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Solvothermal in Situ Ligand Synthesis through Disulfide Cleavage: 3D (3,4)-Connected and 2D Square-Grid-Type Coordination Polymers

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Two novel coordination polymers, $Cu_3(4\text{-pyt})_3$ (**1**) and $Co(4\text{-pyt})_2$ (**2**) (4-pyt = pyridine-4-thiolate), have been synthesized by in situ generation of a 4-pyt ligand from a 4,4′-dithiodipyridine precursor through reductive cleavage of the disulfide bond under solvothermal conditions. **1** and **2** exhibit a three-dimensional (3,4)-connected network and a two-dimensional square-grid-type structure, respectively.

Metal–organic frameworks have attracted much interest because of their intriguing topologies and exploitable properties for potential applications such as gas storage, ion exchange, catalysis, magnetism, and electrical conductivity.[1–5] Since the mid-1990s, a number of structures have been synthesized through judicious assembly of appropriate metal ions (or clusters) and bi- or multifunctional ligands. In such materials, functionality can be introduced from either the inorganic vertexes or the organic building blocks. Furthermore, the molecular-level integration of inorganic and organic subunits is expected to produce cooperative effects so as to initiate or enhance desirable properties. Therefore, the selection or design of organic ligands containing predefined features, such as electronic properties and versatile binding modes, is crucial to the construction of metal–organic frameworks.

In contrast to the large and increasing amount of work on the synthesis with ligands containing O or N donors, there have been fewer reports of studies based on organothiolate ligands.[6–8] Two kinds of organothiolate ligands, thiolatopyridine[6] and thiolatocarboxylate,[7] have been explored to construct structures with luminescent or magnetic properties. Pyridine-4-thiol (4-Hpyt), which exists in solution as an equilibrium mixture of thiol and thione forms, is an interesting ligand in the thiolatopyridine system because of its different structural forms and coordination modes. Although it was previously investigated, only a few crystal structures, usually discrete metal complexes, have been reported.[9–11] Additionally, 4-Hpyt in these compounds tends to adopt the *neutral* thione form (pyridinium-4-thiolate) that coordinates with metal atoms through the S donor. There is only one example in which the *negative* pyridine-4-thiolate (4-pyt)

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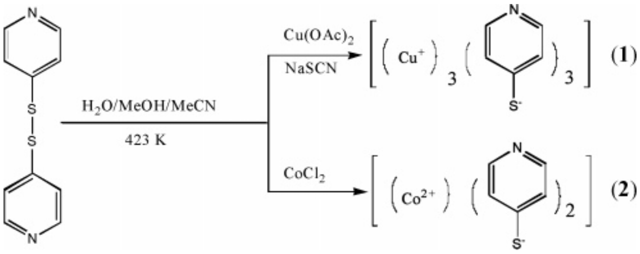
Scheme 1. Self-assembly of the in Situ Generated 4-pyt with Metal Ions



uses both N and S donors to form a coordination polymer. In this case, the 4-pyt ligand is in situ generated from (4-pyridylthio)acetic acid.[11]

A biological process such as protein folding and unfolding makes extensive use of the reversible cleavage of the disulfide bond. A hydro(solvo)thermal system, however, tends to favor the oxidative formation of the disulfide bond. As a result, few examples are known in which the reductive cleavage of the disulfide bond is utilized to create new materials. Here, we explore in situ generation of the 4-pyt ligand from a 4,4′-dithiodipyridine precursor through cleavage of the S−S bond as a strategy for assembling extended coordination polymers (Scheme 1). We isolated two new compounds, $Cu_3(4\text{-pyt})_3$ (**1**) and $Co(4\text{-pyt})_2$ (**2**), with a three-dimensional (3D) (3,4)-connected network and a two-dimensional (2D) square-grid-type structure, respectively.

The solvothermal reaction of $Cu(OAc)_2 \cdot H_2O$, 4,4′-dithiodipyridine, and NaSCN in the mixed $H_2O/MeOH/MeCN$ solution at 150 °C for 3 days afforded yellow crystals of **1**.[12] This reaction resulted in the reduction of Cu^{II} to Cu^{I} (possibly by SCN^-),[11] in addition to the in situ synthesis of the 4-pyt ligand. Single-crystal X-ray analysis[13] revealed that the asymmetric unit of compound **1** contains one and a half Cu^{I} atoms and one and a half 4-pyt ligands, respectively. As shown in Figure 1, two types of Cu^{I} coordination environments are present: the Cu(1) atom is located in the nearly trigonal-planar coordination environment through bonding to two S donors and one N donor of three separate ligands, while Cu(2) adopts a slightly distorted tetrahedral coordination geometry through bonding to three S donors and one N donor of four separate ligands. The Cu(1)···Cu(2) separation is 3.959 Å. The Cu−N bond distances are 2.007(4) and 2.035(3) Å, and the Cu−S bond lengths range from 2.2279(11) to 2.4306(12) Å. Such distances are similar to those found in other Cu^{I} complexes.[6c,11]

It is noteworthy that there are also two kinds of bridging coordination modes of the 4-pyt ligands in **1** that mirror those of two Cu sites: one acts as a μ_3 bridge in which the S donor coordinates to two Cu atoms [Cu(2)−S(2)−Cu(2A), 142.17(6)°], and the other acts as a μ_4 bridge in which the S donor coordinates to three Cu atoms [Cu(1)−S(1)−Cu(2), 120.00(5)°; Cu(1)−S(1)−Cu(2B), 118.26(4)°; Cu(2)−S(1)−Cu(2B), 74.90(3)°].

