

Cuprophilicity-Induced Cocrystallization of $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ Sheets and $[\text{Cu}(\text{SCN})]_n$ Chains into a 3-D Pseudopolyrotaxane

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The cocrystallization of $[\text{Cu}(\text{SCN})]_n$ chains and $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ ($4,4'\text{-bpy} = 4,4'\text{-bipyridine}$) layers generated a 3-D pseudopolyrotaxane compound, $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n \cdot [\text{Cu}(\text{SCN})]_n$ (**1**), which can also be viewed as a 3-D network constructed by linkages of 2-D sheets and 1-D chains via unsupported $\text{Cu}^I\text{--Cu}^I$ interactions. The $\text{Cu}^I\text{--Cu}^I$ contact of 2.651(4) Å in **1** is the shortest unsupported $\text{Cu}^I\text{--Cu}^I$ distance documented to date, indicating cuprophilic attractions.

The attractive interactions between closed-shell d^{10} metal centers have received extensive attention because they play an important role in the optical and electronic properties of polynuclear d^{10} metal complexes.¹ This behavior has been particularly well documented for gold, with the term “aurophilicity” being used to describe $\text{Au}^I\text{--Au}^I$ interactions that are theoretically attributed to correlation and relativistic effects.² The occurrence of analogous metallophilic effects involving lighter copper atoms has been the subject of a long debate because most structurally characterized complexes featuring short $\text{Cu}^I\text{--Cu}^I$ contacts are associated with ligand-bridged, hydrogen-bonded, electrostatic-attracted, and $\pi\text{--}\pi$ -stacked effects.^{1c,d,3,4} Unambiguous experimental evidence for cuprophilicity relies on the isolation of complexes featuring unsupported $\text{Cu}^I\text{--Cu}^I$ contacts that are not associated with network restrictions, hydrogen bonds, electrostatic forces, and $\pi\text{--}\pi$ -stacking interactions. To date, the structur-

ally characterized complexes having reliable cuprophilic interactions are neutral $[\text{CuLA}]_3$ {HLA = 2-[3(5)-pyrazolyl]pyridine} and $[\text{tBuCu}(\text{CN})\text{Li} \cdot (\text{OEt})_2]$ as well as a negatively charged $([\text{CuCl}_2]^-)_2$ dimer.⁵ It remains a great challenge to give direct evidence of cuprophilicity by the synthesis of Cu^I complexes with unsupported $\text{Cu}^I\text{--Cu}^I$ contacts.

One the other hand, polycatenanes, polyrotaxanes, pseudopolyrotaxanes, and polyknots are also of current interest because their linkages are related to the classification of isomers within organic molecules, organic polymers and biopolymers, natural and synthetic forms of DNA, and so on.⁶ In our continuing effort to develop copper complexes,⁷ we synthesized a cocrystallized compound $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n \cdot [\text{Cu}(\text{SCN})]_n$ ($4,4'\text{-bpy} = 4,4'\text{-bipyridine}$) (**1**), which is a 3-D pseudopolyrotaxane constructed by $[\text{Cu}(\text{SCN})]_n$ chains and $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layers. Selectively, **1** can be viewed as a (3,4)-connected 3-D network formed by linkages of 2-D (6,3) sheets and $[\text{Cu}(\text{SCN})]_n$ chains via unsupported $\text{Cu}^I\text{--Cu}^I$ interactions.

Hydrothermal reaction of $\text{Cu}(\text{MeCO}_2)_2$, NH_4SCN , $4,4'\text{-bpy}$, and water in the molar ratio of 2:2:1:1300 at 150 °C for 10 days resulted into pale brown block crystals of **1** in 45% yield.⁸ The infrared spectra show intense stretching

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- (8) Anal. Calcd for $\text{C}_{13}\text{H}_8\text{N}_5\text{Cu}_3\text{S}$ (**1**): C, 34.17; H, 1.76; N, 15.33; S, 7.02. Found: C, 34.14; H, 1.82; N, 15.27; S, 7.06. IR (KBr, cm^{-1}): 3319s, 2918w, 2344w, 2216m, 2158s, 2074m, 1700m, 1616s, 1394s, 1257w, 1131m, 1056m, 951m, 866m, 824w, 507s.

