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Synthesis and characterization of two copper cyanide complexes with hexagonal Cu_6 units

Yingjun Zhao,[a] Maochun Hong,[a]* Weiping Su,[a] Rong Cao,[a]* Zhongyuan Zhou[b] and Albert S. C. Chan*[b]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: hmc@ms.fjirsm.ac.cn*

[b] *Open Laboratory of Chirotechnology and Department of Applied Biology and Chemical Technology, the Hong Kong Polytechnic University, Hong Hum, Hong Kong*

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Reaction of CuCN with PPh_3 and PPh_4Br induced by the pyridine-2-thiolate anion in DMF resulted in a discrete hexanuclear $[Cu(CN)(PPh_3)_2]_6$ (1) complex with a large hexagonal cavity and a polymer $[(PPh_4)\{Cu_2(CN)_3\}]_n$ (2) with a graphite-like lamellar structure, respectively.

Design and research of complexes with macrocyclic and cavity structures are a subject of current interest because of their potential abilities for selective inclusion of ions and molecules and catalysis for specific chemical transformations.[1–7] Transition metal cyanide complexes have a long and distinguished history in the chemical sciences, of which copper(I) cyanide, in particular, has enjoyed popularity among chemists due to its unique role in structural elaboration *via* cyano-Gilman chemistry.[8] However, attempts to obtain single crystals adequate for diffraction studies have been confounded by its insolubility in most solvents. Recently, a series of unusual copper cyanide complexes have been detected in the gas phase.[9]

Laser ablation of CuCN yields positive and negative ions of composition $[Cu_n(CN)_{n+1}]^-$ ($n = 1–5$) and $[Cu_n(CN)_{n-1}]^+$ ($n = 1–6$).[10] Calculations showed that the possible structural identities of these species are chain, cyclic or metal-bridged arrangements. Thus, an interesting challenge is generation, stabilization, isolation, and structural characterization of such structures from solution.[11] Very recently, several Cu–CN complexes with intricate one-dimensional and layered structures, $[Cu_2(CN)_2(L)]_n$ [L = 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane],[12] $[Cu_2(bpy)_2(CN)Cu_5(CN)_6]$, $[Cu_3(CN)_2(trz)(bpy)]$, $[Cu_3(CN)_2(trz)(phen)]$, $[Cu_4(CN)_3(trz)(phen)]$ (trz = triazolato, $C_2N_3H_2^-$), $[\{Cu_2(bipy)_2(CN)\}_2Cu_5(CN)_7]$ and $[Cu_6(CN)_5(trz)]$, $[Cu_5(CN)_3(trz)_2(bpy)]$[13,14] have been synthesized and characterized. However, up to now, no discrete complex with a hexagonal $[Cu_6(CN)_6]$ unit has been reported. Herein, two copper cyanide complexes are reported, a discrete hexagonal cavity framework $[CuCN(PPh_3)_2]_6$ (**1**) and a graphite-like lamellar structure $[(PPh_4)\{Cu_2(CN)_3\}]_n$ (**2**), prepared from the reaction of CuCN with PPh_3 and PPh_4Br, respectively, induced by the pyridine-2-thiolate anion in DMF.