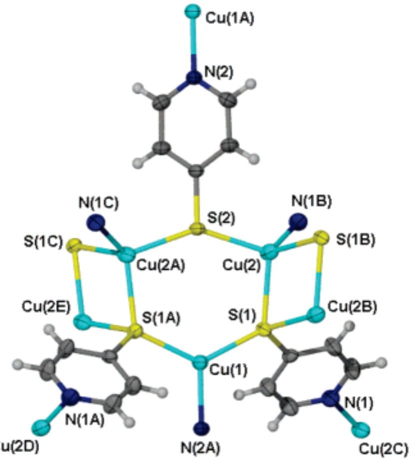


Figure 1. View of the coordination environment of Cu^+ and 4-pyt in **1**. Thermal ellipsoids for non-H atoms are shown at the 50% probability level.

Interestingly, a unique Cu−S chain containing alternating Cu_2S_2 four-ring and Cu_3S_3 six-ring structures is formed with two adjacent rings sharing a common edge. Each Cu−S chain is then cross-linked to six adjacent Cu−S chains through pyridal groups of the 4-pyt ligands, forming a 3D network with one-dimensional (1D) triangular-prism-type channels running along the crystallographic *c* axis (Figure 2).

From the above analysis, both the Cu^{I} cation and the 4-pyt ligand can be considered as 3-connected triangular and 4-connected tetrahedral nodes. Compound **1** therefore possesses a (3,4)-connected topology. Compared to known (3,4)-connected nets such as boracite and cubic C_3N_4,[14] the topology of **1** is complicated because 3- and 4-connected nodes are not alternating (Figure 2). Furthermore, the topology of **1** represents an uncommom example of (3,4)-connected nets in which either metal sites or ligands alone can make up both 3- and 4-connected nodes.

Compound **2** was prepared by a procedure similar to that of **1**.[15] X-ray diffraction analysis[16] shows that it is a 2D square-grid-type structure. In **2**, each Co^{II} center exhibits a tetrahedral geometry with two N atoms and two S atoms from four different ligands. The Co−N and Co−S distances are 2.020(5) and 2.276(2) Å, respectively. Different from **1**, each 4-pyt ligand in **2** acts as a single μ_2 bridge linking two Co ions through its N atom and S atom. Thus, each Co ion connects four ligands to form a layer structure consisting of

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(12) Preparation of **1**:A mixture of $Cu(OAc)_2 \cdot H_2O$ (200.4 mg), NaSCN (80.8 mg), 4,4′-dithiodipyridine (111.7 mg), H_2O (2 mL), MeOH (3 mL), and MeCN (3 mL) was placed in a 23-mL Teflon autoclave and then heated at 150 °C for 3 days. After cooling to room temperature, yellow prismatic crystals of **1** were obtained in 40% yield.

(13) Crystal data for $C_{15}H_{12}Cu_3N_3S_3$ (**1**): monoclinic, space group *C*2/*c*, $M = 521.08$, $a = 18.2915(6)$ Å, $b = 10.6420(3)$ Å, $c = 11.5508(4)$ Å, $\beta = 129.16°$, $V = 1743.42(10)$ Å^3, $Z = 4$, $T = 298(2)$ K, $D_c = 1.985$ g cm^{-3}, $F(000) = 1032$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $\mu = 3.986$ mm^{-1}, R1 = 0.0348 and wR2 = 0.0579, $S = 0.712$.

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(15) Preparation of **2**: A mixture of $CoCl_2 \cdot 6H_2O$ (120.3 mg), 4,4′-dithiodipyridine (220.6 mg), H_2O (2 mL), MeOH (3 mL), and MeCN (3 mL) was placed in a 23-mL Teflon autoclave and then heated at 150 °C for 3 days. After cooling to room temperature, deep-blue block crystals of **2** were obtained in 65% yield.

(16) Crystal data for $C_{10}H_8CoN_2S_2$ (**2**): monoclinic, space group *C*2/*c*, $M = 279.23$, $a = 11.073(3)$ Å, $b = 10.213(3)$ Å, $c = 11.570(4)$ Å, $\beta = 112.341°$, $V = 1210.2(6)$ Å^3, $Z = 4$, $T = 298(2)$ K, $D_c = 1.533$ g cm^{-3}, $F(000) = 564$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $\mu = 1.730$ mm^{-1}, R1 = 0.0594 and wR2 = 0.1706, $S = 1.044$.

