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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]$_n$ (**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.[1] 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.[2,3] Although a large number of metal−organic coordination polymer networks or cyclophanes such as squares and grids are documented in the recent literature,[4,5] 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,[6−8] 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}$_n$ (**1**), containing

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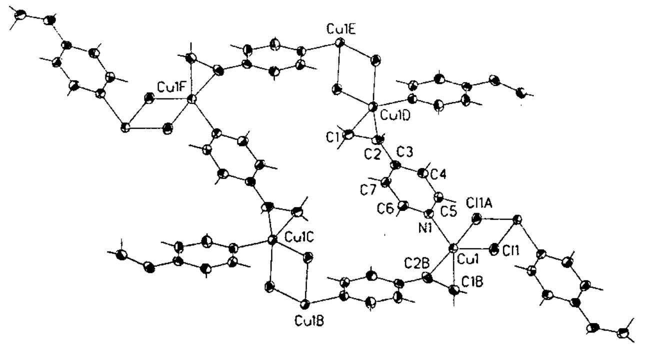
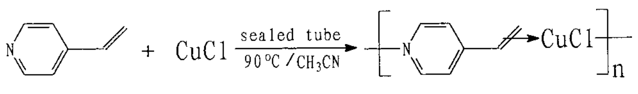


Figure 1. Rectangular unit representation of $\{Cu(4\text{-}VPY)Cl\}_n$ (**1**). The thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Cu(1)−N1 2.006(2), Cu(1)−C(1B) 2.025(3), Cu(1)−C(2B) 2.064(3), Cu(1)−Cl(1) 2.2599(8), Cu(1)−Cl(1A) 2.6751(8), C(1B)−C(2B) 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



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a η^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 endothermal 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 × 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 Cu_2Cl_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 packing view (Figure 4) shows that the two adjacent layers are in a staggered arrangement and adopt an AB type layer.

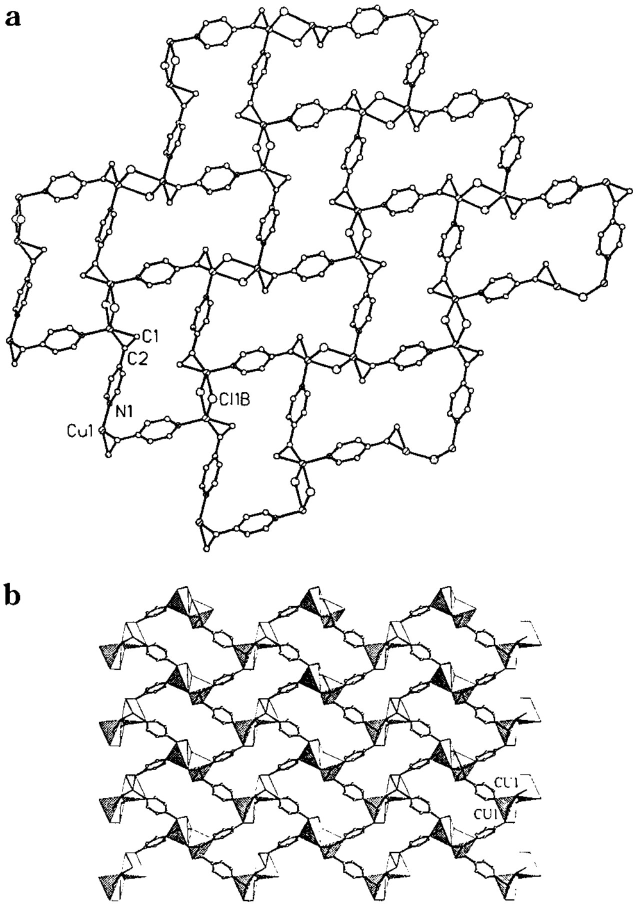

Figure 2. (a) 2-D rectangular grid representation of $\{Cu(4\text{-}VPY)Cl\}_n$ (**1**); (b) 2-D rectangular grid highlighting the Cu atom pseudo-trigonal pyramid.

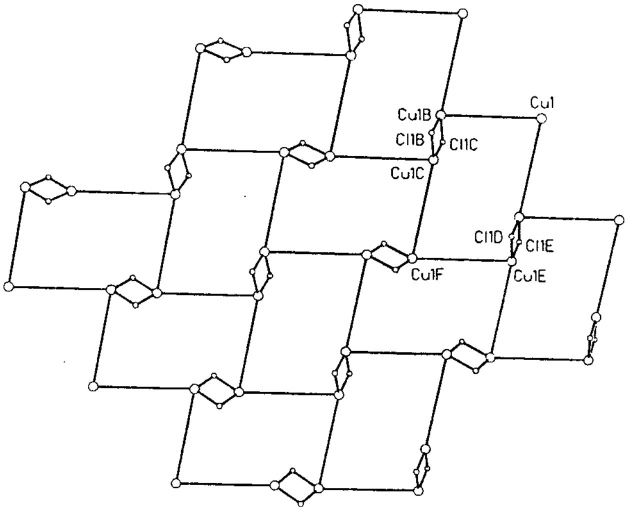

Figure 3. Simplified brick-wall 2-D framework view of $\{Cu(4\text{-}VPY)Cl\}_n$ (**1**) in which long straight lines and open circles with increasing sizes represent 4-VPY, Cl, and Cu atoms, respectively.

