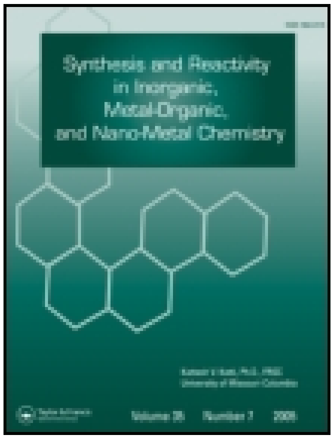
This article was downloaded by: [Case Western Reserve University]
On: 01 December 2014, At: 13:27
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Isolation and Properties of a Chain of Cyano-Bridged Complex $\{LCu^{II}(\mu\text{-}CN)\}_n$ With Triazenido Ligand and a Cyano-Bridged Mixed-Valence Complex $\{Cu^{II}Cu^{I}(\mu\text{-}CN)_3\}_n$

Wan-Yuan Jian [a], Wei Li [a], Qi-Ying Lv [a], Xin Min [a], Yue-Yun Liu [a] & Shu-Zhong Zhan [a]
[a] College of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou, P. R. China

Accepted author version posted online: 30 Jul 2012.Published online: 05 Oct 2012.

To cite this article: Wan-Yuan Jian, Wei Li, Qi-Ying Lv, Xin Min, Yue-Yun Liu & Shu-Zhong Zhan (2012) Isolation and Properties of a Chain of Cyano-Bridged Complex $\{LCu^{II}(\mu\text{-}CN)\}_n$ With Triazenido Ligand and a Cyano-Bridged Mixed-Valence Complex $\{Cu^{II}Cu^{I}(\mu\text{-}CN)_3\}_n$, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:10, 1375-1380, DOI: 10.1080/15533174.2012.680147

To link to this article: http://dx.doi.org/10.1080/15533174.2012.680147

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:1375–1380, 2012

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.680147

Isolation and Properties of a Chain of Cyano-Bridged Complex $\{LCu^{II}(\mu\text{-}CN)\}_n$ With Triazenido Ligand and a Cyano-Bridged Mixed-Valence Complex $\{Cu^{II}Cu^{I}(\mu\text{-}CN)_3\}_n$

Wan-Yuan Jian, Wei Li, Qi-Ying Lv, Xin Min, Yue-Yun Liu, and Shu-Zhong Zhan
College of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou, P. R. China

One reaction of 1-[(2-carboxymethyl) benzene]-3-[2-pyridine] triazene (HL) with $CuCl_2\cdot 2H_2O$, and NaCN gives a chain of cyano-bridged complex $\{LCu^{II}(\mu\text{-}CN)\}_n$ 1 and a cyano-bridged mixed-valence complex $\{Cu^{II}Cu^{I}(\mu\text{-}CN)_3\}_n$ 2, respectively. The X-ray crystal structures of both complexes have been obtained. Magnetic studies indicate significant antiferromagnetic coupling between the copper(II) centers for complex 1, with coupling constants (J) of –129.6 cm^{-1}.

Keywords crystal structures, cyano-bridged complexes, magnetic property

INTRODUCTION

In recent years, much research interest has been focused on crystal engineering of cyano-bridged homocopper and mixed valence copper (I, II) complexes.[1–4] 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 can not be isolated easily. Nevertheless, a few cyano-bridged Cu^{II}/Cu^{II} complexes have been reported.[5,6] In addition, some cyanobridged Cu^{I}/Cu^{II} mixed-valence compounds such as $[Cu^{II}(dien)Cu^{I}(CN)_3]$,[7] $[Cu^{II}(tn)_2Cu^{I}(CN)_3]$,[8] $[\{Cu^{II}(CN)_2\}_2Cu^{I}(cyclam)]$,[9] $[Cu^{II}(pn)_2Cu^{I}_2(CN)_4]$,[10] and $[Cu^{II}_2(oxpn)Cu^{I}(CN)_2]$[11] have been reported.

