

## Notes

## Two-Dimensional Luminescent Rectangular Molecular Grids Containing Copper(I)–Olefin Bonds as Bridging Spacers

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**Summary:** The reaction of CuCl with 4-vinylpyridine (4-VPY) under hydrothermal conditions affords a 2-D copper(I)–olefin luminescent coordination polymer, [Cu(4-VPYA)Cl]<sub>n</sub> (**1**), with an approximately molecular rectangular grid dimension of 10.576 × 7.322 Å.

## Introduction

Supramolecular motifs containing a olefin–copper(I) bond as bridging spacer have recently attracted much attention.<sup>1</sup> Copper(I)–olefin complexes are known to play an important role in biochemistry and modern organic chemistry and are involved as catalytically active species or resting states in copper-catalyzed addition of carbanions to α,β-unsaturated carbonyls and copper-catalyzed cyclopropanation of alkenes by α-carbonyl diazoalkanes.<sup>2,3</sup> Although a large number of metal–organic coordination polymer networks or cyclophanes such as squares and grids are documented in the recent literature,<sup>4,5</sup> the functional (luminescent) molecular grid or square grid (molecular box) containing

copper(I)–olefin bonds still remains, to the best of our knowledge, unknown. Successful access to luminescent molecular grids with olefin–copper(I) bonds remains a great challenge. Inspired by the pioneering work of Hupp and other groups on luminescent molecular boxes,<sup>6–8</sup> we have used 4-vinylpyridine (4-VPY) as bridging ligand to react with CuCl under hydrothermal reaction conditions to construct a novel luminescent 2-D rectangular neutral grid, {Cu(4-VPY)Cl}<sub>n</sub> (**1**), containing

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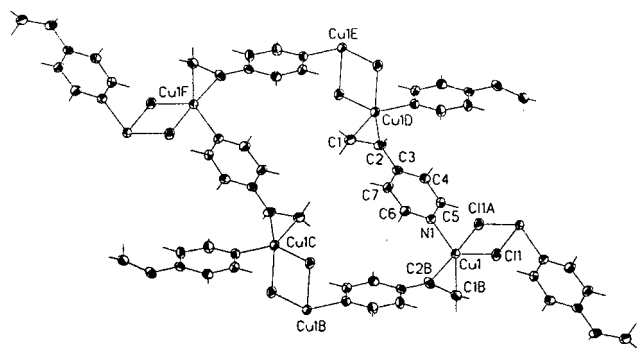
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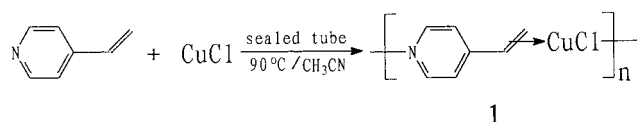
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**Figure 1.** Rectangular unit representation of  $\{\text{Cu}(4\text{-VPY})\text{Cl}\}_n$  (**1**). The thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Cu(1)–N(1) 2.006(2), Cu(1)–C(1B) 2.025(3), Cu(1)–C(2B) 2.064(3), Cu(1)–Cl(1) 2.2599(8), Cu(1)–Cl(1A) 2.6751(8), C(1B)–Cu(1) 1.364(4); C(1B)–Cu(1)–Cu(2B) 38.97(1), N(1)–Cu(1)–C(1B) 148.16(11), N(1)–Cu(1)–C(2B) 110.78(10), N(1)–Cu(1)–Cl(1) 105.56(7), N(1)–Cu(1)–Cl(1A) 94.66(7), C(1B)–Cu(1)–Cl(1) 100.88(10), C(2B)–Cu(1)–Cl(1A) 138.78(9), C(1B)–Cu(1)–Cl(1A) 99.01(10), C(2B)–Cu(1)–Cl(1A) 97.9(8), Cl(1)–Cu(1)–Cl(1A) 97.87(3), Cu(1)–Cl(1A)–Cu(1G) 82.13(3).

