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An Unusual Mixed-Valence Cu(I)–Cu(II) 3-D Framework

Hong Zhao, Zhi-Rong Qu, Qiong Ye, Xi-Sen Wang, Jing Zhang,* Ren-Gen Xiong,* and Xiao-Zeng You

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry,
Nanjing University, 210093 Nanjing, P. R. China

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The reaction of $Cu(CH_3CN)_4ClO_4$ with 2-pyridylacrylic acid (2-HPYA) affords an unusual mixed-valence Cu(I)–Cu(II) 3-D framework $\{[Cu(II)(2\text{-}PYA)_2]_3 \cdot [Cu(I)(2\text{-}PYA)]_2 \cdot (H_2O)_2\}_n$ (**1**) with a novel topology which features Cu(II) dimeric units (or paddle-wheel unit). The almost perpendicular coordinating direction between the N atom of pyridyl and the O atom of carboxylate groups may be responsible for the formation of such a novel network.

Over the past decade, there have been many examples of the use of pyridyl-based bridging ligands in the construction of metal-organic coordination networks. The ligands used include simple 2-connecting ligands such as 4,4′-bipyridine,[1,2] 3-connecting ligands such as 2,4,6-tripyridyl-1,3,5-triazine,[3] and even 4-connecting ligands such as tetrapyridylporphyrin.[4] The result of this work has been a fascinating assortment of novel network structures. More recently, carboxylate-based ligands such as 1,4-benzenedicarboxylate[5] (2-connecting) and 4,4′,4″-benzene-1,3,5-triyl-tribenzoate[6] (3-connecting) have been successfully employed in the synthesis of porous and particularly robust networks where the ligands link small metal clusters or aggregates. The successful use of the aforementioned ligands in the construction of coordination polymers provides strong encouragement that bridging ligands combining carboxylate and pyridyl metal binding units will provide access to a novel range of coordination networks.[7] In this present work we report the reaction of Cu(I) with 2-pyridylacrylic acid (2-HPYA).

In the cases where metal coordination environments can be successfully predicted, it is possible to make accurate predictions as to the connectivity (topology) of the resulting network. The situation is more complicated when ligands containing 2 different types of binding units are employed, especially when one of the units (carboxylate) displays a high degree of variability in its coordination. Nevertheless, it is not unreasonable to expect that a Cu(I) center bound to four pyridyl groups will behave as a 4-connecting center. In the case of carboxylate units binding to Cu(I) centers, we note that copper(II) benzoate has a tetrameric structure with 4 carboxylates bridging an almost square arrangement of particularly close Cu(II) centers.[8] If a similar type of unit is formed in the reaction of Cu(I) with $2\text{-}PYA^-$, then one might expect a network based on two types of 4-connecting centers, a tetrapyridyl Cu(I) center and a tetracarboxylate $Cu(I)_4$ center that is similar to that found in $[Cu(I)_4(4\text{-}PYA)_2(H_2O)(BF_4)]$ (4-PYA = 4-pyridylacrylate) in which a $Cu^+{}_4(CO_2)_4$ cluster serves as a 4-connecting node.[8,9]

Unexpectedly, the reaction of $Cu(CH_3CN)_4ClO_4$ with 2-pyridylacrylic acid (2-HPYA) results in partial oxidation

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* To whom correspondence should be addressed. E-mail: xiongrg@netra.nju.edu.cn (R.-G.X.). Fax: (+86)- 25-3314502 or (+86)-25-3317761 (R.-G.X.).

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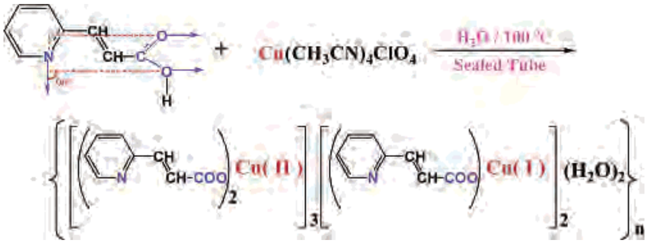
Scheme 1



of the copper to give an unprecedented mixed-valence Cu(I)−Cu(II) 3-D framework, $\{[Cu(II)(2\text{-}PYA)_2]_3{\cdot}[Cu(I)(2\text{-}PYA)]_2{\cdot}(H_2O)_2\}_n$ (**1**) (Scheme 1). Herein, we report its synthesis, its crystal structure, and details relating to its thermal stability.

