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A Notable Difference in Photoluminescent Efficiency between a Newly Synthesized Asymmetric Dinuclear Cu(I) Cyano Complex Building Unit $[Cu_2(CN)_5]^{3-}$ and a Symmetric Unit $[Cu_2(CN)_6]^{4-}$

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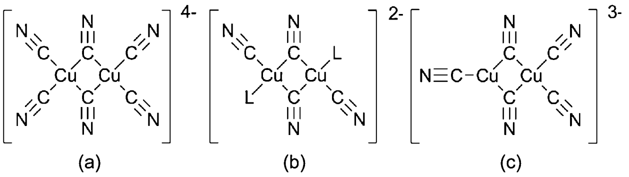
A new cyano-bridged Cu(I)/Cd(II) coordination polymer $K[CdCu_2(CN)_5]\cdot dce\cdot 3H_2O$ (dce = 1,2-dicyanoethane) containing a novel asymmetric dinuclear Cu(I) building unit $[Cu_2(CN)_5]^{3-}$ was synthesized, and its emission intensity was very weak in contrast to very strong emission of $CdCu(CN)_3\cdot hpn\cdot 2H_2O$ (hpn = 3-hydroxypropionitrile) containing an already known symmetric building unit $[Cu_2(CN)_6]^{4-}$.

Cyano-bridged coordination polymers have been attracting much interest and been widely studied in the aspects of synthesis, structure, physical and chemical properties.[1] In most of these compounds the coordination mode of cyano ligands is a linear μ_2 fashion. On the other hand, a cyano ligand which coordinates to two metal ions with its C atom in a bifurcate fashion is in a minority. Most of this type of coordination appears in a dinuclear Cu(I) cyano complex as shown in Schemes 1a and 1b. In such a cyano complex, the C atom of a cyano ligand coordinates to two Cu(I) ions in a bifurcated fashion and two cyano ligands of this type link two Cu(I) ions to form the core of a dinuclear structure. Each Cu(I) ion has a tetrahedral coordination form, and its remaining two coordination sites are occupied by two C atoms of two normal cyano ligands. All cyano ligands including the two bifurcate cyano ligands have potential to coordinate to other metal ions using their N atoms. Therefore, this dinuclear Cu(I) cyano complex can work as a building unit in the formation of a coordination polymer. The first prototype of this structure was reported in 1965 by Cromer et al. in a Cu(I) cyanide–ammonia adduct $CuCN\cdot NH_3$.[2] After this report, several examples were known.[3] Recently, along the development of coordination polymers, its unique structural character as a building unit attracts attention again, and it has been used for constructing many coordination polymers.[4–6] A considerable number of these compounds are occupied by organic-ligand-supported dinuclear Cu(I) cyano complexes, in which organic ligands, such as pyridine and piperazine, are coordinated to Cu(I) ions instead of normal cyano ligands. A typical case is shown in Scheme 1b. Dinuclear Cu(I) cyano complexes are also interesting from the viewpoint of d^{10}–d^{10} interaction, which is called "cuprophilicity" or "cuprophilic interaction" in the case of Cu(I), because the two Cu(I) ions are considerably close to each other.[7] However, it is difficult to say that cuprophilic interaction has been sufficiently understood and established. Recently, photoluminescence of many cyano-bridged Cu(I) coordination polymers was also reported,[5,6] and investigation for understanding its nature is in progress.[8]



Scheme 1. Structural scheme of symmetric (a), organic ligand supported (b), and asymmetric (c) dinuclear Cu(I) cyano complex.

Here, we report the syntheses, structures, and photoluminescent properties of new cyano-bridged coordination polymers $K[CdCu_2(CN)_5]\cdot dce\cdot 3H_2O$ (**1**, dce = 1,2-dicyanoethane) and $CdCu(CN)_3\cdot hpn\cdot 2H_2O$ (**2**, hpn = 3-hydroxypropionitrile). **1** contains an unusual asymmetric dinuclear Cu(I) cyano complex $[Cu_2(CN)_5]^{3-}$ in which one Cu(I) ion adopts a tetrahedral coordination form and another Cu(I) has a trigonal coordination form as shown in Scheme 1c. Although some compounds with trigonal Cu(I) ions were already known in the organic-ligand-supported dinuclear Cu(I) cyano complexes,[4,5] our case is the first example of asymmetric dinuclear Cu(I) cyano complex made of pure cyanide ligands. On the other hand, **2** contains a symmetric dinuclear Cu(I) cyano complex $[Cu_2(CN)_6]^{4-}$ which belongs to the symmetric structure shown in Scheme 1a.