In contrast to the rich Cu^{I}/Cu^{I} Cyanide chemistry, the Cu^{II}/Cu^{II} cyanide systems and the mixed-valence Cu^{I}/Cu^{II} systems are rare. 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 a triazenido ligand (HL = 1-[(2-carboxymethyl) benzene]-3-[2-pyridine] triazene) to react with NaCN, and isolated two kinds of cyano-bridged copper complexes such as a chain of cyano-bridged complex $\{LCu^{II}(\mu\text{-}CN)\}_n$ **1** and a cyano-bridged mixed-valence complex $\{Cu^{II}Cu^{I}(\mu\text{-}CN)_3\}_n$ **2**. In this work, we describe an unusual reaction of NaCN, $CuCl_2\cdot 2H_2O$, and HL, molecular structures of complexes **1** and **2**, and magnetic property of **1** thereof.

EXPERIMENTAL

Physical Measurements

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

Synthesis of 1-[(2-carboxymethyl) benzene]-3-[2-pyridine] triazene (HL)

Methyl anthranilate (10 mmol) in water (5 mL) was mixed with 1 $mol\cdot L^{-1}$ HCl 30 mL (30 mmol, 3 equiv) at 0°C. An aqueous solution (15%) of sodium nitrite (15 mmol, 1.5 equiv) was added dropwise with stirring. Once the amine was dissolved, a 15% solution of 2-aminopyridine in ethanol (10 mmol, 1 equiv) was added at 0°C and stirred for 6 h. The reaction mixture was neutralized with a 15% aqueous of $NaCH_3CO_2$ to give a yellow precipitate. The reaction mixture was filtered, and the solid was purified by crystallization at –4°C from 9:1 ethyl acetate/hexanes to obtain yellow crystals. The crystals were collected and dried *in vacuo* (70%). Anal. Calcd. for $C_{26}H_{26}N_8O_4$ (%): C, 60.64; H, 5.05; N, 21.77. Found (%): C, 60.17; H, 5.04; N, 21.56. ^1H NMR (CD_2Cl_2): δ 8.58 (d, J = 1 Hz, 1H, py), 8.05 (d, J = 2.6 Hz, 1H, Py), 7.96 (d, J = 2.8 Hz, 1H, Py), 7.82 (t, J = 2.7 Hz, 1H, Py), 7.60 (t, J = 2.7 Hz, 2H, Ar), 7.25 (t, J = 1.7 Hz, 1H, Py), 7.16 (t, J = 2.7 Hz, 1 Hz, Py), 3.97 (s, 3H, $-OCH_3$).

Received 15 September 2011; accepted 1 January 2012.

This work was supported by the Research Foundation for Returned Chinese Scholars Overseas of Chinese Education Ministry (No. B7050170), the National Science Foundation of China (No. 20971045), and the Student Research Program (SRP) of South China University of Technology.

Address correspondence to Shu-Zhong Zhan, College of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou, 510640, P. R. China. E-mail: shzhzhan@scut.edu.cn

Synthesis of 1 and 2

To a solution containing ligand (0.515 g, 2 mmol) and triethylamine (0.20 g, 2 mmol) in ethanol (15 mL), $CuCl_2{\cdot}2H_2O$ (0.32 g, 2 mmol) was added and stirred for 10 min. After addition of NaCN (0.20 g, 4 mmol) in ethanol (10 mL) to the previous solution, the mixture was stirred at room temperature for 1 h. The solution color turned from brown to deep green. Brown crystals were obtained from the filtrate, which was allowed to stand at room temperature for several days, be collected by filtration, and dried *in vacuo* (0.25 g, 78.4%). Anal. Calcd. for $C_{13}H_{11}CuN_4O_2$ **1** (%): C, 48.9; H, 3.5; N, 17.6. Found (%): C, 48.7; H, 3.5; N, 17.6. IR bands (KBr pellets, cm^{-1}): $\nu = 2135$ $\nu(C{\equiv}N)$. Slow evaporating above filtrate at room temperature, yellow crystals appeared. The crystals were collected and dried *in vacuo* (0.075 g, 24.5%). Anal. Calcd. for $C_9H_{15}Cu_2N_4$ **2** (%): C, 35.3; H, 4.9; N, 18.3. Found (%): 35.2; H, 4.9; N, 18.3; IR bands (KBr pellets, cm^{-1}): $\nu = 2129, 2087$ $\nu(C{\equiv}N)$.

