

Note

Assembly of cyano-bridged Cu(II)/Cu(I) and Cu(I)/Cu(II) compounds obtained by controlled ration of cyanide

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Abstract

One reaction system of Cu^{2+} , dipn, and CN^- with two different molar ratio sets of 1:1:5, and 2:1:8 produced two compounds **1** $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{I}}(\text{CN})_4]$, and **2** $[\text{Cu}^{\text{II}}(\text{dipn})_2][\text{Cu}_4^{\text{I}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$, respectively (dipn = dipropylentriamine). Their structures were determined by X-ray crystallography. Compound **2** is built from Cu(I) and Cu(II) centers, which are bridged by cyanide groups and metal–metal bonds. The magnetic properties of **1** and **2** were investigated in 2–300 K. Compound **1** exhibits an antiferromagnetic exchange interaction between copper(II) ions mediated by cyano-bridges.

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Keywords: Cyanide; Cu compounds; Metal–metal bond; Magnetic properties

1. Introduction

In recent years, much research interest has been focused on crystal engineering of cyano-bridged homocopper and mixed valence copper (I, II) compounds [1–3]. The rational design of these structures has important implications for the development of new magnetic materials and the metabolic roles of copper metalloenzymes involving transfer electrons from a substrate molecule to molecular oxygen. For the cyano-bridged homocopper (I) systems, the diverse structural feature, initially observed in the spiral polymer chain system $\text{KCu}(\text{CN})_2$ [4a] and the polymer sheets.

$\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ [4b] and $\text{CuCN} \cdot \text{NH}_3$ [4c] has recently become more evident through the works of Zubieta et al. [5], and other groups [6] who exploited the chemistry of copper(I) cyanide. In addition, some cyano-bridged $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ mixed-valence compounds such as $[\text{Cu}^{\text{II}}(\text{dien})\text{Cu}^{\text{I}}(\text{CN})_3]$

[7], $[\text{Cu}^{\text{II}}(\text{tn})_2\text{Cu}^{\text{I}}(\text{CN})_3]$ [8], $[\{\text{Cu}^{\text{II}}(\text{CN})_2\}_2\text{Cu}^{\text{I}}(\text{cyclam})]$ [9], $[\text{Cu}^{\text{II}}(\text{pn})_2\text{Cu}_2^{\text{I}}(\text{CN})_4]$ [10], and $[\text{Cu}_2^{\text{II}}(\text{oxpn})\text{Cu}^{\text{I}}(\text{CN})_2]$ [11] have been reported.

It is well known that in aqueous solution copper(II) is easily reduced to copper(I) by cyanide and that simple C-bonded cyano complexes of copper(II) are unstable with respect to reduction and cannot be isolated easily. In contrast to the rich Cu^{I} and $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ cyanide chemistry, the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{II}}$ cyanide systems are limited [12]. In order to expand the system of homometallic cyano-bridged copper complexes involving Cu^{II} units, we have employed Cu^{II} cations as a copper source and tridentate ligand (dipn = dipropylentriamine) to react with CN^- at different condition, and isolated two kinds of cyano-bridged copper compounds such as one $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ compound **1** $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{I}}(\text{CN})_4]$, and one hexa-nuclear mixed valence $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ compound **2** $[\text{Cu}^{\text{II}}(\text{dipn})_2][\text{Cu}_4^{\text{I}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$. In the present study, we report on the synthesis as well as the structural, magnetic and IR spectroscopic characterization of two homometallic cyano-bridged copper complexes.

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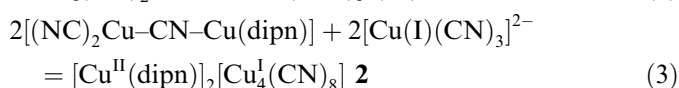
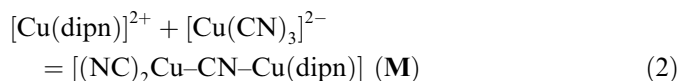
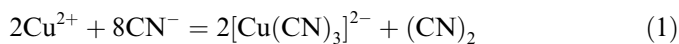
2. Results and discussion

2.1. Synthesis and general properties

The overall synthetic routes to the homometallic copper cyanide compounds **1** and **2** are summarized in Scheme 1. The reaction systems of Cu^{2+} , dipn, and CN^- were run with two different molar ratio sets of 1:2:5, and 2:1:8 in water, and gave two compounds **1** and **2**, respectively.