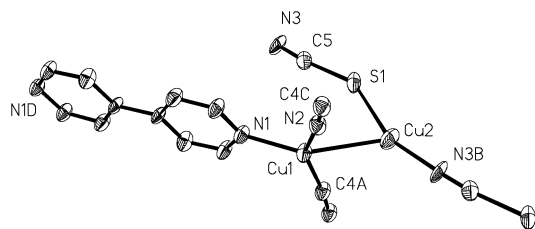


Figure 1. View of the coordination environments of copper atoms in **1** with 35% thermal ellipsoid probability. Selected bond lengths (Å) and angles (deg): Cu1–N2, 1.899(8); Cu1–C4a, 1.899(8); Cu1–N1, 2.082(10); Cu2–S1, 2.455(4); Cu2–N3b, 1.889(19); Cu1–Cu2, 2.651(4); N2–C4c, 1.129(16); N2–Cu1–C4a, 145.7(6); N2–Cu1–N1, 107.0(3); C4a–Cu1–N1, 107.0(3); N3b–Cu2–S1, 156.7(9). Symmetry codes: (a) $x, -y + 1, z$; (b) $x, y, z - 1$; (c) $-x + 1/2, -y + 1/2, -z$.

absorptions at 2158 and 2074 cm^{-1} assigned to the $\text{C}\equiv\text{N}$ vibration from thiocyanate and cyanide, respectively. The wavenumber of the $\text{C}\equiv\text{N}$ vibration from SCN^- is higher than that of the corresponding stretch in $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]$ and $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bpy})]$, reflecting the stronger coordination of the S donor in **1**.⁹ The desulfuration of thiocyanate anions to form cyanides was documented recently by us, which indicates that sulfur atoms of thiocyanate anions are converted into sulfate anions.^{7c} The similar oxidization–desulfuration of thiocyanate anions to form cyanides was documented by Schug et al.¹⁰

X-ray crystallography¹¹ reveals that **1** is a 3-D pseudopolyrotaxane with $[\text{Cu}(\text{SCN})]_n$ chains penetrating $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layers. Compound **1** crystallizes in monoclinic space group $C2/m$, and the asymmetric unit consists of 10 crystallographically independent non-hydrogen atoms, as shown in Figure 1. The C1, C2, and C4/N2 atoms localize general positions. Cu2 and SCN^- are imposed by a crystallographic C_2 axis, which causes the disorder of Cu2 and the SCN^- group. The crystallographic mirror plane passes through the Cu1, Cu2, N1, C3, S1, C5, and N3 sites. The indistinguishable C4 and N2 atoms of cyanide occupy the same sites. The C4–N2 distance of 1.129(16) Å is the typical $\text{C}\equiv\text{N}$ bond length of cyanide.^{7c} Cu1 shows a trigonal geometry, coordinated by one pyridine N and one C and one N from two cyanides. Cu2 shows close to linear geometry, coordinated by one S and one N from two SCN^- groups. Compound **1** is EPR-silent, which indicates that both Cu1

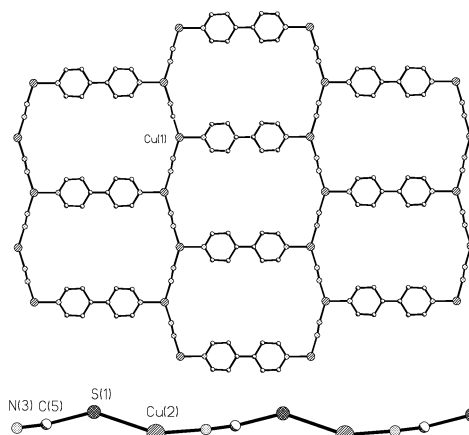


Figure 2. View of the neutral 2-D $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layer (top) and 1-D $[\text{Cu}(\text{SCN})]_n$ chain (bottom) in **1**.