We previously obtained a cyano-bridged coordination polymer $CdCu(CN)_3\cdot CH_3CN\cdot 3H_2O$ (**3**) from an aqueous solution containing CuCN, $K_2[Cd(CN)_4]$, and acetonitrile.[3d] This compound is built with the symmetric building $[Cu_2(CN)_6]^{4-}$ unit and Cd(II) ions. **1** and **2** were synthesized by a method similar to that for **3**. Colorless crystals of **1** and **2** were obtained from a solution of two equivalent CuCN and $K_2[Cd(CN)_4]$ and excess of nitriles.[9] The crystal structures of **1** and **2** were revealed by single-crystal X-ray diffraction analysis[10] and solid-state NMR.[11]

Figure 1 and Figure S1 in Supporting Information (SI)[12] show the structure of $[Cu_2(CN)_5]^{3-}$ building unit in **1**. The coordination form of Cu(1) is planar trigonal and that of Cu(2) is tetrahedral. The distance between Cu(1) and Cu(2) is 2.4626(5) Å, shorter than the interatomic distance in metallic Cu (2.56 Å) indicating cuprophilic interaction. The coordination geometry of Cu(2) is distorted from a regular tetrahedron. The bond angle of C(2)–Cu(2)–C(3) and that of C(4)–Cu(2)–C(5) are 94.90(9) and 129.53(11)°, respectively. The distance between Cu(2)–C(2) and that between Cu(2)–C(3) are remarkably long. Upon this structural situation, $[Cu_2(CN)_5]^{3-}$ is regarded as a planar trigonal $[Cu(CN)_3]^{2-}$ attached to a bent $[Cu(CN)_2]^{-}$. In the crystal of **1**, the $[Cu_2(CN)_5]^{3-}$ building unit makes linkages to the equatorial sites of an octahedral Cd(II) with four N atoms of N(1), N(2), N(3), and N(5) to form a 2D grid sheet parallel to

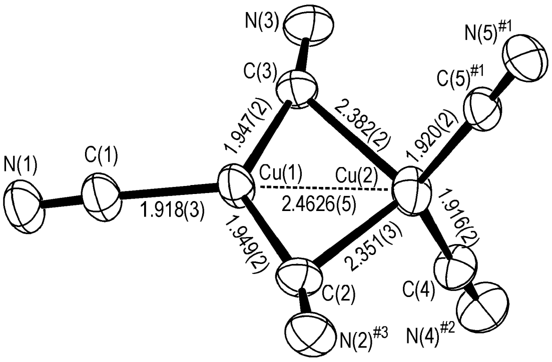


Figure 1. ORTEP view of the asymmetric $[Cu_2(CN)_5]^{3-}$ building unit in **1** at 293 K with thermal ellipsoids drawn at 50% probability level. Numerical values are interatomic distances in Å around Cu(I) ions. Symmetry code: #1: $x + 1/2$, $1/2 - y$, $1 - z$; #2: $1 - x$, $1 - y$, $1 - z$; #3: x, $1/2 - y$, $z - 1/2$.

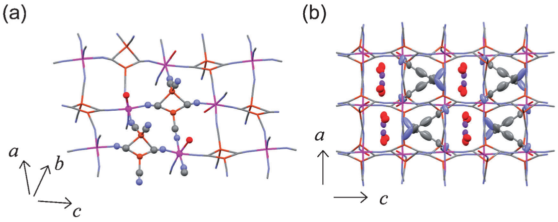


Figure 2. (a) The 2D grid sheet in **1**. The grid is formed by linkages between four cyano ligands of $[Cu_2(CN)_5]^{3-}$ and four equatorial sites of Cd(II). (b) The crystal structure of **1**. The linkage between the remaining cyano ligand of $[Cu_2(CN)_5]^{3-}$ and one axial sites of Cd(II) connects the 2D grid sheets to form a 3D framework. K^+, water, and disordered dce molecules, illustrated with thermal ellipsoids, are trapped as guests in the 3D framework.

