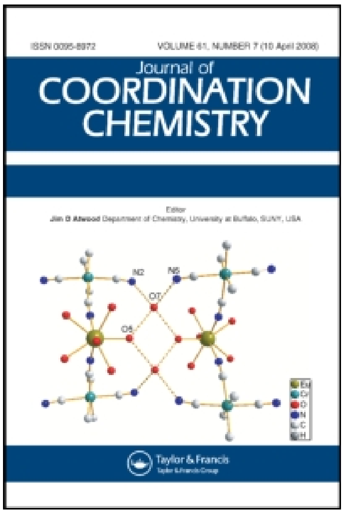

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Synthesis, crystal structure, magnetic properties and electrochemical behavior of the mixed valence compound $[Cu^I(CN)_3Cu^{II}(dipn)]$

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Synthesis, crystal structure, magnetic properties and electrochemical behavior of the mixed valence compound [$\mathrm{Cu^I(CN)_3Cu^{II}(dipn)}$]

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A mixed-valence cyano-bridged $\mathrm{Cu^{II}/Cu^{I}}$ complex, **1**, has been prepared. Complex **1** was fully characterized spectroscopically (UV-Vis and IR), and its structure was determined by X-ray crystallography. The magnetic property was measured in the temperature range 2–300 K. Electrochemical studies of **1** reveal a one-electron oxidation-reduction process associated with the Cu(II)/Cu(I) couple.

Keywords: Cyanides; Mixed valence complex; Crystal structure

1. Introduction

Research has focused on crystal engineering of cyano-bridged homocopper and mixed valence copper (I, II) complexes [1–3]. The rational design of these structures has important implications for development of new magnetic materials and the metabolic roles of copper metalloenzymes involving transfer electrons from a substrate molecule to molecular oxygen. For cyano-bridged homocopper(I) systems, diverse structural features, initially observed in the spiral polymer chain $\mathrm{KCu(CN)_2}$ [4a], and the polymer sheets $\mathrm{KCu_2(CN)_3 \cdot H_2O}$ [4b] and $\mathrm{CuCN \cdot NH_3}$ [4c] have become more evident through the work of Zubieta *et al.* [5], and other groups [6] who exploited the chemistry of copper(I) cyanide. 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.

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Nevertheless, a few cyano-bridged Cu^{II}/Cu^{II} complexes have been reported [7]. In addition, some cyano-bridged Cu^{I}/Cu^{II} mixed-valence compounds such as $[Cu^{II}(dien)Cu^{I}(CN)_3]$ [8], $[Cu^{II}(tn)_2Cu^{I}(CN)_3]$ [9], $[\{Cu^{II}(CN)_2\}_2Cu^{I}(cyclam)]$ [10], $[Cu^{II}(pn)_2Cu^{I}_2(CN)_4]$ [11], and $[Cu^{II}_2(oxpn)Cu^{I}(CN)_2]$ [12] have been reported. In order to expand the system of homometallic cyano-bridged Cu^{I}/Cu^{II} mixed-valence complexes, we have employed Cu^{II} cations as a copper source and the tridentate ligand (dipn = dipropylenetriamine) to react with CN^-, and isolated a cyano-bridged copper complex, $[Cu^{II}(dipn)][Cu^{I}(CN)_3]$ (**1**). In the present study, we report the synthesis as well as structural, magnetic, electrochemical and spectroscopic characterization of **1**.

2. Experimental

$CuCl_2 \cdot 2H_2O$, dipropylenetriamine, and KCN were purchased from commercial sources and used as received.

2.1. *Preparation $[Cu^{I}(CN)_3\text{–}Cu^{II}(dipn)]_n$ (1)*

A solution of dipropylenetriamine (0.52 g, 4 mmol) in water (8 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.34 g, 2 mmol) in water (5 mL). The mixture was stirred for 2 min before addition of potassium cyanide (0.65 g, 8 mmol) dissolved in a minimum of water. After warming at 60°C for 1 h and filtering, the solution was left standing for several days, which led to formation of blue blocks. They were collected by filtration and dried in air (0.21 g, 63%). The elemental analysis (Found C, 32.17; H, 5.04; N, 24.88; $C_9H_{17}Cu_2N_6$ requires C, 32.11; H, 5.05; N, 24.97) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2102(s), 2056(s) cm^{-1} (ν_{CN}).