Compound **1** was synthesized by the reaction of $Cu(CH_3CN)_4ClO_4$ with 2-HPYA under hydrothermal reaction conditions.[10] In its IR spectrum, three strong peaks at 1658, 1612, and 1400 cm^{-1} suggest that the carboxylate group persists in **1** and is deprotonated. The absence of a peak at ca. 1100 cm^{-1} indicates the perchlorate ion is not present in **1**. One weight loss step occurred at ca. 50−130 °C (2.36% loss), corresponding to the removal of two water molecules per formula unit (2.34%). Most important is the fact that no weight loss was recorded between the temperature 130 and 170 °C, suggesting that the host is a stable molecular network. The framework decomposes beyond 225 °C. The XPS spectrum results (shoulders peaks at 934.6 and 954.2 eV (Cu(I) character) with satellite peaks at 943.5 and 962.8 eV (Cu(II) character)) and magnetic susceptibility (antiferromagnetic coupling, $2J = -2.80$ cm^{-1}, similar to those of copper(II) acetate[11]) indicate that both Cu(I) and Cu(II) may be present in the coordination polymer of **1**.

Figure 1. A diagram showing a $Cu_2(CO_2)_4$ dimer unit and distorted tetrahedral Cu(I) coordination environment in (**1**): Cu(II) purple, Cu(I) green, O red, N blue, C black.

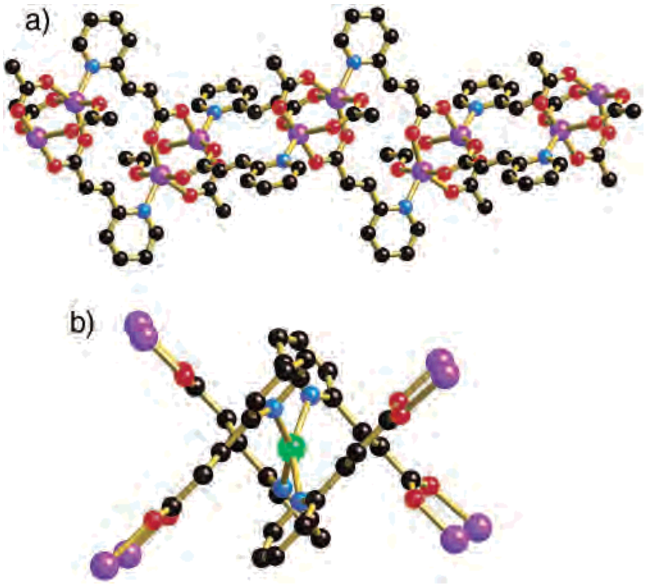


Figure 2. PYA⁻ links between Cu centers. (a) PYA⁻ ligands bridging Cu(II) dimers in a "strip" extending in the [110] direction. (b) The connections between Cu(I) centers and Cu(II) dimeric units: Cu(II) purple, Cu(I) green, O red, N blue, C black.

The three-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction investigation.[12] As indicated in Figure 1, Cu(I) centers (green spheres) are four-coordinate with the nitrogen atoms of 4 pyridyl groups lying at the vertices of a significantly distorted tetrahedron (flattened almost toward a square plane). Figure 1 also shows the Cu(II) centers (purple spheres) present in the form of the familiar tetracarboxylate dimer (or paddle-wheel unit) with axial positions occupied by pyridyl groups.[8,9]

A notable structural feature within this network is the presence of $[Cu(II)_2pya_2]_n$ strips of the Cu(II) dimer units which extend in the [110] direction (see Figure 2a). It can be seen that each dimeric unit is doubly bridged to adjacent dimeric units resulting in the formation of 14-membered rings. Symmetry related strips extend in the $[1\bar{1}0]$ direction.

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(10) Preparation of $\{[Cu(II)(2\text{-}PYA)_2]_3{\cdot}[Cu(I)(2\text{-}PYA)]_2{\cdot}(H_2O)_2\}_n$ (**1**): Hydro(solvo)-thermal treatment of $Cu(CH_3CN)_4ClO_4$ (1.0 mmol), 2-H-PYA (2.0 mmol), and H_2O (2 mL) for 2 days at 100 °C yielded a green block crystalline product (only one pure phase). The yield of **1** was about 45% on the basis of $Cu(CH_3CN)_4ClO_4$. Anal. Calcd for $C_{64}H_{52}N_8O_{18}Cu_5$: [%] C, 49.91; H, 3.38; N, 7.28. Found: [%] C, 50.15; H, 3.42; N, 7.42. IR (KBr, cm^{-1}): 3400(br, w), 1658(s), 1612(s), 1480(w), 1400(s), 1300(w), 1250(w), 1100(w), 1080(w), 980(w), 880(w), 785(m), 750(w), 620(w), 500(w).