Compound **1** was obtained by the reaction of Cu^{2+} , dipn, and CN^- (at the molar ratio sets of 1:1:5), and suggesting cyano-bridged complex of copper(II) is stable enough and can be isolated in aqueous solution.

Compound **2** was obtained from the reaction of Cu^{2+} , dipn, and CN^- (at the molar ratio sets of 2:1:8). The mechanism of the reaction is illustrated by Eqs. (1)–(3). The chemical reduction of excess aqueous solution of KCN yield a $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ mixed-valence compound, $[\text{Cu}^{\text{I}}(\text{CN})_3-\text{Cu}^{\text{II}}(\text{dipn})]$ (**M**). The resulting $[\text{Cu}^{\text{I}}(\text{CN})_3]^{2-}$ anion acting as a building block for formation of the cyano-bridged $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ coordination polymer reacts with (**M**) to give **2**



The formation of cyanide bridges in compound **1** was evidenced by the IR spectrum in the region of the stretching vibration of the cyanide ligands. The IR spectrum of compound **1** $[\text{Cu}^{\text{II}}(\text{CN})_4\text{Cu}^{\text{II}}(\text{dipn})]$ shows two bands at 2169, and 2129 cm^{-1} , which is assigned to the intermetallic $\text{Cu}^{\text{II}}\text{C}\equiv\text{NCu}^{\text{II}}$ bonds ($\nu[\text{C}\equiv\text{N}(\text{b})]$) and terminal $\text{C}\equiv\text{N}$ stretching mode, respectively.

The CN stretching mode of the isolated $[\text{Cu}^{\text{I}}(\text{CN})_3]^{2-}$ complex ion ($\text{D}_{3\text{h}}$ symmetry) is observed at 2111 cm^{-1} for $\text{Na}_2[\text{Cu}^{\text{I}}(\text{CN})_3] \cdot 3\text{H}_2\text{O}$ [13] at 2094 cm^{-1} for an aqueous solution of $\text{K}_2[\text{Cu}^{\text{I}}(\text{CN})_3]$ [14,15] and at 2066 cm^{-1} for crystalline $[\text{Cu}^{\text{I}}(\text{CN})_3][\text{Cu}^{\text{II}}(\text{en})_3]$ [16]. Compound **2** $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{I}}(\text{CN})_3]$ shows three bands at 2132 (s), 2111, and 2095 cm^{-1} , which is assigned to the intermetallic $\text{Cu}^{\text{I}}-\text{C}\equiv\text{N}-\text{Cu}^{\text{II}}$ bond ($\nu[\text{C}\equiv\text{N}(\text{b})]$) and the terminal CN group, respectively.

2.2. Structure of compound 1

An ORTEP drawing of compound **1** is shown in Fig. 1. One asymmetric unit of the structure of **1** consists of one $[\text{Cu}(\text{dipn})]^{2+}$ cation and one $[\text{Cu}(\text{CN})_4]^{2-}$ anion. Nitrogen of cyanide N(4) coordinates with the adjacent $[\text{Cu}(\text{dipn})]^{2+}$, the bond angle $176.8(2)^\circ$ of C7–N4–Cu2 is nearly linear. Cu(2) is coordinated by three N atoms from dipropylene-triamine and two cyanide N, the average value for the $\text{Cu}(2)-\text{N}_{\text{triamine}}$ distance is 2.028(2) Å, and $\text{Cu}(2)-\text{N}_{\text{cyanide}}$ distance is 2.024(2) Å. Cu(1) is in a quadrilateral planar coordination sphere, revealing the first example of a structurally characterized bridging $[\text{Cu}^{\text{II}}(\text{CN})_4]^{2-}$ unit. Among the bond distances between Cu(1) and cyano-carbon atoms, two bridging cyano groups form the average distance of 1.866(3) Å, whereas the other two cyano groups show an average distance of 1.873(3) Å. The shortest $\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}$ separation is 4.870 Å. The 1-D chain is formed with the $-\text{Cu}(1)-\text{C}-\text{N}-\text{Cu}(2)-\text{N}-\text{C}-$ linkages, and the extended nets of compound **1** are formed by H-bonds (Fig. 2).