X-Ray Crystallography

Data were collected with a Bruker SMART CCD area detector (Germany) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program (University of Göttingen, Germany, 1996).[12] Structures are 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 (University of Göttingen, Germany, 1997).[13] Details of the crystal parameters, data collection, and refinement for complexes **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 complexes **1** and **2**

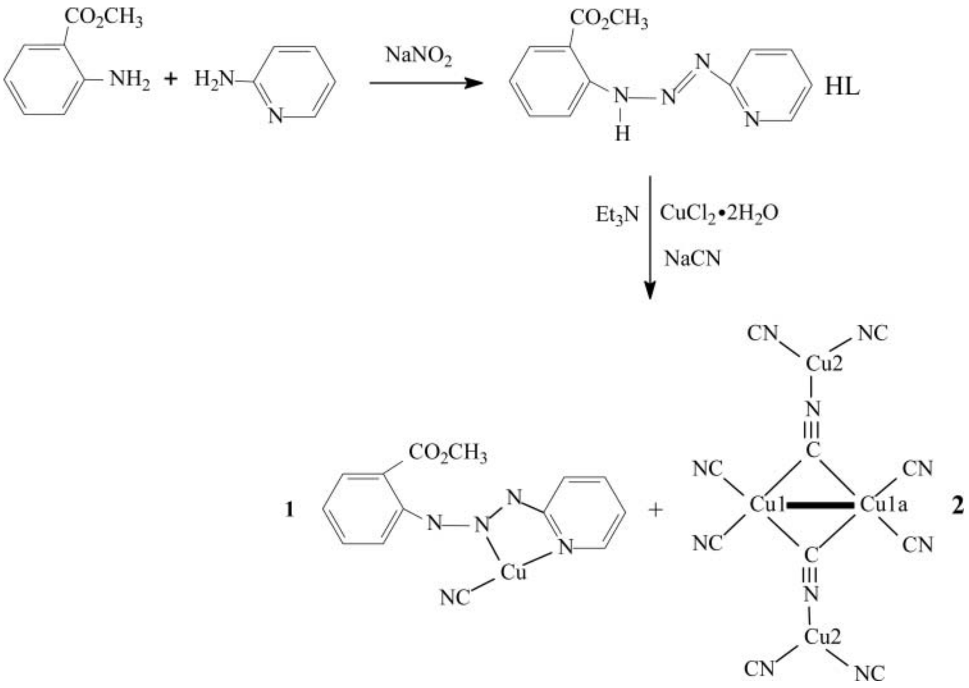
Parameter	**1**	**2**
Empirical formula	$C_{13}H_{11}CuN_4O_2$	$C_9H_{15}Cu_2N_4$
Formula weight	318.80	306.33
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P2(1)/n	p2(1)/n
a/Å	12.923(3)	8.3412(17)
b/Å	8.9349(18)	13.511(3)
c/Å	13.133(3)	11.398(2)
α/°	90	90
β/°	101.90(3)	91.71(3)
γ/°	90	90
V/Å^3	1483.8(5)	1283.9(4)
Z	4	4
Dc/Mg m^{-3}	1.427	1.585
F(000)	648	620
θ range for data collection	3.04 to 27.48°	3.02 to 27.48
Reflections collected/unique	14149/3397	2885/1822
Data/restraints/ parameters	3397/0/200	2885/0/127
Goodness-of-fit on F^2	1.065	1.145
Final R indices [I > 2sigma(I)]	R1 = 0.0587 wR2 = 0.1448	R1 = 0.0462 wR2 = 0.0997
R indices (all data)	R1 = 0.1300 wR2 = 0.2127	R1 = 0.0958 wR2 = 0.1609

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

Bond distances			
Cu(1)-C(14)	1.925(5)	Cu(1)-N(5)	1.943(7)
Cu(1)-N(4)	2.047(5)	Cu(1)-N(1)	2.339(4)
N(1)-N(2)	1.281(6)	N(1)-N(3)	1.337(6)
Cu(1)-N(5)	2.545		
Bond angles			
C(14)-Cu(1)-N(5)	128.3(2)	C(14)-Cu(1)-N(4)	98.2(2)
N(5)-Cu(1)-N(4)	126.9(2)	C(14)-Cu(1)-N(1)	118.3(1)
N(5)-Cu(1)-N(1)	100.8(1)	N(4)-Cu(1)-N(1)	71.7(1)
N(2)-N(1)-N(3)	110.8(4)	N(2)-N(1)-Cu(1)	111.8(3)
N(3)-N(1)-Cu(1)	129.0(3)	N(1)-N(2)-C(5)	112.7(4)
C(5)-N(4)-Cu(1)	118.7(4)	N(4)-C(5)-N(2)	119.0(4)
N(5)-C(14)-Cu(1)	166.1(5)	C(14)-N(5)-Cu(1)	176.6(5)

