WB···O2 <sup>i</sup>	2.037(2)	2.813(2)	0.790(2)	167.14(19)
C6-H6B···O1W	2.332(2)	3.161(2)	0.990	140.74

<sup>i</sup>[ x,1/2-y,-1/2+z], <sup>ii</sup> [-x,-1/2+y,1/2-z]

**Table 7.** Magneto-structural parameters for compounds **1** and **5a**.

Compound	$\theta_{Cu-O-Cu}, \tau$ (°)	$-2J$ (cm <sup>-1</sup> )
<b>1</b> [46]	104.3, 11.2	-587
<b>3</b>	101.3, 26.5	-535
<b>5a</b>	103.5, 11.2	-571

**Table 8.** Crystallographic data for **1**, **2** and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>14</sub> H <sub>22</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>24</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>11</sub> CuN <sub>3</sub> O <sub>4</sub>
Formula weight	476.33	414.81	264.73
<i>T</i> (K)	100(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
System, space group	Triclinic P $\bar{1}$	Orthorhombic Pccn	Monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions			
<i>a</i> (Å)	4.2990(2)	23.8198(12)	13.880(2)
<i>b</i> (Å)	8.2451(4)	10.6354(5)	4.7765(9)
<i>c</i> (Å)	12.9432(6)	14.6124(8)	16.127(3)
$\alpha$ (°)	82.066(2)	90	90
$\beta$ (°)	87.584(2)	90	114.798(6)
$\gamma$ (°)	79.200(2)	90	90
<i>V</i> (Å <sup>3</sup> )	446.28(4)	3701.8(3)	970.6(3)
<i>Z</i>	1	8	4
<i>D</i> <sub>calc</sub> (g cm <sup>3</sup> )	1.772	1.489	1.812
$\mu$ (mm <sup>-1</sup> )	2.697	1.482	2.249
<i>F</i> (000)	242	1720	540
Crystal size (mm <sup>3</sup> )	0.205x0.144x0.060	0.163x0.140x0.078	0.314x0.120x0.031
<i>hkl</i> ranges	-6 ≤ <i>h</i> ≤ 6 -11 ≤ <i>k</i> ≤ 11 -18 ≤ <i>l</i> ≤ 18	-33 ≤ <i>h</i> ≤ 34 -15 ≤ <i>k</i> ≤ 15 -20 ≤ <i>l</i> ≤ 20	-19 ≤ <i>h</i> ≤ 19 -6 ≤ <i>k</i> ≤ 6 -22 ≤ <i>l</i> ≤ 23
$\theta$ range (°)	3.168 to 30.593	2.518 to 30.601	2.566 to 30.613
Reflections collected/ unique/[ <i>R</i> <sub>int</sub> ]	23008/ 2733 [ <i>R</i> <sub>int</sub> ] = 0.0223	163709/5675 [ <i>R</i> <sub>int</sub> ] = 0.0526	12549/2916/ [ <i>R</i> <sub>int</sub> ] = 0.0561]
Completeness to $\theta$ = 25.242	99.3	99.8	99.7
Absorption Correction	Semi-empirical	Semi-empirical	Semi-empirical
Max. and min. transmis.	0.7461 and 0.6649	0.7461 and 0.6897	0.7461 and 0.6202
Refinement method	Full matrix least- squares on <i>F</i> <sup>2</sup>	Full matrix least- squares on <i>F</i> <sup>2</sup>	Full matrix least- squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2733/1/111	5675/1/212	2916/0/138
Goodness of fit (GOF) on <i>F</i> <sup>2</sup>	1.100	1.086	1.056
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0162, w <i>R</i> 2 = 0.0432	<i>R</i> 1 = 0.0280, w <i>R</i> 2 = 0.0632	<i>R</i> 1 = 0.0490, w <i>R</i> 2 = 0.0864
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0175, w <i>R</i> 2 = 0.0439	<i>R</i> 1 = 0.0361, w <i>R</i> 2 = 0.0663	<i>R</i> 1 = 0.0699, w <i>R</i> 2 = 0.0931
Extinction coefficient	n/a	n/a	n/a
Largest. Diff. peak and hole (e Å <sup>-3</sup> )	0.444 and -0.409	0.460 and -0.426	0.800 and -1.146

**Table 9.** Crystallographic data for **4** and **5b**.

	<b>4</b>	<b>5b</b>
Empirical formula	C <sub>14</sub> H <sub>24</sub> CuN <sub>6</sub> O <sub>8</sub>	C <sub>18</sub> H <sub>40</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>12</sub>
Formula weight	467.93	631.62
<i>T</i> (K)	100(2)	150(2)
Wavelength (Å)	0.71073	0.71073
System, space group	Monoclinic, P2 <sub>1</sub> /c	Monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions		
<i>a</i> (Å)	17.6305(14)	10.5582(5)
<i>b</i> (Å)	8.8369(7)	14.3727(6)
<i>c</i> (Å)	13.0285(10)	9.1424(4)
$\alpha$ (°)	90	90
$\beta$ (°)	92.447(3)	90.643(2)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	2028.03	1387.27(11)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.533	1.512
$\mu$ (mm <sup>-1</sup> )	1.131	1.595
<i>F</i> (000)	972	660
Crystal size (mm <sup>3</sup> )	0.241x0.068x0.047	0.313x0.076x0.057
<i>hkl</i> ranges	-22 ≤ <i>h</i> ≤ 22 0 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 16	-15 ≤ <i>h</i> ≤ 15 -20 ≤ <i>k</i> ≤ 18 -13 ≤ <i>l</i> ≤ 13
$\theta$ range (°)	2.312 to 27.565	2.394 to 30.579
Reflections collected/ unique/[ <i>R</i> <sub>int</sub> ]	4667/4667/ [ <i>R</i> <sub>int</sub> = 0.1826]	45761/4228 [ <i>R</i> <sub>int</sub> = 0.0270]
Completeness to $\theta$ = 25.242	99.6	99.1
Absorption Correction	Semi-empirical	Semi-empirical
Max. and min. transmis.	0.7456 and 0.6571	0.7461 and 0.6182
Refinement method	Full matrix least- squares on <i>F</i> <sup>2</sup>	Full matrix least- squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4667/0/257	4228/10/184
Goodness of fit (GOF) on <i>F</i> <sup>2</sup>	0.855	1.132
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0329, w <i>R</i> 2 = 0.0488	<i>R</i> 1 = 0.0232, w <i>R</i> 2 = 0.0592
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0748, w <i>R</i> 2 = 0.0549	<i>R</i> 1 = 0.0276, w <i>R</i> 2 = 0.0616
Extinction coefficient	n/a	n/a
Largest. Diff. peak and hole (e Å <sup>-3</sup> )	0.378 and -0.660	0.427 and -0.470