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Two New Cyano-Bridged Cu(II)–Fe(II) Complexes: Synthesis and Crystal Structures[1]

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Abstract—Two new cyano-bridged Cu(II)–Fe(II) binuclear complexes, $[Cu(L^1)Fe(CN)_5(NO)]$ (**I**) [L^1 = 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane and $[Cu(L^2)Fe(CN)_5(NO)] \cdot 2H_2O$ (**II**) L^2 = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane, have been assembled and structurally characterized by spectroscopy and X-ray crystallography. Complex **I** crystallizes in the monoclinic crystalline system of space group $P2_1/c$, while complex **II** crystallizes in the monoclinic crystalline system of space group $P2_1/n$. These two complexes assume a binuclear structure in which the Fe^{2+} ion is in an octahedron environment and the Cu^{2+} ion is in a square-prism geometry environment.

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INTRODUCTION

In the past decades, cyano-bridged coordination polymers have drawn an intense interest of scientists among the world and an enormous amount of research work have been devoted to it. As the fabulous properties of these kinds of functional solid materials have been discovered, it shows potential application as catalysts, optical devices as well as molecule-based magnets [1–6]. To further investigate the magneto-structural correlation of the cyano-bridged complexes coupled with $[CuL]^{2+}$, we have prepared and characterized the two new compounds, $[Cu(L^1)Fe(CN)_5(NO)]$ (**I**), L^1 = 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane and $[Cu(L^2)Fe(CN)_5(NO)] \cdot 2H_2O$ (**II**) L^2 = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane, via designing and assembly of nitroprusside anion of $[Fe(CN)_5(NO)]^{2-}$ in order to formed a binuclear Cu(II)–Fe(II) systems [7–11]. In this paper, we report the synthesis, crystal structures and spectra properties of the two new cyano-bridged Cu(II)–Fe(II) compounds.

EXPERIMENTAL

Materials and physical measurements. All reagents are of analytical grade and were used without further purification. Distilled water was used for all procedures. The procedure for the syntheses of $[Cu(L^1)Cl]ClO_4$, (L^1 = 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane) and $[Cu(L^2)](ClO_4)_2$, (L^2 = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane) have been reported previously [12]. Elemental analyses for C, H, and N were carried out on a PerkinElmer elemental analyzer (model 240). The infrared spectrum was obtained on a Shimadzu IRAffinity-1 Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} region as a KBr pellet.

Synthesis of I. 5 mL of an aqueous solution of $Na_2[Fe(CN)_5(NO)]$ (59.58 mg, 0.2 mmol) was added dropwise to a solution of $[Cu(L^1)Cl]ClO_4$ (90.58 mg, 0.2 mmol) in MeOH (10 mL). The mixture was stirred at room temperature for 1 h. The resulting solution was filtered and kept at room temperature, and well-shaped crystals were obtained after a few days. The resulting crystals were collected, washed with H_2O and MeOH respectively, and dried in air.

For $C_{17}H_{26}N_{12}OFeCu$

anal. calcd., %:	C, 38.21;	H, 4.87;	N, 31.47.
Found, %:	C, 38.48;	H, 4.81;	N, 31.56.

Synthesis of II. To a solution of $[Cu(L^2)](ClO_4)_2$ (90.58 mg, 0.2 mmol) (2 mL DMF) was added dropwise a DMF solution of $Na_2[Fe(CN)_5(NO)]$ (59.58 mg, 0.2 mmol) (2 mL). The mixture was stirred at room temperature for 1 h. The resulting solution was filtered and kept at room temperature and well-shaped crystals were obtained after a few days. The resulting crystals were collected, washed with H_2O and MeOH respectively, and dried in air.

For $C_{17}H_{30}N_{12}O_3FeCu$

anal. calcd., %:	C, 35.79;	H, 5.26;	N, 29.48.
Found, %:	C, 35.54;	H, 5.55;	N, 29.59.