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

Bond distances			
Cu(1)-C(8)	1.925(7)	Cu(1)-C(9)	1.959(6)
Cu(1)-C(7)	2.018(7)	Cu(1a)-C(7)	2.211(7)
Cu(1)-Cu(1)	2.5175(17)	Cu(2)-N(3)	1.917(8)
Cu(2)-N(2)	1.918(6)	Cu(2)-N(4)	1.956(6)
C(7)-N(2)	1.140(9)	C(7)-Cu(1)	2.018(7)
C(8)-N(4)	1.160(9)	C(9)-N(3)	1.131(9)
N(3)-C(9)	1.131(9)	N(4)-C(8)	1.160(9)
Bond angles			
C(8)-Cu(1)-C(9)	108.8(3)	C(8)-Cu(1)-C(7)	118.7(3)
C(9)-Cu(1)-C(7)	109.1(3)	C(8)-Cu(1)-Cu(1a)	131.3(2)
C(9)-Cu(1)-Cu(1a)	118.3(2)	C(7)-Cu(1)-Cu(1a)	57.1(2)
N(3)-Cu(2)-N(2)	128.4(3)	N(3)-Cu(2)-N(4)	121.5(3)
N(2)-Cu(2)-N(4)	109.8(3)	N(2)-C(7)-Cu(1)	151.3(6)
N(2)-C(7)-Cu(1a)	135.5(6)	Cu(1)-C(7)-Cu(1)	72.9(2)
C(7)-N(2)-Cu(2)	173.0(7)	C(7)-Cu(1)-C(7)	107.1(2)



SCH. 1. Schematic representation of the synthesis of HL and complexes **1** and **2.**

RESULTS AND DISCUSSION

Synthesis and General Properties

The ligand 1-[(2-carboxymethyl) benzene]-3-[2-pyridine] triazene (HL) is synthesized by the reaction of methyl anthranilate, sodium nitrite, and 2-aminopyridine (Scheme 1; see also Figure S1NMR of HL).

In the presence of Et_3N, NaCN reacts with $CuCl_2{\cdot}2H_2O$ and HL in C_2H_5OH solvent to form an unexpected chain of cyano-bridged complex $\{LCu^{II}(\mu\text{-CN})\}_n$ **1** and a cyano-bridged Cu^{II}/Cu^{I} complex **2.** The infrared spectrum of **1** shows one $\nu(C{\equiv}N)$ stretching at 2135 cm^{-1} at higher energies than free CN^- (2080 cm^{-1}), assigning to the cyano-bridged mode of **1** (Figure S2). Complex **2** exhibits two bands at 2129, and 2087 cm^{-1}, which are assigned to the bridged CN and the terminal CN groups, respectively (Figure S3).

Crystal Structure of Complex 1

The unit of **1** is shown in Figure 1, the copper atom is four coordinated with two nitrogen atoms and two cyanides. The Cu-C distance is 1.925(5) Å, and the Cu-N bond lengths fall in the range 2.047(5)–2.545 Å. An infinite chain $\{\text{-}LCu^{II}\text{-}CN\text{-}LCu^{II}\text{-}CN\text{-}\}$ is built by cyano-bridges, and two copper centers are separated by 3.217 Å (Figure 2).

Crystal Structure of 2

The symmetric units of **2** are illustrated in Figures 3 and 4. Mixed-valence complex **2** is completed by two copper atoms, three cyanides, and one Et_3N molecule. Cu(1) is four-coordinated by four cyano-C atoms, and the Cu-C distances fall in range 1.925(7) to 2.018(7) Å. Cu(2) is three-coordinated by

