

Diamond-Shaped Heterometallic Complexes of Iron(II) and Copper(I) Bridged by Cyanide Groups

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The self-assembly of polygons of transition-metal complexes has remained an interest of chemists for some time.¹ More recently there has been considerable focus on the synthesis and structural characterization of tetrametallic “molecular squares”.² Prominent among these studies are the numerous reports from the research groups of Stang³ and Fugita and Ogura.⁴ Some potential utility of these engaging complexes includes their serving as hosts for small molecule guests and functioning as solution phase sensors. In addition to “molecular squares” there are recent reports of “molecular rectangles” involving dinuclear rhenium thiolates or alkoxide derivatives bridged by 4,4'-bipyridine ligands.^{5,6} Klausmeyer, Rauchfuss, and Wilson have extended these molecular designs to assemble cyanide-linked molecular squares and cubes containing octahedral building blocks of rhodium and cobalt derivatives.⁷ Indeed, there is a large body of literature involving molecular ensembles containing cyano-linked metal complexes.⁸ In an effort to expand the supramolecular structural motif of tetrametallic complexes, and to continue our studies of transition-metal cyanide derivatives serving as ligands to Cu(I) and Zn(II),⁹

we wish to communicate on the synthesis and characterization of novel diamond-shaped molecules derived from the η^5 -C₅H₅Fe(CO)(CN)₂⁻ anion.

The reaction of [K][η^5 -C₅H₅Fe(CO)(CN)₂] with 1 equiv of [Cu(CH₃CN)₄][BF₄] in acetonitrile immediately yielded a yellow solution of [η^5 -C₅H₅Fe(CO)(μ -CN)₂Cu(CH₃CN)₂]₂ (**1**) and a fine white precipitate of KBF₄. The infrared spectrum of **1** in CH₃CN exhibits two ν (CN) vibrational modes at 2125s and 2118s cm⁻¹ and a ν (CO) vibration at 1974 cm⁻¹. These vibrations are shifted to higher frequencies when compared with the corresponding values in the parent anion, η^5 -C₅H₅Fe(CO)(CN)₂⁻, which occur at 2088, 2094, and 1949 cm⁻¹, respectively.^{10,11} Substitution of the CH₃CN ligands on the copper centers by PCy₃ was found to readily take place at ambient temperature as evidenced by infrared and ³¹P NMR spectroscopies. That is, the addition of 2 equiv of PCy₃ to complex **1** in CH₃CN led to immediate formation of a yellow precipitate of [η^5 -C₅H₅Fe(CO)(μ -CN)₂Cu(PCy₃)₂]₂ (**2**).¹² Upon removal of acetonitrile by cannulation and vacuum, the precipitate of **2** was dissolved in CH₂Cl₂ for spectral analysis. In contrast, the reaction of complex **1** with 4 equiv of PCy₃ in acetonitrile afforded a clear yellow solution of [η^5 -C₅H₅Fe(CO)-(μ -CN)₂Cu(PCy₃)₂]₂ (**3**). Yellow crystals suitable for single-crystal X-ray diffraction of complex **2** were grown from CH₂Cl₂/CH₃CN over several days at 10 °C, and of complex **3** from THF/hexane under similar conditions. Both air-sensitive complexes, **2** and **3**, were characterized in solution by FTIR and ³¹P NMR spectroscopies.¹³

The solid-state structures of **2** and **3** were determined by X-ray crystallographic analysis.^{14,15} Both complexes exhibit a diamond-shaped motif composed of two η^5 -C₅H₅Fe(CO) fragments, two Cu(I) centers, and four bridging CN⁻ ligands. One PCy₃ ligand is bound to each copper ion in **2**, and two PCy₃ ligands are bound to each copper ion in **3**. A thermal ellipsoid drawing of **2** is provided in Figure 1, whereas that of **3** may be found in the Supporting Information. Also included in the Supporting Information is a space-filling model of complex **2**, where a methylene chloride solvent molecule is shown to be located near one of the faces of the diamond. As indicated in Chart 1, the copper centers exhibit trigonal and tetrahedral geometries in **2** and **3**, respectively. The copper atoms in complex **2** each lie 0.023 Å out of