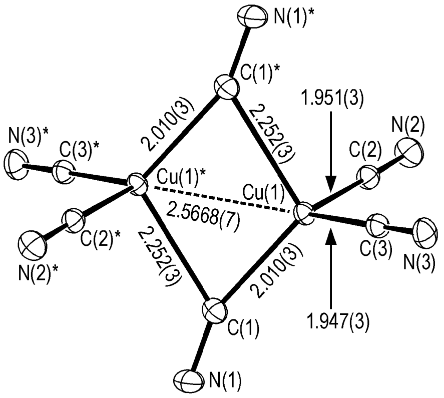


Figure 3. ORTEP view of the symmetric $[Cu_2(CN)_6]^{4-}$ building unit at 173 K in **2** with thermal ellipsoids drawn at 50% probability level. Numerical values are interatomic distances in Å around Cu(I) ions. Symmetry code; *: $1 - x$, $1 - y$, $1 - z$.

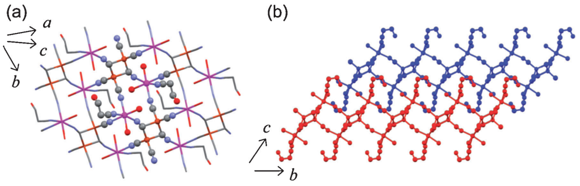


Figure 4. (a) The 2D network in **2** formed with $[Cu_2(CN)_6]^{4-}$ hexa-connecting units and octahedral Cd(II), whose three facial sites are occupied by hpn and two water molecules. (b) In the crystal of **2** the 2D networks are stacked along the *c* axis. Adjacent networks are interlocked with each other through water and hpn molecules protruding from Cd(II).

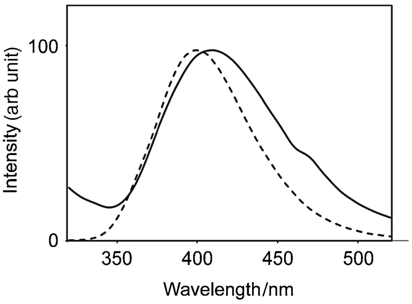


Figure 5. Normalized emission spectra of **1** (solid line) and **2** (dashed line) in solid state at room temperature (excitation wavelength 300 nm).

the *ac* plane. The axial positions of Cd(II) are coordinated by one water molecule and N(4) from $[Cu_2(CN)_5]^{3-}$ unit in the adjacent 2D grid sheet to form a $[Cd(H_2O)Cu_2(CN)_5]_n^{n-}$ 3D framework. This framework has large internal space which is occupied by a K^+ cation, water, and dce molecules as shown in Figure 2 and Figure S2 in SI.[12] The dce molecule exists as a guest, coordinating to neither Cu(I) nor Cd(II). Such guest-driven structure formation was also reported in the acetonitrile inclusion compound **3** synthesized under a similar condition except for the nitrile.[3d]

Figure 3 and Figure S3 in SI[12] show the structure of $[Cu_2(CN)_6]^{4-}$ building unit in **2**, which is centrosymmetric. Both Cu(I) ions are crystallographically equivalent to each other, and their coordination tetrahedral forms are slightly distorted. The interatomic distance between the two Cu(I) ions is 2.5668(7) Å, indicating weak cuprophilic interaction. The distance between Cu(1) and C(1)* (2.252(3) Å) is remarkably longer than that between Cu(1) and C(1) (2.010(3) Å). This dinuclear structure can be regarded as two trigonal $[Cu(CN)_3]^{2-}$ units coupled. The $[Cu_2(CN)_6]^{4-}$ unit works as hexa-connecting unit to make linkages to octahedral Cd(II) cations of which three facial coordination sites are occupied by two water and one hpn molecules. The resultant structure is a 2D network of $\{[Cd(H_2O)_2(hpn)]_2[Cu_2(CN)_6]\}_\infty$ extending parallel to the *ab* plane, and these networks are stacked along the *c* axis as shown in Figure 4 and Figure S4 in SI.[12] The adjacent networks are interlocked with each other by steric engagement and hydrogen bonding among the water and hpn molecules protruding from the surfaces of the networks. This structural scheme is similar to that found in **3**.[3d]

Our quantitative quantum yield analysis revealed remarkable difference in photoluminescent between **1** and **2**.[13] As shown in Figure 5, upon excitation at 300 nm at room temperature **2** showed very strong emission around 400 nm, whose quantum yield was 0.77. In contrast, emission of **1** was very weak. Its quantum yield measured was ca. 0.005. This finding suggests that the quenching in dinuclear Cu(I) cyano complexes is strongly affected by their structure and symmetry. Several papers on photoluminescence of Cu(I) cyano-coordination polymers, in which some organic ligand is involved in many cases, have been already published.[5] Although the variety of their luminescent properties depending on coordination environment was reported, the information about quantum yield is few. Our finding suggests that the efficiency of luminescence in Cu(I) cyano complexes is sensitive to their structure even in such a "simple" system with no organic ligand. At the present stage, however, there are not sufficient data for detailed discussion about the relationship between the structure of dinuclear Cu(I) cyano complexes with no organic ligand and their photoluminescent behavior. Accumulation of more data are now in progress.[14]