2.2. *Physical measurements*

Infrared spectrum was recorded (between 4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. Electronic spectra were recorded on a Hitachi U-3010 (UV-Vis) spectrophotometer from aqueous solution. Magnetic susceptibility data for powder samples 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 $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility. Electrochemical experiments were carried out with an Auto Lab instrument with a platinum wire working electrode, a platinum plate counter electrode, and a standard calomel electrode (SCE) as the reference electrode. The values given for the potential are always corrected to those of the SCE electrode. Characterization voltammograms of the complexes were recorded at ca $1 \times 10^{-4}\,mol\,L^{-1}$ complex concentration in 1.0 $mol\,L^{-1}$ KNO_3.

2.3. *X-ray crystallography*

The X-ray diffraction measurements for $[Cu^{I}(CN)_3\text{–}Cu^{II}(dipn)]$ were performed on a Bruker Smart 1000 CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [13]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All 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. The hydrogen atoms of the water molecules were located in the difference Fourier map and refined isotropically. All calculations were performed using the SHELXTL program [14]. Details of the crystal parameters, data collection and refinement for complex [$Cu^{I}(CN)_3$–Cu^{II}(dipn)] (**1**) are listed in table 1, and selected bond distances and angles are given in table 2.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_9H_{17}Cu_2N_6$
Formula weight	336.37
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	7.7869(12)
b (Å)	22.833(4)
c (Å)	8.2092(13)
α (°)	90
β (°)	106.146(2)
γ (°)	90
V (Å^3)	1402.0(4)
Z	4
D_c (Mgm^{-3})	1.594
Absorption coefficient (mm^{-1})	3.022
$F(000)$	684
Crystal size (mm^3)	$0.33 \times 0.20 \times 0.09$
Theta range for data collection (°)	2.72 to 27.49
Limiting indices	$-10 \le h \le 10$, $-29 \le k \le 29$, $-10 \le l \le 10$
Reflections collected/unique	12267/3222 [$R_{(int)} = 0.0349$]
Max. and min. transmission	0.7706 and 0.4373
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3222/0/158
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0861$
R indices (all data)	$R_1 = 0.0579$, $wR_2 = 0.0977$
Largest diff. peak and hole (e A^{-3})	0.573 and −0.386

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

Cu(1)–N(3)	2.005(3)	Cu(1)–N(4)	2.022(3)
Cu(1)–N(1)	2.030(3)	Cu(1)–N(2)	2.064(3)
Cu(1)–N(6)#1	2.174(3)	Cu(2)–C(8)	1.927(4)
Cu(2)–C(9)	1.940(4)	Cu(2)–C(7)	1.943(3)
N(6)–Cu(1)#2	2.174(3)		
N(4)–Cu(1)–N(1)	85.32(12)	N(4)–Cu(1)–N(2)	163.29(12)
N(3)–Cu(1)–N(6)#1	98.79(14)	N(4)–Cu(1)–N(6)#1	102.23(12)
C(8)–Cu(2)–C(9)	124.25(14)	C(8)–Cu(2)–C(7)	121.66(14)
C(9)–Cu(2)–C(7)	114.02(14)	C(1)–N(1)–Cu(1)	117.5(2)
C(7)–N(4)–Cu(1)	169.3(3)	C(9)–N(6)–Cu(1)#2	159.1(3)
N(4)–C(7)–Cu(2)	172.4(3)	N(5)–C(8)–Cu(2)	177.5(3)
N(6)–C(9)–Cu(2)	178.2(3)		

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

3. Results and discussion

3.1. *Synthesis and characterization*

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 at normal temperatures with respect to reduction. The chemical reduction of excess aqueous solution of KCN yield a one-dimensional chain structured CuII/CuI mixed-valence complex **1** $[Cu^I(CN)_3–Cu^{II}(dipn)]_n$, which is air stable in solution and in the solid state. The mechanism of the reaction is illustrated by equations (1)–(2). The resulting $[Cu(I)(CN)_3]^{2-}$ anion acting as a building block for formation of the cyano-bridged Cu^{II}/Cu^I coordination polymer reacts with $[Cu(dipn)]^{2+}$ to produce **1**.

$$2Cu^{2+} + 8CN^- = 2[Cu(CN)_3]^{2-} + (CN)_2 \tag{1}$$

$$[Cu(dipn)]^{2+} + [Cu(CN)_3]^{2-} = [(NC)_2Cu - CN - Cu(dipn)] \tag{2}$$

3.2. *Crystal structure of 1*

The ORTEP view of **1** is shown in figure 1. The crystal structure analysis confirms that **1** is built up by binuclear $[Cu^I(CN)_3–Cu^{II}(dipn)]$, one cyanide acts as a 1,2-μ_2 bridging ligand between the $[Cu(I)(CN)_3]^{2-}$ anion and the Cu(II) centre of $[Cu(dipn)]^{2+}$. The two copper atoms are separated by 5.166(14) Å.