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- (12) The PPh₃ derivatives of **2** and **3** were insoluble in most organic solvents, including benzene, toluene, THF, CH₃CN, CH₂Cl₂, and methanol.
- (13) IR (CH₂Cl₂) of **2**: ν (CN) 2116s cm⁻¹, ν (CO) 1974vs cm⁻¹. ³¹P NMR (C₆D₆, 298 K): δ 13.80 (s, PCy₃). IR (CH₃CN) of **3**: ν (CN) 2105m, 2095s cm⁻¹; ν (CO) 1959vs cm⁻¹. ³¹P NMR (C₆D₆, 298 K): δ 12.01 (s, PCy₃). ³¹P NMR of free PCy₃ (C₆D₆, 298 K): δ 10.42 (s).
- (14) Crystal data for **2**: C₂₇H₄₀Cl₂CuFeN₂O₂P, fw = 629.87, triclinic, *P* $\bar{1}$, *a* = 9.615 Å, *b* = 10.700(11) Å, *c* = 14.918(11) Å, α = 84.06(7)°, β = 82.86(6)°, γ = 75.56(8)°, *T* = 190(2) K, *Z* = 2, *V* = 1471(2) Å³, 5521 reflections with *I* > 2 σ (*I*) used, *R* = 0.0384, *R*_w = 0.0934.
- (15) Crystal data for **3**: C₄₄H₆₆CuFeN₂O₂P₂, fw = 884.36, triclinic, *P* $\bar{1}$, *a* = 13.370(9) Å, *b* = 13.876(2) Å, *c* = 15.115(2) Å, α = 67.049(9)°, β = 69.703(7)°, γ = 80.748(9)°, *T* = 190(2) K, *Z* = 2, *V* = 2411.2(4) Å³, 14 646 reflections with *I* > 2 σ (*I*) used, *R* = 0.0898, *R*_w = 0.223.

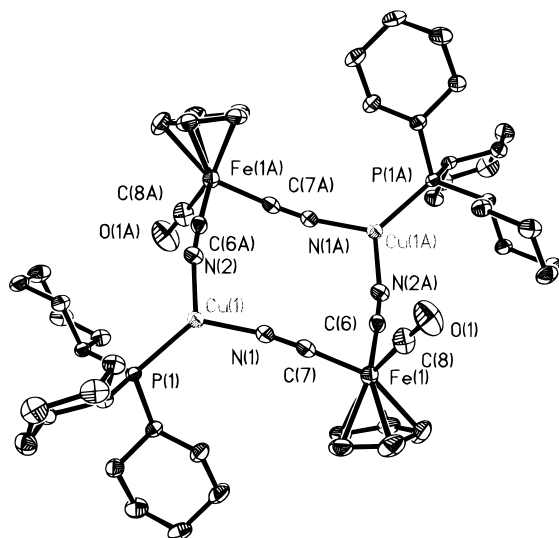
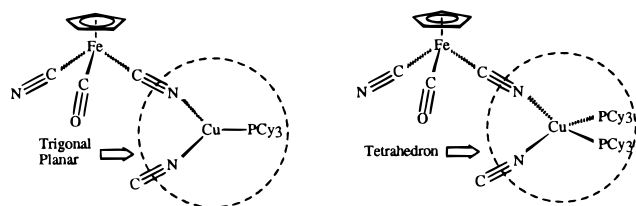


Figure 1. Molecular structure of complex **2**; thermal ellipsoids at 50% probability.