In summary, a novel coordination polymer containing an asymmetric dinuclear Cu(I) cyano complex building unit $[Cu_2(CN)_5]^{3-}$ was synthesized based on the Cu(I)/Cd(II)/CN/nitrile system. This system potentially affords diverse dinuclear Cu(I) cyano complex units which are attractive in photoluminescent properties as well as structural interest.

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9 Synthetic details of **1** and **2**: $K_2[Cd(CN)_4]$ (2.06 g, 7 mmol) and CuCN (1.26 g, 14 mmol) were added to water (100 mL). The mixture was warmed to 80 °C, stirred for 30 min, and then filtered on hot. The filtrate was divided into 25 mL each, kept at 80 °C, and 1,2-dicyanoethane (0.56 g, 7 mmol) or 3-hydroxypropionitrile (0.2 mL, 3.5 mmol) was added into each portion. The solutions were cooled down, and allowed to stand at room temperature. The crystals of **1** and **2** were obtained as colorless platelets in a few days (**1**: 0.49 g, 51% and **2**: 0.35 g, 57%). **1**: Found: C, 19.95; H, 2.03; N, 17.82%. Calcd for $C_9H_{10}CdCu_2KN_7O_3$: C, 19.91; H, 1.86; N, 18.06%. **2**: Found: C, 19.69; H, 2.58; N, 15.27%. Calcd for $C_6H_9CdCuN_4O_3$: C, 19.96; H, 2.51; N, 15.51%.

10 Crystal data for **1** and **2**: **1**: $C_9H_{10}CdCu_2KN_7O_3$, $M = 542.82$, orthorhombic, space group *Pbca*, $a = 12.2042(2)$ Å, $b = 14.3786(2)$ Å, $c = 20.3859(7)$ Å, $V = 3577.30(14)$ Å^3, $T = 293(2)$ K, $Z = 8$, $\mu(\mathrm{Mo}\,K\alpha) = 3.787\ \mathrm{mm}^{-1}$. Final $R1$ (all data) $= 0.0383$, $wR2$ $(I > 2\sigma(I)) = 0.0783$ and $S = 1.049$, 209 parameters were refined for 6182 unique reflections. **2**: $C_6H_9CdCuN_4O_3$, $M = 361.12$, triclinic, space group $P\bar{1}$, $a = 7.6948(2)$ Å, $b = 8.6781(3)$ Å, $c = 9.2592(7)$ Å, $\alpha = 73.8829(9)°$, $\beta = 75.8686(10)°$, $\gamma = 67.9294(11)°$, $V = 543.63(5)$ Å^3, $T = 173(2)$ K, $Z = 2$, $\mu(\mathrm{Mo}\,K\alpha) = 3.902\ \mathrm{mm}^{-1}$. Final $R1$ (all data) $= 0.0213$, $wR2$ $(I > 2\sigma(I)) = 0.0655$ and $S = 1.227$, 150 parameters were refined for 3696 unique reflections. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-752682 and CCDC-752683 for **1** and **2**, respectively. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

11 The assignment of atomic species in the bridging cyano ligands was confirmed using ^{113}Cd CP-MAS NMR. For details, see SI.[12]

12 Supporting Information (SI) is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

13 Crystals of the compounds were washed with water and air-dried, and then powdered. After confirmation by powder X-ray diffraction method each powder sample was packed into a flat cylindrical cell with a quartz window, and the cell was attached to a JASCO ISF-513 calibrated integrating sphere system. Emission spectra and absolute quantum yield were measured using a JACSO FP-6500 spectrophotometer equipped with the integrating sphere system.

14 As other examples, strong emission of $CdCu(CN)_3 \cdot EtCN \cdot 2H_2O$ which includes a $[Cu_2(CN)_6]^{4-}$ unit and weak emission of $K[CdCu_2(CN)_5] \cdot dcp \cdot 2H_2O$ (dcp = 1,2-dicyanopropane) which includes $[Cu(CN)_5]^{3-}$ were also indicated by preliminary measurements.