2.3. Structure of compound 2

The asymmetric units of the complex $[\text{Cu}^{\text{II}}(\text{dipn})]_2-[\text{Cu}_4^{\text{I}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ are illustrated in Figs. 3 and 4. There are six types of Cu sites in **2**: a distorted trigonal planar Cu(3) site, coordinating with one cyano-C atom and two cyano-N atoms, the average $\text{Cu}-\text{N}$ distance is 1.976(3)

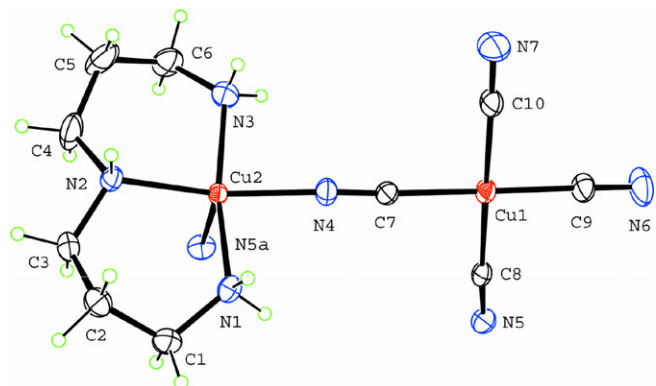
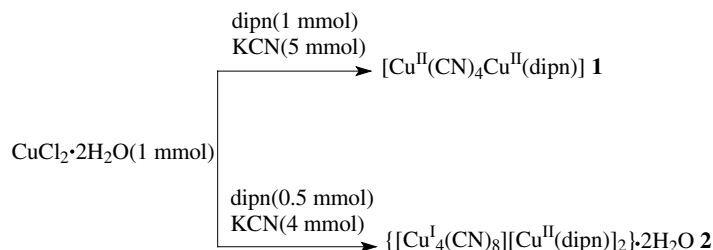


Fig. 1. The ORTEP view of **1** $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{II}}(\text{CN})_4]$.



Scheme 1.

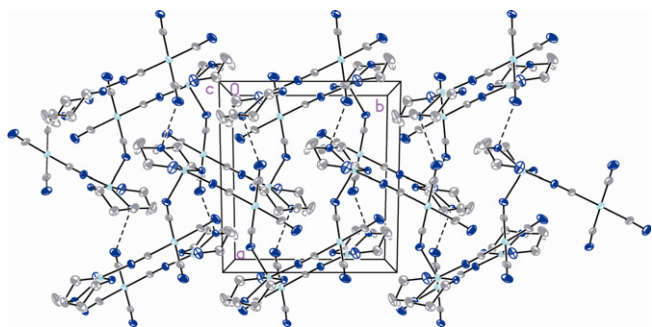


Fig. 2. Crystal packing diagram of compound **1** $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{II}}(\text{CN})_4]$.

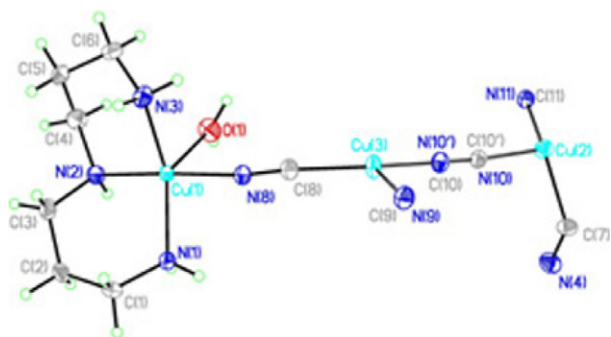


Fig. 3. Illustration showing the coordination sphere of CuII and CuI of **2**.