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
F_w	533.89	569.92
Temperature, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a, Å	14.157(5)	10.350(7)
b, Å	9.739(3)	12.739(9)
c, Å	16.365(6)	19.193(13)
β, deg	94.460(4)	96.874(7)
V, Å^3	2249.5(13)	2513(3)
Z	4	4
ρ, g cm^{-3}	1.576	1.507
μ, mm^{-1}	1.627	1.467
F(000)	1100	1180
Crystal size, mm	0.3 × 0.28 × 0.18	0.3 × 0.2 × 0.2
Theta range for data collection, deg	3.26–25.00	3.17–25.00
Limiting indices	$-16 \le h \le 16, -11 \le k \le 11, -19 \le l \le 19$	$-12 \le h \le 12, -15 \le k \le 15, -22 \le l \le 22$
Reflections collected/unique (R_{int})	18819/3963 (0.0371)	21146/4417 (0.0639)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3963/0/289	4417/12/323
Goodness-of-fit on F^2	1.054	1.039
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0269$, $wR_2 = 0.0686$	$R_1 = 0.0507$, $wR2 = 0.1089$
R indices (for all data)	$R_1 = 0.0297$, $wR_2 = 0.0708$	$R_1 = 0.0739$, $wR2 = 0.1225$
Largest diff. peak and hole, e Å^{-3}	0.353 and –0.316	0.565 and –0.685

X-ray structure determination. All measurements were made on a Rigaku XtaLAB mini CCD detector with graphite monochromated MoK_α radiation (λ = 0.71073 Å). The empirical absorption corrections by semi-empirical from equivalents were carried out. The structure was solved by direct methods using the SHELXS-97 program [13] and refined with SHELXL-97 [13] by full-matrix least-squares techniques on F^2. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Complete crystallographic data and collection parameters for the two structures are listed in Table 1. The selected bond lengths and angles of **I** and **II** are listed in Table 2.

Table 2. Selected bond lengths (Å) and angles (deg) for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I			
Cu(1)–N(10)	2.0147(18)	Cu(1)–N(8)	2.0176(18)
Cu(1)–N(9)	2.0211(18)	Cu(1)–N(7)	2.0308(19)
Cu(1)–N(1)	2.2296(19)	Fe(1)–N(6)	1.6493(18)
O(1)–N(6)	1.13 8(2)	N(1)–C(1)	1.142(3)
N(2)–C(2)	1.144(3)	N(3)–C(3)	1.140(3)
N(5)–C(5)	1.149(3)	N(4)–C(4)	1.141(3)
II			
Cu(1)–N(9)	1.990(4)	Cu(1)–N(7)	2.010(4)
Cu(1)–N(8)	2.052(4)	Cu(1)–N(10)	2.058(4)
Cu(1)–N(1)	2.306(4)	N(6)–O(1)	1.141(5)
C(3)–N(3)	1.139(6)	C(4)–N(4)	1.148(5)
C(2)–N(2)	1.160(6)	N(1)–C(1)	1.155(6)
N(5)–C(5)	1.159(6)		
Angle	ω, deg	Angle	ω, deg
I			
N(1)C(1)Fe(1)	175.08(19)	O(1)N(6)Fe(1)	177.31(18)
N(2)C(2)Fe(1)	177.9(2)	N(3)C(3)Fe(1)	177.8(2)
N(5)C(5)Fe(1)	175.2(2)	N(4)C(4)Fe(1)	178.1(2)
C(1)N(1)Cu(1)	162.70(18)		
II			
C(1)N(1)Cu(1)	155.5(4)	N(2)C(2)Fe(1)	178.6(5)
N(5)C(5)Fe(1)	179.0(5)	N(1)C(1)Fe(1)	176.8(4)
N(4)C(4)Fe(1)	178.5(4)	N(3)C(3)Fe(1)	177.8(5)
O(1)N(6)Fe(1)	177.6(4)		

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 848587 (**I**) and 848588 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Strong peaks at 2170 cm^{-1} for **I** and 2144 cm^{-1} for **II** which occurred red shifting, is attributed to the bridging ν(C≡N) [11]. It is noted that the weaker band at 2132 cm^{-1} of **I** and 2137 cm^{-1} of **II** may be due to the terminal uncoordinated cyano groups [14, 15]. The very strong peaks at 1910 cm^{-1} of **I** and 1915 cm^{-1} of **II** are reasonably assigned to the N=O stretching vibration, which are almost the same as those bands reported in complexes containing the nitroprusside fragment [14–17]. Meanwhile, a peripheral peak at 3242 cm^{-1} of **I** is reasonably assigned to the N–H vibration of the primary amido groups (in general, the complexes show ν(NH) bands for the secondary amines of the ligands in the region 3143–3237 cm^{-1}). A similar band at 3225 cm^{-1} is also found in **II**. Furthermore, a strong wide band ranges in 3481–3385 cm^{-1} can be attributed to the crystal water of **II**.