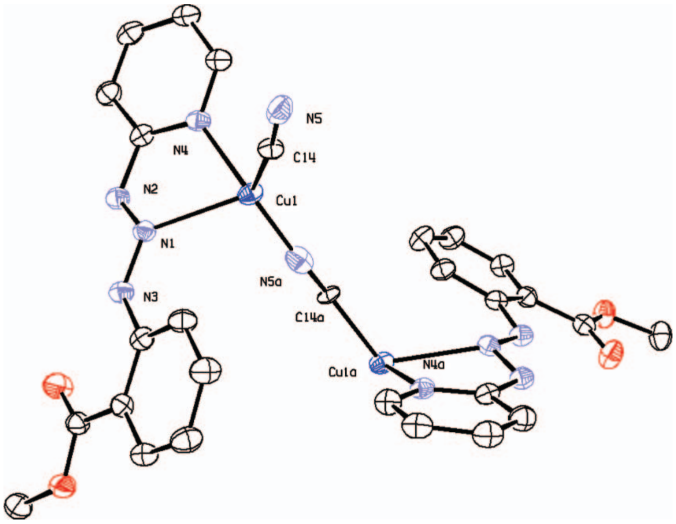


FIG. 1. The crystal structure of units of **1** (color figure available online).

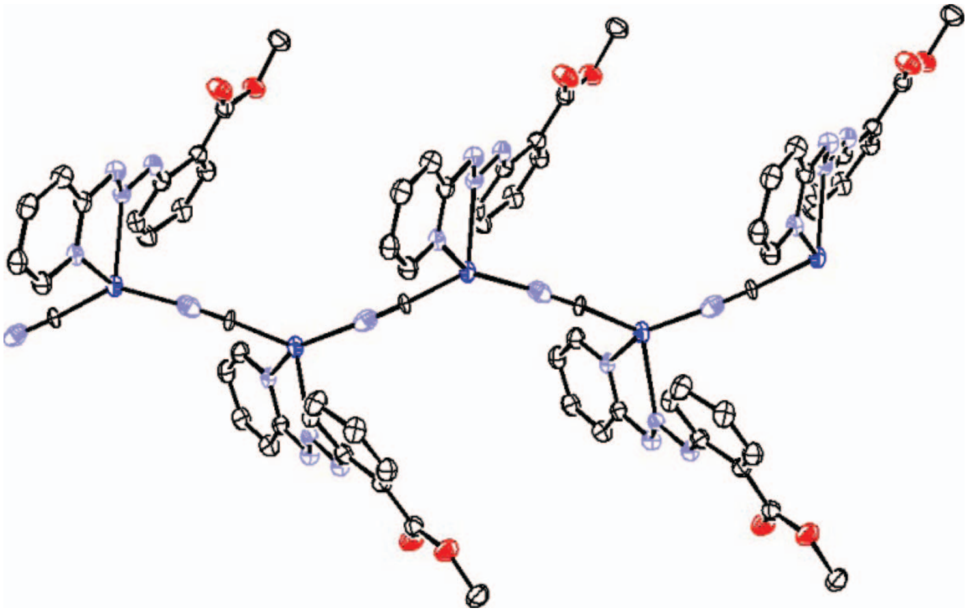


FIG. 2. Cell packing of **1** (color figure available online).

three nitrogen atoms of cyanide groups, and the average bond lengths between Cu and N is 1.330 Å.

The interesting feature is that Cu(1) is linked with Cu(1a) via metal-metal bond and two cyanides. The distance of Cu(1) and Cu(1a) is 2.5175 Å, and the distances between Cu(1) and C are 2.018(7) and 2.211(7) Å, respectively. The Cu(1)-C(7)-Cu(1a) bond angle is 72.9(2), and the C(7)-Cu(1)-C(7a) bond angle is 107.1(2)°. The bridging pane ($Cu_2(CN)_2$) containing Cu(1), C(7), Cu(1a), C(7a) is planar with the torsion angle C(7)-Cu(1)-C(7a)-Cu(1a) of 0.0°. Three $Cu_2(CN)_2$ dimers are linked to Cu(2) via cyanides, the three-coordinated cyanide-Cu-cyanide angles are 109.8(3), 121.5(3), and 128.4(3), respectively. The resulting sheets are tiled from alternating $Cu_2(CN)_2$ dimers and three-coordinated centers, Cu(2) (Figure 5).