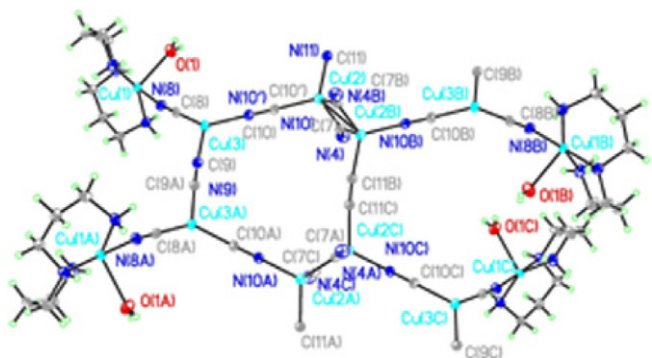


Fig. 4. The ORTEP view of **2** $[\text{Cu}^{\text{II}}(\text{dipn})_2][\text{Cu}^{\text{I}}_4(\text{CN})_8] \cdot 2\text{H}_2\text{O}$.

and the distance of Cu and C atom is 1.929(3) Å (two C–Cu3–N bond angles and one N–Cu2–N bond angle are 122.94(11)°, 122.23(11)° and 111.67(10)°, respectively); a distorted trigonal planar Cu(3B) site, coordinating with three cyano-C atoms, the average Cu–C distance is 1.960(3) Å; two copper(II) (Cu(1) and Cu(1B)) sites, which take a distorted square-pyramidal coordination with three nitrogen atoms of the dipn ligand, one cyano-N atom and one oxygen atom of H₂O; one distorted tetragonal pyramidal Cu(2) site, coordinating with three cyano-C atoms, one cyano-N atom and connecting with Cu(2B) atom, the average Cu–C distance is 2.088(3) Å, the Cu–N distance is 1.992(3) Å (three C–Cu(2)–C are 107.18(10)°, 109.24(11)°, and 108.71(11)°, respectively); one distorted tetragonal pyramidal Cu(2B) site, coordinating with three cyano-C atoms,

one cyano-N atom and Cu(2B) atom, the Cu–N distance is 1.992(3), the average Cu–C distance is 2.088(3) Å.

The interesting feature is that Cu(2) is linked with Cu(2B) via metal–metal bond and cyanide groups, and one (Cu₂)₂C₂ rhombus is built from two equivalent Cu(I) centers and two cyano-C atoms. The distance of Cu(2) and Cu(2B) is 2.5369(8) Å, and the distances between Cu2 and C are 2.085(3) and 2.187(3) Å, respectively. The Cu(2)–C(7)–Cu(2B) bond angle is 72.82(10), and the C(7)–Cu(2)–C(7B) bond angle is 107.18(10)°. The bond angles of C(11)–Cu(2)–Cu(2B), N(10)–Cu(2)–Cu(2B), C(7)–Cu(2)–Cu(2B), and C(7B)–Cu(2)–Cu(2B) are 122.38(8)°, 123.21(8)°, 55.46(9)°, and 51.72(8)°, respectively.

The extended structure of compound **2** is a two-dimensional netlike layer consisting of $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_2(\text{CN})_8]$ unit, as shown in Fig. 5. Each ring is built from five Cu(I) and one Cu(II) centers, which are bridged by cyanide groups and metal–metal bonds. The bridging fragments Cu(II)–NC–Cu(I) or Cu(I)–NC–Cu(I) are not linear with both Cu(II)–N–C and Cu(I)–C–N bond angles showing wide variation (142.7(3)–176.8(2)°).

2.4. Magnetic properties of **1**

The magnetic properties of compounds **1** and **2** were investigated in the temperature range 2–300 K.

The magnetic behavior of complex **1** is shown in Fig. 6 in the form of χ_M vs. T . The value of $\chi_M T$ at room temperature, 1.2 cm³ K mol^{−1} (3.1 μ_B), is larger than the value of 1.0 cm³ K mol^{−1} (2.83 μ_B) of two isolated Cu(II) ions ($S = 1/2$, $g = 2.1$) and decreases rapidly with decreasing temperature between 300 and 4 K, and then decreases slightly to 0.015 emu K mol^{−1} at 2.0 K.