The ORTEP diagram of **I** with the atom numbering scheme is shown in Fig. 1a. The crystal structure of **I** consists of one $[Fe(CN)_5(NO)]^{2-}$ and one $[Cu(L^1)]^{2+}$ cation. As shown in Fig. 1, the copper atom of **I** exhibits a square-pyramidal structure with four nitrogen atoms from the L^1 ligands in the equatorial positions. Meanwhile, one nitrogen atom of cyanide from the $[Fe(CN)_5(NO)]^{2-}$ occupies the apical positions. The four nitrogen atoms (N(7), N(8), N(9), and N(10)) are nearly coplanar and the copper atom lies 0.2067 Å out of the plane towards the apical N(1) atom. The Cu–N (equatorial) distances range from 2.0147(2) to 2.0308(2) Å, which is shorter than the distance of axial Cu(1)–N(1) bond (2.2296(2) Å). The phenomena may be attributed to the Jahn–Teller effect of Cu^{2+} ion. The bridging cyanide coordinates to the copper(II) ion in a bent fashion with the C(1)N(1)Cu(1) bond angle of 162.70(2)°. As usual, the $[Fe(CN)_5(NO)]^{2-}$ anion exhibits a distorted octahedral structure. The bond distances of Fe(1)–O(1) and N(6)=O(1) are 1.6493(2) and 1.138(2) Å, respectively. The bond distances of the C≡N (average 1.143 Å) are almost consistent with those observed in other nitroprussides [18–21]. The intermolecular H-bonding interactions have been observed. It is believed that the weak interactions play an important role in stabilizing the structure. In addition, the packing of **I** is shown in Fig. 2a.

As shown in Fig. 1, crystal structure of **II** and **I** is basically similar. It is similarly made up of one $[Fe(CN)_5(NO)]^{2-}$ and one $[CuL_2]^+$ cation. The Cu(1)