In **1**, each Cu(II) is coordinated by three N atoms from dipn ligand and one cyanide N. The average value for the CuII–$N_{triamine}$ distance is 2.033(3) Å lower than

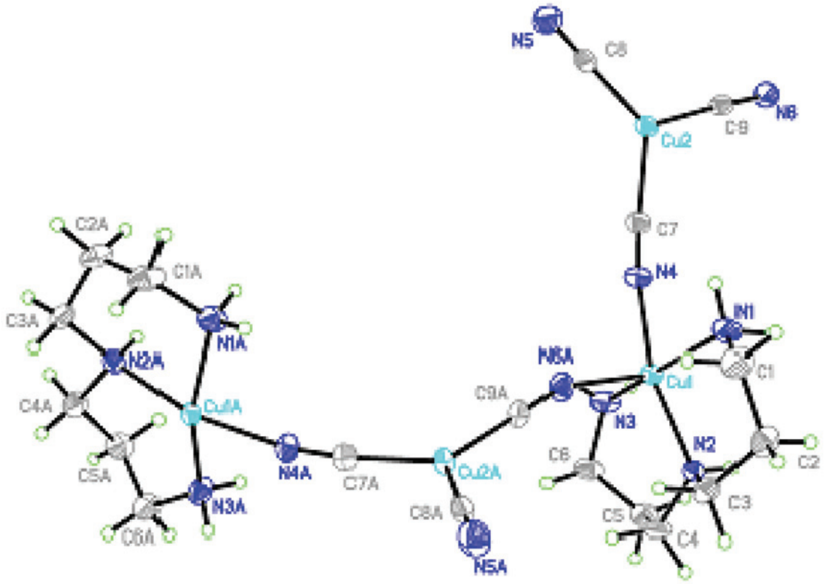

Figure 1. The ORTEP view of $[Cu^I(CN)_3–Cu^{II}(dipn)]$.

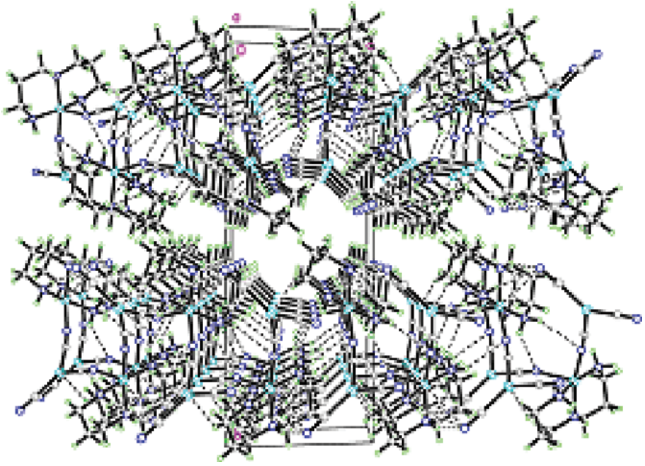

Figure 2. Crystal packing diagram of **1**.

that for CuI–$N_{cyanide}$ (2.098(3) Å). Cu(I) is in a distorted trigonal-planar coordination (three C–Cu^I–C bond angles are 121.66(14), 114.02(14), and 124.25(14)°).

The extended structure of **1** is a 1-D chain formed with –Cu(2)–C–N–Cu(1)–N–C– linkages, and extended 2D networks of **1** are formed by H-bonds between N of cyanide and H of dipn (figure 2).

3.3. *Infrared and UV-Vis spectroscopy*

The CN stretching mode of $[Cu^I(CN)_3]^{2-}$ (D_{3h} symmetry) is observed at 2111 cm^{-1} for $Na_2[Cu^I(CN)_3] \cdot 3H_2O$ [15], at 2094 cm^{-1} for an aqueous solution of $K_2[Cu^I(CN)_3]$ [16, 17] and at 2066 cm^{-1} for crystalline $[Cu^I(CN)_3][Cu^{II}(en)_3]$ [18]. The IR spectrum of **1** $[Cu^{II}(dipn)][Cu^I(CN)_3]$ shows two bands at 2169 and 2129 cm^{-1}, assigned to the bridging Cu^I–C≡N–Cu^{II} (νC≡N(b)) and the terminal CN group, respectively.

UV-Vis spectra of **1** recorded both in the solid state and for aqueous solution show similar features, indicating that **1** is stable in aqueous solution. The room temperature absorption spectra for an aqueous solution of **1** exhibits a strong charge-transfer absorption with a maximum centered around 591 ($\varepsilon = 971\ mol^{-1}\ dm^3\ cm^{-1}$) nm, which can be assigned to the electron transfer from Cu^{II} to cyanide.