The 1-D magnetic coupling system of compound **1** can be simplified as interacting dimeric units with coupling constant J . On this basis, it should be possible to interpret the

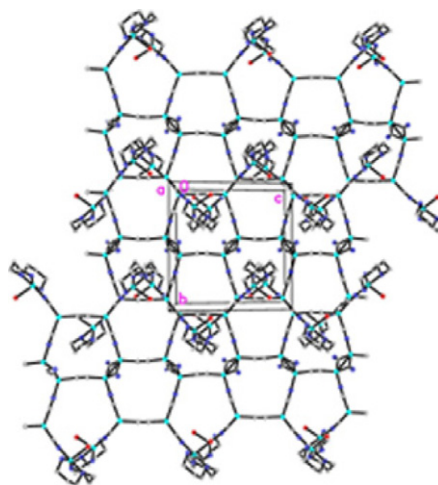


Fig. 5. Cell packing diagram along the crystallographic c axis showing one set of 2D frameworks of **2** $[\text{Cu}^{\text{II}}(\text{dipn})_2][\text{Cu}^{\text{I}}_4(\text{CN})_8] \cdot 2\text{H}_2\text{O}$.

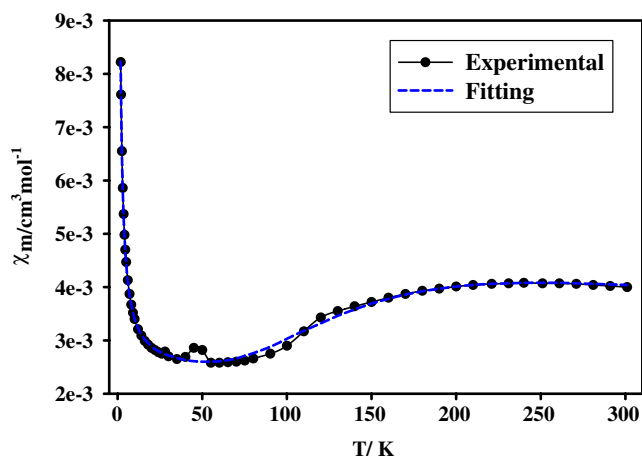


Fig. 6. Plot of the temperature dependence of the χ_M for compound 1.

data by means of a modified Beleaney–Bowers equation [17]

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \left[3 + \exp\left(-\frac{J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{N\beta^2 g^2}{2kT} \rho + 2N\alpha$$

Least-squares fitting of the experimental data led to $J = -406.2 \text{ cm}^{-1}$, $g = 2.1$, $N\alpha = 1.2 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ and $\rho = 0.0012$. As a consequence, there is a strong antiferromagnetic exchange interaction between copper(II) ions mediated by cyano-bridges.

2.5. Magnetic properties of 2

The magnetic behavior of compound 2 is shown in Fig. 7 in the form of $\chi_M T$ vs. T . From room temperature down to 40 K, the $\chi_M T$ remains constant and it is equal to $0.993 \text{ cm}^3 \text{ K mol}^{-1}$ ($2.82 \mu_B$), which is close to the value of $1.0 \text{ cm}^3 \text{ K mol}^{-1}$ ($2.83 \mu_B$) of two isolated Cu(II) ions ($S = 1/2$). Below 40 K, the $\chi_M T$ decreases, reaching a value of $0.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This variation is indicative of

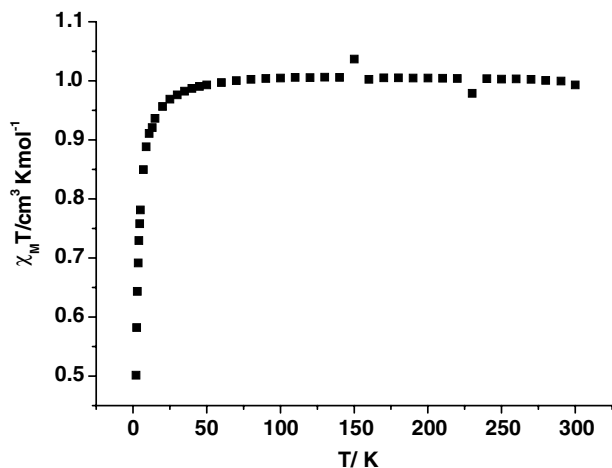


Fig. 7. Temperature dependence of $\chi_M T$ for compound 2.

an overall weak antiferromagnetic behavior of compound 2. Since the Cu(II) ions interact through diamagnetic $[\text{Cu(I)(CN)}_3]^{2-}$ units, the coupling between them is expected to be very weak.

3. Experimental

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, dipropylenetriamine, and KCN were purchased from commercial sources and used as received.