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(12) Crystal data for **1**: $C_{64}H_{52}N_8O_{18}Cu_5$, orthorhombic, *Fddd*, $a = 15.913(2)$ Å, $b = 21.616(4)$ Å, $c = 42.739(10)$ Å, $V = 14702(5)$ $Å^3$, $Z = 8$, $M = 1538.84$, $D_c = 1.390$ Mg m^{-3}, R1 = 8.92%, wR2 = 24.59%, $T = 293$ K, $\mu = 1.492$ mm^{-1}, $S = 0.993$.

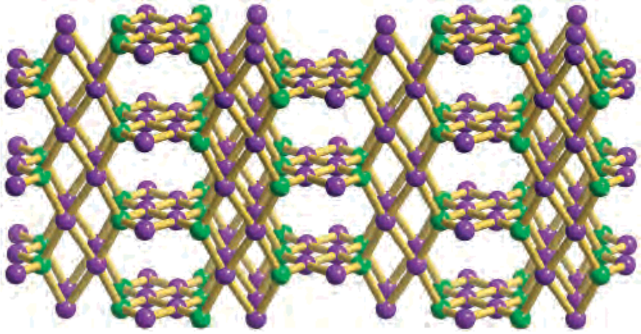

Figure 3. The connectivity of **1**. Planar centers represent Cu(II) dimers; “tetrahedral” centers represent Cu(I) centers. Single purple spheres represent Cu(II) pairs; green spheres represent tetrahedral Cu(I) centers. Identical Cu(II) dimer strips extend in an almost vertical direction and a direction almost normal to the plane of the page.

Inspection of Figure 2a reveals two incomplete 2-PYA ligands per dimer. These ligands extend from the strips depicted in Figure 2a to Cu(I) centers shown in Figure 2b. The two Cu(II) pairs indicated in the top half of Figure 2b belong to the same $[\mathrm{Cu(II)pya_2}]_n$ strip while the lower pairs belong to another strip which runs in the $[1\bar{1}0]$ direction.

Given the complexity of the coordination network, it is perhaps useful to simplify the connectivity of the structure by representing each dimeric unit and Cu(I) center by multiconnecting centers. Each Cu(I) atom links to 4 dimeric units, and as a consequence, it may be considered as a 4-connecting center. Although the dimeric units are coordinated by six different ligands, each of the units only links to two other dimeric units and two Cu(I) centers, and thus, from a topological perspective the Cu(II) pair may be considered as a 4-connecting center as well. A representation of the net formed by these two types of 4-connecting centers is presented in Figure 3. In this net the approximately square planar centers represent bimetallic units while the centers with a distorted tetrahedral environment represent the Cu(I) atoms. Connections between “square planar” centers result in the formation of broad strips that contain double rows of square planar centers. These strips which represent the atoms depicted in Figure 2a extend in the [110] and $[1\bar{1}0]$ dirctions. The tetrahedral 4-connectors link these strips together.

The network has strong similarities with the PtS structure. In the tetragonal PtS structure, “strips” composed of edge sharing square planar centers (Pt atoms) extending in the direction normal to the page are linked through tetrahedral centers (S atoms) to strips running in a vertical direction (see Figure 4). The main difference between the net discussed above and PtS is that the strips in the PtS net contain only single rows of square planar centers. The mixed-valence Cu(I)−Cu(II) 3-D coordination polymer is, to the best of our knowledge, the first example of a coordination polymer with this novel topology. There are however examples of the PtS topology in other coordination polymers.[4,13] The network found for **1** is not without precedent, and we are grateful to a referee for pointing out that the network has the same topology as the Ge net in LiGe[14] and has the Schafli symbol $[4^2.8^4][4^3.8.6^2]$.

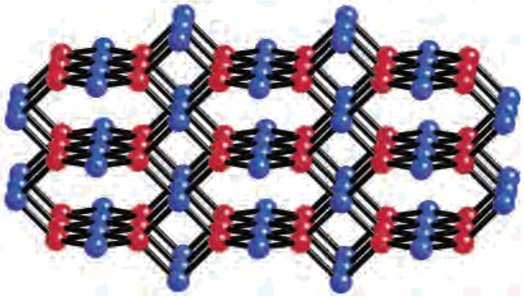

Figure 4. The structure of PtS. Square planar centers represent Pt(II) (blue) and tetrahedral centers represent S atoms (red).

In conclusion, the present results provide encouragement that the use of ligands combining carboxylate and pyridyl groups as buildings blocks in coordination polymers may provide access to a novel range of extended structures.

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Note Added after ASAP: An error appeared in the Acknowledgment in the version posted ASAP on January 10, 2004. The corrected version appeared on January 22, 2004. Also, there has been a change in authorship since the original ASAP posting. The revised version was posted on February 26, 2004.

Supporting Information Available: X-ray data in CIF format. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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