Worthy of note are $[C_8H_8CuCl]$ and $(C_7H_8CuCl)_4$ (C_8H_8 = cyclooctatetraene and C_7H_8 = bicyclo[2.2.1]-hepta-2π,5-diene) reported by Doyle and co-workers,[9] in which the Cu atom was bridged by only one Cl atom,

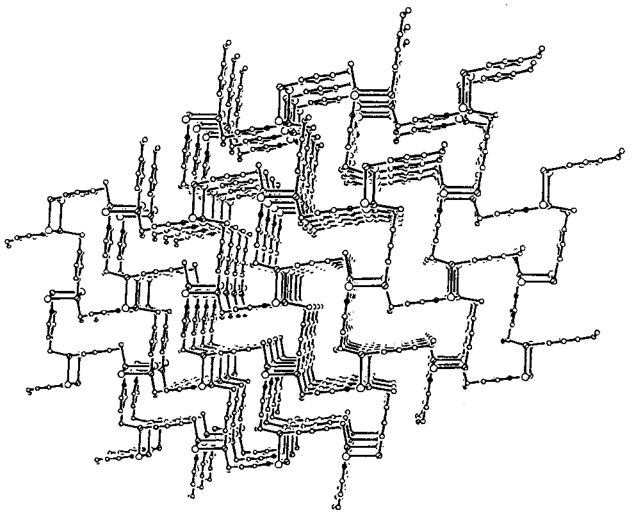

Figure 4. Packing view of $\{Cu(4\text{-}VPY)Cl\}_n$ (**1**) along the *a*-axis.

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.[10] However, it is worthy of noting that these π-complexes with CuCl are very unstable and decompose easily at room temperature even if they also display polymeric structures.[10]

The C−C bond distance (1.364(4) Å) for the coordinated olefin **1** is slightly longer than that found in $[Cu_2Cl_2(C_5H_8)]$ (C_5H_8 = 2-methylbutadiene) (1.358(7) Å)[10c] but slightly shorter than those found in $[CuCl(C_5H_8O)]$ (C_5H_8O = 1-penten-3-one) (1.383(8) Å)[10a] and $[CuCl(C_4H_6O_2)]$ ($C_4H_6O_2$ = methylpropenoate) (1.370(8) Å).[10b] It is interesting to note that the C−C bond lengths of the coordinated olefin in the two copper(I) π-complexes Cu_4Cl_4L (1.33(2) Å) and Cu_4Br_4L (1.34(2) Å) (L = C_7H_8, 1,4-pentadiene) containing a Cu_4X_4 cubane core are slightly shorter than that of **1**, but the Cu−C bond distances in Cu_4Cl_4L (2.10(1)−2.06(1) Å) and Cu_4Br_4L (2.05(1)−2.10(1) Å) are almost comparable to that in **1** (2.025(3)−2.064(3) Å).[10e] In addition, the Cu−Cl bond lengths in the Cu_2Cl_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).[11,12] However, the metal center d to s orbital transition could not be ruled out.[12] The luminescent spectrum of **1** in the solid state at room temperature is shown in Figure 5, with a maximum at ca. 580 nm (λ_{ex} = 240 nm) that is similar to those found in $Cu_4I_4(pyridine)_4$ (λ_{emax} = 580 nm), $[Cu(3,4'\text{-bipyridine})(Br)]_n$ (λ_{emax} = 580 nm),[11,12] and $[Cu(3\text{-PYA})]_n$ as well as $\{[(2\text{-PYA})Cu(I)]\cdot(H_2O)\}_n$ (λ_{emax} = 580 nm, PYA = acrylate).[1] 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. τ = 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, Cu(CO)Cl(4-VPY) (**2**).[2e,f,10f] However, the intermediate can be converted into **1** (and the luminescence can be recovered) after heating since CO is very labile and easily lost.[13] 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.

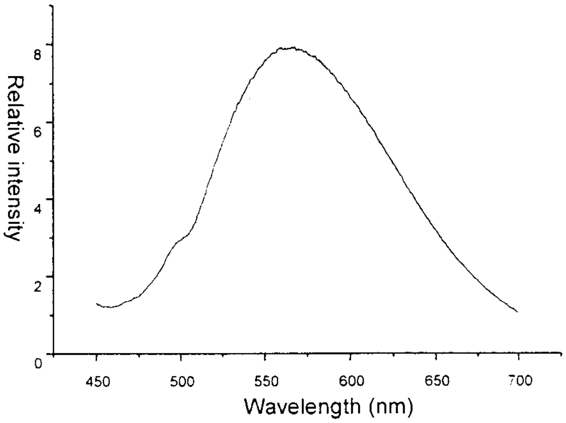

Figure 5. Luminescent spectrum of $\{Cu(4\text{-}VPY)Cl\}_n$ (**1**) in the solid state at room temperature.

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 CH_3CN, the tube was frozen with liquid 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, 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}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, $P2_1/c$, $a = 7.9377(11)$ Å, $b = 9.4600(12)$ Å, $c = 10.7491(12)$ Å, $\alpha = 90.00°$, $\beta = 109.494(11)°$, $\gamma = 90.00°$, $V = 760.89(17)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\rho_{\mathrm{cacl}} = 1.782$ g.cm^{-3}. Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 3.134$ 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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