**Scheme 1**

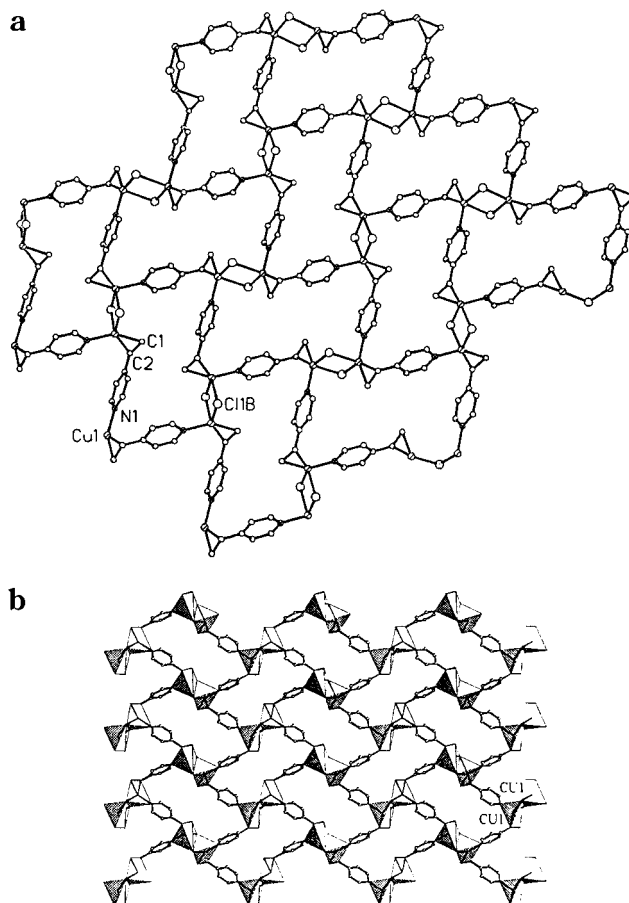


a  $\eta^2$ -copper(I)–olefin bond as connecting spacer. Herein we report its synthesis, crystal structure, and luminescent property.

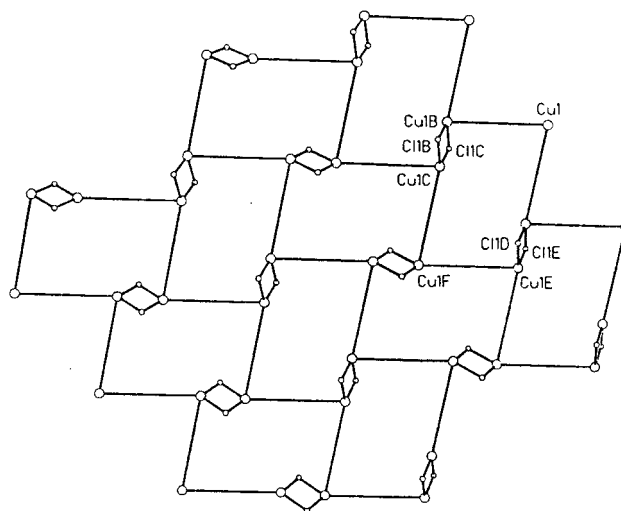
## Results and Discussion

**1** was synthesized under hydrothermal conditions through the reaction between CuCl and 4-VPY (Scheme 1). **1** possesses high thermal stability, as shown in its thermogravimetric analysis (TGA). The TGA of the polycrystalline **1** showed no weight loss between ca. 50 and 160 °C, while an endothermic reaction occurred at 160 °C with a weight loss of ca. 4.1%, probably corresponding to the removal of the absorbed 0.5 water (4.409%). The framework was stable up to 350 °C and collapsed beyond that temperature. The EPR spectrum of a single crystal of **1** is silent, indicating that the status of the Cu atom in **1** is Cu(I).

The X-ray crystal analysis of complex **1** (Figure 1) revealed that the Cu(I) ion in **1** is coordinated in a distorted tetrahedral geometry, which is defined by two chloride atoms and one nitrogen atom and the C–C moiety of the olefin. Thus, 4-VPY acts as bidentate spacer to link two Cu atoms, while the Cl atom also bridges two Cu atoms, leading to the formation of a 2-D framework, as shown in Figure 2. The framework belongs to a wall-brick net type, as shown in Figure 3. Each rectangular net in **1** has an approximate dimension of  $10.576 \times 7.322$  Å, as defined by Cu1–Cu1B–Cu1F–Cu1E. It is interesting to note that the two longer sides of each rectangle contain the  $\text{Cu}_2\text{Cl}_2$  dimer moiety to extend this side, and the distance between Cu1B and Cu1C is about 3.254 Å. This suggests that the cavity can intercalate or include a guest molecule. The pack-