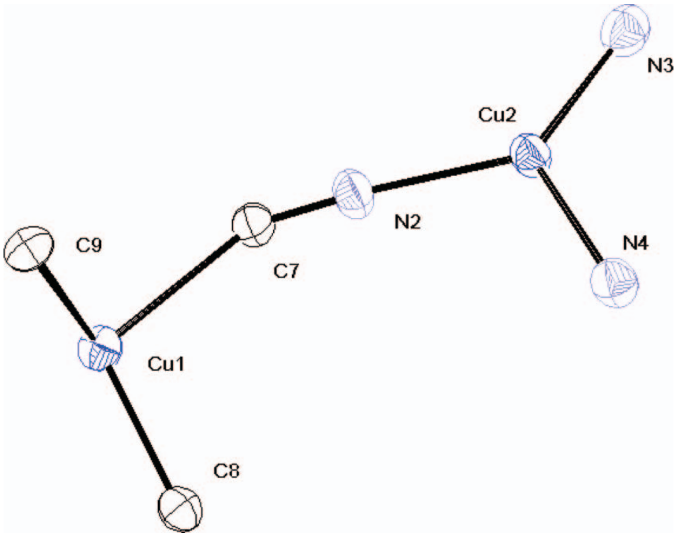


FIG. 3. Illustration showing the coordination sphere of Cu^{II} and Cu^{I} of **2** (color figure available online).

Magnetic Behavior of 1

The magnetic behavior of complex **1** is shown in Figure 6 in the form of χ_M versus T. **1** is characterized by having low room-temperature magnetic moment [$\mu_{eff} = 0.32\ \mu_B$ (300 K)], indicating significant antiferromagnetic coupling between the copper(II) centers. The data are fitted on the basis of the Heisenberg model $\mathbf{H} = -2JS_1 \cdot S_2$. The molar magnetic susceptibility for Cu(II)-Cu(II) units is expressed as in Eq. 1.[14]

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

Least-squares fitting of the experimental data led to J = –192.6 cm^{-1}, $N\alpha = 1.1 \times 10^{-3}$ cm^3mol^{-1}, and $\rho = 0.1$. As a consequence, there was a strong antiferromagnetic exchange interaction between copper(II) ions mediated by cyano-bridges.