and Cu2 are monovalent. The Cu1–Cu2 distance is 2.651(4) Å, which is not associated with ligand-bridged, hydrogen-bonded, electrostatic-attracted, or π – π -stacked effects, indicating genuine unsupported Cu^I – Cu^I contacts. Only a few ligand-unsupported Cu^I – Cu^I contacts have been reported up to now, and some of them are associated with hydrogen-bonded, electrostatic-attracted, or π – π -stacked effects. These ligand-unsupported Cu^I – Cu^I contacts are usually formed between linear two-coordinate Cu^I centers such as $[\text{Cu}_3(\text{CN})(\text{IN})_2]_n$,^{4c} $[\text{Cu}(\text{NH}_3)\text{Cl}]$,^{4b} $[\text{CuL}]^+[\text{CuCl}_2]^-$ [$\text{L} = 1,1'$ -bis(2-pyridyl)octamethylferrocene],^{4a} $[\text{Cu}(\text{NH}_3)_2\text{Br}, (\text{CuCl}_2)^-]$,^{5b} and $[\text{tBuCu}(\text{CN})\text{Li}(\text{OEt}_2)_2]$ ^{5c} or between three-coordinate Cu^I centers such as $[\text{CuLA}]_3$ ^{5a} and $[\text{Cu}_2(\text{obpy})_2]_2$ ^{4d} (Hobpy = 1*H*-2,2'-bipyridinyl-6-one). Different from them, the Cu^I – Cu^I contact in **1** is formed between two- and three-coordinate Cu^I centers. It is worth noting that the ligand-unsupported Cu1–Cu2 distance of 2.651(4) Å in **1** is the shortest among the observed ligand-unsupported Cu^I – Cu^I distances (including hydrogen bonded, electrostatic attracted, and π – π stacked).

Compound **1** consists of two types of neutral coordination polymers, as shown in Figure 2. One is a $[\text{Cu}(\text{SCN})]_n$ chain, and the other is a $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layer with (6,3) topology. The linkage of thiocyanate in a μ -S,N mode to Cu2 atoms generates a $[\text{Cu}(\text{SCN})]_n$ chain. The coordination of Cu1 atoms and cyanides forms the $[\text{Cu}(\text{CN})]_n$ chain, and the adjacent $[\text{Cu}(\text{CN})]_n$ chains are further bridged by 4,4'-bpy to finish the (6,3)-topological $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layer. Within the layer, there are hexagonal units sized at ca. 13.8×9.4 Å, and each is enclosed by six Cu1 atoms, four cyanides, and two 4,4'-bpy groups. The layers are stacked along the *a*-axis direction in a parallel fashion with the sequence of AB, and this gives rise to channels of ca. 6×6 Å along the *c*-axis direction (Figure S1 in the Supporting Information). One should note that the $[\text{Cu}(\text{SCN})]_n$ chain in **1** is dually disordered (Figure S2 in the Supporting Information) and each channel is penetrated by one $[\text{Cu}(\text{SCN})]_n$ chain (albeit it looks like two $[\text{Cu}(\text{SCN})]_n$ chains, as shown in Figure S3 in the Supporting Information) in an inclined way to form the 3-D pseudopolyrotaxane (Figure 3). Pseudopolyrotaxanes are uncommon in coordination polymers.^{6b} As for pseudopolyrotaxanes with 2-D sheets penetrated by

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(11) Crystal data for **1**: monoclinic, space group $C2/m$, $M_r = 456.92$, $a = 12.598(9)$ Å, $b = 9.471(6)$ Å, $c = 7.095(6)$ Å, $\beta = 117.768(12)^\circ$, $V = 749.0(9)$ Å³, $Z = 2$, $D_c = 2.026$ g cm⁻³, $\mu = 4.359$ mm⁻¹, $F(000) = 448$, $T_{\text{min}} = 0.4338$, $T_{\text{max}} = 0.7799$, $2\theta_{\text{max}} = 54^\circ$, $S = 1.146$, $R_1 = 0.0737$. X-ray single-crystal diffraction data were collected on a Bruker SMART APEX CCD diffractometer at 298(2) K using Mo $K\alpha$ radiation ($\lambda \leq 0.71073$ Å) by ω and φ scan modes. The program SAINT was used for integration of the diffraction profiles. The structure was solved by direct methods using the SHELXS¹⁴ program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.¹⁵ All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms of the organic group were generated theoretically onto the specific carbon atoms and refined isotropically with fixed thermal factors. The indistinguishable C and N atoms of the cyanide occupy the same sites and are refined by EXYZ and EADP constraints.

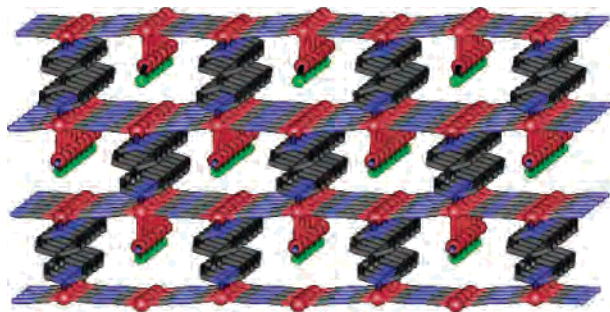


Figure 3. View of the 3-D pseudopolyrotaxane along the *c*-axis direction showing $[\text{Cu}(\text{SCN})]_n$ chains penetrating $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layers and unsupported $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ interactions. The Cu and S atoms are represented by brown and green balls, respectively.