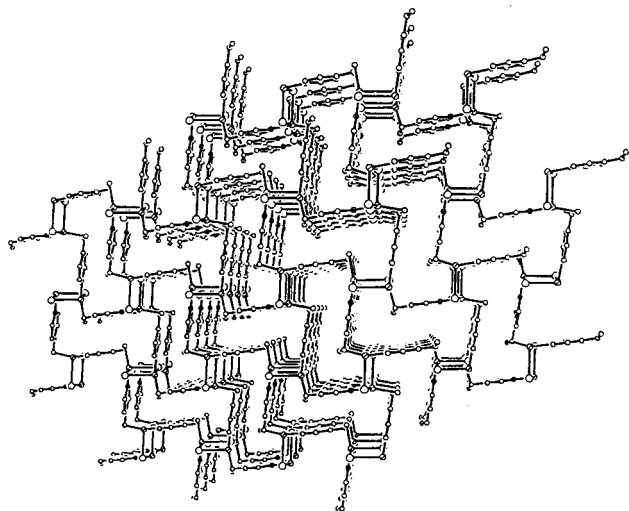
**Figure 2.** (a) 2-D rectangular grid representation of  $\{\text{Cu}(4\text{-VPY})\text{Cl}\}_n$  (**1**); (b) 2-D rectangular grid highlighting the Cu atom pseudo-trigonal pyramidal.



**Figure 3.** Simplified brick-wall 2-D framework view of  $\{\text{Cu}(4\text{-VPY})\text{Cl}\}_n$  (**1**) in which long straight lines and open circles with increasing sizes represent 4-VPY, Cl, and Cu atoms, respectively.

ing view (Figure 4) shows that the two adjacent layers are in a staggered arrangement and adopt an AB type layer.

Worthy of note are  $[\text{C}_8\text{H}_8\text{CuCl}]$  and  $(\text{C}_7\text{H}_8\text{CuCl})_4$  ( $\text{C}_8\text{H}_8$  = cyclooctatetraene and  $\text{C}_7\text{H}_8$  = bicyclo[2.2.1]hepta-2 $\pi$ ,5-diene) reported by Doyle and co-workers,<sup>9</sup> in which the Cu atom was bridged by only one Cl atom,

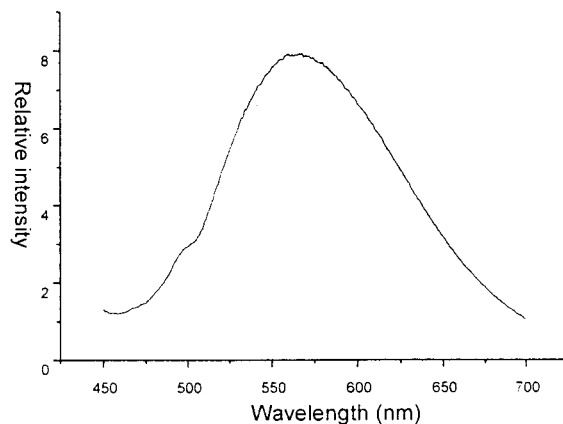


**Figure 4.** Packing view of  $\{\text{Cu}(4\text{-VPY})\text{Cl}\}_n$  (**1**) along the *a*-axis.

and the former is a one-dimensional chain, while the latter is a tetramer. Recently some copper(I)–olefin complexes containing Cl or Br atoms as counterions have been also documented in the literature. Most of these complexes are monomeric, and a few are an infinite chain.<sup>10</sup> However, it is worthy of noting that these  $\pi$ -complexes with CuCl are very unstable and decompose easily at room temperature even if they also display polymeric structures.<sup>10</sup>

The C–C bond distance (1.364(4) Å) for the coordinated olefin **1** is slightly longer than that found in  $[\text{Cu}_2\text{Cl}_2(\text{C}_5\text{H}_8)]$  ( $\text{C}_5\text{H}_8 = 2\text{-methylbutadiene}$ ) (1.358(7) Å)<sup>10c</sup> but slightly shorter than those found in  $[\text{CuCl}(\text{C}_5\text{H}_8\text{O})]$  ( $\text{C}_5\text{H}_8\text{O} = 1\text{-penten-3-one}$ ) (1.383(8) Å)<sup>10a</sup> and  $[\text{CuCl}(\text{C}_4\text{H}_6\text{O}_2)]$  ( $\text{C}_4\text{H}_6\text{O}_2 = \text{methylpropenoate}$ ) (1.370(8) Å).<sup>10b</sup> It is interesting to note that the C–C bond lengths of the coordinated olefin in the two copper(I)  $\pi$ -complexes  $\text{Cu}_4\text{Cl}_4\text{L}$  (1.33(2) Å) and  $\text{Cu}_4\text{Br}_4\text{L}$  (1.34(2) Å) (L =  $\text{C}_7\text{H}_8$ , 1,4-pentadiene) containing a  $\text{Cu}_4\text{X}_4$  cubane core are slightly shorter than that of **1**, but the Cu–C bond distances in  $\text{Cu}_4\text{Cl}_4\text{L}$  (2.10(1)–2.06(1) Å) and  $\text{Cu}_4\text{Br}_4\text{L}$  (2.05(1)–2.10(1) Å) are almost comparable to that in **1** (2.025(3)–2.064(3) Å).<sup>10e</sup> In addition, the Cu–Cl bond lengths in the  $\text{Cu}_2\text{Cl}_2$  dimer of **1** are not equal to each other; thus the distance between Cu and Cu is slightly too long for a Cu–Cu interaction in **1**.