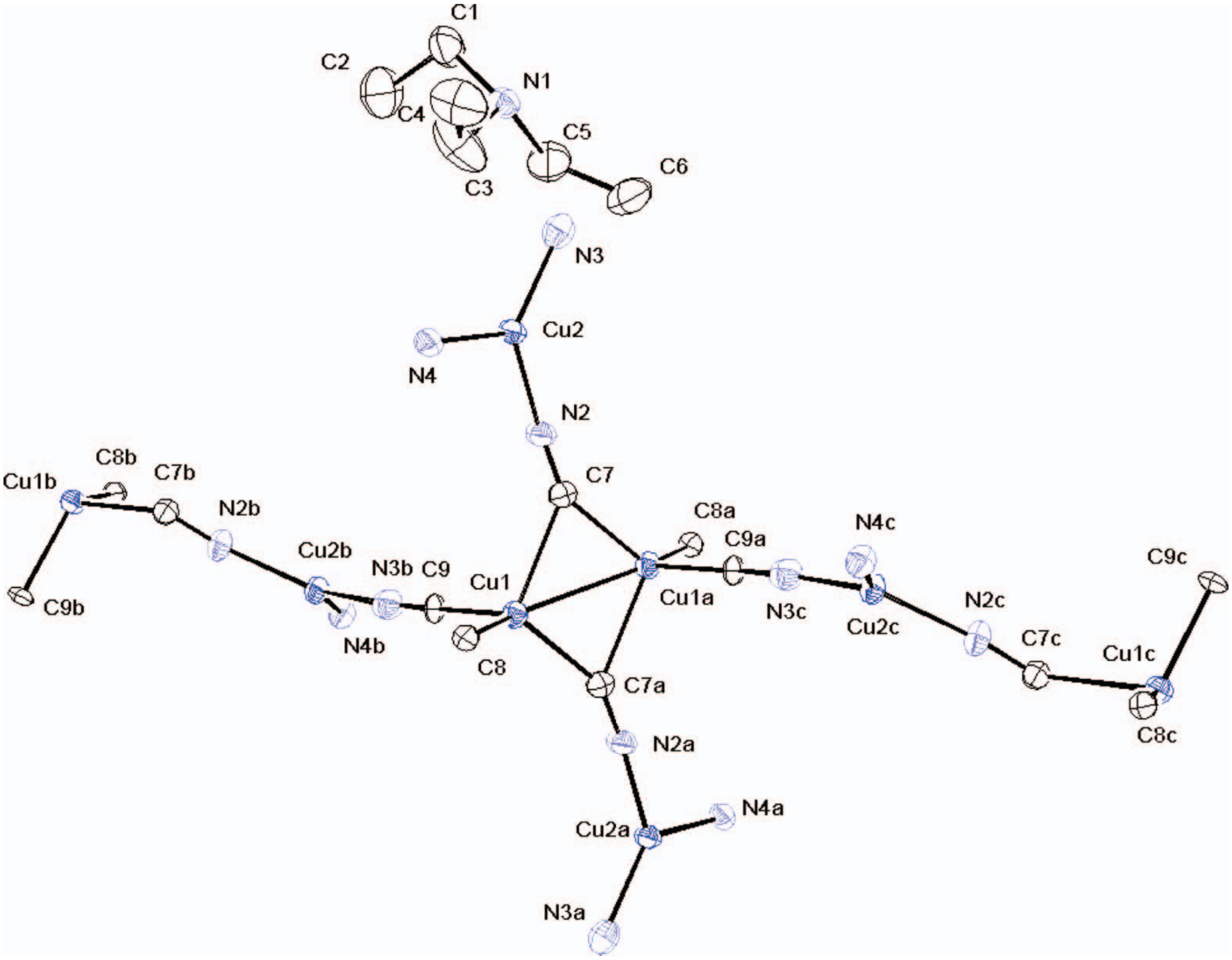


FIG. 4. The ORTEP view of **2** (color figure available online).

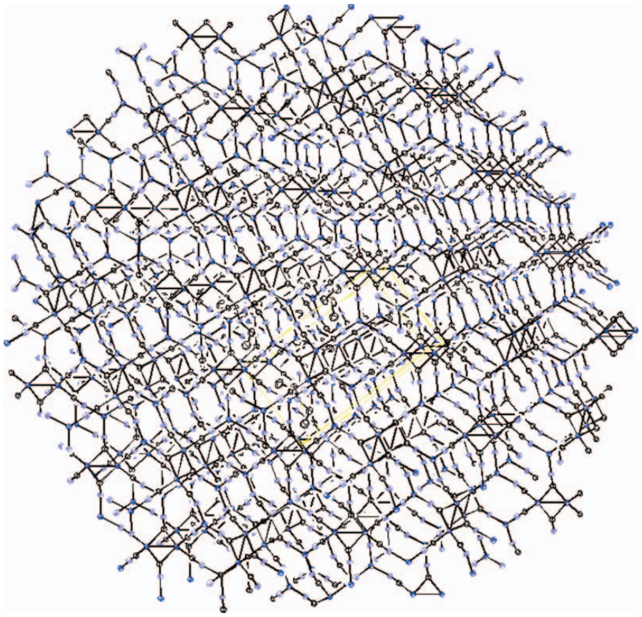


FIG. 5. Cell packing of **2** (color figure available online).