3.1. Physical measurements

Infrared spectrum was recorded (in the $4000\text{--}400 \text{ cm}^{-1}$) as KBr disks on a Bruker 1600 FTIR spectrometer. Magnetic susceptibility data for powder sample were collected in the temperature range 2–300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility.

3.2. Synthesis of compounds

3.2.1. $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{II}}(\text{CN})_4] \mathbf{1}$

A solution of dipropylenetriamine (0.65 g, 4 mmol) in water (6 ml) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.68 g, 4 mmol) in water (5 ml). The mixture was stirred for 2 min before the addition of potassium cyanide (0.65 g, 10 mmol) dissolved in a minimum of water. After stirring for 10 min at room temperature and filtering, the solution was left standing for several days, which lead the formation of blue pellet. They were collected by filtration and dried in air (0.24 g, 67%). The elemental analysis results (Found: C, 32.87; H, 4.72; N, 27.25%. $\text{C}_{10}\text{H}_{17}\text{Cu}_2\text{N}_7$ requires C, 33.11; H, 4.69; N, 27.04) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2169 (s), 2129 (s) cm^{-1} (ν_{CN}).

3.2.2. $[\text{Cu}^{\text{II}}(\text{dipn})]_2[\text{Cu}_4^{\text{I}}(\text{CN})_8] \cdot 2\text{H}_2\text{O} \mathbf{2}$

A solution of dipropylenetriamine (0.52 g, 4 mmol) in water (8 ml) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.34 g, 2 mmol) in water (5 ml). The mixture was stirred for 2 min before the addition of potassium cyanide (0.97 g, 15 mmol) dissolved in a minimum of water. After foiling for 5 min and filtering, the solution was left standing for several days, which lead the formation of blue needles. They were collected by filtration and dried in air (0.17 g, 58%). The elemental analysis results (Found: C, 27.37; H, 3.82; N, 22.06%. $\text{C}_{20}\text{H}_{38}\text{Cu}_6\text{N}_{14}\text{O}_2$ requires C, 27.15; H, 3.85; N, 22.18) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2132 (s), 2111, 2095 (s) cm^{-1} (ν_{CN}).

3.3. X-ray crystallography

Data were collected with a Bruker SMART CCD area detector using graphite monochromated $\text{MoK}\alpha$ radiation

($\lambda = 0.71073 \text{ \AA}$) at room temperature. All empirical absorption corrections were applied by using the SADABS program [18]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer program [19]. Details of the crystal parameters, data collection and refinement for compounds **1**, and **2** are listed in Table 1, and selected bond distances and angles are given in Tables 2 and 3.

Table 1
Crystallographic data for **1** and **2**

	1	2
Empirical formula	C ₁₀ H ₁₇ Cu ₂ N ₇	C ₂₀ H ₃₈ Cu ₆ N ₁₄ O ₂
Formula weight	362.39	887.88
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	11.4035(13)	17.6569(17)
<i>b</i> (Å)	10.0638(12)	13.4038(17)
<i>c</i> (Å)	13.7289(16)	13.3552(14)
α (°)	90	90
β (°)	108.3350(10)	105.712(2)
γ (°)	90	90
<i>V</i> (Å ³)	1495.6(3)	3042.7(6)
<i>Z</i>	4	4
<i>D</i> _c (Mg m ⁻³)	1.609	1.938
<i>F</i> (000)	384	1784
θ Range for data collection (°)	2.56–27.49	2.29–25.50
Reflections collected/unique	9575/3400	11062/2834
Maximum and minimum transmission	0.7623 and 0.3645	0.9114 and 0.6689
Data/restraints/parameters	3400/0/172	2834/0/193
Goodness-of-fit on <i>F</i> ²	0.985	1.058
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0581	<i>R</i> ₁ = 0.0281, <i>wR</i> ₂ = 0.0782
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0784	<i>R</i> ₁ = 0.0381, <i>wR</i> ₂ = 0.0832