chains, only one Cd complex and one Ag complex have been reported.¹² The Cd complex having the formula $[(\text{A})(\text{B})(\text{C})]\text{NO}_3$ [$(\text{A}) = [\text{Cd}(\text{L})_2(\text{NO}_3)_2]$, $(\text{B}) = [\text{Cd}_4(\text{L})_4(\text{NO}_3)_6(\text{MeOH})_6]^{2+}$, $(\text{C}) = [\text{Cd}(\text{L})(\text{NO}_3)_3]^-$, where $(\text{L}) = 4,4'$ -bis(4-pyridyl)biphenyl] was reported by Fujita, in which 2-D large square grids stack in an offset fashion, forming channels that are threaded by ladders B and chains C. The Ag complex is formulated as $[\text{Ag}(\text{bpp})][\text{Ag}_2(\text{bpp})_2(\text{ox})](\text{NO}_3)$ [bpp = 1,3-bis-(4-pyridyl)propane, ox = oxalate], which has 3-D architecture with 1-D polymeric $[\text{Ag}(\text{bpp})]^+$ chains penetrating 2-D (6,3)-topological $[\text{Ag}_2(\text{bpp})_2(\text{ox})]$ sheets. The co-crystallization of two neutral structural motifs and unsupported $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ interactions make **1** quite different from the two documented pseudopolyrotaxanes.

Considering weak unsupported $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ interactions, the pseudopolyrotaxane of **1** is a (3,4)-connected 3-D network constructed by $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layers and $[\text{Cu}(\text{SCN})]_n$ chains via unsupported $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ interactions. To be noted, after consideration of the dual disorder of the $[\text{Cu}(\text{SCN})]_n$ chain, half of the Cu1 atoms remain 3-connected in the (3,4)-connected network (this can also be easily understood from the 2:1 molar ratio of Cu1 to Cu2). The short *Schläfli* symbol for a trinodal (3,4)-connected network is $(6^3)_{\text{Cu1}}(10^2 \cdot 12)_{\text{Cu2}}(6^3 \cdot 10^3)_{\text{Cu1}}$ (Figure S4 in the Supporting Information).

Compared to the metal-metal distance in the open-shell metallic copper (2.556 Å) and the sum of the van der Waals radii of Cu^{I} atoms (2.80 Å),¹³ the unsupported Cu-Cu distance of 2.651(4) Å in **1** is closer to the former. From a space-filling point of view, the penetration of $[\text{Cu}_2(4,4'\text{-bpy})-$

$(\text{CN})_2]_n$ layers by $[\text{Cu}(\text{SCN})]_n$ chains via the centers of the channels formed by stacking of $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layers is advantageous in minimizing intermolecular repulsion forces. However, the $[\text{Cu}(\text{SCN})]_n$ chains in **1** apparently deviate from the centers of the channels, indicating that $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ contact in **1** is not dictated by space-filling effects. Therefore, the $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ contact in **1** represents genuine cuprophilicity.

A solid UV-vis spectrum shows little absorption in the visible range, consistent with pale brown color of **1**. Compound **1** is thermally stable up to 175 °C in air, and the decomposition of ligands is not finished up to 650 °C. In solid state, **1** shows an intense emission band centered at 372 nm upon photoexcitation ($\lambda_{\text{ex}} = 220$ nm). In view of the short $\text{Cu}^{\text{I}} \cdots \text{Cu}^{\text{I}}$ distance in **1**, the emission is tentatively assigned to originate from the ligand 4,4'-bpy-centered excited state modified by $\text{Cu}^{\text{I}} \cdots \text{Cu}^{\text{I}}$ interactions.

In summary, the co-crystallization of $[\text{Cu}(\text{SCN})]_n$ chains and $[\text{Cu}_2(4,4'\text{-bpy})(\text{CN})_2]_n$ layers generated a pseudopolyrotaxane or a (3,4)-connected 3-D network. The shortest unsupported Cu-Cu distance of 2.651(4) Å was observed. The preparation of **1** also demonstrates that the weak cuprophilicity can be used to construct an interesting supramolecular array.

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Supporting Information Available: Crystallographic data in CIF format, additional structural plots, and X-ray powder diffraction, thermogravimetric analysis, and solid UV-vis spectra. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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