In the study on the Cu–CN reaction system, we hoped that a discrete complex with a $[Cu_6(CN)_6]$ hexagonal unit might be formed if terminal ligands such as PPh_3 were introduced into the system. However, the directed reaction of CuCN with PPh_3 in DMF initially resulted in the formation of an uncharacterized precipitate, which is not soluble in any solvent. On addition of sodium pyridine-2-thiolato to the reaction system of CuCN and PPh_3, surprisingly, the precipitate smoothly turned into a single product after the solution was stirred for 6 hours. From the solution, the complex **1** was isolated as red crystals in 66% yield by slowly diffusing diethyl ether into the solution. Complex **1** is very soluble in CH_2Cl_2 and THF, and soluble in DMF. The ^{31}P NMR spectrum of **1** in THF showed two signals at 15.5 and 17.2 ppm downfield from the resonances for free PPh_3. An IR spectrum of **1** showed a strong peak at 2106 cm^{-1}, indicating that there is only one kind of coordination mode for the CN^- group. Elemental analysis was consistent with the formula $[CuCN(PPh_3)_2]$.† The actual formula $[CuCN(PPh_3)_2]_6$ was confirmed by X-ray single crystal diffraction analyses.‡ As shown in Fig. 1, the core structure of **1** is a hexagonal macrocycle 9.8 Å in diameter, formed from six Cu(I) and six CN^- bridging groups. Two phosphine ligands coordinate to each copper atom to complete the tetrahedral coordination sphere of the copper atoms.

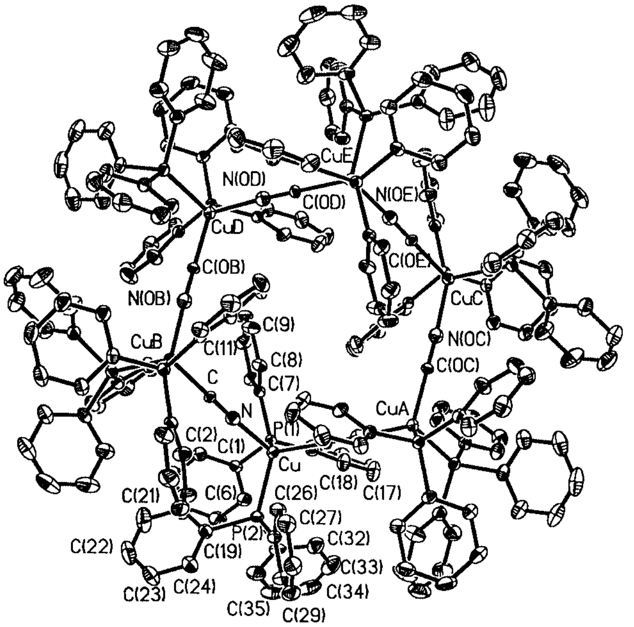

Fig. 1 Molecular structure of **1**.

After careful studies on the structure of **1**, we deduced that the replacement of the PPh_3 terminal ligand by a bridging cyanide ligand may generate infinite lamellar structures with $[Cu_6(CN)_6]$ hexagonal units. The cyanide ion is a good choice for the bridging ligand. Thus, by addition of PPh_4Br into the reaction system to remove some part of Cu(I), yellow crystals of **2** were isolated in 58% yield by slowly diffusing diethyl ether into the resulting reaction solution. Complex **2** is not soluble in organic solvents, such as CH_2Cl_2, THF or DMF. The IR spectrum of **2** showed two strong peaks at 2098 and 2114 cm^{-1}. Elemental analysis was consistent with the formula $[(PPh_4)Cu_2(CN)_3]$.† X-Ray single crystal diffraction analyses ‡ revealed that **2** exhibits anionic infinite 2D graphite-like structure sheets