Table 2
Selected bond distances (Å) and angles (°) for complex **1**

<i>Bond distances</i> (Å)			
Cu(1)–C(10)	1.863(3)	Cu(1)–C(7)	1.869(3)
Cu(1)–C(8)	1.873(3)	Cu(1)–C(9)	1.873(3)
Cu(2)–N(3)	2.017(3)	Cu(2)–N(1)	2.021(2)
Cu(2)–N(4)	2.024(2)	Cu(2)–N(2)	2.046(2)
N(5)–Cu(2)	2.200(2)		
<i>Bond angles</i> (°)			
C(10)–Cu(1)–C(7)	89.24(12)	C(10)–Cu(1)–C(8)	178.03(12)
C(7)–Cu(1)–C(8)	91.95(11)	C(10)–Cu(1)–C(9)	90.70(13)
C(7)–Cu(1)–C(9)	178.51(14)	C(8)–Cu(1)–C(9)	88.07(12)
N(4)–Cu(2)–N(5)	100.01(10)	C(7)–N(4)–Cu(2)	176.8(2)
C(8)–N(5)–Cu(2)	141.1(2)	N(4)–C(7)–Cu(1)	176.9(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y + 1/2, -z + 1/2$; #2 $-x + 1/2, y - 1/2, -z + 1/2$.

Table 3
Selected bond distances (Å) and angles (°) for complex **2**

<i>Bond distances</i> (Å)			
C(8)–N(8)	1.141(4)	C(8)–Cu(3)	1.929(3)
N(8)–Cu(1)	2.001(2)	C(9)–Cu(3)	1.973(3)
C(10)–N(10)	1.153(4)	C(10)–Cu(3)	1.978(3)
N(10)–Cu(2)	1.992(3)	C(11)–Cu(2)	1.991(3)
Cu(1)–N(3)	2.009(2)	Cu(1)–N(1)	2.023(2)
Cu(1)–N(2)	2.028(2)	Cu(1)–O(1)	2.304(2)
Cu(2)–C(7)	2.085(3)	Cu(2)–C(7)#3	2.187(3)
Cu(2)–Cu(2)#3	2.5369(8)	Cu(3)–Cu(3)#4	3.0232(8)
C(7)–Cu(2)#3	2.187(3)		
<i>Bond angles</i> (°)			
N(8)–C(8)–Cu(3)	174.2(3)	C(8)–N(8)–Cu(1)	171.8(3)
C(9)#1–C(9)–Cu(3)	177.10(8)	N(10)–C(10)–Cu(3)	176.8(2)
C(10)–N(10)–Cu(2)	175.5(2)	C(11)#2–C(11)–Cu(2)	174.59(13)
C(11)–Cu(2)–N(10)	114.21(11)	C(11)–Cu(2)–C(7)	111.04(11)
N(10)–Cu(2)–C(7)	108.71(11)	C(11)–Cu(2)–C(7)#3	106.20(11)
N(10)–Cu(2)–C(7)#3	109.24(11)	C(7)–Cu(2)–C(7)#3	107.18(10)
C(11)–Cu(2)–Cu(2)#3	122.38(8)	N(10)–Cu(2)–Cu(2)#3	123.21(8)
C(7)–Cu(2)–Cu(2)#3	55.46(9)	C(7)#3–Cu(2)–Cu(2)#3	51.72(8)
C(8)–Cu(3)–C(9)	122.94(11)	C(8)–Cu(3)–C(10)	122.23(11)
C(9)–Cu(3)–C(10)	111.67(10)	C(8)–Cu(3)–Cu(3)#4	65.76(9)
C(9)–Cu(3)–Cu(3)#4	113.06(8)	C(10)–Cu(3)–Cu(3)#4	109.91(8)
N(4)–C(7)–Cu(2)	142.7(3)	N(4)–C(7)–Cu(2)#3	144.4(3)
Cu(2)–C(7)–Cu(2)#3	72.82(10)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z - 1/2$; #2 $-x, y, -z + 1/2$; #3 $-x, -y, -z$; #4 $-x, -y + 1, -z$.

4. Conclusions

Two new cyano-bridged compounds **1** and **2** have been prepared. The formation of these compounds is strongly affected by the amount of cyanide anion in the reaction media and can be controlled by the ratio of Cu²⁺, dipn ligand and CN⁻. The present example is one new demonstration of the versatility of cyanometalates in building molecule-based assemblies from discrete species to polynuclear molecules.

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Appendix A. Supplementary material

CCDC 614309 and 636935 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: depos-

it@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.032.

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