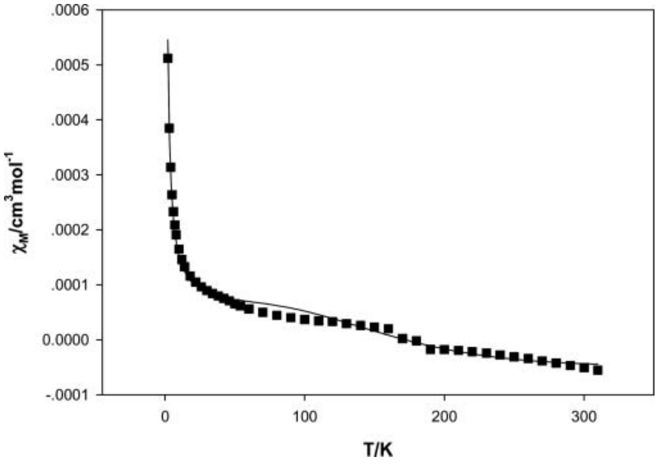


FIG. 6. Temperature dependence of χ_M at 3000 Oe for **1.**

SUPPLEMENTARY MATERIALS

CCDC 758981 and 772978 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

REFERENCES

1. Lim, M.J.; Murray, C.A.; Tronic, T.A.; deKrafft, K.E.; Ley, A.N.; deButts, J.C.; Pike, R.D.; Lu, H.; Patterson, H.H. Copper(I) cyanide networks: synthesis, structure, and luminescence behavior. Part 2. piperazine ligands and hexamethylenetetramine. *Inorg. Chem.* **2008**, *47*, 6931–6947.
2. Atanasov, M.; Comba, P.; Hanson, G.R.; Hausberg, S.; Helmle, S.; Wadepohl, H. Cyano-bridged homodinuclear copper(II) complexes. *Inorg. Chem.* **2011**, *50*, 6890–6901.
3. Xu, F.; Huang, W.; You, X.Z. Novel cyano-bridged mixed-valent copper complexes formed by completely *in situ* synthetic method via the cleavage of C–C bond in acetonitrile. *Dalton Trans.* **2010**, *39*, 10652–10658.
4. Zhan, S.Z.; Li, W.; Wang, J.; Liang, A.; Deng, Y. Assembly of cyano-bridged Cu(II)/Cu(II) and Cu(I)/Cu(II) compounds obtained by controlled ration of cyanide. *J. Organomet. Chem.* **2007**, *692*, 3568–3573
5. Duggen, D.M.; Jungst, R.G.; Mann, K.R.; Stucky, D.G.; Hendrickson, D.N. Electronic and crystallographic study of two cyanide-bridged copper(II) dimers. Magnetic exchange interactions through a linear copper-cyanide-copper bridge and a hydrogen-bonded copper-cyanide...hydrogen-nitrogen-copper system. *J. Am. Chem. Soc.* **1974**, *96*, 3443–3450.
6. Duggen, D.M.; Hendrickson, D.N. X-ray structural characterization of an outer-sphere copper(II) dimer, dicyanobis(2,2′,2′′-triaminotriethylamine)dicopper(II) tetraphenylborate. Hydrogen-bonding between two trigonal-bipyramidal copper cations. *Inorg. Chem.* **1974**, *13*, 1911–1916.
7. Huang, S.F.; Wei, H.H.; Wang, Y. A new cyano-bridged one-dimensional polymeric mixed-valence $\mathrm{Cu^{II}}$/CuI complex formed from reduction of a binuclear $\mathrm{Cu^{II}}$ complex with sodium cyanide. *Polyhedron* **1997**, *16*, 1747.
8. Pretsch, T.; Ostmann, J.; Donner, C.; Nahorska, M.; Mrozinski, J.; Hartl, H. Synthesis, crystal structure, magnetic properties and electrochemical behaviour of the mixed valence compound> $[\mathrm{Cu^{I}(CN)_3Cu^{II}(C_3H_{10}N_2)_2}]$. *Inorg. Chim. Acta* **2005**, *358*, 2558–2564.
9. Kim, D.-H.; Koo, J.-E., Hong, C.S.; Oh, S.O.; Do, Y. Novel examples of high-dimensional mixed-valence copper cyanide complexes. *Inorg. Chem.* **2005**, *44*, 4383–4390.
10. Colacio, E.; Kivekas, R.; Lloret, F.; Sunberg, M.; Suarez-Varela, J.; Bardaji, M.; Laguna, A. Architecture dependence on the steric constrains of the ligand in cyano-bridged copper(I) and copper(II)−copper(I) mixed-valence polymer compounds containing diamines: rystal structures and spectroscopic and magnetic properties. *Inorg. Chem.* **2002**, *41*, 5141–5149.
11. Kou, H.-Z.; Zhou, B.C.; Wang, R.-J. Assembly of an interpenetrating three-dimensional mixed-valence $\mathrm{Cu^{II}/Cu^{I}}$ coordination polymer. *J. Organometallic Chem.* **2004**, *689*, 369–373.
12. Sheldrick, G.M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, Germany, **1996**.
13. Sheldrick, G.M. *SHELXS 97, Program for Crystal Structure Refinement*; University of Göttingen, Germany, **1997**.
14. Bleaney, B.; Bowers, K.D. Anomalous paramagnetism of copper acetate. *Proc. R. Soc. London, Ser. A.* **1952**, *214*, 451–465.