3.4. *Magnetic properties*

The magnetic properties of **1** were investigated in the temperature range 2–300 K for molar susceptibility. The magnetic behavior of the mixed valence compound is shown in figure 3 in the form of $\chi_M T$ *versus* T. The room temperature value of $\chi_M T$ for compound **1** is 0.473 emu K mol^{-1} (1.95 μ_B) which is larger than the expected value for one Cu(II) ($S = 1/2$) ion (1.73 μ_B), and lower than the value of 0.75 emu K mol^{-1} (2.45 μ_B) of two isolated Cu(II) ions ($S = 1$, $g = 2.0$) and gradually decreases with decreasing temperature between 300–2 K (1.5 μ_B at 2 K). The magnetic analysis was carried out using the Bleaney-Bowers equation based on the Heisenberg mode

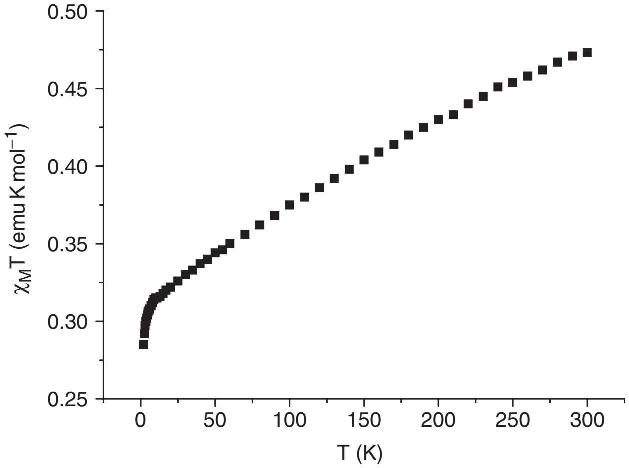

Figure 3. Temperature dependence of $\chi_M T$ at an applied field of 1000 Oe for [Cu^I(CN)$_3$–Cu^{II}(dipn)].

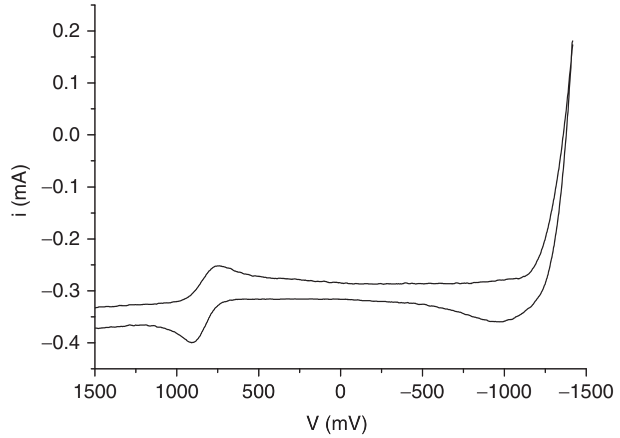

Figure 4. Cyclic voltammogram of **1**, in water (m Vs^{-1}). Concentrations ca 1.0×10^{-4} mol dm^{-3}.

$H = -2JS_1S_2$ [equation (3)] [19], where p is the fraction of monomeric impurity and χ_M is the magnetic susceptibility. The susceptibility of **1** can be well reproduced by the Bleaney–Bowers equation using the magnetic parameters $g = 2.00$, $J = -0.48\,\text{cm}^{-1}$, $N_\alpha = 1.0 \times 10^{-4}\,\text{mol}^{-1}$ and $p = 0.5$. As a consequence, there is a weak antiferromagnetic exchange interaction between copper(II) ions mediated by the CN–Cu(I)–CN diamagnetic bridge.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \frac{1-p}{3 + \exp(-2J\ KT^{-1})} + \frac{0.45p}{T} + N_\alpha \tag{3}$$

3.5. *Electrochemistry*

Complex **1** shows one reversible one-electron potential at 0.83 V, assigned to the CuII/I couple. The closeness of the observed redox potential to the potential of +0.84 V, for a cyano-bridged Cu(II/I) aziridine complex [20], allows the assumption that the following one-electron oxidation and reduction takes place:

$$[\mathrm{Cu(II)}\cdots\mathrm{Cu(II)}\overset{+\mathrm{e}}{\underset{-\mathrm{e}}{\Longleftrightarrow}}[\mathrm{Cu(I)}\cdots\mathrm{Cu(II)}] \qquad (4)$$

Complex **1** with dipn is an electronic donor–acceptor system, whereas with cyanide the mixed-valence species is obtained.

Supplementary data

CCDC-614309 contains 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.

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