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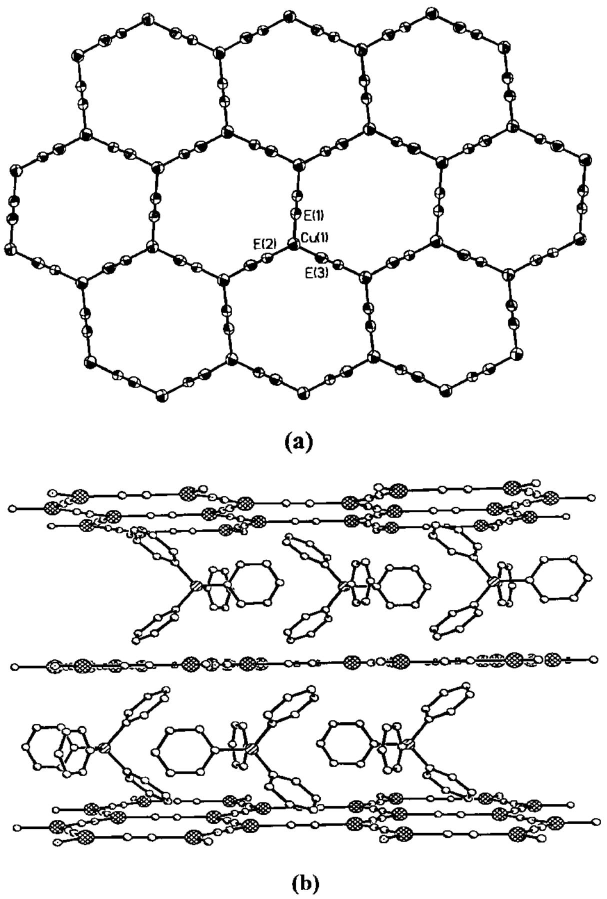

Fig. 2 (a) The graphite-like lamellar network in **2**. (b) Structure of **2** showing the lamellar network with PPh_4^+ cations protruding into the interlayer region.

with [$Cu_6(CN)_6$] hexagonal units. As shown in Fig. 2a, each Cu(I) is coordinated to three CN^- and each CN^- links two Cu(I) to produce the lamellar structure. The layer is exactly co-planar and PPh_4^+ ions lie between two adjacent layers (Fig. 2b), which is different to [$Cu(OH_2)_4$][$Cu_4(CN)_6$] which has tetraquacupric dications intercalated into alternate interlayer spaces[14] and K[$Cu_2(CN)_3$]·H_2O with a water molecule in the [$Cu_6(CN)_6$] unit.[15]

In conclusion, attempts to prepare complexes **1** and **2** from directed syntheses of CuCN with phosphine and PPh_4^+, always provided uncharacterized products. By introducing pyridine-2-thiolate into the solution, **1** and **2** were isolated in high yield. The results illustrate the anion effect of pyridine-2-thiolate in the formation of the two complexes.

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Notes and references

† Elemental analyses: for **1**, calc.: C, 72.36; H, 4.92; N, 2.28; found: C, 71.76; H, 5.01; N, 2.05%; for **2**, calc.: C, 59.55; H, 3.70; N, 7.72; found: C, 60.16; H, 3.55; N, 7.65%.

‡ Crystallography. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at room temperature. All of the calculations were performed by using the SHELXTL-PLUS[16] version 5.10 package on a Hewlett Packard computer. The structures were solved by direct methods and refined by full matrix least squares. For **1**: red hexagonal, dimensions 0.12 × 0.18 × 0.18 mm, $M_r = 3684.60$, hexagonal, space group R-3; $a = 34.402(2)$, $c = 13.7159(11)$ Å, $V = 14058(2)$ Å^3; $D_{calc} = 1.306$ g cm^{-3}, $Z = 3$; μ(Mo-Kα) = 0.828 mm^{-1}; 31566 reflections collected, 7165 [$I > 2\sigma(I)$] reflections observed; $R_1 = 0.0346$; $wR_2 = 0.0934$. For **2**: yellow block, dimensions 0.14 × 0.16 × 0.18 mm, $M_r = 544.51$, orthorhombic, space group $Pnma$; $a = 14.362(2)$, $b = 19.037(3)$, $c = 8.9251(14)$ Å, $V = 2440.2(7)$ Å^3; $D_{calc} = 1.482$ g cm^{-3}, $Z = 4$; μ(Mo-Kα) = 1.834 mm^{-1}; 15707 reflections collected, 2888 [$I > 2\sigma(I)$] reflections observed; $R_1 = 0.0432$; $wR_2 = 0.1156$. CCDC reference number 186/1934. See http://www.rsc.org/suppdata/dt/b0/b002096f/ for crystallographic files in .cif format.

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