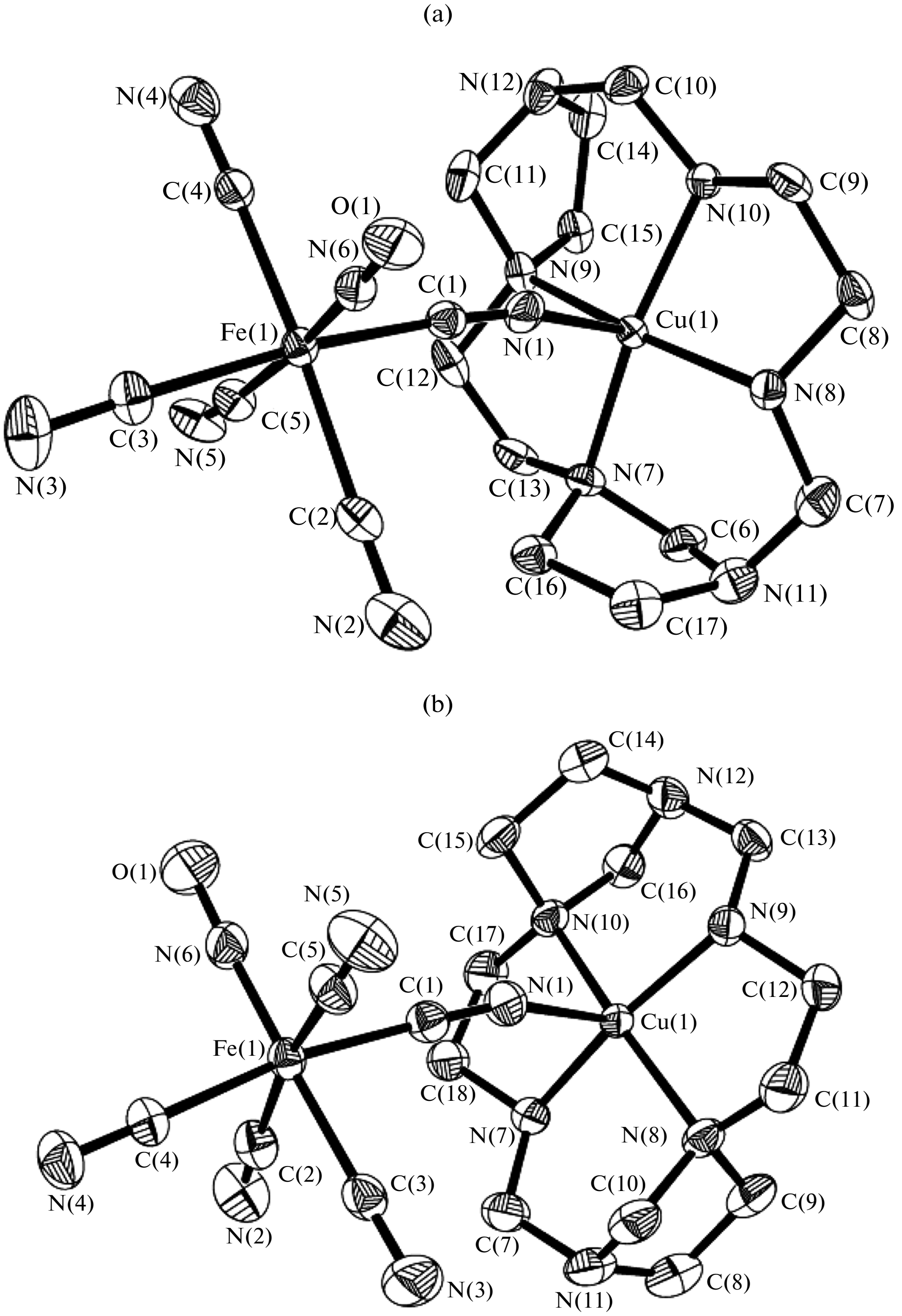

Fig. 1. ORTEP diagram of **I** (a) and **II** (b) with atom labeling scheme, thermal ellipsoids are drawn at the 30%. Hydrogen atoms are omitted for clarity.

atom also exhibits a square-pyramidal environment and contains the analogous nitrogen coordination form with four equatorial nitrogen atoms and one axial nitrogen atoms bonded with $[Fe(CN)_5(NO)]^{2-}$ group. The four equatorial nitrogen atoms present a nearly coplanar structure, just like **I** dose, and the copper atom lies 0.2053 Å out of the plane. But the bond angle of C(1)N(1)Cu(1) is 155.5(4)°, which is smaller than **I**. Moreover, a different from **I**, oxygen atoms coming from crystal water extended the binuclear unit into a

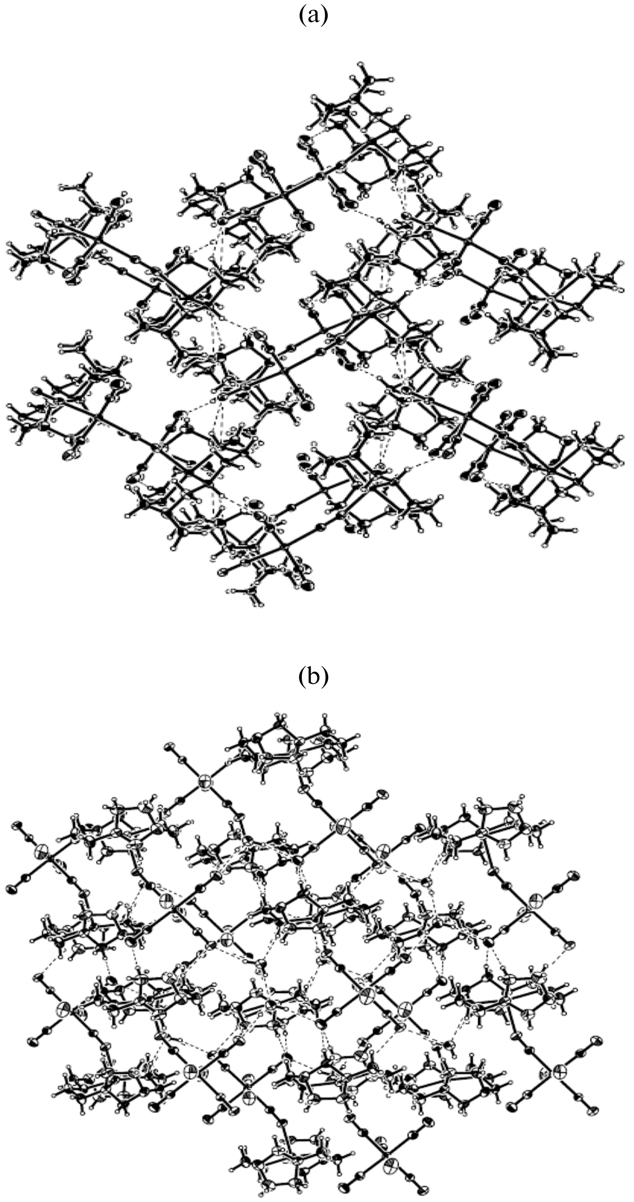

Fig. 2. View of the stacking of **I** (a) and **II** (b).

three-dimensional network by means of the hydrogen bonding interactions. The packing of **II** is shown in Fig. 2b.

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