Chart 1



the plane defined by the phosphorus and nitrogen donor groups. As a consequence, the sum of the three angles is 358.6° , where the average $\text{N}-\text{Cu}-\text{P}$ angle is 124.6° . A skeletal drawing of the lozenge-shaped metal framework with metric parameters indicating the various metal-metal distances for complex **2** is provided in Figure 2. The area inside of the diamond was calculated to be approximately 24 \AA^2 . It is noteworthy that the terminal, iron-bound CO ligands are on opposite sides of the plane defined by the four metal atoms. The copper atoms in complex **3** are each located at the center of a distorted tetrahedron, where, due to the bulky tricyclohexylphosphine ligands, the $\text{P}-\text{Cu}-\text{P}$ bond angle of 127.8° is much larger than the average $\text{P}-\text{Cu}-\text{N}$ angle (106.3°) or the $\text{N}-\text{Cu}-\text{N}$ angle (100.6°). As would be anticipated, the average $\text{Cu}-\text{N}$ bond distance in three-coordinate complex **2** of 1.955 \AA is shorter than the corresponding distance in complex **3** of 2.035 \AA . Similarly, the average $\text{Cu}-\text{P}$ bond length in **3** of 2.28 \AA is slightly longer than that observed in **2** of 2.206 \AA . The $(\text{N})\text{C}-\text{Fe}-\text{C}(\text{N})$ angles in both complexes **2** and **3** are near right angles at 88.4° and 88.8° , respectively. Because of the two obtuse angles in the diamond-shaped structures, the $\text{Cu}-\text{N}\equiv\text{C}-\text{Fe}$

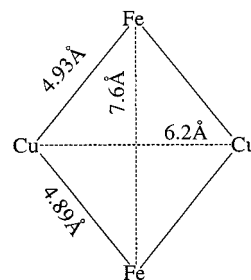


Figure 2. Metric parameters of the $\text{Fe}_2\text{Cu}_2(\text{CN})_4$ faces of complex **2**. The mean deviation from planarity of these 12 atoms is 0.190 \AA in **2** and 0.0964 \AA in **3**.

linkage is nonlinear with average $\text{Cu}-\text{N}\equiv\text{C}$ angles of 160.4° and 166.6° and average $\text{Fe}-\text{C}\equiv\text{N}$ angles of 175.5° and 178.8° in complexes **2** and **3**, respectively.¹⁶ Studies of these $\text{Cu}-\text{N}\equiv\text{C}-\text{Fe}$ interactions are of much current interest in understanding the mode of cyanide binding to the binuclear sites of heme-copper oxidases.^{16,17}

The synthetic strategy employed herein can be adapted for the preparation of a variety of metal and phosphine derivatives. For example, reactions of the $[\text{K}]_2[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CN})_3]$ complex¹⁸ with $[\text{Zn}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ in the presence of tricyclohexylphosphine affords a derivative where the iron-CN linkages are bonded to a zinc phosphine fragment. Although the derivatives reported upon herein are fairly robust in solution, prolonged standing of complex **3** in acetonitrile ultimately led to the formation of the dimeric $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CN})(\text{PCy}_3)(\mu\text{-CN})\text{Cu}(\text{PCy}_3)_2$ derivative, which has been structurally characterized ($\text{Fe}-\text{C}\equiv\text{N}$ and $\text{Cu}-\text{N}\equiv\text{C}$ angles are 172.2° and 166.7° , respectively).

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Supporting Information Available: Ball and stick drawings of **2** and **3**, a thermal ellipsoid drawing of **3**, a space-filling model of **2** indicating the presence of CH_2Cl_2 above the face of the diamond, and tables of X-ray crystallographic results for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) Lim and Holm have reported the crystal structures of two complexes containing a cyanide-bridged Fe^{II} to Cu^{I} unit where X-ray refinement favors an $\text{Fe}^{\text{II}}-\text{N}-\text{C}-\text{Cu}^{\text{I}}$ assembly. In this instance the $\text{Fe}^{\text{II}}-\text{N}-\text{C}$ and $\text{N}-\text{C}-\text{Cu}^{\text{I}}$ angles were found to be 175.6° and 174.7° , respectively. Lim, B. S.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 4898. In our case, interchanging carbon for nitrogen in the cyanide bridges of complex **2** led to an increase in the *R* value from 3.84% to 4.43%. Indeed on the basis of our synthetic methodology we would not have anticipated any linkage isomerization to have occurred.
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