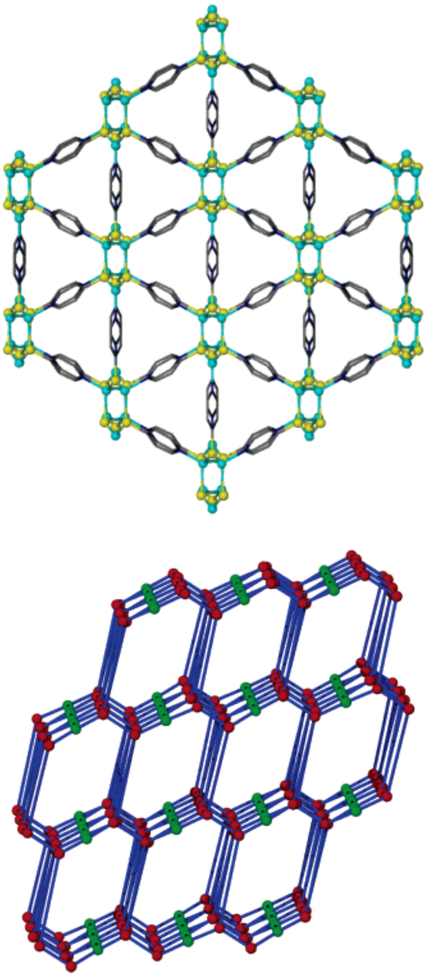

Figure 2. Top: 3D framework for **1** viewed down the *c* axis. Bottom: schematic representation of **1**, simplified as the (3,4)-connected network, viewed down the *b* axis (red ball = 4-connected node; green ball = 3-connected node).

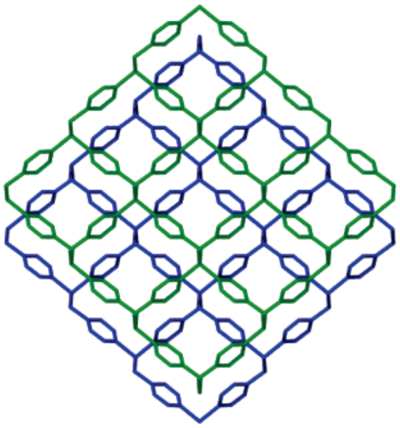

Figure 3. Two adjacent layers in **2**, showing the square-grid-type structure.

a (4,4) net with dimensions of 7.5 × 7.5 Å based on the metal-to-metal distances. As shown in Figure 3, the two layers are stacked along the *c* axis to give a noninterpenetrating topology.

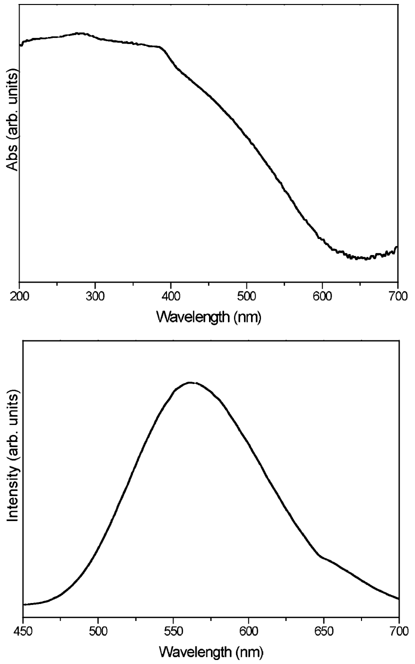

Figure 4. UV−vis absorption spectrum (top) and photoluminescent emission spectrum (bottom) for **1** in the solid state at room temperature.

The optical properties of **1** were studied by solid-state diffuse-reflectance UV−vis−near-IR spectroscopy (Figure 4). The spectrum shows an optical transition with a band gap of 1.9 eV. The transition likely results from the charge transfer from the S-dominated valence band to the Cu-dominated conduction band. When excited at 380 nm at room temperature, **1** emits a strong green luminescence, with the maximum wavelength centered at 560 nm (Figure 4). The emission likely originates from ligand-to-metal charge transfer and/or metal-to-ligand charge transfer. More detailed theoretical and spectroscopic studies are necessary for a better understanding of the luminescent mechanism.

In conclusion, two new metal organosulfides have been successfully synthesized by in situ generation of a 4-pyt ligand from a 4,4′-dithiodipyridine precursor through the reductive cleavage of the S−S bond under solvothermal conditions. These results are relevant for the development of a possible strategy for the in situ synthesis of new ligands and construction of polymeric metal organosulfides.

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Supporting Information Available: X-ray crystallographic files for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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