The diffuse reflectance UV–vis spectrum of **1** shows a high-energy band at ca. 244 nm and a low-energy band at ca. 369 nm. The former may be assigned to the intraligand transition of the ligand 4-VPY, as 4-VPY as a free ligand in solution shows a band at ca. 250 nm, while the low-energy band could be assigned to a metal-to-ligand charge transfer (MLCT).<sup>11,12</sup> However, the metal center d to s orbital transition could not be ruled out.<sup>12</sup> The luminescent spectrum of **1** in the solid state at room temperature is shown in Figure 5, with a



**Figure 5.** Luminescent spectrum of  $\{\text{Cu}(4\text{-VPY})\text{Cl}\}_n$  (**1**) in the solid state at room temperature.

maximum at ca. 580 nm ( $\lambda_{\text{ex}} = 240$  nm) that is similar to those found in  $\text{Cu}_4\text{I}_4(\text{pyridine})_4$  ( $\lambda_{\text{emax}} = 580$  nm),  $[\text{Cu}(3,4'\text{-bipyridine})(\text{Br})]_n$  ( $\lambda_{\text{emax}} = 580$  nm),<sup>11,12</sup> and  $[\text{Cu}(3\text{-PYA})]_n$  as well as  $\{[(2\text{-PYA})\text{Cu}(\text{I})\cdot(\text{H}_2\text{O})]_n$  ( $\lambda_{\text{emax}} = 580$  nm, PYA = acrylate).<sup>1</sup> Thus, the emission at 580 nm in **1** can be tentatively assigned to MLCT since the fluorescent emission of the free ligand is observed at about 320 nm. In addition, the shorter luminescent lifetime of **1** (ca.  $\tau = 1.02$  ns) in the solid state suggests its emission should be fluorescent emission. Interestingly, the luminescence of **1** can be quenched in an atmosphere of CO (carbon monoxide), probably suggesting that **1** reacts with CO to give an unstable intermediate,  $\text{Cu}(\text{CO})\text{Cl}(4\text{-VPY})$  (**2**).<sup>2e,f,10f</sup> However, the intermediate can be converted into **1** (and the luminescence can be recovered) after heating since CO is very labile and easily lost.<sup>13</sup> Thus, the luminescent emission of **1** makes it a good candidate for sensing applications on the basis of recognition and inclusion of appropriate guest molecules.

## Experimental Section

**Preparation of 1.** CuCl (1 mmol) and 4-VPY (2 mmol) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of 2.0 mL of  $\text{CH}_3\text{CN}$ , the tube was frozen with liquid  $\text{N}_2$ , evacuated under vacuum, and sealed with a torch. The tube was heated at 90 °C for 2 days to give yellow block crystals (pure phase) in 55% yield based on CuCl. Anal. Found: C, 41.24; H, 3.56; N, 6.45. Calcd: C, 41.15; H, 3.43; N, 6.86. IR (KBr,  $\text{cm}^{-1}$ ): 3081(w), 1608(s), 1559(w), 1523(m), 1485(w), 1423(m), 1400(w), 1323(w), 1258(m), 1216(m), 1106(w), 1064(m), 1014(m), 944(w), 915(w), 837(s), 799(m), 753(w), 684(w), 567(m), 523(m). CP-MAS  $^{13}\text{C}$  NMR (ppm): 150.5, 147.4, 124.8, 118.5, 102.6, and 90.3.

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**X-ray Crystallographic Determination of 1.** Crystal data for **1**:  $C_7H_7ClCuN$ ,  $M_r = 204.13$ , monoclinic, space group,  $P2_1/c$ ,  $a = 7.9377(11) \text{ \AA}$ ,  $b = 9.4600(12) \text{ \AA}$ ,  $c = 10.7491(12) \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 109.494(11)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 760.89(17) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 293(2) \text{ K}$ ,  $\rho_{\text{calc}} = 1.782 \text{ g.cm}^{-3}$ . Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ),  $\mu = 3.134 \text{ mm}^{-1}$ ,  $R1 = 0.0282$ ,  $wR2 = 0.0664$  for 1313 observed reflections from 1737 independent reflections,  $GOF = 1.021$ .

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**Supporting Information Available:** Crystallographic CIF (excluding structure factors) and tables of atomic coordinates, thermal parameters, and bond distances and angles for **1** as well as the preparation of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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